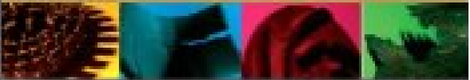
COMPREHENSIVE
CORROSION



4.01 Surface Pretreatment

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Glossary

Millscale An oxide that forms on steel during high temperature processing (e.g., hot rolling) and must be effectively removed prior to the application of any subsequent surface protection.

Surfactant A substance that lowers the surface tension of a liquid, allowing easier spreading across the surface of a material.

Workpiece The item, component, or material that is undergoing surface pretreatment.

Abbreviations

BS British Standard

EDTA Ethylene diamine tetra-acetic acid

EN European Norm
ISO International Standards Organisation
TLV Threshold limit values
VOC Volatile organic compounds

4.01.1 Introduction

The attainment of a clean surface prior to the application of any subsequent treatment or coating is essential, whether this subsequent operation is electroplating, anodizing, chemical treatment, or organic coating. The standard of cleanliness which must be achieved has been stated to be “that which will allow the subsequent process to be carried out satisfactorily”; however, this is an almost meaningless statement. Often it is industry experience that provides a guide to the standard of surface preparation required. As an example, the degree of cleanliness required to satisfactorily zinc plate from an acid solution is somewhat higher than that required prior to zinc plate from a high-cyanide alkali zinc solution. However, this should never be taken as a license to skimp on surface preparation and in another example the arguments over the degree of pretreatment required for ‘surface-tolerant’ paint coatings abound and will probably continue. It should be remembered that it is to a large extent true that problems of early failure in metal finishing are traceable to incorrect or insufficient surface preparation.

4.01.2 Chemical Cleaning

Chemical contamination consists of oils, greases, preservatives, or old paint coatings which must be removed prior to further finishing. Paint coatings can be removed by chemical paint strippers (e.g., solvent or alkali based); however, these methods will not be discussed further here. Sources of most organic contamination are, for example, cutting and machining fluids, preservatives, oils, and greases from, for example, rolling operations, press lubricants, and mechanical or manual handling operations. Various means of removal have been proposed: mechanical action; solvency; detergency; and chemical reaction. In all cleaning operations one or more of these mechanisms will contribute more or less to the overall cleaning procedure, dependent upon the cleaning method and solution employed.

With chemical cleaning, performance will be enhanced by the use of mechanical action, such as brushing, air agitation, spraying, electrolysis or ultrasonic agitation. Solvency is where the materials to be removed dissolve in the cleaning medium, for example mineral oil in chlorinated solvents. Detergency is the ‘lifting’ action attributed to some alkalis and to special surface-active agents commonly referred to as surfactants. Chemical reaction is characterized by, for example, the saponification of some oils in strong alkali, or the reaction of rust with acid solutions. The main types of cleaners used for the removal of organic contaminants are solvent cleaners, neutral cleaners, acid cleaners, and alkali cleaners.

4.01.2.1 Solvent Cleaning

The traditional use of flammable hydrocarbon solvents (e.g., white spirit or paraffin) used either by immersion or by manual application is not to be recommended as an effective or particularly safe method of degreasing. When used by immersion, the holding tank can become heavily contaminated and the contaminants will remain on the work after the solvent has evaporated. The use of solvent-soaked rags, although a time-honored procedure, is now being frowned upon on the grounds of operator safety; aqueous based prewipes are available.

4.01.2.1.1 Vapor degreasing

The use of hot/boiling solvents, with either immersion of the articles to be cleaned in the bulk solvent or in the overlying vapor using specially designed installations, is an effective use of solvents for cleaning purposes. The solvent, which traditionally was of a halogenated hydrocarbon type, is held in a sump at the base, which is heated by any suitable means and under thermostatic control. Above this may be a wire mesh on which the workpieces are rested. The solvent is condensed near the top of the chamber by cooling coils; thus, between the mesh and the coils is created a region where the solvent is in vapor form. When cold items are introduced, the vapor condenses upon them and liquid solvent flows off, thereby removing contamination. To a large extent, only clean solvent is vaporized, thus ensuring that only fresh solvent is used to clean the workpiece until the sump becomes overcontaminated, when the solvent must be cleaned or replaced. Care should be exercised with some metals, notably aluminum, that solvent with free chloride is not used, as this could lead to pitting of the metal surface.

Currently, the use of chlorinated solvents is increasingly deprecated in view of the extent of release of volatile organic compounds (VOC). Therefore, the advice of the manufacturers of the installation and the suppliers of the solvent should always be heeded in the operation of these installations to ensure their trouble-free running. Effective fume control must be available above the installation and the work must be removed slowly enough to ensure that all the solvent has evaporated from the work before it leaves the extracted area. Also, as per governing legislative rules, exposure limits for solvents are increasingly being reduced and current advice must be sought.

4.01.2.1.2 Emulsifiable cleaners (water rinsable cold solvent cleaning)

Emulsifiable cleaners (sometimes incorrectly referred to as emulsion cleaners) are blends of organic solvent (often hydrocarbons) with surface active agents and dispersed in an aqueous medium. The work is immersed in the unheated solution for a sufficient time for the cleaner to penetrate the surface thoroughly. The articles are then removed and water rinsed. Additives in the cleaner allow the solvent to emulsify in the water thus removing the contamination. Spray rinsing or agitation in an immersion rinse will aid removal of the residues. This form of cleaning creates disposal problems as the rinse water cannot be merely disposed of into sewerage systems. Thus, the effluent will require storage and the emulsion is broken up before discharge of the water layer and approved disposal of the organic material. As with all solvent-based materials, the need to observe threshold limit values (TLV) for personal exposure and the need for the work to be carried out only under effective fume extraction must be taken into account when considering this type of cleaning product.

The cleanliness of the surface produced by emulsifiable cleaners is not of the highest standard, and additional cleaning may well be necessary before further finishing operations. However, in the use of this method prior to some chemical conversion coating processes (e.g., immersion in phosphate baths), the crystal growth can be quite refined because of the absence of the passivation effect often encountered with some heavy-duty alkali cleaners. Needless to say, manufacturers' recommendations should be followed at all times and the suitability of any particular cleaning/pretreatment combination should be confirmed. Another benefit gained from the use of emulsifiable cleaners is that the surface produced is usually hydrophobic and therefore, to an extent, resistant to tarnishing and corrosion in storage.

4.01.2.1.3 Emulsion cleaners

These are materials, containing blends of organic solvents and surfactants, which are added to water to form an emulsion. Typical concentrations are in the range 0.5–5%. Such emulsions are normally used by spray, as either a preclean in a multistage pretreatment line, or as the cleaner in an industrial washing machine. Such washing machines are often used to clean parts which are contaminated with cutting oils and which require inspection before storage. Like the emulsifiable cleaners, the emulsion cleaners, after rinsing, often leave a hydrophobic surface which is resistant to short-term corrosion. Emulsion cleaners can be used hot or cold. Heat generally improves the cleaning action but, in most cases, leads to an objectionable increase in the smell associated with solvent products.

4.01.2.2 Neutral Cleaners

These are rapidly replacing emulsion and alkali products for use in industrial washing machines and are generally used at pH 7.5–9, which is considerably lower than that of the corresponding alkali products. Neutral cleaners are on the basis of chemical soaps, with additions of surfactant (to improve cleaning, wetting, penetration, and defoaming), corrosion inhibitors (which may be nitrite or organic), and a bactericide.

Neutral cleaners provide the benefits of generally lower operating temperatures, reduced odor, easier effluent treatment, and improved health and safety considerations over the alkali or emulsion products. Because of the inhibited nature of the surface produced, such products are used for inter stage cleaning and prior to assembly. The surface is generally not suitable for immediate painting.

4.01.2.3 Acidic Cleaners

The vast majority of acid-based cleaning products are designed for the removal of scale, rust, and other oxide films. These products may also contain solvents and surfactants to degrease and derust simultaneously. There are, however, certain acid-based materials which can primarily be construed as cleaners. One such type of material is used in the cleaning of aluminum cans prior to treating and lacquering. Such cleaners are normally on the basis of sulfuric or phosphoric acid, with, generally, additions of hydrofluoric acid and surfactants. These materials are sprayed on to preformed cans to remove the lubricant used during the can-forming operation. The fluoride is present to enhance the removal of fine metal swarf as well as to remove the oxide film.

Fluoride-free acid cleaners are used for general pretreatment cleaning of aluminum as an alternative to strong alkali materials. Although more expensive in terms of initial make-up and plant requirements the rate of material loss through cleaning and etching is reduced. Furthermore, the need for an acid de-smut (required after alkali cleaning) can be eliminated.

As the surface smoothing and leveling effects are somewhat limited, the use of acid cleaners prior to anodizing or electropainting, where surface defects can be enhanced, is not common. Care must be taken here not to confuse acid cleaners with high-strength, phosphoric acid-based chemical polishes and chemical brighteners, which are used to obtain specific types of attractive surface finish. Also in the category of acid cleaners could be considered the lightweight alkali–metal phosphating cleaner–coater solutions; a fuller discussion of such materials is best left to specialist publications on metal pretreatment chemicals.

4.01.2.4 Alkaline Cleaners

Alkali cleaners can be used before almost every conceivable metal finishing operation at one stage or another; they can be used by spray, by immersion, by manual application or by all three, or maybe by two out of the three methods. They can come as powders or as made-up liquids. They may be single or multipack, to be used as supplied or at a range of dilutions. They may require high temperatures or work successfully at ambient temperature. They may be suitable for cleaning one metal only or have multimetal capability. The user thus has an immense range from which to choose.

Consideration will first be given to the inorganic species used to produce the base material. The pH values of several commonly used materials are shown in Table 1. Hydroxides are the simplest, strongest alkalis and most commonly used. A major effect of hydroxides in cleaning is saponification: the conversion of certain oils and greases to water-soluble soap-type materials.

Beside the benefits of hydroxides must be placed certain disadvantages:

1. The possible passivation of iron and steel surfaces; this can be a problem prior to chemical conversion coatings.
2. The soaps produced by saponification may give excessive foam during spray cleaning or react with hard-water salts to form scum and scale.
3. Amphoteric metals, such as zinc and aluminum, can be attacked (i.e., corroded) more than is desirable.
4. Powder products formulated with too much hydroxide can be hygroscopic and thus tend to form solid blocks in storage rather than remaining as free-flowing powders.
5. Spray cleaners based on hydroxide can pick up carbon dioxide from the atmosphere and such carbonated solutions become less effective.

Table 1 pH values of selected alkalis as 1 wt% solution at 50°C

Alkali	*pH*
NaOH	12.7
Na_2CO_3	11.3
Na_2SiO_3	12.2
Na_3PO_4	11.8
$Na_2P_2O_7$	10.6
$Na_5P_3O_{10}$	9.8
$Na_2B_4O_7$	9.3
$NaC_7H_{13}O_8$	7.8

Carbonates and bicarbonates are used as lower alkalinity adjuncts or substitutes for hydroxide and are more resistant to carbonation during spraying than hydroxide-only solutions. Powder products blended with light sodium carbonate are much less hygroscopic and the carbonate can be a useful ‘carrier’ for liquid additives, such as surfactants and solvents.

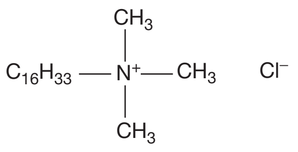
Silicates can offer an almost complete cleaning system on their own. Sodium silicate, the most commonly used of these materials, has a high enough pH value to cause saponification on its own and the anion formed gives a certain degree of detergency and inhibition. Thus, silicates are often found in multimetal cleaners. Light metals, such as zinc and aluminum will generally not be attacked if the silicate level is sufficiently high and the free hydroxide level sufficiently low. However, cleaners containing silicate can cause problems. They should not be used prior to an alkaline process on aluminum, owing to the formation on the surface of alkali-insoluble aluminum silicate. Cleaners containing silicates can also cause problems if used prior to some surface-sensitive treatments, such as use of zinc phosphating solutions.

Other common ingredients of alkaline cleaners include phosphates, which have both detergent and dispersive properties; also, the polyphosphates have water softening capabilities. In addition, borates are often the base for light-duty cleaners, because of their inhibiting action and less alkaline pH. They can also be used, to a certain extent, as a substitute for phosphates when a phosphate-free product is required. The organic acid salts, such as EDTA and heptonate, are included for water softening properties and to assist in the removal of solid particles. Gluconate and heptonate, in particular, are effective in the highly alkaline solutions used for etching aluminum and prevent the precipitation of aluminum hydroxide scale and sludge.

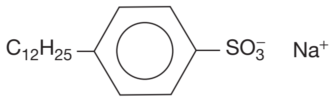
Surfactants are probably the materials which most affect the performance of alkali cleaners. Surfactants are chemicals that modify the solubility of various materials in, and their surface affinity for, oil and water. The diverse composite which makes up the surface of a metal object must be fully wetted out if the cleaner is to perform properly. Surfactants lower the surface tension to allow wetting out to occur. Oils and greases must either be dissolved off the surface or lifted from it; surfactants assist in both areas.

There are four broad categories of surfactant on the basis of the charge associated with the active part of the molecule (typical examples of each are given in Figure 1):

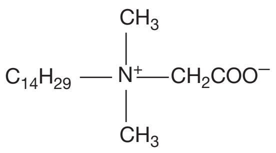
1. cationic, where the residual charge is positive;
2. anionic, where the residual charge is negative;
3. amphoteric, where there exists both positive and negative charge centers;
4. nonionic, where there is no residual change.



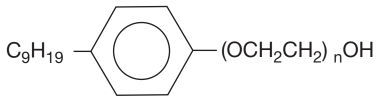
Cetyl trimethyl ammonium chloride (cationic)



Sodium dodecyl benzene sulphonate (anionic)



Myristyl dimethyl betaine (amphoteric)



Polyethoxylated nonyl phenol (nonionic)

Figure 1 Common surfactants of each main category.

Care must be taken with some surfactant-containing cleaners not to exceed certain temperature and concentration limits. Thus, it is not always true that the hotter and more concentrated the solution, the better the cleaning. Many commonly used surfactants have limited solubility in alkali and become less soluble as the alkalinity, ionic strength, and temperature rise. A point can, therefore, be reached when the surfactants come out of solution and, in immersion cleaning especially, performance will suffer drastically. Similarly, some spray cleaners are designed to work above a certain minimum temperature and strength. In this case, a surfactant is designed to come out of solution to act as a defoamer for the system. Examples of typical simple formulations for various types of alkali cleaners are given in Table 2.

4.01.2.5 Acid Pickling of Ferrous Materials

The hot rolling of steel produces a surface layer of complex oxides known as 'millscale.' It is unstable and must be removed prior to painting if reliable performance is to be obtained. Removal of millscale may be accomplished by a variety of methods but it is traditionally removed by pickling in strong acid containing one or more corrosion inhibitors.

4.01.2.5.1 Formation of millscale

When mild steel is heated in air an oxide or scale will form on the steel surface. This scale consists of three well defined layers, whose thickness and composition depend on the duration and temperature of heating. In general, the layers, from the steel base outwards,

Table 2 Typical formulations for alkali cleaners

Constituent	*Composition (%)*				
NaOH	20	60	20	0	0
Na_2SiO_3	50	20	40	60	0
$Na_2CO_3/NaHCO_3$	20	10	20	10	20
Na_3PO_4	–	–	12	20	20
$EDTANa_4$	5	5	5	5	8
$Na_2B_4O_7$	–	–	–	–	50
Surfactant	5	5	3	5	2
Substrate application	Steel immersion	Steel electrocleaning	Zinc electrocleaning	Multimetal immersion	Aluminium spray

comprise a relatively thick layer of wüstite, the composition of which approximates to the formula FeO, a layer of magnetite (Fe_3O_4), and a thin layer of hematite (Fe_2O_3).

When the steel is rapidly cooled, the thickness and composition of these layers remain more or less unchanged, but when it is slowly cooled through 575 °C the scale becomes enriched in oxygen and the remaining wüstite layer breaks down to some extent into an intimate mixture of finely divided iron and magnetite.[1] Holding the temperature between 400 and 575 °C causes the iron particles to agglomerate and the scale becomes further enriched in oxygen. As wüstite is unstable below 575 °C, scales produced at temperatures lower than this contain magnetite and hematite only. In addition, the scales are often cracked and porous. This is due to the difference in contraction between scale and metal on cooling and to the change in volume when the metal is oxidized.

4.01.2.5.2 Mechanism of scale removal

When steel that has been slowly cooled through 575 °C is immersed in mineral acid, the acid penetrates through the cracks and pores in the upper layers of scale and rapidly attacks the oxide layers (Figure 2). The iron, being anodic, dissolves to form ferrous ions and the magnetite, being cathodic, is reduced, forming more ferrous ions. As the three constituents of these cells are good electrical conductors, their resistance is sufficiently small so that the rate of dissolution is largely governed by the rate at which acid diffuses in through the cracks and the rate at which spent acid diffuses out through them. A similar but slower action occurs between the exposed metal and the magnetite and hematite layers which have not been detached.

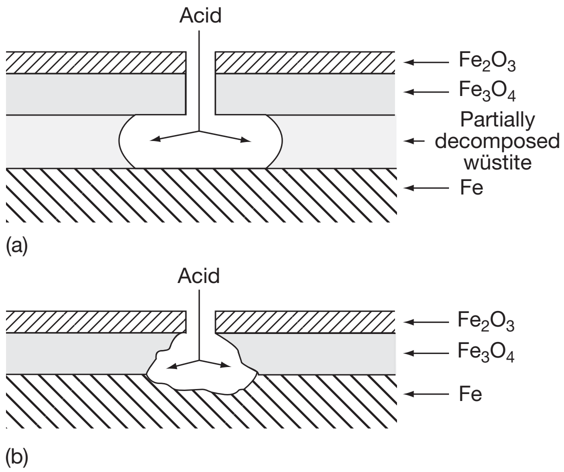


Figure 2 Mechanism of scale removal with acid: (a) high temperature scale and (b) low-temperature scale.

The mechanisms of oxide dissolution and scale removal have been widely studied and have been thoroughly reviewed by Frenier and Growcock,[2] who concluded, in agreement with others,[3] that oxide removal from the surface of steel occurs predominantly by a process of reductive dissolution, rather than by chemical dissolution, which is slow in mineral acids. In this process the reduction of the ferric components of the scale is coupled to oxidation of the base metal, both reactions yielding ferrous species readily soluble in the acid. For magnetite the processes are:

1. $Fe_3O_4 + 8H^+ + 2e^- = 3Fe^{2+} + 4H_2O$
2. $Fe = Fe^{2+} + 2e^-$

Scale removal is also assisted by the dissolution of the underlying metal by normal acid corrosion processes, which undermines the scale, and by the physical effect of hydrogen gas evolved in this latter reaction.

In general there does not appear to be any direct correlation between the rate of the chemical dissolution of oxides and the rate of scale removal, although most work on oxide dissolution has concentrated on magnetite. For example, Gorichev and coworkers have studied the kinetics and mechanisms of dissolution of magnetite in acids[4,5] and found that it is faster in phosphoric acid than in hydrochloric, while scale removal is slower in the former. Also, ferrous ions accelerate the dissolution of magnetite in sulfuric, phosphoric and hydrochloric acids, whereas the scale removal rate is reduced by the addition of ferrous ions. These observations appear to emphasize the importance of reductive dissolution and undermining in scale removal, as opposed to direct chemical dissolution.

As further confirmation of this Rozenfeld[3] has reviewed Russian work on this subject and reports that in pickling with sulfuric acid the amount of acid used in scale dissolution is only about one-tenth that consumed by the dissolution (corrosion) of the underlying metal. However, in hydrochloric acid the direct scale dissolution occurs to a much greater degree, and is responsible for about 40% of the acid consumption.

A mechanism such as that given above provides explanations for the known effects of many process variables. The reductive dissolution and undermining processes require access of the acid to the metal surface, hence the benefits obtained by the deliberate introduction of cracks in the oxide by cold-working prior to pickling. Also the increase in pickling rate with agitation or strip velocity can be explained in terms of the avoidance of acid depletion at the oxide–solution interface.

4.01.2.5.3 Hydrogen embrittlement

Although the majority of the hydrogen produced on the cathodic areas is evolved as gas and assists the removal of scale, some of it diffuses into the steel in the atomic form and can render it brittle. Hardened and higher carbon ferritic steels are particularly susceptible to this hydrogen embrittlement and cracks may appear during pickling. Austenitic steels, however, are much more resistant to embrittlement because of the lower diffusivity of hydrogen in the face-centered cubic lattice. Certain impurities (e.g., arsenic, sulfur, antimony, etc.) promote the dissolution of hydrogen into the metal (or inhibit the hydrogen recombination reaction generating hydrogen gas, which amounts to the same thing). Consequently, this increases the quantity of hydrogen that diffuses into the steel and the consequent risk of embrittlement. Several theories of the mechanism of embrittlement have been put forward[6,7] and these are discussed in more detail elsewhere in this volume.

As well as causing brittleness, absorbed gas may combine to form molecular hydrogen on the surface of inclusions and voids within the steel. Thus a gas pressure is set up in the voids and this may be sufficient to cause blisters to appear either during pickling or during subsequent processing such as hot-dip galvanizing. The embrittlement effect can be largely removed by heat treatment of the steel at 150–200 °C, but even then the original ductility may not be entirely restored. In estimating the degree of embrittlement, the temperature and rate of testing have an important effect. Thus the embrittlement tends to disappear at very low and very high temperatures and is reduced at high strain rates.

4.01.2.5.4 Pickling of alloy steels

The furnace scales which form on alloy steels are thin, adherent, complex in composition, and more difficult to remove than from nonalloy steels. Several mixed acid pickles have been recommended for stainless steel, the type of pickle depending on the composition and thickness of the scale.[8] For lightly-scaled stainless steel, a nitric–hydrofluoric acid mixture is suitable, the ratio of the acids being varied to suit the type of scale. Strict chemical control of this mixture is necessary, as it tends to pit the steel when the acid is nearing exhaustion. For heavy scale, two separate pickles are often used. The first conditions the scale and the second removes it. For example, a sulfuric–hydrochloric acid mixture is recommended as a scale conditioner on heavily scaled chromium steels and a nitric–hydrochloric acid mixture for scale removal. A ferric sulfate–hydrofluoric acid mixture has advantages over a nitric–hydrofluoric acid mixture in that the loss of metal is reduced and the pickling time is shorter, but strict chemical control of the bath is necessary.

Electrolytic pickling of stainless steel in 5–10% (w/v) sulfuric acid at 50 °C can be used for removing the majority of the scale. The strip is first made anodic, when a little metal dissolves, and then cathodic, when the evolved hydrogen removes the loosened scale. To complete the pickling, a nitric plus hydrofluoric acid dip is given for austenitic steels and a nitric acid dip for ferritic steels.

The chromium-containing oxides on stainless steels are more resistant to reductive dissolution and harder to remove than oxides on mild steel. Typically mixed acids and multistage treatments are used and many formulations have been reported.[9] Scale conditioning can be carried out in acids, in molten salts (e.g., sodium hydroxide plus sodium nitrate) or in alkaline solutions (e.g., alkaline permanganate). Scale removal can be obtained with a variety of acids, the commonest being a nitric/hydrofluoric mixture. Rozenfeld[3] also reports effective pickling with ferric sulfate plus sulfuric acid mixtures and considers that the effect of the ferric ions is to speed up the dissolution of the underlying metal. Organic acids, such as citric acid, also have a role in the cleaning of lightly corroded alloy steels.[10]

4.01.2.5.5 Pickling inhibitors

Organic inhibitors

During the pickling of scaled steel, the thinner and more soluble scale is removed before the thicker and less soluble scale. Consequently, some exposed base metal is attacked before the pickling operation is complete. In order to reduce this acid attack to a minimum, corrosion inhibitors are used. Although an effective inhibitor reduces acid attack, it does not prevent the attack of oxidizing agents on the exposed base metal. Thus, the ferric ions resulting from the gradual dissolution of the detached magnetite and hematite may, even in the presence of an inhibitor, attack the exposed steel causing pitting.

Clearly, the selected inhibitor should not decompose during the life of the pickle nor decrease the rate of scale removal appreciably. Some highly efficient inhibitors, however, do reduce pickling speed a little. It would be expected that as the hydrogen evolution is reduced the amount of hydrogen absorption and embrittlement would also be reduced. This is not always the case; thiocyanate inhibitors, for example, actually increase the absorption of hydrogen.

Many organic substances soluble in acid or colloidally dispersible have been shown to have inhibiting properties. The most effective types contain a nonpolar group such as a hydrocarbon chain and a polar group such as an amine. They contain oxygen, nitrogen, sulfur, or other elements of the fifth and sixth groups of the Periodic Table. They include alcohols, aldehydes, ketones, amines, proteins, amino acids, heterocyclic nitrogen compounds, mercaptans, sulfoxides, sulfides, substituted ureas, thioureas, and thioazoles.

The efficiency of an inhibitor (I) under a given set of conditions can be expressed by the ratio of the decreased corrosion rate as a function of the original uninhibited corrosion rate (as a percentage):

$$I = \frac{\begin{array}{c}(\text{Unhibited corrosion rate} - \\ \text{Inhibited corrosion rate})\end{array}}{\text{Inhibited corrosion rate}} \times 100\%$$

In general the efficiency increases with an increase in inhibitor concentration; typically an effective inhibitor gives >95% inhibition at a concentration of 0.01 wt% and ∼90% at ∼0.005 wt%. Provided the inhibitor is stable, increase in temperature usually increases the efficiency although the actual acid attack may be greater. A change in acid concentration, or in type of steel, may also alter the efficiency. Thus, the conditions of a laboratory determination of efficiency should closely simulate the conditions expected in commercial practice.

Figure 3 shows the relationship between efficiency and concentration of some thiourea derivatives and gelatin in the pickling of cold-reduced and annealed strip in 6 wt% sulfuric acid at 85 °C. The thiourea derivatives, diluted with sodium chloride, gelatin and a wetting agent, are used commercially. Mono- and di-*O*-tolyl thioureas are stable in this pickle for at least 50 h, but diphenyl thiourea and gelatin decompose after 4 or 5 h.

The principles behind the selection of effective inhibitors for steel in the various acids have been reviewed by Schmitt[11] and Gardner.[12] The selection of an inhibitor is dependent on both the metal and the acid. For steel, in general, nitrogen-based inhibitors (e.g., amines and heterocylic compounds) are used in hydrochloric acid, whereas sulfur-containing ones (e.g., thiourea and its derivatives) find more favor in sulfuric acid.

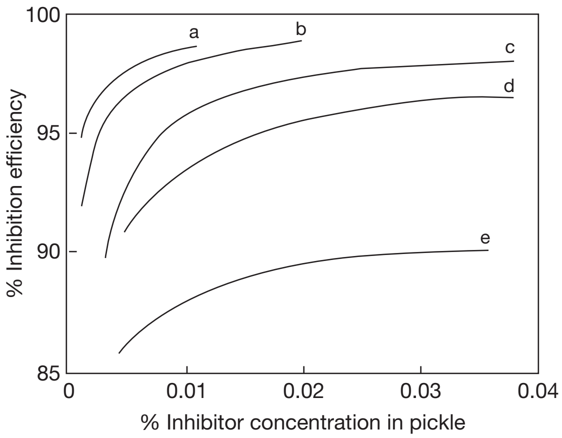


Figure 3 Relationship between % inhibitor efficiency and inhibitor concentration in 6 wt% H_2SO_4: (a) di-*o*-tolyl thiourea; (b) mono-*o*-tolyl thiourea; (c) commercial inhibitor containing 20% di-*o*-tolyl thiourea; (d) commercial inhibitor containing 20% diphenyl thiourea; and (e) gelatin.

Given the reductive dissolution process involved and the contributions from undermining and hydrogen evolution in scale removal, inhibitors might be expected to affect the rate of this removal. Also, if the inhibitor adsorbs on the oxide surface then the rate of chemical dissolution of the oxide may be affected. Experimental evidence suggests that these effects may occur, depending on the acid and the inhibitor. Cumper[13] has shown that pyrrole and indole can increase the rate of dissolution of magnetite in hydrochloric acid. It has been reported[14] that commercial amine-based inhibitors can either increase or decrease the rate of scale removal in the same acid. Other reports suggest that the presence of inhibitor has little effect on scale removal rate in hydrochloric acid but markedly decreases it in sulfuric acid. One area that has not been widely studied is the effectiveness of inhibitors on scaled surfaces, but there is experimental evidence that the presence of magnetite scales can significantly affect the performance of nitrogen-based inhibitors in alkaline solutions used for chemical cleaning.

Inorganic inhibitors

Inorganic inhibitors are salts of metals having a high hydrogen overvoltage, for example, antimony and arsenic salts. The inhibiting action is associated with the formation of a coating of the metal, which, being cathodic to the steel and having a high hydrogen overvoltage, prevents the discharge of hydrogen ions and so stops the dissolution of the steel. These inhibitors are seldom used in commercial practice, but antimony chloride dissolved in concentrated hydrochloric acid is used in the laboratory for stripping deposits of zinc, cadmium, tin, and chromium from steel, and with the addition of stannous chloride for removing scale and rust.[15]

4.01.2.6 Acid Pickling of Nonferrous Metals

Although less common, acids are also used for the removal of oxide and scale from nonferrous metals and alloys. Table 3 summarizes a number of pickling solutions for selected materials.

4.01.2.6.1 Electrochemical cleaning

A significant increase in immersion cleaning performance can be achieved by local agitation caused by vigorous gas evolution on the surface of the workpiece. Thus, the use of an applied cathodic voltage evolves hydrogen, which provides a ‘scrubbing’ action, greatly enhancing the cleaning process. However, during cathodic cleaning any dissolved metal ions in solution will tend to plate-out on the metal surface, so the work will normally be given a short anodic cycle at the end of the cleaning time to dissolve this contamination. Also, periodic reverse cathodic–anodic cycling is another way of achieving the same effect. Anodic cleaning can also be performed as a small fraction of the metal is dissolved, thereby simultaneously removing any contamination; however, this should be done with care, as otherwise the workpiece may be destroyed.

For electrocleaning, care must be taken that a solution of sufficiently high conductivity is used to prevent solution voltage drops and ‘burning’ of workpieces in high current density areas. Clearly, excessively high anode current densities should be avoided as these will cause excess corrosion/dissolution of the workpiece. Care must also be taken during cathodic cleaning of steel alloys as hydrogen embrittlement, which must always be considered a risk during cathodic cleaning, must be either avoided or allowed for.

4.01.2.7 Ultrasonic Cleaning

Another method for introducing mechanical action into immersion cleaning is by the use of ultrasonic agitation. Here, a high frequency vibration is imparted to the solution. At the surface to be cleaned, minute bubbles are formed by local cavitation of the fluid. When they collapse, they impart a high degree of local agitation, thereby efficiently removing any surface contamination.

4.01.3 Mechanical Cleaning

4.01.3.1 Flame Cleaning

Now little used as a preparatory method, flame cleaning is a process whereby an intensely hot flame is played on the surface of the steel. In theory, differential expansion causes millscale to detach. In practice, there is evidence that the treatment may not remove thin, tightly adhering millscale. Also, steel less than 5 mm thick can buckle. Finally, the process can ‘burn in’ chemicals deposited on the surface, causing premature paint failure.

4.01.3.2 Manual Cleaning

The term encompasses all manual and mechanical methods of cleaning other than blast-cleaning, for example abrasive discs, wire brushes, scrapers, vibratory needle guns and chipping hammers are all

Table 3 Pickling solutions for nonferrous metals

Metal	*Acid*	*Temperature*	*Time*
Copper and brass (60–90% Cu, 10–40% Zn)	7–25% (w/w) H_2SO_4 or 15–25% (w/w) HCl	15–60 °C 15 °C	1–10 min 1–3 min
Aluminimum bronze (82–95% Cu, 5–10% Al, 0–5% Fe, 0–5% Ni)	Scale conditioned with 10% (w/w) NaOH followed by H_2SO_4 or HCl as above	75 °C	2–5 min
Copper–silicon alloys (96–97% Cu, 1–3% Si)	7–25% (w/w) H_2SO_4 + 1–3% (w/w) HF	15 °C	1–5 min
Nickel–copper alloys (55–90% Cu, 10–30% Ni, 0–27% Zn)	10% (w/w) HCl + 1.5% (w/w) $CuCl_2$	80 °C	30 min
Nickel–chromium alloys (35–80% Ni, 16–20% Cr, 0–45% Fe, 0–2% Si)	Scale conditioned with 20% NaOH + 5% (w/w) $KMnO_4$ followed by 20% (w/w) HNO_3 + 4% (w/w) HF	100 °C 50 °C	1–2 h 5–30 min
Aluminium alloys (0–10% Cu, 0–30% Mg, 0–6% Zn, 0–12% Si)	25% (w/w) H_2SO_4 + 5% (w/w) CrO_3 40% (w/w) HNO_3 + 1–5% (w/w) HF	65 °C 15 °C	20 min 1–5 min
Magnesium alloys (0–10% Al, 0–3% Zn. 0–0.2% Mn)	10–20% (w/w) CrO_3 + 3% (w/w) H_2SO_4	100 °C 25 °C	1–30 min 15 s

available. Manual cleaning removes neither tightly adhering millscale nor deep-seated rust from pits. None the less, it is often used for maintenance work or for the preparation of new steelwork to be exposed in nonaggressive conditions. Manual cleaning is rarely used in conjunction with, as it is inappropriate for, high-performance long-life systems, for example, two-pack chemically curing coatings which require a high standard of blast cleaning.

4.01.3.3 Abrasive Blast Cleaning

Abrasive blast cleaning uses the action of abrasive particles suspended in a fluid (e.g., air or water) in order to remove surface contamination by mechanical action. Thus, abrasive particles are directed at high velocity against the blasted surface by means of compressed air, high-pressure water, or centrifugal force from an impeller wheel. As the surface removal rate can be controlled by choice of equipment, abrasive grit and blast parameters, all kinds of surfaces may be prepared including heavily rusted steel and concrete, as well as lightly contaminated surfaces.

4.01.3.3.1 Surface finish

Surface ‘finish’ commonly means surface cleanliness. It is important to remember that cleanliness refers not only to the degree of residual rust present, but also to the level of surface chemical contamination from soluble salts and from condensed moisture layers, all of which will detrimentally affect coating adhesion and ultimate performance.

4.01.3.3.2 Surface profile

Blast-cleaning produces a roughened surface, the size and nature of which is largely determined by the type and size of the abrasive used. The nature of the profile is important, especially for application of organic coatings (paints) and for thermally sprayed metal coatings. This is because the profile acts to aid the mechanical ‘keying’ of the coating to the surface and, hence, greatly increases coating adhesion. Likewise, the peak-to-trough profile roughness should not be excessive as this causes rogue peaks from the substrate to penetrate beyond the coating surface. Finally, profiles should be relatively open as excessively compressed surfaces will contain pores and defects underneath the coating that can act as reservoirs for chemical contamination and certainly will prevent coating penetration to the complete surface.

4.01.3.4 Ultrahigh Pressure Water Jetting

Water jetting is a convenient method for light cleaning and washing of surfaces. However, if the pressure of the water is increased significantly, the fluid becomes capable of removing, with high efficiency, relatively loosely adherent materials on a surface, including organic coatings. Water jetting also leaves surfaces relatively free of soluble salt contamination, which is a considerable advantage. Because of the kinetic energy of the water droplets on hitting the blasted surface, ultrahigh pressure water jetting leaves a dry, slightly warm surface that is free of dust and which dries relatively quickly; therefore, repainting can be carried out without significant delay.

The recent trend is to increase pressures as less volume of water is used. Thus, ultrahigh pressure (>170 MPa) water jetting equipment is becoming preferred as disposal costs for contaminated water are reduced. Water jetting cannot change an existing surface profile; hence if this is inadequate, abrasive blasting is to be preferred. However, for surfaces that have an adequate abrasive blast profile, it is sufficient to merely remove the defective coating and water jetting can be a highly economical option to achieve this end.

4.01.3.5 Health, Safety, and the Environment

In all surface preparation methods, including chemical and mechanical cleaning options, health, safety and environmental concerns are essential. Organic solvents are toxic and clearly have high VOC levels while aqueous alternatives may still possess significant organic content; in both cases operator protection and chemical disposal need to addressed adequately. Organic-free chemical cleaners are frequently highly corrosive (acidic or alkaline), and also require correct neutralization and disposal procedures. Mechanical cleaning operations contain their own danger, not the least of which is the safety of the operator; to this end correct operator training, especially for abrasive and water jetting operations, is essential. Finally, waste abrasive grit and paint are frequently contaminated by toxic heavy metals previously used as corrosion inhibitive pigments (i.e., lead, chromium, etc). Removal and disposal of such materials often require a special license and certainly require great care and attention to detail.

4.01.4 Standards

Generally standards for surface preparation, especially for surfaces subsequently to be painted, use visual comparisons. In all such standards, some caution should be exercised because the color reproduction may vary from one copy to another.

Standards for degrees of surface rusting are described in ISO 8501-1 as follows:

(a) Steel surface largely covered with adhering mill scale, but little if any rust.
(b) Steel surface which has begun to rust and from which mill scale has begun to flake.
(c) Steel surface on which the mill scale has rusted away or from which it can be scraped, but with slight pitting visible under normal vision.
(d) Steel surface on which the mill scale has rusted away and on which general pitting is visible under normal vision.

Surface rust and millscale must be removed before surface protection is applied. Where this is done by abrasive blasting, standards of surface cleanliness are also described in ISO 8501-1 and are on the basis of the original Swedish SIS 05 5900:

Sa 1: Light blast cleaning.
Sa 2: Thorough blast cleaning.
Sa 2½: Very thorough blast cleaning.
Sa 3: Blast cleaning to visually clean steel.

The minimum standard that is normally accepted for organic coating of steel structures is the Sa 2½ grade, which is generally achievable in the field using handheld equipment. Sa 3, which is effectively blasting to white metal, can be achieved using modern automated shot-blast plant under factory conditions.

References

1. Pfeil, L. B. *J. Iron Steel Inst.* **1931**, 123, 237.
2. Freiner, W. W.; Growcock, F. B. *Corrosion* **1984**, *40*, 663.
3. Rozenfeld, I. L. *Corrosion Inhibitors*; McGraw-Hill, 1981.
4. Gorichev, I. G.; Klyuchnikov, N. G.; Bibikova, Z. P.; Boltovskaya, I. G. *Russ. J. Phys. Chem.* 1976, 50.
5. Gorichev, I. G.; Gorsheneva, V. F.; Boltovskaya, I. G. *Russ. J. Phys. Chem.* **1979**, *53*, 1293.
6. Petch, N. J.; Stables, P. *Nature (London)* **1952**, *169*, 842.
7. Morlet, J. G.; Johnson, H. H.; Troiano, A. R. *J. Iron Steel Inst.* **1958**, *189*, 37.
8. Spencer, L. F. *Metal Finish.* **1954**, *52*(2), 54.
9. Roberts, W. J. In *Cleaning Stainless Steel*; ASTM Special publ. 538, 1972; p 77.
10. Blume, W. J. In *Cleaning Stainless Steel*; ASTM Special publ. 538, 1972; p 43.
11. Schmitt, G. *Br. Corros. J.* **1984**, *19*, 165.
12. Gardner, G. In *Corrosion Inhibitors*; Nathan, C. C., Ed.; NACE, 1973; p 156.
13. Cumper, C. W. N.; Grzeskowiak, R.; Newton, P. *Corros. Sci.* **1982**, *22*, 551.
14. Riggs, O. L.; Hurd, R. M. *Corrosion* **1968**, *24*, 45.
15. Clarke, S. G. *Trans. Electrochem. Soc.* **1936**, *69*, 131.

Further Reading

Hudson, R. *Guide to Good Practice in Corrosion Control: Surface Preparation for Coatings*; National Corrosion Service, National Physical Laboratory: UK, 2000.

Freeman, D. B. *Phosphating and Metal Pre-treatment*; Woodhead, 1986.

Plaster, H. S. *Blast Cleaning and Allied Processes;* Industrial Newspapers, 1972/1973; Vol. I/II.

Relevant Websites

www.waterjetting.org.uk – Water Jetting Association.
www.sspc.org – Steel Structures Painting Council/Society for Protective Coatings (SSPC).

Standards

Swedish Standard SIS 05 5900: ''Pictorial surface preparation standards for painting steel surfaces''
BS 7079:2009: ''General introduction to standards for preparation of steel substrates before application of paints and related products''
BS EN ISO 8501: ''Preparation of steel substrates before application of paints and related products: Visual assessment of surface cleanliness''
BS EN ISO 8502: ''Preparation of steel substrates before application of paints and related products: Tests for the assessment of surface cleanliness''
BS EN ISO 8503: ''Preparation of steel substrates before application of paints and related products: Surface roughness characteristics of blast-cleaned steel substrates''
BS EN ISO 8504: ''Preparation of steel substrates before application of paints and related products: Surface preparation methods''
BS EN ISO 11124: ''Preparation of steel substrates before application of paints and related products: Specifications for metallic blast-cleaning abrasives''
BS EN ISO 11125: ''Preparation of steel substrates before application of paints and related products: Test methods for metallic blast-cleaning abrasives''
BS EN ISO 11126: ''Preparation of steel substrates before application of paints and related products: Specification for nonmetallic blast-cleaning abrasives''
BS EN ISO 11127: ''Preparation of steel substrates before application of paints and related products: Test methods for nonmetallic blast-cleaning abrasives''
BS ISO 27831: ''Metallic and other inorganic coatings: Cleaning and preparation of metal surfaces''

4.02 Phosphate Coatings

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Glossary

Diacetone alcohol 4-Hydroxy-4-methyl-2-pentanone: $(CH_3)_2C(OH)CH_2COCH_3$
Hopeite Hydrated zinc phosphate of composition: $Zn_3(PO_4)_2{\cdot}4H_2O$
Hureaulite Hydrated manganese iron phosphate of composition: $(Mn,Fe)_5(PO_4)_4{\cdot}4H_2O$
Phosphophyllite Hydrated iron–zinc phosphate of composition: $FeZn_2(PO_4)_2{\cdot}4H_2O$
Scholzite Hydrated zinc calcium phosphate of composition: $CaZn_2(PO_4)_2{\cdot}2H_2O$
Vivianite Hydrated iron phosphate of composition: $Fe_3(PO_4)_2{\cdot}8H_2O$

Abbreviations

BS British Standard
BSTSA British Surface Treatment Suppliers Association
EN European Norm
ISO International Standards Organisation
Me In a chemical equation, represents the metal ion (e.g., Fe, Zn, Mn, etc.).

4.02.1 Introduction

Phosphate treatments are readily adaptable to production requirements for articles of all sizes, and for large or small numbers. Mild steel sheet is the material most frequently subjected to phosphate treatment, but a great variety of other ferrous surfaces is also processed. Examples include cast-iron plates and piston rings, alloy steel gears, high-carbon steel cutting tools, case-hardened components, steel springs and wire, powdered iron bushes and gears, etc. Phosphate treatments designed for steel can also be used for the simultaneous treatment of zinc die-castings, hot-dipped zinc, and zinc-plated articles. However, if there is a large quantity of these nonferrous articles, it is often more economical to phosphate them without the steel. Aluminum articles may also be phosphated; however, these require somewhat different bath chemistries.

The usual method of applying phosphate coatings is by immersion, using a sequence of tanks that includes degreasing and phosphating stages, with their respective rinses. The treatment time ranges from 3 to 5 min for thin zinc phosphate coatings and up to 30–60 min for thick zinc, iron, or manganese phosphate coatings. The accelerated zinc phosphate processes lend themselves to application by power spray, and the processing time may then be reduced to 1 min or less. Power spray application is particularly advantageous for mass-production articles such as motorcars and refrigerators, as the conveyor can run straight through the spray tunnel, which incorporates degreasing, rinsing, phosphating, rinsing, and drying stages. Flow-coating and hand spray-gun application are sometimes employed when a relatively small number of large articles have to be phosphated.

4.02.2 Phosphate Coating Formation

4.02.2.1 Deposition Mechanism

All conventional phosphate coating processes are based on dilute phosphoric acid solutions of iron, manganese, and zinc dihydrogen phosphates either separately or in combination. The free phosphoric acid in these solutions reacts with the iron surface undergoing treatment in the following manner[1]:

$$\mathrm{Fe} + \mathrm{H_3PO_4} \leftrightarrows \mathrm{Fe(H_2PO_4)_2} + \mathrm{HHh{\cdot}H_2} \qquad [1]$$

Thus, ferrous dihydrogen phosphate is produced and hydrogen is liberated. Local depletion of phosphoric acid occurs at the metal–solution interface. As the dihydrogen phosphates of iron, manganese, and zinc dissociate readily (i.e., are soluble) in aqueous solution, the following reactions take place:

$$\mathrm{Me(H_2PO_4)_2} \leftrightarrows \mathrm{MeHPO_4} + \mathrm{H_3PO_4} \qquad [2]$$

$$3\mathrm{MeHPO_4} \leftrightarrows \mathrm{Me_3(PO_4)_2} + \mathrm{H_3PO_4} \qquad [3]$$

$$3\mathrm{Me(H_2PO_4)_2} \leftrightarrows \mathrm{Me_3(PO_4)_2} + 4\mathrm{H_3PO_4} \qquad [4]$$

The neutralization of free phosphoric acid by reaction [1] alters the position of equilibrium of equations [2]–[4] towards the right and thereby leads to the deposition of the sparingly soluble hydrogen phosphates and insoluble phosphates on the metal surface.

As reaction [1] takes place even when the phosphating solution contains zinc or manganese phosphate with little or no dissolved iron, it will be seen that the simple (or nonaccelerated) phosphate treatment gives coatings that always contain iron phosphate derived from the ferrous parts being processed. After prolonged use, a manganese phosphate bath often contains more iron in solution than manganese and produces coatings with an iron content 2–3 times that of manganese.

The relation between free phosphoric acid content and total phosphate content in a processing bath, whether based on iron, manganese, or zinc, is very important; this relation is generally referred to as the acid ratio. An excess of free acid will retard the dissociation of the dihydrogen and hydrogen phosphates and hinder the deposition of the insoluble phosphate coating; sometimes excessive loss of metal takes place and the coating is loose and powdery. When the free acid content is too low, dissociation of phosphates takes place in the solution as well as at the metal/solution interface and leads to precipitation of insoluble phosphates as sludge. Nonaccelerated processes operated near boiling generally work best with a free-acid titration between 12.5% and 15% of the total acid titration.

A zinc phosphate solution tends to produce coatings more quickly than iron or manganese phosphate solutions, and dissociation of zinc dihydrogen phosphate proceeds rapidly through reaction [2] to [3] or directly to zinc phosphate via reaction [4]. Even so, a processing time of 30 min is usual with the solution near boiling. Another factor in the initiation of the phosphate coating reaction is the presence in the processing solution of phosphate, either as a colloidal suspension or as fine particles.[2] This effect is most apparent in zinc phosphate solutions, which produce good coatings only when turbid. The zinc phosphate particles can be present to a greater extent in cold processing solutions and may act as nuclei for the growth of many small crystals on the metal surface, thereby promoting the formation of smoother coatings.

Similarly, the ferric phosphate sludge formed during the processing of steel in a zinc phosphate solution can play a useful part in coating formation.[3] The solubility of ferric phosphate is greater at room temperature than at elevated temperatures, and is increased by the presence of nitrate accelerators. To allow for saturation at all temperatures, it is desirable always to retain some sludge in the processing bath. Coatings with optimum corrosion resistance are produced when the temperature of the bath is rising and causing supersaturation of ferric phosphate.

With zinc/iron/phosphate/nitrate baths, the iron content of the coating comes predominantly from the processing solution and very little from the surface being treated.[4] This greatly diminished attack on the metal surface by accelerated baths has a slight disadvantage in practice in that rust is not removed, whereas the vigorous reaction of the nonaccelerated processes does remove light rust deposits. The solution of iron represented in eqn [1] takes place at local anodes of the steel being processed, while discharge of hydrogen ions with simultaneous dissociation and deposition of the metal phosphate takes place at the local cathodes.[1] Thus, factors that favor the cathode process will accelerate coating formation and, conversely, factors favoring the dissolution of iron will hinder the process.

Application of a cathodic potential to the treated surface exerts an accelerating action, as the reaction at all cathodic areas is assisted and the formation of a phosphate layer is speeded accordingly. Conversely, an anodic potential results in the dissolution of iron at local anodes and hinders phosphate coating formation. An oxidizing agent acts as an accelerator by depolarization of the cathodes, raising the density of local currents so that rapid anodic passivation of active iron in the pores takes place. This inactivation of local anodes favors the progression of the cathodic process. The accelerating effect of alternating current is explained by the practical observation that the cathodic impulse acting protectively greatly exceeds in its effect the anodic impulse which dissolves iron. In a similar manner, the electrolytic pickling of iron with alternating current can dissolve iron at a slower rate than when no current is used.

Reducing agents have the same ultimate effect as cathodic depolarization in that they convert anodic regions into cathodic regions and increase the ratio of cathodic to anodic areas. Nitrogenous organic components such as toluidine, quinoline, aniline, etc. all act as inhibitors to the anodic reaction between metal and acid and thereby favor the cathodic reaction and accelerate the process.

4.02.2.2 Accelerators

The majority of phosphate processes in use are ‘accelerated’ to obtain shorter treatment times and lower processing temperatures. The most common mode of acceleration is by the addition of oxidizing agents such as nitrate, nitrite, chlorate, and hydrogen peroxide. By this means, a processing time of 1–5 min can be obtained at temperatures of 45–70 °C. The resultant coatings are much smoother and thinner than those from nonaccelerated processes, and, while the corrosion resistance is lower, they cause less reduction of paint gloss and are more suited to mass-production requirements.

The presence of nitrate as accelerator has a pronounced effect on the amount and composition of gas evolved from the work being treated[1] (**Table 1**). It will be observed that hydrogen evolution drops to a very low figure with the zinc/nitrate baths. The formation of nitrite arises from the oxidation of ferrous ion by nitrate leading to ferric ions, which will then deposit out as ferric phosphate:

$$2Fe^{2+} + NO_3^- + 2H^+ \leftrightarrows 2Fe^{3+} + NO_2^- + H_2O$$

In acid solution, the nitrite ion acts as an oxidizing agent. A slight degree of acceleration can be obtained by introducing traces of metals which are more noble than iron, for example nickel, copper, cobalt, and silver. These metals are deposited electrochemically over the iron surface undergoing treatment, thereby providing more active cathodic centers and promoting phosphate deposition. This method of acceleration has the disadvantage of leaving minute particles of the noble metal in the coating, and, in the case of copper, this can seriously inhibit the drying of some types of paint coatings.

4.02.3 Nature of Coatings

4.02.3.1 Types of Coating

Although there is a limited number of phosphate coating types, there are many specific bath compositions

Table 1 Amount and composition of the gases evolved on phosphating of 1 m^2 of sheet metal for deep drawing

Phosphate solution	*Pointage*[a]	*Time (min)*	*Amount of gas (cm^{3}m^2)*	*H_2 (%)*	*N_2 (%)*	*O_2 (%)*	*$N_2O + NO$ (%)*
Manganese phosphate	30	60	7000	87.5	11.4[b]	1.1	–
Zinc phosphate	40	30	2540	92.7	6.4[b]	0.9	–
Manganese phosphate (accelerated with nitrate)	30	15	3500	84.6	9.1	1.3	3.0
Zinc phosphate (accelerated with nitrate)	70	5	78	16.7	75.3	8.0	–
Zinc phosphate containing 1.5–2 g l^{-1} iron (accelerated with nitrate)	70	5	85	32.1	57.0	1.6	9.3

[a] A measure of the total of a phosphatine solution, as indicated by the number of ml of 0.1 s sodium hydroxide (4.0 g l^{-1}) needed to neutralise 10 ml of the phosphating solution to phenolphthalcin.

[b] Presumably from anrides present in the steel.

that have been formulated for optimization of particular applications and processes.[5] Lightweight amorphous iron phosphates provide excellent paint adhesion and are of low cost; however, the corrosion resistance is relatively poor. Lightweight (microcrystalline) zinc phosphate coatings offer higher corrosion resistance while still retaining very good adhesion for organic coatings. Heavy macrocrystalline zinc phosphates are used in applications such as fastener coatings or wire and tube drawing aids. Where used in this fashion, the coating provides excellent adhesion and a slightly porous surface that can act as a reservoir for drawing lubricants such as soaps and/or oils. Likewise, heavy-weight manganese–iron phosphates and calcium–zinc phosphates may be used to reduce galling on mating surfaces such as valve train components or hypoid gears. These coatings have good oil absorbing properties and provide good corrosion resistance when used with a rust-preventing oil. Military ordnance components are often finished by this method. Table 2 provides a summary of some types and applications of phosphate coatings.

4.02.3.2 Effect of Metal Surface

The state of the metal surface has a pronounced effect on the texture and nature of phosphate coating produced by orthodox processes. Heavily worked surfaces tend to be less reactive and lead to patchy coatings. Surface abrasive blasting greatly simplifies treatment and gives uniform phosphate coatings. Accidental contamination of sheet steel with lead has been shown to have an adverse effect on the corrosion resistance and durability of phosphate coatings and paint.[6]

Cleaning operations that make use of strong acids or strong alkalis tend to lead to the formation of excessively large phosphate crystals which do not completely cover the metal surface and therefore show inferior corrosion resistance; this is particularly serious if rinsing is inadequate between the preparatory treatment and the phosphating. Adherent dust particles can also lead to the formation of relatively large phosphate crystals, whereas surfaces that have been wiped beforehand show much smoother and more uniform phosphate coatings.

On the other hand, the provision of vast numbers of minute nuclei assists the phosphate coating reaction to start at a multitude of centers, resulting in a finely crystalline coating. This effect can be obtained chemically by a predip in a solution of sodium phosphate containing minutely dispersed traces of titanium or zirconium salts[7] or in weak solution of oxalic acid. This type of predip entirely eliminates any coarsening effect due to previous treatment in strong alkalis or acids.

4.02.3.3 Effect of Phosphate Solution

Improved nucleation within the phosphate solution itself can produce smoother coatings without the necessity of recourse to preliminary chemical treatment. This may be accomplished by introducing into the phosphating bath the sparingly soluble phosphates of the alkaline-earth metals or condensed phosphates such as sodium hexametaphosphate or sodium tripolyphosphate. Such modified phosphating baths produce smoother coatings than orthodox baths and are very much less sensitive to cleaning procedures.

Very thin coatings of iron phosphate can be produced by treatment with solutions of alkali-metal phosphate. These serve a useful purpose for the treatment of office furniture, toys, etc. where a high

Table 2 Types of phosphate coating

Type	*Mineral name*	*Formula*	*Coating weight ($g\,m^{-2}$)*	*Appearance*
Lightweight iron phosphate	Vivianite	$Fe_3(PO_4)_2{\cdot}8H_2O$	0.3–0.9	Iridescent pink/yellow/ blue to light gray
Microcystalline zinc phosphate	Hopeite or phosphophyllite	$Zn_3(PO_4)_2{\cdot}4H_2O$; $FeZn_2(PO_4)_2{\cdot}4H_2O$	1.4–2.7	Light gray
Macrocrystalline zinc phosphate	Hopeite or phosphophyllite	$Zn_3(PO_4)_2{\cdot}4H_2O$; $FeZn_2(PO_4){\cdot}4H_2O$	7.5–30	Light gray
Manganese iron phosphate	Hureaulite	$(Mn,Fe)_5(PO_4)_4{\cdot}4H_2O$	7.5–30	Dark gray to black
Calcium zinc phosphate	Scholzite	$CaZn_2(PO_4)_2{\cdot}2H_2O$	1.6–6.5	Light gray

Source: British Surface Treatment Suppliers Association, Technical Brochure: ''Metal pre-treatment.'' Available for download from http://www.bstsa.org.uk.

degree of protection is not required, and also as a base for phenolic varnishes or resin varnishes requiring high temperature curing, for example, at over 200 °C. The coating is of heterogeneous nature and contains less than 35% iron phosphate ($FePO_4 \cdot 8H_2O$) with the remainder probably γ-Fe_2O_3.[8]

Thin phosphate coatings can be formed by application of phosphoric acid solution alone, that is, not containing metallic phosphates, to a steel surface, sufficient time being allowed after application to enable complete reaction to take place. In this way, a thin film of iron phosphate can be formed. In practice, it is difficult to obtain complete conversion, and the remaining traces of phosphoric acid can cause blistering of paint coatings. This effect may be insignificant on rough, absorbent steel surfaces, for example, ship's plating, where heavy coats of absorbent paint are applied, and under these circumstances the treatment can enhance the corrosion resistance of the finishing system.

4.02.3.4 Composition and Structure

The simplest phosphate coating that is formed from a solution containing only ferrous phosphate and phosphoric acid consists of dark gray to black crystals of ferrous phosphate, $Fe_3(PO_4)_2$ and ferrous hydrogen phosphate, $FeHPO_4$, with a small proportion of ferric phosphate, $FePO_4$. Coatings formed from manganese phosphate solutions consist of $Mn_3(PO_4)_2$, and those from zinc phosphating solutions consist of $Zn_3(PO_4)_2$. With both the manganese and zinc type of coating, insoluble iron phosphates, derived from iron present in the bath, may also be present in solid solution. Iron from the surface being treated can also be present in the coating, particularly at the metal–phosphate interface. The PO_4^{3-} content of coatings may vary from 33% to 50%, whereas the theoretical PO_4^{3-} content is lowest, at 41%, in $Zn_3(PO_4)_2 \cdot 4H_2O$ and highest, at 63%, in $FePO_4$.

X-ray diffraction studies have given very good correlation between the mineral hopeite, $Zn_3(PO_4)_2 \cdot 4H_2O$, and the zinc phosphate coatings that form on steel.[9] $Zn_3(PO_4)_2 \cdot 4H_2O$ appears in three crystal forms: α-hopeite (rhombic plates), β-hopeite (rhombic crystals), and δ-hopeite (triclinic crystals). Their transition points are at 105, 140, and 163 °C, respectively. It has been observed[10] that zinc phosphate coatings heated in the absence of air lose their corrosion resistance at between 150 and 163 °C probably due to disruption in coating integrity due to the volume changes arising from the phase change. Likewise, manganese phosphate coatings lose their corrosion resistance at between 200 and 218 °C, where they lose between 75 and 80% of their water of hydration. It is assumed that this results in a volume decrease of the coating which causes voids and thereby lowers the corrosion resistance. Figure 1 shows the loss of water of hydration from zinc, iron, and iron–manganese phosphate coatings.

The heating of phosphate coatings in the absence of air provides conditions similar to those prevailing during the stoving of paint on phosphated articles, but in general the paint stoving temperatures and times are well below those at which damage to zinc phosphate coatings takes place. The loss of water from conventional zinc and manganese phosphate coatings heated in air is from 10 to 20% higher than the loss on heating in the absence of air. It is thought that this greater loss may be due to oxidation of the iron phosphate present in the coatings.

The most important uses for phosphate coatings entail sealing with oil or paint and it is therefore of interest to study absorption values. Table 3 compares the absorption of diacetone alcohol into coatings of widely differing thicknesses and composition; despite these differences, values of 10.5–13 g m^{-2} are obtained throughout. It is therefore evident that absorption is predominantly a surface effect and not appreciably influenced by coating thickness.

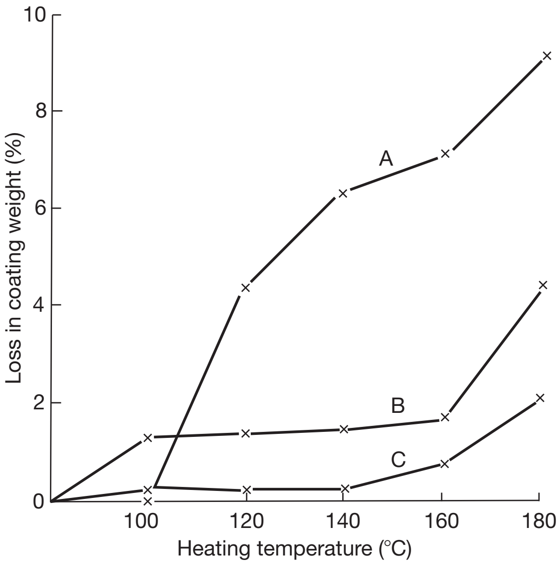

Figure 1 Effect of heating on phosphate coatings for 16 h at various temperatures, showing loss of water of hydration: (a) zinc phosphate; (b) iron phosphate, and (c) iron manganese phosphate. Reproduced from B.S.I. Phosphate Coatings (Drafting) Panel, *J. Iron Steel Inst.* **1952**, *170*, 13.

Table 3 Analytical tests on industrial phosphate coatings

Process[a]	*P*	*S*	*T*	*Q*	*V*	*R*
Main cation in phosphate bath	*Fe*	*Mn*	*Zn*	*Zn*	*Zn*	*Zn*
Method of application	*Immersion*	*Immersion*	*Spraying*	*Immersion*	*Immersion*	*Immersion*
Duration of treatment (min)	*15*	*30*	*1.5*	*4*	*5*	*12*
Change in weight on phosphating ($g\,m^{-2}$)	−26.1	−26.4	2.61	3.37	1.63	5.87
Coating weight ($g\,m^{-2}$)	14.2	21.2	4.46	5.43	3.48	12.28
PO_4^{3-}($g\,m^{-2}$)	7.0	8.9	1.96	2.07	1.20	4.46
Moisture ($mg\,m^{-2}$)	81.5	76.1	152.2	396.6	173.9	771.7
PO_4^{3-} content of coating (%)	49.0	42.0	44.0	38.0	34.0	36.0
Moisture content of coating (%)	0.6	0.4	3.4	6.9	5.0	6.4
Hygroscopicity of coating (%)	0.3	0.2	1.2	1.3	1.0	1.5
Absorption value (diacetone alcohol ($g\,m^{-2}$)	11.4	10.9	10.9	13.04	10.87	11.96

[a] The letters used for designation indicate proprietory process.
Data reproduced courtesy of the *Journal of the Iron and Steel Institute*, **1952**, *170*, 11.

4.02.3.5 Post-phosphating Treatment: Rinses

After phosphating, thorough rinsing with water is necessary in order to remove soluble salts which would otherwise tend to promote blistering under a paint film. Care should also be taken to ensure that the water supply itself is sufficiently free from harmful salts. Experience has shown that a water supply is potentially injurious if it exceeds any one of the three following limits:

1. 70 ppm total chlorides and sulfates (calculated as $Cl^- + SO_4^{2-}$);
2. 200 ppm total alkalinity (calculated as $CaCO_3$); and
3. a maximum of 225 ppm of (1) and (2) together.

Improved corrosion resistance and reduced tendency to blistering was traditionally obtained by treating the final rinse with chromic acid, or preferably with phosphoric and chromic acids combined. Normally, a total acid content of 0.05% was used, with higher concentrations of chromate increasing corrosion resistance. However, legislation restricting the use of chromates has now eliminated this practice. The use of demineralized water for rinsing purposes is recommended, especially before electrophoretic painting, as this practice reduces residual surface contamination. The demineralized water is generally applied by misting jets at the end of all other pretreatment stages and allowed to flow back into the last rinse tank. In certain cases, rinsing may be dispensed with after nonaccelerated phosphate treatment, but blistering of paint due to local concentration of solution in seams and crevices may occur. Thus, it is good practice to employ rinsing, regardless of the type of phosphate process.[11]

4.02.4 Performance

4.02.4.1 Corrosion Protection

The corrosion protection provided by phosphate coatings without a sealing treatment is of a low order; their value when sealed is considerably greater. Unsealed corrosion tests are therefore of little value except perhaps for studying porosity or efficiency of coatings destined to be sealed only with oil. It is usually necessary to control the acid ratio of phosphating baths, particularly those of iron, manganese, and zinc operating near boiling point that produce heavy coatings. The best performing coatings are obtained when the free acidity is maintained between 12.5% and 15%; above this figure, coatings with progressively lower corrosion resistance are obtained. Note that heavy, that is, thicker phosphate coatings do not necessarily have better corrosion resistance than lighter coatings. Even with a single process, for example, zinc/iron/phosphate/nitrate, no consistent relationship has been found between corrosion resistance and either coating weight or weight of metal dissolved. Jaudon[12] tested phosphate coatings and found the salt-spray resistance, as judged by the first appearance of rust, while only a few minutes for base steel, was around a few hours for phosphated steel.

Table 4 Typical phosphate coating processes

Phosphate coating solution	*Accelerator*	*Immersion time (min)*	*Type of coating*	*Coating weight (g m^{-2})*
Iron	None	30	Heavy	10.87–32.61
Iron/manganese	None	30	Heavy	10.87–32.61
Manganese	Nitrate	15	Heavy	8.70–32.61
Zinc	Nitrate	15	Medium	3.26–32.61
Zinc	Nitrate/nitrite or chlorate	3	Light	1.09–6.52
Sodium/ammonium	None	1–2 (spray)	Very light	0.22–0.65

Phosphating prior to painting doubled the observed time to first rusting.

Phosphate processes containing little or no oxidizing agent and based on manganese or zinc tend to accumulate iron in solution from the work being processed. With a manganese content from 0.2% to 0.5%, it is best to control the iron between 0.2% and 0.4%; a higher iron content reduces the corrosion resistance and may lead to the formation of thin powdery coatings, while a lower iron content gives soft coatings. Similarly, a zinc process operates best with 0.15–0.5% zinc and 0.4–0.5% iron. Again, with a higher iron content corrosion resistance falls off and powdery coatings may be formed, and soft coatings result from lower iron content.

Within broad limits, phosphate processes can be classified according to the main metallic radical of the processing solution and the type of accelerator used; typical processes are given in Table 4. The selection of process and of coating weight is mainly dependent on the end-use of the article being processed; the general requirements for corrosion resistance and wear prevention are given in Table 5.

Table 5 Typical uses of phosphate coatings on steel

Coating weight (g m^{-2})	*For corrosion resistance*	*For wear prevention and metal forming*
21.74–32.61	–	Critical cold extrusion
10.87–21.74	Military equipment, etc. requiring oil or grease finish	Normal cold extrusion ‘Running in’ treatment for piston rings, gears and tappets
5.43–10.87	Nuts, bolts, clips, brackets	Wire and tube drawing Sheet steel pressing
2.17–2.72	Cars, refrigerators, washing machines	Light metal pressing
1.63–2.17	Steel drums, bicycles, office machinery	
0.22–0.65	Toys, office furniture Strip steel, for painting and forming	

4.02.4.2 Testing

Heavy phosphate coatings are generally used as protection against corrosion in conjunction with a sealing film of oil or grease. The porosity or free pore area of these coatings should be kept to a minimum. Machu[13] devised a method of examination based on the quantity of electricity necessary to effect passivation of the bare steel and used this to determine the free pore area which, in the phosphate coatings tested, varied from 0.27% to 63%; however, this method is insufficiently sensitive to evaluate thin zinc phosphate coatings. A method for making rapid measurements of the electrical resistance of phosphate coatings has been described by Scott and Shreir.[14]

The most widely used accelerated tests are based on salt spray, whose main value is in the evaluation of the effectiveness of phosphate coatings in restricting the spread of rust from scratches or other points of damage in a paint film.[15] This feature is of particular interest to the automotive industry, as vehicles are often exposed to marine atmospheres and to moisture and salt when the latter is used to disperse ice and frost from road surfaces. Great care is needed in the interpretation of a salt-spray test, as it has been found to favor thin iron phosphate coatings more than is justified by experience with natural weathering. Humidity tests are generally of more practical use than salt-spray tests, particularly where painting is employed, as the thoroughness of rinsing may be checked by this means. The use of contaminated water can leave water-soluble salts in the phosphate

Table 6 Weights of phosphate coatings

Class of phosphate process	*Coating weight ($g\ m^{-2}$)*	
	Min.	*Max.*
A 1. Heavyweight (Mn or Fe)	7.61	–
A 2. Heavyweight (Zn)	7.61	–
B Medium weight (Zn, etc.)	4.34	–
C Lightweight (Zn, etc.)	1.09	4.34
D Extra lightweight (Fe)	0.33	1.09

Source: BS EN 12476: Phosphate conversion coatings of metals. Method of specifying requirements.

coating and lead to blistering of the paint film under humid conditions, as paint films are permeable to water vapor. Immersion in water, or subjection to high humidity in a closed cabinet, will generally show any defects of this kind within a few days.

Phosphate coating weight determinations are generally performed by dissolving the coating from weighed panels using inhibited acid (e.g., by immersion in a solution of $20\,g\,dm^{-3}$ of antimony trioxide in concentrated hydrochloric acid at a temperature of 13–21 °C. Thin iron or zinc phosphate coatings can be removed for weight determination by immersion in 5% chromic acid solution at 70 °C, but this solution should also be used only once, as the presence of more than a trace of phosphate leads to pitting of the steel and false results. Zinc phosphate coatings can be removed by immersion in 10% sodium hydroxide at boiling temperature, aided by rubbing during rinsing.

BS EN 12476 contains information on the operation of phosphate processes to obtain optimum results and on the testing of phosphate coatings.[16] The classification of coatings according to composition and weight is shown in Table 6. The inspection and testing includes determination of coating weight, freedom from corrosive residues as shown by a humidity test, and resistance to corrosion by salt spray. BS EN ISO 12944-1 is also a valuable source of information.[17]

4.02.4.3 Phosphophyllite–Hopeite Ratio

There is evidence that the ratio of phosphophyllite to hopeite (the so-called $P/(P+H)$ ratio) can be used as a predictive measure of the performance of phosphated steel when coated with cathodic electroprimer and paint.[18,19,20,21] In this context, P is defined as the intensity of X-rays diffracted from the (100) plane of phosphophyllite, $FeZn_2(PO_4)_2{\cdot}4H_2O$, and H is defined as the intensity of X-rays diffracted from the (020) plane of hopeite, $Zn_3(PO_4)_2{\cdot}4H_2O$, and it has been suggested that higher values of this ratio (i.e., a low volume fraction of hopeite) are synonymous with good corrosion performance.[18] However, other factors to be considered include the need for homogeneous phosphate layers of controlled thickness, the direct attachment of the primer to a coherent layer, and the level of interlayer cohesion within the coating. Some papers[21] indicate that adhesion failure results from internal fracture of the phosphate coating and that it is concentrated at the junction between a primary microcrystalline or even amorphous layer close to the metal substrate and a secondary layer exhibiting relatively coarse crystallinity. The primary layer is comprised essentially of a zinc phosphate material, and the Zn/P ratio in the retained primary layer after fracture is lower than that in the detached material, though close enough to be considered essentially similar.

Finally, it is worth noting that the quality of the steel substrate can have an effect on the corrosion resistance promoted by any subsequent treatment by phosphating and painting. Indeed, it has been reported[22] that interesting results are obtained when cold-rolled steel panels, with different amounts of surface contamination, are zinc phosphated, then coated with anionic or cationic electrocoat primers, and followed by a conventional filler-topcoat system. In salt-spray, scab, and filiform corrosion tests, it is apparently possible to distinguish between different surface contamination levels and primer coatings. Carbonaceous residues on the steel can have a detrimental effect, and this can be confirmed in the case of anionic primer during salt-spray tests. In the scab corrosion and filiform corrosion tests, however, anionic primer performance actually increases with surface contamination. It can be concluded that the steel condition and the type of coating affect the corrosion resistance of the entire system by inducing changes in the phosphate layer. With the current low level of surface contamination of commercial steels and the highly resistant modern coating formulations, it is suggested[22] that the phosphate layer is the weakest link in the entire system.

References

1. Machu, W. *Die Phosphatierung — Wissenschaftliche Grundlagen und Technik*; Verlag Chemie: Weinheim, 1950.
2. Wusterfeld, H. *Arch. Metallk* **1949**, *3*, 233.
3. Determination of the solubility of ferric phosphate in phosphating solutions using radioiron, US Department of Commerce, Office of Technical Services, Rep. no. PB 111, 1953; p 399.

4. Radiometric study of phosphating problems, US Department of Commerce, Office of Technical Services, Rep. no. PB 111, 1951; p 396.
5. British Surface Treatment Suppliers Association, Technical Brochure: ‘‘Metal pre-treatment.’’ Available for download from http://www.bstsa.org.uk.
6. Wirshing, R. J.; McMaster, W. D. *Can. Paint Varn. Mag.* **1956**, *30*(5), 42, 55.
7. Jernstedt, G. *Chem. Eng. News* **1943**, *21*, 710; *Trans. Electrochem. Soc.* **1943**, *83*, 361.
8. A radiometric study of the iron phosphating process, US Department of Commerce, Office of Technical Services, Rep. no. PB 111, 1953; p 400.
9. X-ray diffraction study of zinc phosphate coatings on steel, US Department of Commerce, Office of Technical Services, Rep. no. PB 111, 1954, p 486.
10. Doss, J. *Org. Finish.* **1956**, *17*(8), 6.
11. B.S.I. Phosphate Coatings (Drafting) Panel. *J. Iron Steel Inst.* **1952**, *170*, 13.
12. Jaudon, E. *Peint.-Pigm.-Vernis.* **1949**, *25*, 224.
13. Machu, W. *Korros, Metallsch.* **1944**, *20*, 1.
14. Scott, J. W.; Shreir, L. L. *Chem. Ind. (Rev.)* **1957**, 807.
15. BS EN ISO 9227: Corrosion tests in artificial atmospheres: Salt spray tests.
16. BS EN 12476: Phosphate conversion coatings of metals. Method of specifying requirements.
17. BS EN ISO 12944-1: Paints and varnishes. Corrosion protection of steel structures by protective paint systems.
18. Miyawaki, T.; Okita, H.; Umehara, S.; Okabe, M. *Proc. Interfinish.* **1980**, *80*, 303.
19. Richardson, M. O. W.; Freeman, D. B.; Brown, K.; Djaroud, N. *Trans. I.M.F.* **1983**, *61*, 155.
20. Freeman, D. B.; Brown, K.; Richardson, M. O. W.; Tiong, H. *Finishing* **1984**, 27–28.
21. Cooke, B. A. Proceedings of the IX International Conference on Organic Science and Technology, Athens; 1983; pp 29–46.
22. Soepenberg, E. N.; Vrijburg, H. G.; van Ooij, W. J.; Vries, O. T. The Influence of Steel Quality, Pretreatment and Coating Systems on the Corrosion of Automotive Steel, 1984; pp 381–393.

Relevant Websites

http://www.bstsa.org.uk – British Surface Treatment Suppliers Association, Birmingham, UK.

4.03 Coatings Produced by Anodic Oxidation

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Glossary

Barrier anodic film An oxide coating deliberately formed on a valve metal (commonly aluminum) that is generally relatively featureless and provides an electrical and physical barrier to the bare metal surface.

Porous anodic film An oxide coating deliberately formed on a valve metal (commonly aluminum) that generally contains self-organized directional porosity; all porous anodic films are terminated by a form of barrier anodic film adjacent to the base metal surface.

Plasma electrolytic oxidation A process for anodizing that uses relatively high voltages that deliberately induce dielectric breakdown, with associated sparking, on the treated component; also called micro-arc oxidation.

Valve metal An element from the group: aluminum, titanium, zirconium, hafnium, tungsten, niobium and tantalum. Such elements will develop protective oxide films when polarized anodically in a suitable electrolyte.

Symbols

MAO Micro-arc oxidation
PEO Plasma electrolytic oxidation
SHE Standard Hydrogen Electrode

4.03.1 Practice of Anodizing

Anodic oxidation or anodizing, as applied to metallic surfaces, is the production of a coating, generally of oxide, on the surface by electrolytic treatment in a suitable solution, the metal being the anode. Although a number of metals,[1] including aluminum, magnesium, tantalum, titanium, vanadium and zirconium, can form such anodic films, only aluminum and its alloys, and to a lesser extent magnesium, are anodized on a significant commercial scale for corrosion protection.

The anodic oxidation of magnesium does not normally produce a film that has sufficient corrosion resistance to withstand exposure without further protection by painting, and the solutions used are complex mixtures containing phosphates, fluorides and chromates. In the case of aluminum, a relatively simple treatment produces a hard, compact, strongly adherent film of oxide, which affords considerably increased protection against corrosive attack.[2,3]

A further advantage of this process lies in the decorative possibilities of the oxide film, which may be almost completely transparent on very high purity aluminum (99.99% Al) and certain alloys based on this purity, and thus protects the surface without obscuring its polish or texture. On metal of lower purity, and other alloys, the oxide layer may become slightly milky, or colored grey or yellowish, although the deterioration is hardly apparent with purities down to 99.7–99.8% Al. The appearance and character of the film may also be influenced by the type of anodizing treatment, and the oxide film may be dyed to produce a wide range of colored finishes. Anodizing characteristics of a number of aluminum alloys are listed by Wernick and Pinner.[3] The anodizing procedures in general use are shown in **Table 1**, sulfuric acid being the most commonly used electrolyte. Treatment time is 15 min to 1 h.

The articles to be anodized should be free from crevices where the acid electrolyte can be trapped. They may be given a variety of mechanical and chemical pretreatments, including polishing, satin-finishing, etching, etc. but before anodizing, the surface must be clean and free from grease and polishing compound.

After the anodic treatment, the work is removed from the tank and carefully swilled with cold water to remove all traces of acid. At this stage, the anodic film is absorptive, and care should be taken to avoid contamination with oil or grease, particularly if the work is to be dyed. Dyeing may be carried out by immersion for about 20 min in an aqueous solution of the dyestuff at a temperature of 50–60 °C. Inorganic pigments may also be incorporated in the oxide layer by a process involving double decomposition. Finally, both dyed and undyed work are sealed by treatment in boiling water (distilled or deionized) or steam, which enhances the corrosion resistance and prevents further staining or leaching of dye. Solutions of metal salts, for example nickel or cobalt acetates, are often used to seal work after dyeing. Traditionally sealing in 5–10% dichromate solution, which gives the coating a yellow color, was used to impart the highest degree of corrosion resistance. However, the use of chromates is being increasingly phased out due to environmental concerns.[4]

In the architectural field, use is being made of integral color anodizing which is capable of producing self-colored films in a number of fade-resistant tints ranging from gray, through bronze and brown, to a warm black. The electrolytes are developments of the oxalic acid solution and consist of various dibasic organic acids, such as oxalic, malonic or maleic, or sulfonated organic acids such as sulfosalicylic acid, together with a small proportion of sulfuric acid. For constant and reproducible results, a close analytical control of the electrolyte must be maintained, particularly with respect to aluminum which dissolves as

Table 1 Traditional anodizing processes for aluminum (the chromic acid treatment is historic and is being increasingly phased out)

Electrolyte	*Temperature (°C)*	*Applied voltage (V)*	*Current density ($A\,m^{-2}$)*	*Film thickness (μm)*	*Appearance*
5–10% sulfuric acid	17–22	12–24	110–160	3–25	Transparent: colorless to milky
3–10% chromic acid	30–45	30–45	30–35	2–8	Opaque: light to dark gray
2–5% oxalic acid	20–35	30–60	110–215	10–60	Transparent: light yellow to brown

treatment proceeds, and ion-exchange resins are frequently used to regenerate the relatively expensive electrolyte and keep the aluminum in solution between controlled limits. Some typical color anodizing treatments are summarized in Table 2.

Alloys are generally of the Al–Mg–Si type with additions of copper and chromium or manganese. Color varies with the particular alloy and the film thickness. For optimum control of color, the alloy must be carefully produced with strict attention to composition, homogenization and heat-treatment, where appropriate, and the anodizing conditions must be maintained within narrow limits. It is usual to arrange matters, preferably with automatic control, such that current density is held constant with rising voltage up to a selected maximum, after which voltage is held steady; the whole cycle being for a fixed time. Refrigeration of the electrolyte may be necessary to maintain the temperature at the working level, owing to the relatively high wattage dissipation.

Hard anodic films, 50–100 μm thick, for resistance to abrasion and wear under conditions of slow-speed sliding, can be produced in sulfuric acid electrolytes at high current density and low temperature.[5–7] Current densities range from 250 to 1000 $\mathrm{A\,m^{-2}}$, with or without superposed alternating current in 20–100 $\mathrm{g\,l^{-1}}$ sulfuric acid at −4 to 10 °C. Under these conditions, special attention must be paid to the contact points to the article under treatment, in order to avoid local overheating.

The films are generally dark in color and often show a fine network of cracks due to differential expansion of oxide and metal on warming to ambient temperature. They are generally left unsealed, since sealing markedly reduces abrasion resistance, but may be impregnated with silicone oils[8] to improve the frictional properties. Applications include movable instrument parts, pump bodies and plungers, etc. Decorative self-colored films[9] can also be produced in sulfuric acid under conditions intermediate between normal and hard anodizing.

Continuously anodized sheet, foil and wire, which may be given a dyed finish, are produced through a series of cleaning, etching and anodizing tanks, with a film thickness up to about 6 μm. Uses include electrical windings for transformers and motors, where the light weight of aluminum and the insulating and heat-resistant properties of the film are of value, and production of small or light-section articles by stamping or roll-forming.

4.03.2 Mechanism of Formation of Porous Oxide Coatings

It has been established that in the case of electrolytes, such as boric acid or ammonium phosphate solutions, in which aluminum oxide is insoluble, this anodic passivity is due to the formation of a thin compact layer of aluminum oxide whose thickness is proportional to the applied voltage. In neutral phosphate solutions, for example, film growth practically ceases when the thickness corresponds to about 1.4 $\mathrm{nm\,V^{-1}}$, and a similar value has been found for many other electrolytes of this type. These thin films have a high electrical resistance, and can withstand several hundred volts under favorable conditions.

In electrolytes in which the film has a moderate solubility, film growth is possible at lower voltages, for example, in the range 12–60 V, since the rate of formation of the oxide exceeds its rate of solution and current flow continues owing to the different structure of the oxide layer. Electron microscopy has revealed the characteristic porous structure of these films.[10] The pore diameter appears to be a function of the nature and concentration of the electrolyte and of its temperature, being greatest in a solution of high solvent activity, while the number of pores per unit area varies inversely with the formation voltage. In any given electrolyte, the lower the temperature and concentration, and the higher the voltage, the denser will be the coating, as the number of pores per unit

Table 2 Traditional integral color anodizing processes

Electrolyte	*Temperature (°C)*	*Current density ($\mathrm{A\,m^{-2}}$)*	*Voltage (V)*	*Time (min)*
Sulfosalicylic acid (100 $\mathrm{g\,l^{-1}}$) + sulfuric acid (50 $\mathrm{g\,l^{-1}}$)	22–25	215–320	25–70	20–45
4- or 5-Sulfophthaic acid (75–100 $\mathrm{g\,l^{-1}}$) + sulfuric acid (8–10 $\mathrm{g\,l^{-1}}$)	15–30	130–370	>70	30
Oxalic acid (80 $\mathrm{g\,l^{-1}}$ to saturation)	15–25	130–160	35–70	50–90

area are reduced under these conditions; **Table 3** illustrates these points.

In order to account for the relatively high potential required to maintain the current it was suggested by Setoh and Miyata[11] that a thin barrier-layer, similar to that formed in nonsolvent electrolytes, is present below the porous layer. This view has been supported by later work involving capacity and voltage–current measurements, which have allowed the thickness of the barrier-layer to be computed.[12] As in the case of electrolytes which produce barrier films, the thickness has been found to be proportional to the anodizing voltage, but is lower than the limiting growth rate of 1 nm V^{-1} and varies with the anodizing conditions (**Table 4**). The morphology of the anodic film is shown in **Figure 1** and diagrammatically in **Figure 2**.

The more or less regular pattern of pores imposes a cellular structure on the film, with the cells approximating in plan to hexagons, each with a central pore.[13–15] A barrier layer separates the pores from the aluminum, the alumina cells can self-organize to a close-packed arrangement,[13,16] with groups of cells having a potential for organization into regular patterns.[13,16–18] The pore diameter and barrier layer thickness are related to the anodizing voltage, with ratios of about 1.0 nm V^{-1}, with an increased ratio of about 2.8 nm V^{-1} for the cell width.[19] The metal surface underlying the film, therefore, consists of a close-packed regular array of nearly hemispherical depressions which increase in size with the anodizing voltage. The thickness of the individual cell walls is approximately equal to that of the barrier-layer.[20]

Table 3 Number of pores in anodic oxide coatings

Electrolyte	*Temperature (°C)*	*Applied voltage (V)*	*Pores (cm^{-2})*
15% sulfuric acid	10	15	77×10^9
	10	20	51×10^9
	10	30	28×10^9
3% chromic acid	49	20	22×10^9
	49	40	8×10^9
	49	60	4×10^9
2% oxalic acid	24	20	36×10^9
	24	40	12×10^9
	24	60	6×10^9

Data reproduced from Keller, F.; Hunter, M. S.; Robinson, D. L. *J. Electrochem. Soc.* **1953**, *100*, 411.

Table 4 Barrier-layer thickness in various electrolytes

Electrolyte	*Temperature (°C)*	*Barrier layer growth ratio*
15% sulfuric acid	10	1.00
3% chromic acid	38	1.25
2% oxalic acid	24	1.18

Data reproduced from Hunter, M. S.; Fowle, P. *J. Electrochem. Soc.* **1954**, *101*, 481.

In view of its position in the electrochemical series (E^0 $Al^{3+}/Al = -1.66$ V (SHE)), aluminum would be expected to be rapidly attacked even by dilute solutions of relatively weak acids. In fact, the rate of chemical attack is slow, owing to the presence on the aluminum of a thin compact film of air-formed oxide. When a voltage is applied to an aluminum anode there is a sudden initial surge of current, followed by a rapid fall to a lower, fairly steady value. It appears that this is due to the formation of a barrier-layer. Before the limiting thickness is reached; however, the solvent action of the electrolyte initiates a system of pores at weak points or discontinuities in the oxide barrier-layer.

Pore initiation may be associated with irregularities in original air-formed film on the metal. The development of locally thicker film regions with subsequent pore initiation in the thinner film region is related to the substrate texture. Initial uniform film thickening is apparent, followed by development of locally thicker film material above the distinct metal ridges upon the aluminum surface after pretreatment, and eventual pore development in preferred regions of thinner film between the protuberances, as shown in **Figure 3**.[21–23]

Growth of oxide continues on a series of hemispherical fronts centered on the pore bases, provided that the effective barrier-layer thickness between the metal surface and the electrolyte within the pores, represented by the hemisphere radius, is approximately 1 nm V^{-1}. As anodic oxidation proceeds at a uniform rate, a close-packed hexagonal cell-pattern is produced, the inward extension of the pore due to solution of oxide keeping pace with the inward movement of the oxide–metal interface, as shown by the arrows in **Figure 2**.

Radiochemical and electron microscopy studies[21–25] indicate that the pore base is the actual site of formation of aluminum oxide. The high electric field that exists across the barrier layer drives the transport of Al^{3+} and O^{2-} ions through the barrier layer, which is necessary for film growth.[23,26] The formation of porosity has mainly been attributed to field-accelerated dissolution of anodic alumina at the base of each pore,[22,23] which is also enhanced by the heating

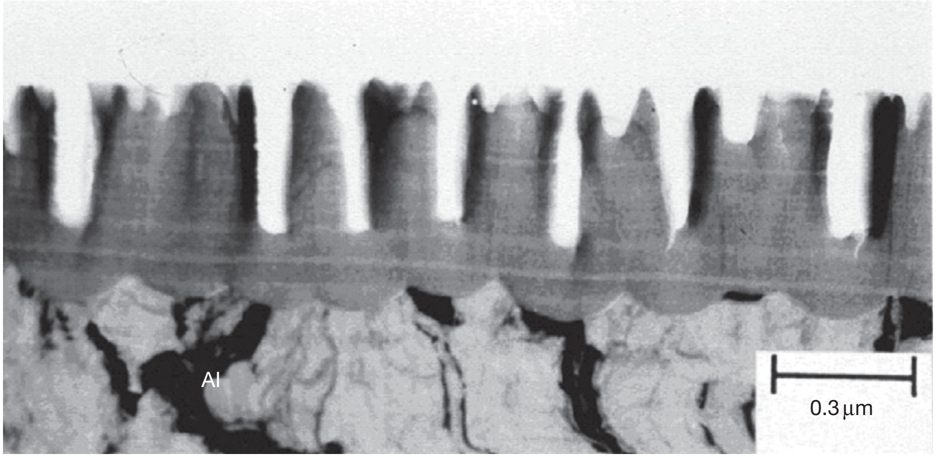

Figure 1 Transmission electron micrographs of ultramicrotomed cross section of porous anodic film, revealing pores at the centers of cells that pass perpendicular to metal surface and the barrier layer present at the base of pore.

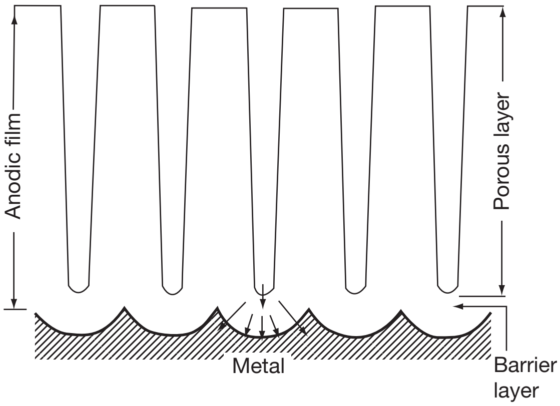

Figure 2 Diagrammatic cross-section of porous anodic oxide film.

effect of the current, but will also be limited by diffusion. In a process that is separate to field-assisted dissolution, the Al^{3+} ions that migrate to the pore base are ejected directly to the electrolyte,[23] that is, without formation of anodic alumina, such that new film is formed due to the inward migration of O^{2-} ions. It has been shown that the freshly formed oxide, α-Al_2O_3, is amorphous.[27] The very early stages of pore growth have been extensively studied, and the importance of surface topography and flaw sites in the preexisting oxide established by O'Sullivan, Wood[24] and Thompson and Wood[28] using electron microscopy. Prolonged action of the acid electrolyte on thick films may cause the pores to become conical in section, widening towards the upper surface of the film. This will impose an upper limit on film thickness in solvent electrolytes, as found in practice.

For color anodizing, although it might seem at first sight that dyestuffs are merely held mechanically within the pores, and this view is probably correct in the case of inorganic pigments, there is some support for the opinion that only those dyestuffs which form aluminum–metal complexes produce really light-fast colorations. The effect of hot water sealing is to convert anhydrous γ-Al_2O_3 into the crystalline monohydrate, $Al_2O_3{\cdot}H_2O$, which occupies a greater volume and blocks up the pores, thus preventing further absorption of dyes or contaminants. The monohydrate is also less reactive.

4.03.3 Properties of Coatings

4.03.3.1 Composition

The main constituent of the film is aluminum oxide, in a form which varies in constitution between amorphous Al_2O_3 and γ-Al_2O_3, together with some monohydrate, $Al_2O_3{\cdot}H_2O$. In the presence of moisture, both the anhydrous forms are gradually transformed into the monohydrate, and the water content of as-formed films is, therefore, somewhat variable.

After sealing in boiling water, the composition of the completely hydrated film obtained when using sulfuric acid approximates to: 70% Al_2O_3, 17% H_2O, 13% SO_3. It is probable that the SO_3 is combined with the aluminum as a basic sulfate. Sealed films show the electron diffraction pattern of the monohydrate, beohmite.

Anion incorporation in the film is a further important factor affecting film characteristics. It has been

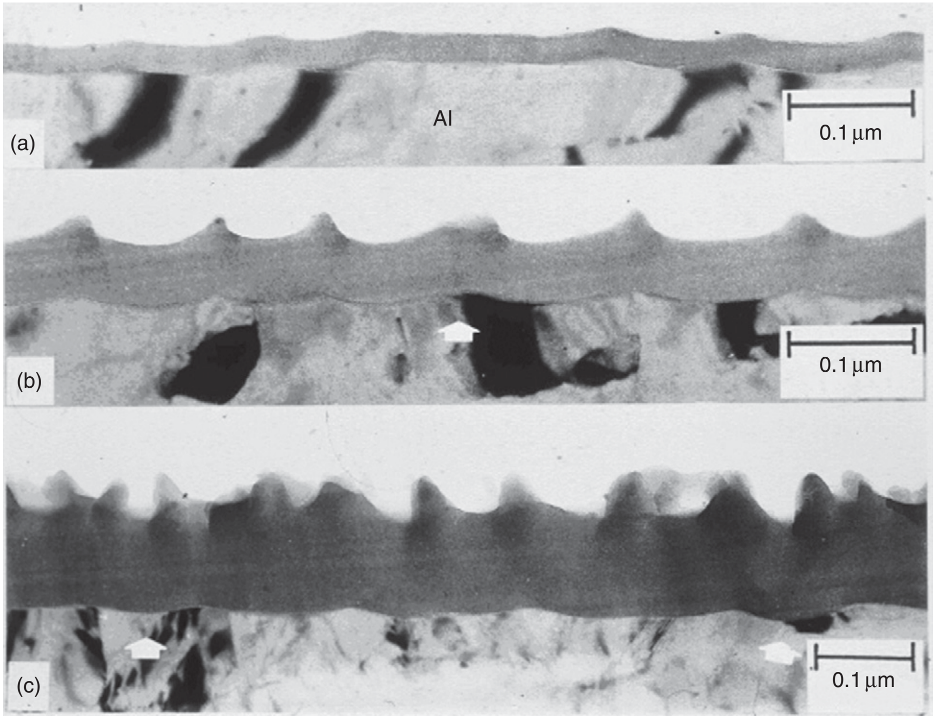

Figure 3 Transmission electron micrographs of ultramicrotomed cross-section of porous anodic film in the early stages of development. The arrow in (b) highlights a local crack/repair event.

found that anion species are incorporated into the films produced in the main acids, including oxalic acid, sulfuric acid, phosphoric acid and boric acid–formamide electrolytes.[29] The levels of acid anion incorporation are generally in the order: sulfuric acid > phosphoric acid > oxalic acid > chromic acid. Using a radiotracer technique and electron probe microanalysis, sulfur incorporation in films formed in sulfuric acid were determined. A typical level of 4–18 wt% sulfur was found, distributed uniformly throughout film thickness, by different researchers.[30–33] Anodizing in chromic acid produces contrasting results from films formed in sulfuric, oxalic, phosphoric acids; the films contain relatively low levels of chromate incorporation.

The distribution of the anion present after anodizing in oxalic acid has been studied by Rutherford back scattering (RBS) and Auger electron spectroscopy (AES).[34] Carbon is present in the oxide layer in measurable concentrations. The carbon concentration shows a maximum at the surface, a slow decrease through the oxide, and with no signal within a thin oxide region adjacent to the metal. An oxalate content of about 2.4 wt% in films formed in oxalic acid was reported.[35]

4.03.3.2 Density

Owing to the variable degree of porosity of the anodic film, it is only possible to determine the apparent density, which varies with the anodizing conditions and also with the film thickness. Figure 4 shows the variation in density with thickness for steam-sealed anodic films produced in sulfuric acid on aluminum of 99.99% and 99.5% purity. A mean figure of 2.7 g cm^{-3} for sealed, and 2.5 g cm^{-3} for unsealed films is accepted by the British Standard for anodized aluminum.[36]

4.03.3.3 Mechanical Properties

4.03.3.3.1 Hardness

It is not possible to obtain a reliable figure for the hardness of anodic coatings with either the indentation or scratch methods, because of the influence of the relatively soft metal beneath the anodic film, and the presence of a soft outer layer on thick films. On Moh's scale, the hardness of normal anodic films lies between 7 and 8, that is, between quartz and topaz.

Methods are available for the determination of relative abrasion resistance using either a mixed jet

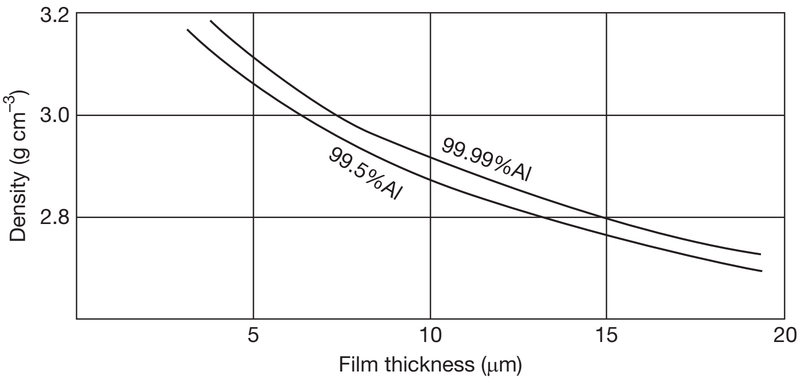

Figure 4 Apparent density of anodic film as a function of film thickness. Reproduced from *Aluminium, Berl.* **1938**, *32*, 126.

of air and abrasive, as recommended in the appropriate British Standard[37] or an abrasive wheel or disc. Owing to variations in the quality of the abrasive, and the performance of individual jets, a standard comparison sample is included in each batch.

The hardness of the film is markedly affected by the conditions of anodizing. By means of special methods involving dilute electrolytes at low temperatures and relatively high voltages, with or without superimposed alternating current, it is possible to produce compact abrasion-resistant films with thicknesses of 50–75 μm and hardness of 200–500 Vickers, for special applications.

4.03.3.3.2 Flexibility

The normal anodic film begins to crack if subjected to an extension exceeding about 0.5%. Thinner films up to 5 μm in thickness appear to withstand a greater degree of deformation without obvious failure, and are often used for dyed coatings on continuously anodized strip from which small items may be punched or stamped. Continuously anodized wire can be bent round a radius of 10–15 times its diameter without visible crazing. A greater degree of flexibility is also shown by the more porous coatings produced in 20–25% sulfuric acid at 35–40 °C, while hard films are much less flexible. Unsealed films are only slightly more flexible than films sealed in water or dichromate solution.

4.03.3.4 Electrical Properties

The specific resistance of the dry anodic film is $4 \times 10^{15}\,\Omega$ cm at 20 °C,[38] while the dielectric constant of anodic oxide films has been found to be 5.0–5.9 for sulfuric films, and 7–8 for oxalic films. A mean value of 7.45 has been quoted for barrier-layer films,[1] but more recent work favors a value closer to 8.7.[39]

The breakdown voltage of an anodic film varies with the method of measurement and conditions of anodizing, and shows fluctuations over the surface. In the case of unsealed films, breakdown voltage also depends on the relative humidity at the time of measurement. It is normally measured by applying a slowly increasing alternating voltage between a loaded hemispherical probe on the upper surface of the film, and the underlying metal, contact to which may be established by removing a portion of the film. The breakdown voltage–thickness relationship for sealed films up to about 20 μm is approximately linear, and the slope of the curve for sulfuric acid films varies from 30 to 40 V μm^{-1}. These results were obtained with a relatively high loading on the probe; with reduced load (approx. 60 g and below on a hemispherical probe of 1.6 mm radius) values of 60–100 V μm^{-1} can be reached. The higher figures probably represent limiting values which will apply to the conditions between adjacent laps or turns on coils wound from anodized strip or wire.

4.03.3.5 Physical Properties

The thermal expansion of the film is only about one-fifth that of aluminum,[1] and cracking or crazing is observed when anodized aluminum is heated above 80 °C. The fine hair-cracks produced do not seem to impair the protective properties of the coating if anodizing conditions have been correct.

The thermal conductivity of anodized films is approximately one-tenth that of aluminum.[2] Also, apart from hair-cracks, little change is observable in the anodic film on heating up to 300–350 °C, although some dyed finishes may change color at 200–250 °C, but at higher temperatures up to the melting point of the metal, films may become opaque or change color, owing to loss of combined water, without losing their adhesion.

4.03.3.6 Thermal Properties

Table 5 shows the total heat emissivity of various aluminum surfaces, as a percentage of that of a black body. The emissivity of anodized aluminum rises rapidly with film thickness up to 3 µm after which the rate of increase diminishes.

The heat reflectivity of as-rolled aluminum is about 95%, but this high value may not be maintained for long in a corrosive atmosphere, although it is less affected by surface finish than is optical reflectivity. Anodizing reduces the heat reflectivity, owing to absorption by the oxide layer; this effect increases with film thickness. There is a deep absorption trough in the region corresponding to a wavelength of 3 µm; this is probably due to the –OH grouping in the hydrate, the effects of which may be minimized by sealing the heated film in oil instead of water.[40] This treatment is particularly valuable for heat reflectors in apparatus using sources running at 900–1000 °C, which show a peak emission in the 2–3 µm region. Figure 5 shows the heat reflectivity of anodized superpurity aluminum for a source of this type plotted against film thickness. The benefits of the modified sealing treatment are obvious.

Table 5 Relative heat emissivity of various aluminum surfaces

Surface	*Heat emissivity (%)*
Highly polished	4.3–6.4
Etched	6.4–8.5
Bright roll finish	5.3–7.4
Malt roll finish	8.5–16
Aluminum paint	17–32
Diecast	16–26
Sandcast	26–36
Anodized, according to film thickness	38–92
Black body	100

Data recalculated from Hase, R. *Aluminium, Berl.* **1942**, *24*, 140.

4.03.3.7 Optical Properties

The refractive index of the clear anodic film produced on aluminum of the highest purity in sulfuric acid is 1.59 in the as-formed condition, rising to 1.62 after sealing.[41] The total and specular reflectivities of an anodized aluminum surface are controlled by both the condition of the metal surface, polished or matt, and the absorption or light-scattering properties of the oxide layer. Total reflectivity may be defined as the percentage of the incident light reflected at all angles, while specular reflectivity is that percentage reflected within a relatively narrow cone with its axis along the angle of reflection. For many years, the standard instrument for measuring specular reflectivity has been that designed by Guild,[42] but more recently a modified gloss head giving rather greater discrimination has been described by Scott.[43] Other instruments, while placing a number of surfaces of varying specularity in the same relative order, may give different values for the specular reflectivity.

The general brightness of a surface is chiefly dependent upon the total reflectivity T, while specular reflectivity S controls the character of the reflected image. In assessing the subjective brightness of a surface the eye tends to be influenced more by

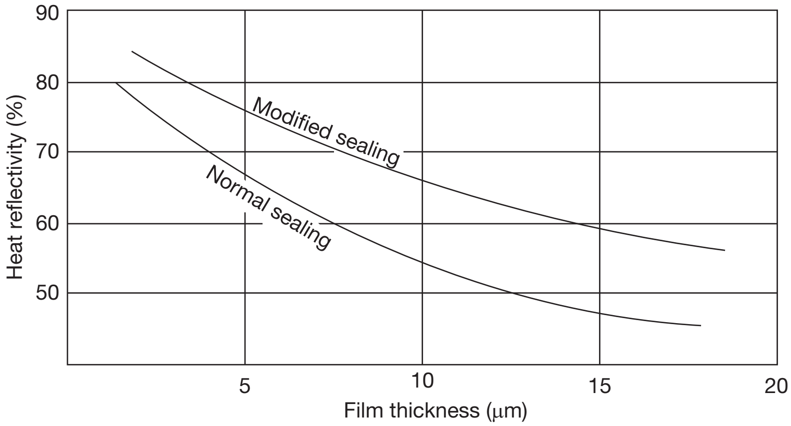

Figure 5 Heat reflectivity of anodized aluminum. Reproduced from Pearson, T. G.; Phillips, H. W. L. *Metallurg. Rev.* **1957**, *2*(8), 348.

the S/T ratio or image clarity than by the total reflectivity.

For a high degree of specularity, the metal surface must be given a high polish by mechanical means; this may be followed (or replaced) by electrochemical or chemical brightening. When such a brightened surface is protected by anodizing, however, insoluble impurities (mainly iron and silicon) present in the aluminum will be incorporated in the anodic film and will increase its tendency to absorb or scatter light. Only metal of the highest purity, 99.99% Al, produces a fully transparent oxide film, while lower purities show decreased total reflectivities and the fraction of specular reflectivity (S) as a function of total reflectivity (T), the S/T ratio, after anodizing because of the increased opacity of the anodic film. Table 6 demonstrates these effects. The figures were obtained using the Guild meter on electrobrightened and anodized metal.

4.03.3.8 Effect of Anodizing on Mechanical Properties

The tensile strength of thin sections of aluminum may be somewhat reduced by anodizing, owing to the brittleness of the coating and the reduction in metallic cross-section, but this effect is normally very slight. Thin sheet, less than about 0.6 mm with a relatively thick anodic coating, also has a tendency to break more easily on bending. The incompressibility of the anodic film on the inside of the bend probably enhances this effect, which is also seen on anodized wire.

Table 6 Effect of metal purity and anodic film thickness on reflectivity

Metal purity (%)	*Film thickness (μm)*					
	2		*5*		*10*	
	T	*S/T*	*T*	*S/T*	*T*	*S/T*
99.5	80	0.84	79	0.83	77	0.78
99.8	82	0.95	83	0.95	–	–
99.99 (super purity)	84	0.99	84	0.99	84	0.99
Super purity + 0.5 Mg	84	0.98	84	0.98	83	0.97
Super purity + 1.25 Mg	83	0.99	83	0.99	82	0.99
Super purity + 0.7 Mg, 0.3 Si. 0.25 Cu	82	0.99	79	0.98	–	–

S, Specular reflectivity; *T*, Total reflectivity.
Data reproduced form Pearson, T. G.; Phillips, H. W. L. *Metallurg. Rev.* **1957**, *2*(8), 348.

Anodizing should be used with caution on components likely to encounter high stresses, owing to the deterioration in fatigue properties liable to result under these conditions, but under light loading and with the thinner coatings, the reduction is negligible. In some cases,[44] an actual improvement has been reported. The coefficient of friction of the sealed anodic film is 0.76, falling to 0.19 after impregnation with silicone oil.[45] These results were obtained with anodized wire.

4.03.3.9 Measurement of Film Thickness

The thickness of an anodic film may be determined by a variety of nondestructive methods. Some of these are capable of a high degree of precision, while simpler methods are available for rough sorting. A number of instruments employing the eddy-current principle, with which, after prior calibration, a rapid estimate of film thickness may be made, are now available. With the best instruments, an accuracy of ±1 μm can be obtained. For approximate determinations of thickness, the breakdown voltage of the film may be measured. Breakdown voltage shows wide variations with anodizing conditions and metal or alloy composition. A separate calibration curve is, therefore, needed for each treatment. Accuracy is comparatively low, rarely being greater than ±2% of the total film thickness.

Alternatively, the loss in weight[46] of an anodized sample of known area may be found after the film has been stripped in a boiling solution made up with phosphoric acid (specific gravity 1.75) 3.5 vol.% and chromic acid 2.0 wt%. Immersion for 10 min is usually sufficient to remove the film without the metal being attacked. Further, film thickness can be precisely determined by cross-sectional examination in a scanning electron microscope or a transmission electron microscope.

4.03.4 Corrosion Resistance

Since the natural passivity of aluminum is due to the thin film of oxide formed by the action of the atmosphere, it is not unexpected that the thicker films formed by anodic oxidation afford considerable protection against corrosive influences, provided the oxide layer is continuous, and free from macropores. The protective action of the film is considerably enhanced by effective sealing, which plugs the mouths of the micropores formed in the normal course of anodizing with hydrated oxide, and still further improvement may be afforded by the incorporation of corrosion inhibitors, such as dichromates, in the sealing solution. Chromic acid films, in spite of their thinness, show good corrosion resistance.

The protective action of sulfuric films is mainly controlled by the anodizing conditions, compact films formed at temperatures below 20 °C in 7% (v/v) sulfuric acid being more resistant than the films formed at higher temperatures in more concentrated acid. The wider pores of the latter result in less protection but these films are more readily dyed. Greater protection is also given by thicker films, and a thickness of about 25 μm is generally considered adequate for architectural work in a normal urban environment. In a heavily polluted industrial area, even thicker films may be desirable, while in rural areas some reduction would be permissible. Bright anodized motorcar trim is generally given a film thickness of about 7 μm.

Alumina monohydrate in the mass is very unreactive, being rapidly attacked only by hot sulfuric acid or caustic soda solutions, and the anodic coating shows similar characteristics to some degree. The presence in the film of macropores due to localized impurities, intermetallic particles or contaminations in the metal and overlying oxide can bring about rapid penetration, owing to the concentration of attack at the few vulnerable points. Metal of good quality specially produced for anodizing should therefore be used in order to ensure that such weak points are absent. For vessels and tanks for holding liquids, it may be preferable to use unanodized aluminum, and to accept generalized corrosive attack rather than run the risk of perforation, which may occur with anodized metal.

For ordinary atmospheric exposure, it is usually possible to arrange that thin spots of the film, such as the contact points of the anodizing jigs, are located in relatively unimportant positions on the article and are hidden from view.

Since the corrosion resistance of anodic films on aluminum is markedly dependent on the efficacy of sealing (provided the film thickness is adequate for the service conditions), tests for sealing quality are frequently employed as an index of potential resistance to corrosion. While it is admitted that an unequivocal evaluation of corrosion behavior can only be obtained by protracted field tests in service, accelerated corrosion tests under closely controlled conditions can also provide useful information in a shorter time within the limitations of the particular test environment employed.

Tests for sealing include dye staining tests such as that specified in BS EN 12373-4:1999, involving preliminary attack with acid, followed by treatment with dye solution. Nitric acid[47,48] or a sulfuric acid/fluoride mixture may be used for the initial attack, and a rapid spot test[49] has been developed using the acid/fluoride mixture, followed by a solution of $10\,\mathrm{g\,l^{-1}}$ Aluminum Fast Red B3LW. Poor sealing is revealed by a deep pink to red spot, while good sealing gives nearly colorless to pale pink colorations. The test can be applied to architectural or other material on site.

Physical tests of film impedance[50] using an a.c. bridge have also been recommended, although the correlation with corrosion resistance is necessarily empirical. Film impedance increases at an approximately linear rate with sealing time and film thickness.

Exposure of the samples to a controlled moist atmosphere containing sulfur dioxide, as recommended in ISO 12473:2006, is an example of a test bridging the gap between sealing tests and accelerated corrosion tests. After exposure for 24 h at 25 ± 2 °C, poorly sealed films show a persistent heavy white bloom, while good sealing produces at the most a slight superficial bloom.

A rapid immersion test in a hot aqueous solution containing sulfur dioxide has also been developed by Kape[44] and is specified in ISO 12473:2006. Results are similar to those obtained in the preceding test, Method H. The method can also be made quantitative by measuring the weight loss.

The accelerated corrosion test in most general use is the copper accelerated acetic acid (CASS) test[51] in which the articles are sprayed intermittently with a solution made up with 5% NaCl, 0.026% $CuCl_2 \cdot H_2O$ acidified to pH 2.8–3.0 with acetic acid. The specimens are clamped at an angle of 15° to the vertical in a baffled enclosure maintained at 50 °C, and the exposure time is 24–96 h. Corrosive attack of inadequately sealed or thin films is shown by pitting.

A derivative of the CASS test is known as the Ford Anodized Aluminium Corrosion Test (FACT).[52] This makes use of a controlled electrolytic attack using the CASS solution. The electrolyte is contained in a glass test cell and clamped against the anodized surface with a Neoprene sealing gasket. A d.c. voltage of 200 V in series with a high resistance is maintained between an anode of platinum wire and the aluminum test piece as cathode. The integrated fall in potential across the cell over a fixed period of 3 min as corrosion proceeds and an increasing current flows, is taken as a measure of the corrosion resistance. Remarkably good correlation has been obtained between the readings of this instrument and the amount of pitting after exposure at a number of outdoor sites.[53,54] Comprehensive reviews of sealing techniques including test methods and corrosion behavior have been published by Thomas[55] and Wood.[56]

The behavior of samples under the actual conditions of service is the final criterion, but unfortunately such observations take a long time to collect and assess, and the cautious extrapolation of data from accelerated tests must be relied on for forecasting the behavior of anodized aluminum in any new environment.

4.03.4.1 Atmospheric Exposure

Table 7 shows the effects of thin anodic oxide films on the resistance to industrial and synthetic marine atmospheres (intermittent salt spray) of three grades of pure aluminum. The results show how relatively thin films produce a marked improvement in both environments.

In an industrial atmosphere, an anodic film only 6.5 μm thick provides a twofold increase in life over unprotected metal, and the effect under salt-spray conditions is even greater. It is interesting to note that both the industrial atmosphere and salt-spray results show parallel trends. A similar improvement in expectation of life for thin anodic coatings has been reported by Phillips[57] for 99.5% Al, and for alloys of the following compositions: Al–1.25Mn; Al–2Mg–1Mn; Al–1Mg–1Si. The results for a high-copper alloy were less good.

An interesting paper by Lattey and Neunzig[58] shows that the better the surface finish of the aluminum the thinner the coating required for protection. Neunzig[59] has also studied the effect of the hair-cracks produced by heating or bending on corrosion resistance. Although pitting was initiated by such cracks in thin films (5 μm), serious pitting in thicker films (15 μm) was observed only if anodizing had been carried out at 25 °C; films produced at 16–17 °C were more resistant to corrosive attack. This reemphasizes the importance of maintaining correct anodizing conditions for maximum corrosion resistance.

Results of exposure tests for 10 years in a severe industrial environment at Stratford, London, have been reported by the Fulmer Research Institute.[60] A range of pure and alloy specimens, anodized to a maximum film thickness of about 25 μm, was exposed at an angle of 45°. Corrosion was assessed visually, by determination of weight loss after cleaning, and by reflectivity measurements. All specimens showed signs of pitting, and there was a considerable loss of reflectivity, the under surface being more affected than the upper. A striking feature of the results was the accelerating rate of deterioration in the final five years of exposure. Although none of the samples was completely protected, results were better for the purer specimens and the thicker films.

4.03.4.2 Maintenance

In architectural work, particular care must be taken to avoid destructive attack of the anodic film by alkaline mortar or cement during erection, and temporary coatings of spirit-soluble waxes, or acetate–butyrate lacquers are frequently applied to window frames and the like to protect against mortar splashes,

Table 7 Corrosion tests on unprotected and anodized pure aluminum

	Corrosive effect	*Grade 1B (99.5%)*			*Grade 1A (99.8%)*		*Super purity (99.99%)*	
		Film thickness (μm)			*Film thickness (μm)*		*Film thickness (μm)*	
		0	*6.5*	*0*	*4*	*6.5*	*0*	*4*
Industrial atmosphere (7 years exposure)	Appearance[a] (life in years)	2.5	5	2.5	.5	5	3.5	6
	Mechanical properties (life in years)	2.75	5.5	3	4.5	6	3	5
	Pitting[b] (depth in mm)	0.18	0.20	0.18	0.25	0.25	0.20	0.13
Marine atmosphere (11 years exposure)	Appearance[a] (life in years)	<1	4	1	4	5	3	4
	Mechanical properties[c] (life in years)	5	>11	8	7	>11	>11	>11
	Pitting[b] (depth in mm)	0.30	0.18	0.15	0.33	0.15	0.15	0.08

[a] No of years to deterioration surface appearance to a fixed arbitrary level.
[b] Mean depth of Pitting obtained statistically.
[c] No of years to deterioration mechanical properties to a fixed arbitrary level.
Data reproduced from Champion, F. A.; Spillett, E. E. *Sheet Metal Ind.* **1956**, *33*, 25.

which in any event should be removed at the earliest possible moment.

The resistance of properly anodized aluminum exposed to the weather can be considerably enhanced by correct and regular cleaning. Deposits of soot and dirt should be removed by washing with warm water containing a nonaggressive detergent; abrasives should not be used. For window frames this washing may conveniently be carried out when the glass is cleaned in the normal way. In such circumstances the life of the coating may be prolonged almost indefinitely, as exemplified by the good condition of the chromic-anodized window frames of Cambridge University Library which were installed in 1933, and of the sulfuric-anodized window frames of the New Bodleian Library, Oxford University, installed in 1938.

4.03.5 Recent Developments

4.03.5.1 Practice of Anodizing

Although there have been few changes in the basic anodizing practices, and sulfuric acid is the electrolyte used in most plants, there have been many developments in the pretreatment, coloring and sealing processes associated with anodizing.

The increasingly stricter regulations on the toxicological and environmental issues associated with hexavalent chromium have pushed research efforts focused on the replacement of chromic acid anodizing.[61–65] Different weak organic acid additions, such as boric acid[66] or tartaric acid[67] to sulfuric acid anodizing baths have been proposed. Tartaric/sulfuric acid anodizing (TSA) has proven to produce porous anodic film comparable to those formed in chromic acid baths.

Over recent years, new anodizing processes have been developed. These processes do not utilize hexavalent chromium species and hydrofluoric acid and as such have environmental advantages over some earlier processes. For instance, research on plasma electrolytic oxidation (PEO),[68–78] also known as microarc oxidation (MAO), has been revived since the late 1980s. PEO is an electrochemical surface treatment process for generating oxide coatings on metals. It is an anodizing processes with the use of relatively high voltages that lead to dielectric breakdown, with sparking, on the treated component. During the process, discharges occur and the resulting plasma modifies (and enhances) the structure of the oxide layer. This process can be used to grow thick (tens or hundreds of micrometers), largely crystalline, oxide coatings on metals such as aluminum, magnesium and titanium. The resultant coatings can offer protection against wear, corrosion or heat as well as electrical insulation due to their high hardness and a continuous barrier layer.

The trend in architectural applications has been towards more matt finishes, and the sodium hydroxide-based etchants used frequently contain additives such as sodium nitrate or nitrite or sodium fluoride. Chelating agents such as gluconates, heptonates or sorbitol are added to complex the aluminum produced, and other additives such as sulfides may be present in the etchant to complex zinc dissolved from the alloy, and allow it to be used continuously without dumping.[79]

In terms of anodizing itself, the introduction of a standard for architectural applications of anodized aluminum,[80] and the European development of the Qualanod quality labeling scheme for architectural anodizing,[81,82] have been significant factors in the general improvement in the standard of anodizing. Both of these standards require the use of thick coatings (20 or 25 μm), which are sealed to a high quality level. The production of such coatings requires good control of operating parameters, particularly the anodizing electrolyte temperature, which should be below 21 °C.[83]

The field of color anodizing has changed considerably since the late 1960s. At that time the integral color anodizing processes were dominant in architectural applications, and electrolytic coloring was relatively new. Now, mainly because of the high energy costs associated with integral color processes, electrolytic coloring is by far the most widely used technique.

In order to produce color by this method, the anodized work is rinsed and transferred to a suitable metal salt solution. The process is electrolytic, and a.c. is passed between the work and a metal or graphite counter-electrode, causing the metal present in the solution to be deposited at the base of the pores of the anodic coating.[84] The height of the metal deposited in the pores controls the depth of color, and a range of shades is produced by varying the applied voltage and time. Ranges of bronze and black finishes are produced in nickel-, cobalt-, or tin-based electrolytes, and pink, maroon, or black finishes in electrolytes based on copper. The electrolytes usually contain the appropriate metal sulfate, with many other additives present to adjust or control pH, to improve throwing power, or to make dark colors easier to produce. Nickel and cobalt electrolytes are used at pH values of 4–6, and tin and copper electrolytes at pH values of 1–2; an applied voltage of the order of 10–20 V and a current density of about 30–50 A m^{-2} are normally required.

The finishes produced have very good light fastness and corrosion resistance, and, unlike integral color finishes, the shade is largely independent of the aluminum alloy and the anodic film thickness used. The whole range of shades can be produced on films as thin as 5 µm, so the finishes are also being used in trim applications.[85] Many patents and publications in the electrolytic coloring field now exist and they have been reviewed by many authors.[86,87]

In order to obtain a wider range of colored finishes, electrolytic coloring processes have been combined with conventional dyeing.[88] The work is anodized normally to the required film thickness, electrolytically colored in a cobalt- or tin-based electrolyte to a light bronze shade, and then over-dyed in an appropriate dyestuff to give muted shades of red, blue, yellow, or brown. Again the main application is architectural, and the finishes have good light fastness and durability. An alternative approach to widening the color range with electrolytic coloring has been the development of finishes based on optical interference effects,[89] whereby quite different colors can be produced in the same electrolyte. An intermediate treatment in a phosphoric acid anodizing electrolyte is normally required, between anodizing and electrolytic coloring, to produce these effects.

With the increasing use of color anodized finishes, sealing quality has become very important, and seal quality tests and standards have all improved. Sealing smut is more visible on colored than on clear anodized surfaces, and it has become common practice to try to eliminate this chemically, rather than removing it by hand wiping. Approaches to this include dipping in mineral acids after sealing,[90] and adding surface active agents which prevent smut forming.[91,92]

Sealing is normally carried out in boiling water and the high energy costs involved have led to the development of alternative, lower-energy methods. Approaches have included the use of boehmite accelerators such as triethanolamines to shorten the sealing time,[93] and the use of so-called ‘cold’ sealing systems. These latter approaches have mainly been developed in Italy,[94] and are based on the use of nickel salts in the presence of fluorides. They are used at a temperature of about 30 °C for a time of 15 min, and are claimed to give good corrosion resistance.

4.03.5.2 Mechanism of Anodizing

The development of sophisticated electron-optical techniques now allows the direct observation of the barrier layer and the pore structure of all types of anodic coating. Much of the most relevant work has been carried out at the University of Manchester.

For example using a tungsten tracer layer that is incorporated into the anodic film from the aluminum substrate has indicated a major role for oxide growth stresses in the origin of porosity.[95–98] The stresses result in flow of the relatively plastic film material in the barrier layer region of the porous film, which proceeds from beneath the pores toward the cell walls. The redistribution of film material contributes to an enhanced thickness of the film relative to that of the metal consumed. Such stress-driven pore generation is probably an important factor in the potential for self-ordering of porosity in anodic alumina.[99, 100] The behavior is contrary to expectations of a dissolution model of pore formation.

The morphology of porous anodic films are significantly affected by alloying elements in aluminum alloys. Thus, morphologies of porous anodic alumina films on aluminum alloys containing copper often differ greatly from that on high purity aluminum, as shown in **Figure 6**. The well-developed cellular morphology of the classic porous film[11,101,102] is largely absent. In contrast, the porosity in the anodic film is irregular and can incorporate a component with a lateral alignment in cross-sections of the film.

From studies of barrier films, it was revealed that alloying elements with Gibbs free energies of oxide formation per equivalent greater than that of alumina enrich at the alloy–film interface; when a critical enrichment is reached, oxidation of the alloying elements occurs; for alloying elements with oxides of lower Gibbs free energies than that of alumina, immediate oxidation, along with aluminum, is evident from the commencement of anodizing.[103–108] For copper-containing alloys, copper can be significantly enriched in the alloy immediately beneath the anodic film, up to 40 at.% Cu, by the initial formation of a copper-free alumina film.[109–111] The enriched alloy layer is typically about 2 nm in thickness. Following enrichment, copper can be oxidized, and incorporated into the anodic film as Cu^{2+} species.[112] About the same time that the oxidation of copper commences, oxygen is generated within the anodic film, with associated formation of bubbles of high pressure gas.[113,114]

The pore morphology of the porous anodic films formed on copper-containing alloys is associated with the generation of oxygen gas bubbles and their subsequent disruption. The film disruption leads to an altered direction of pore propagation, before the pore reestablishes a normal orientation with respect

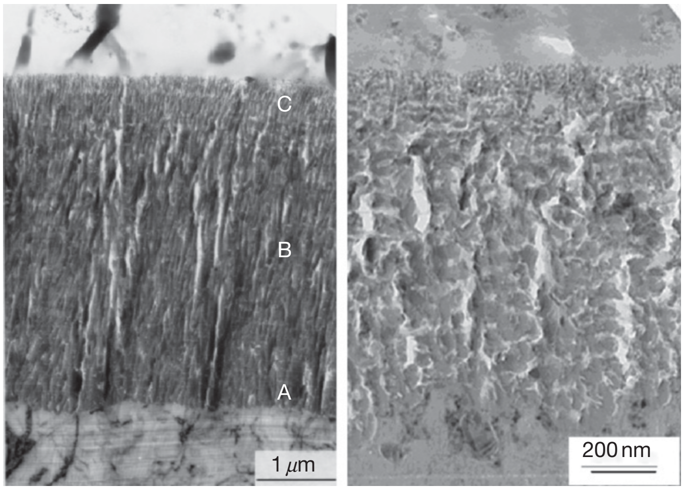

Figure 6 Transmission electron micrographs of ultramicrotomed sections of aluminum alloys following anodizing in chromic acid (DEF STAN 03-24/2): (a) AA1050 and (b) AA2024. Reproduced from Zhou, X.; Thompson, G. E.; Skeldon, P. In Proceedings of the 17th International Corrosion Congress, Las Vegas, USA, 2008; Paper 3972.

to the local alloy–film interface. The changing directions of pores contribute to a lateral aspect of the pore morphology.[101,115]

The mechanism of coloring with integral color finishes has been shown to depend on the presence of free metallic aluminum in the film, as well as on the inclusion of intermetallic constituents.[116] With electrolytic coloring processes, color is produced by light scattering effects, with the tiny metallic deposits within individual pores acting as light scattering centers.[126] Distribution of metal in the pores varies from one electrolyte to another, and this can affect the corrosion resistance of the final product.[127]

The mechanism of sealing has been shown to involve an initial dissolution and reprecipitation of hydrated aluminum oxide on the pore walls, pseudo-boehmite gel formation within the pores, and conversion of this to crystalline boehmite at the film surface.[117] The presence of an intermediate layer close to the film surface, in which the identity of the original pores has been lost, has also been recognized.[118]

4.03.5.3 Properties of Coatings

The hardness and abrasion resistance of anodic coatings have never been easy properties to measure, but the development of a British Standard on hard anodizing[119] has made this essential. Film hardness is best measured by making microhardness indents on a cross-section of a film,[120,121] but a minimum film thickness of 25 μm is required. For abrasion resistance measurements, a test based on a loaded abrasive wheel,[122] which moves backwards and forwards over the film surface, has improved the sensitivity of such measurements.

4.03.5.4 Test Methods

Tests for quality of sealing of anodic coatings have become internationally standardized. They include dye spot tests with prior acid treatment of the surface (ISO 2143:1981 and BS EN 12373-4:1999), measurement of admittance or impedance (ISO 2931:1983 and BS EN 12373-5:1999), or measurement of weight loss after acid immersion (ISO 3210:1983 and 12373-6:1999, BS EN 12373-7:2002). Of these the chromic-phosphoric acid immersion test (ISO 3210) has become the generally accepted reference test.

The revision of the main anodizing standard (BS 1615:1987) has changed it from a 'specification' to a 'method for specifying,' but it provides all the information necessary to write an appropriate specification for any anodized product.

References

1. Young, L. *Anodic Oxide Films*; Academic Press: New York, 1961.
2. Schenk, M. *Werkstoff Aluminium und seine Anodische Oxydation*; Francke: Berne, 1948.
3. Wernick, S.; Pinner, R. *The Surface Treatment and Finishing of Aluminium and its Alloys,* 3rd ed.; Robert Draper: Teddington, 1964.
4. Processes for the Anodic Oxidation of Aluminium and Aluminium Alloy Parts, DTD 910C, H.M.S.O.: London, 1951.

5. Campbell, W. J. Conference on Anodising Aluminium, A.D.A., Nottingham, Paper 11, Sept. 1961.
6. Csokan, P. *Metalloberfläche* **1965**, *19*(8), 252.
7. Csokan, P. *Trans. Inst. Met. Fin.* **1964**, *41*, 51.
8. Tsuji, Y. *Trans. Inst. Met. Fin.* **1963**, *40*, 225.
9. Scott, B. A. *Trans. Inst. Met. Fin.* **1965**, *43*, 1.
10. Edwards, J. D.; Keller, F. *Trans. Amer. Inst. Min. (Metall.) Engrs.* **1944**, *156*, 288.
11. Setoh, S.; Miyata, A. *Sci. Pap. Inst. Phys. Chem. Res. Tokyo* **1932**, *17*, 189.
12. Hunter, M. S.; Fowle, P. *J. Electrochem. Soc.* **1954**, *101*, 481.
13. Masuda, H.; Yamada, H.; Satoh, M.; Asoh, H.; Nakao, M.; Tamamura, T. *Appl. Phys. Lett.* **1997**, *71*, 2770.
14. Shingubara, S.; Morimoto, K.; Sakaue, H.; Takahagi, T. *Electrochem. Solid-State Lett.* **2004**, *7*, 2004.
15. Ono, S.; Saito, M.; Asoh, H. *Electrochem. Solid-State Lett.* **2004**, *7*, B21.
16. Masuda, H.; Fukada, K. *Science* **1995**, *268*, 1466.
17. Li, F.; Zhang, L.; Metzger, R. M. *Chem. Mater.* **1998**, *10*, 2470.
18. Nielsch, K.; Choi, J.; Schwirn, K.; Wehrspohn, R. B.; Gösele, U. *Nano Lett.* **2002**, *2*, 677.
19. Wood, G. C.; O'Sullivan, J. P. *Electrochim. Acta* **1970**, *15*, 1865.
20. Keller, F.; Hunter, M. S.; Robinson, D. L. *J. Electrochem. Soc.* **1953**, *100*, 411.
21. Lewis, J. E.; Plumb, R. C. *J. Electrochem. Soc.* **1958**, *105*, 496.
22. Hoar, T. P.; Mott, N. F. *J. Phys. Chem. Solids* **1959**, *9*, 97.
23. Siejka, J.; Ortega, C. *J. Electrochem. Soc.* **1977**, *124*, 883.
24. O'Sullivan, J. P.; Wood, G. C. *Proc. Royal Soc.* **1970**, *A317*, 511.
25. Thompson, G. E.; Xu, Y.; Skeldon, P.; Shimazu, K.; Han, S. H.; Wood, G. C. *Philos. Mag. B* **1987**, *55*(6), 651–667.
26. Cherki, C.; Siejka, J. *J. Electrochem. Soc.* **1973**, *120*, 784.
27. Verwey, E. J. W. *Z. Kristallogr.* **1935**, *91*, 65.
28. Thompson, G. E.; Wood, G. C. In *Corrosion: Aqueous Processes and Passive Films*; Scully, J. C., Ed.; Academic Press: New York, 1983.
29. Tajima, S.; Baba, N.; Mori, T.; Shimura, M. *Electrochim. Acta* **1967**, *45*, 174.
30. Brace, A. W.; Baker, H. *Trans. IMF* **1963**, *40*, 31.
31. Pullen, N. D. *Metal Ind.* **1939**, *56*, 327.
32. Liechti, F.; Rreadwell, W. T. *Helo. Chim. Acta* **1947**, *30*, 1024.
33. Spooner, R. C. *Proc. Am. Electropl. Soc.* **1951**, *44*, 1321.
34. Surganov, V.; Jansson, C.; Nielsen, J. G.; Morgen, P.; Gorokh, G.; Larsen, A. N. *Electrochim. Acta* **1988**, *33*, 517.
35. Alvay, C. E. Ph.D. Thesis, UMIST, 1974.
36. Aluminium and aluminium alloys anodizing: Method for specifying decorative and protective anodic oxidation coatings on aluminium, BS EN 12373-1: 2001.
37. Aluminium and aluminium alloys anodizing: Measurement of mean specific abrasion resistance of anodic oxidation coatings using an abrasive wheel/jet test apparatus, BS EN 12373-9: 1999; 12373-10: 1999.
38. Franckenstein, G. *Ann. Phys.* **1936**, *26*, 17.
39. van Geel, W. Ch.; Schelen, B. J. J. *Philips Res. Rep.* **1957**, *12*, 240.
40. Gwyer, A. G. C.; Pullen, N. D. *Metallurgia Manchr.* **1939**, *21*, 57.
41. Edwards, J. D. *Mon. Rev. Amer. Electropl. Soc.* **1939**, *26*, 513.
42. Guild, J. *J. Sci. Inst.* **1940**, *17*, 178.
43. Scott, B. A. *J. Sci. Inst.* **1960**, *37*, 435.
44. Kape, J. M. *Metal Industry* **1959**, *95*(6), 115.
45. Vevers, H. H. In Conference on Anodising Aluminium, A.D.A., Nottingham, Discussion on Section 4, Sept. 1961.
46. Aluminium and aluminium alloys anodizing: Assessment of quality of sealed anodic oxidation coatings by measurement of the loss of mass after immersion in phosphoric acid/chromic acid solution with/without prior acid treatment BS EN 12373-7: 2002; 12373-6: 1999.
47. Neunzig, H.; Rohrig, V. *Aluminium* **1962**, *38*(3), 150.
48. Sacchi, F.; Paolini, G. *Aluminio* **1961**, *6*, 9.
49. Scott, B. A. *Electroplating and Metal Finishing*, Feb. 1965.
50. Wood, G. C. *Trans. Inst. Met. Fin.* **1964**, *41*, 99.
51. ASTM B368-97 (2003) e1, Standard Method for Copper-Accelerated Acetic Acid-Salt Spray (Fog) Testing (CASS Test).
52. Quality Laboratory and Chem. Eng. Physical Methods, MA-P, BQ7–1, Ford (USA), Feb. 1970.
53. Carter, V. E.; Edwards, J. *Trans. Inst. Met. Fin.* **1965**, *43*, 97.
54. Carter, V. E. *Trans. Inst. Met. Fin.* **1967**, *45*, 64.
55. Thomas, R. W. In Symposium on Protecting Aluminium, Aluminium Federation: London, 1970.
56. Wood, G. C. *Trans. Inst. Met. Fin.* **1959**, *36*, 220.
57. Phillips, H. W. L. *Institute of Metals Monograph* 1952, Vol. 13.
58. Lattey, R.; Neunzig, H. *Aluminium, Berl.* **1956**, *32*, 252.
59. Neunzig, H. *Aluminium, Berl.* **1958**, *34*, 390.
60. Liddiard, E. A. G.; Sandersen, G.; Penn, J. E. In Annual Technical Conference, Institute of Metal Finishing, Brighton, 28 May 1971.
61. Thompson, G. E.; Zang, L.; Smitz, C. J. E.; Skeldon, P. *Corrosion* **1999**, *55*, 1052.
62. Eichinger, E. *Met. Finish* **1997**, *95*, 36.
63. Smith, C. J. E.; Baldwin, K. R.; Garrett, S. A.; Gibson, M. C.; Hewins, M. A. H.; Lane, P. L. *ATB Metall.* **1997**, *37*, 266.
64. Wilcox, G. D.; Gabe, D. R.; Warnick, M. E. *Corr. Rev.* **1986**, *6*, 327.
65. Moutarlier, V.; Gigandet, M. P.; Ricq, L.; Pagetti, J. *Appl. Surf. Sci.* **2001**, *183*, 1.
66. Moutarlier, V.; Gigandet, M. P.; Pagetti, J. *Appl. Surf. Sci.* **2003**, *206*, 237.
67. Boeing Co. EP 0, 405, 624,1991.
68. Patel, J. L.; Saka, N. *J. Interceram.* **2001**, *50*, 398.
69. Shatrov, A. S.; Samsonov, V. I. U.S. Patent 6,896,785, 2005.
70. Kurze, P.; Banerjee, D.; Kletke, H.-J. U.S. Patent 5,385, 662, 1995.
71. Saakian, L. S.; Yefremov, A. P.; Ropyak, L. Y.; Apelfeld, A. V. *Corrosion Control and Environment Protection*. Informative survey, VNIIOENG, Moscow, 6,1986.
72. Fyedorov, V. A.; Kan, A. G.; Maksutov, R. P. *Surface Strengthening of Oil and Gas Trade Facilities by Micro Arc Oxidation,* VNIIOENG, Moscow, 6,1989, in Russian.
73. Markov, G. A.; Gizatullin, B. S.; Rychazhkova, I.B. USSR Patent 926,083, Bul. Inv. 17, 1982.
74. Snezhko, L. A.; Tchernenko, V.I. USSR Patent 973,583, Bul. Inv. 23, 1982.
75. Gradkovsky, R. J.; Bayles, S. N. U.S. Patent 3,956,080, May 11, 1974.
76. Brown, S. D.; Kuna, K. J.; Van, T. B. *J. Am. Ceram. Soc.* **1971**, *54*(8), 384.
77. Monfort, F.; Berkani, A.; Matykina, E.; Skeldon, P.; Thompson, G. E.; Habazaki, H.; Shimizu, K. *Corros. Sci.* **2007**, *49*(2), 672.
78. Yerokhin, A. L.; Nie, X.; Leyland, A.; Matthews, A.; Dowey, S. J. *Surf. Coat. Technol.* **1999**, *122*(2–3), 73–93.

79. Kape, J. M. *Trans. Inst. Met. Fin.* **1971**, *49*, 22.
80. Specification for anodic oxidation coatings on wrought aluminium for external architectural applications, BS EN 3987: 1991.
81. Qualanod, Specifications for the Quality Sign for Anodic Oxidation Coatings on Wrought Aluminium for Architectural Purposes, Zürich, 1983.
82. Carter, V. E. *Trans. Inst. Met. Fin.* **1977**, *55*, 9.
83. Architectural Anodising: Sulphuric Acid Anodic Film Quality, British Anodising Association, 1981.
84. Sheasby, P. G.; Cooke, W. E. *Trans. Inst. Met. Fin.* **1974**, *52*, 103.
85. Short, E. P.; Fern, D.; Kellermann, W. M. In SAE Conference, Detroit, 1983, Paper 830389.
86. Brace, A. W.; Sheasby, P. G. *The Technology of Anodising;* Aluminium Technology Ltd.: UK, 1979.
87. John, S.; Balasubramanium, V.; Shenoi, B. A. *Fin. Ind.* **1978**, *2*, 32.
88. Grossman, H.; Speier, C. Th. *Aluminium* **1979**, *55*, 141.
89. Sheasby, P. G.; Patrie, J.; Badia, M.; Cheetham, G. *Trans. Inst. Met. Fin.* **1980**, *58*, 41.
90. Aluminium Co. of America, U.S. Patent 3,822,156, 1974.
91. Göhausen, H. J. *Galvanotechnik* **1978**, *69*, 893.
92. Speiser, C. Th. *Aluminium* **1983**, *59*, E350.
93. Olin Mathieson Chemical Corp., U.S. Patent 3,365,377, 1968.
94. Strazzi, E. *Alluminio* **1981**, *50*, 496.
95. Garcia-Vergara, S. J.; Iglesias-Rubianes, L.; Blanco-Pinzon, C. E.; Skeldon, P.; Thompson, G. E.; Campestrini, P. *Proc. R. Soc. A* **2006**, *462*, 2345.
96. Skeldon, P.; Thompson, G. E.; Garcia-Vergara, S. J.; Iglesias-Rubianes, L.; Blanco-Pinzon, C. E. *Electrochem. Solid State Lett.* **2006**, *9*, B47.
97. Garcia-Vergara, S. J.; Skeldon, P.; Thompson, G. E.; Habazaki, H. *Electrochim. Acta* **2006**, *52*, 681.
98. Garcia-Vergara, S. J.; Skeldon, P.; Thompson, G. E.; Habazaki, H. *Corros. Sci.* **2007**, *49*, 3772–3782.
99. Ono, S.; Saito, M.; Asoh, H. *Electrochim. Acta* **2005**, *51*, 827.
100. Jessensky, O.; Müller, F.; Gösele, U. *Appl. Phys. Lett.* **1998**, *22*, 1173.
101. Zhou, X.; Thompson, G. E.; Skeldon, P. In Proceeding of the 17th International Corrosion Congress, Las Vegas, USA, 2008, Paper 3972.
102. Garcia-Vergara, S. J.; El Khazmi, K.; Skeldon, P.; Thompson, G. E. *Corros. Sci.* **2006**, *48*, 2937.
103. Habazaki, H.; Shimizu, K.; Skeldon, P.; Thompson, G. E.; Wood, G. C.; Zhou, X. *Corros. Sci.* **1997**, *39*, 731–737.
104. Paez, M. A.; Foong, T. M.; Ni, C. T.; Thompson, G. E.; Shimizu, K.; Habazaki, H.; Skeldon, P.; Wood, G. C. *Corros. Sci.* **1996**, *38*, 59.
105. Habazaki, H.; Paez, M. A.; Shimizu, K.; Skeldon, P.; Thompson, G. E.; Wood, G. C.; Zhou, X. *Corros. Sci.* **1996**, *38*, 1033.
106. Habazaki, H.; Shimizu, K.; Paez, M. A.; Skeldon, P.; Thompson, G. E.; Wood, G. C.; Zhou, X. *Surf. Interf. Anal.* **1995**, *23*, 892.
107. Zhou, X.; Habazaki, H.; Shimizu, K.; Skeldon, P.; Thompson, G. E.; Wood, G. C. *Thin Solid Films* **1997**, *293*, 327.
108. Habazaki, H.; Zhou, X.; Shimizu, K.; Skeldon, P.; Thompson, G. E.; Wood, G. C. *Electrochim. Acta* **1997**, *42*, 2627.
109. Paez, M. A.; Bustos, O.; Thompson, G. E.; Skeldon, P.; Shimizu, K.; Wood, G. C. *J. Electrochem. Soc.* **2000**, *147*, 1015.
110. Habazaki, H.; Paez, M. A.; Shimizu, K.; Skeldon, P.; Thompson, G. E.; Wood, G. C.; Zhou, X. *Corros. Sci.* **1996**, *38*, 1033.
111. Habazaki, H.; Shimizu, K.; Skeldon, P.; Thompson, G. E.; Wood, G. C.; Zhou, X. *Trans. Inst. Met. Finishing* **1997**, *75*, 18.
112. Zhou, X.; Thompson, G. E.; Robinson, J.; Skeldon, P. *J. Electrochem. Soc.* **2005**, *152*, B393.
113. Skeldon, P.; Thompson, G. E.; Wood, G. C.; Zhou, X.; Habazaki, H.; Shimizu, K. *Philos. Mag. A* **1997**, *76*, 729.
114. Zhou, X.; Thompson, G. E.; Paez, M. A.; Skeldon, P.; Habazaki, H.; Shimizu, K.; Wood, G. C. *J. Electrochem. Soc.* **2000**, *147*, 1747.
115. Iglesias-Rubianes, L.; Garcia-Vergara, S. J.; Skeldon, P.; Thompson, G. E.; Ferguson, J.; Beneke, M. *Electrochim. Acta* **2006**, *52*, 7148.
116. Wefers, K.; Evans, W. T. *Plating Surf. Fin.* **1975**, *62*, 951.
117. Wefers, K. *Aluminium* **1973**, *49*, 553.
118. Thompson, G. E.; Furneaux, R. C.; Wood, G. C. *Trans. Inst. Met. Fin.* **1975**, *53*, 97.
119. Specification for hard anodic oxidation coatings on aluminium and its alloys for engineering purposes *BS EN* 5599:1993.
120. Metallic and other inorganic coatings: Vickers and Knoop microhardness tests, BS EN ISO 4516: 2002.
121. Thomas, R. W. *Trans. Inst. Met. Fin.* **1981**, *59*, 97.
122. Göhausen, H. J. *Trans. Inst. Met. Fin.* **1978**, *56*, 57.
123. Thompson, G. E.; Furneaux, R. C.; Goode, J. S.; Wood, G. C. *Trans. IMF* **1978**, *56*, 159.
124. Thompson, G. E.; Furneaux, R. C.; Wood, G. C. *Trans. IMF* **1979**, *57*, 123.
125. Stickley, G. W.; Howell, F. M. *Proc. Am. Soc. Test. Mater.* **1950**, *50*, 735.
126. Goad, D. G. W.; Moskovits, M. *J. Appl. Phys.* **1978**, *49*, 2929.
127. Sheasby, P. G. Paper presented at Aluminum Finishing Seminar, St. Louis, 1982.

4.04 General Principles of Protection by Coatings

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Abbreviations

ASTM American Society for Testing of Materials
BS British Standard
CVD Chemical vapor deposition
FCC Face centered cubic
GMR Giant magnetoresistive
HE, DTD Aluminum alloy designation codes
NASA National Aeronautics and Space Administration

4.04.1 Introduction

The application of metallic coatings for the protection of metals may be required for one or more of the following reasons:

(a) to prevent or reduce corrosion of the substrate metal;
(b) to modify the physical or mechanical properties of the substrate metal;

[†] Deceased.

(c) to achieve and maintain some desired decorative effect.

Many coatings also have a role in wear resistance and may have other important properties to be considered, for example, silver electrodeposits for electrical contacts.

Although the initial choice of coating material applied for reasons (b) or (c) may be dictated by the particular properties required, the corrosion behavior of the composite metal coating–metal substrate system must also be taken into consideration insofar as it may affect the maintenance of the desired properties. Consequently, in all cases where protective metal coatings are used, the corrosion performance of both coating and substrate requires careful consideration.

The choice of substrate metal is usually governed by cost and weight as well as general physical, mechanical or, fabricational properties, and these factors will normally dictate a very limited number of possible materials none of which may be ideal in resisting the corrosive environment that will be encountered in service. Ideally, a protective metal coating should exclude completely the corrosive environment from the substrate metal and, if this can be achieved, only the resistance of the coating metal itself to that corrosive environment needs to be considered. However, in practice, discontinuities in the coating may occur during application or be produced subsequently by mechanical damage or by the corrosion of the coating itself. In these cases, the corrosion performance of the bimetallic system so produced is of major importance.

4.04.2 Anodic and Cathodic Coatings

A detailed discussion of galvanic corrosion between dissimilar metals in contact in a corrosive environment is given in the chapter on galvanic corrosion in this book. In the case of coating discontinuities, the effect of the anode–cathode area relationship and the nature of any corrosion products formed at small discontinuities may modify any choice made on strict considerations of general galvanic corrosion theory based on the potentials of the coating and substrate in the environment under consideration.

Thus, coatings which are anodic or cathodic to the substrate are both used in practice, but the former will provide sacrificial protection at a coating discontinuity, and the latter may stimulate attack on any exposed substrate. The sacrificial consumption of an anodic coating at a pore or discontinuity results in a gradual increase in the area of substrate exposed and a corresponding decrease in the corrosion current density, which, in time, may become insufficient to maintain protection in the centre of the exposed area. The rate of sacrificial consumption of an anodic coating is reduced by several factors such as the resistance of the electrolyte solution within the discontinuity, blocking of the discontinuity by corrosion products, or the formation of protective films on the exposed substrate which may be encouraged by an increase of electrolyte pH by the cathodic reaction at the discontinuity. Under these circumstances, the life of the anodic coating will be prolonged.

Zinc and cadmium are both anodic to steel and provide sacrificial protection to the substrate when used as coating metals. On exposure to industrial atmospheres, zinc will protect steel for a longer period than cadmium, whereas in many marine or rural environments, cadmium provides a longer period of protection. Layton[1] attributes this difference in behavior to the nature of the corrosion products formed in the different environments. In industrial atmospheres, soluble sulfates of both zinc and cadmium are produced and are removed by rain so that corrosion can continue freely. Under these conditions, zinc, which has a more negative potential than cadmium in most environments, is a more efficient anode than cadmium and gives a longer period of protection to the substrate. In rural and marine exposure, however, the cadmium carbonates and basic chlorides that are formed are insoluble and corrosion is stifled to a greater extent than in the case of the more soluble zinc carbonates and basic chlorides, so tending towards a longer life with cadmium coatings.

When cathodic coatings are used, the sacrificial action is reversed, the substrate being attacked and the coating protected. This attack on the substrate can be highly localized and can lead to rapid penetration through the thickness of the metal. The effect is appreciably reduced by electrolyte resistance and by the stifling action of corrosion products, as mentioned above for anodic coatings, and the production of substrate corrosion products within the discontinuity can significantly decrease the corrosion rate and delay penetration.

Decorative coatings of nickel plus chromium are cathodic to steel or zinc alloy substrates, and with these protective systems, deliberate use may be made of discontinuities in the chromium topcoat where corrosion of the underlying nickel will occur. If the number of these discontinuities in the chromium layer is greatly increased, the current density at each individual corrosion site is reduced; the penetration of corrosion through the thickness of the nickel layer is thus slowed down, and the period of protection of the substrate metal is prolonged.

In general, the choice between cathodic or anodic coatings will be governed by the service application. Where cathodic coatings are used, any attack on the substrate will be highly localized, leading to rapid perforation of thin sections with a consequent loss of functional integrity. Anodic coatings, on the other hand, will protect exposed areas of substrate metal by sacrificial action until the area exposed exceeds that, over which cathodic polarization of the corrosion reaction can be maintained, after which time the substrate itself will corrode freely.

With both anodic and cathodic coating systems, account must be taken of the extent to which the presence and nature of corrosion products on the surface may impair either the decorative aspects or the functional use of the article. For example, the presence of small amounts of corrosion products on the surface of gold-plated electrical contacts can markedly increase the electrical contact resistance and cause malfunctioning; the problem may be overcome by increasing the thickness of the gold deposit – thus reducing its porosity – or by interposing an undercoat of a more resistant metal to act as a barrier layer between the gold and the substrate.

Because of the many variables which can influence the corrosion reaction, the use of the e.m.f. series of metals to predict the behavior of galvanic couples in a given service environment can be hazardous and misleading. Numerous examples of coatings expected to act cathodically but have, in fact, been anodic have been reported in the literature,[2–5] and specialized lists of galvanic couples in different environments have been compiled.[6–8]

4.04.3 Factors Affecting Choice of Coating

Many factors are involved in the choice of coating material to be used for any particular application, and these will now be described.

4.04.3.1 Resistance to the Corrosive Environment

The principal difficulty in assessing the resistance of a coating material to a corrosive environment lies in an adequate and accurate definition of that environment. Metals exposed to natural atmospheres will corrode at markedly different rates depending upon the degree of pollution present and a number of interrelated meteorological factors. Atmospheric corrosion rates for most of the metals in common use have been published by many authors and by official organizations such as the American Society for Testing and Materials (ASTM).[9] These tables may be consulted for general guidance but must always be used with caution by choosing data for environments that most nearly approach the service conditions concerned. However, purely local conditions can markedly affect the rate of attack. An example of this, in the authors' knowledge, involved the corrosion of galvanized-steel air-intake louvres on the roof of a building in a severe industrial environment; most of the louvres gave satisfactory service, but premature rusting occurred on those that faced in a westerly direction where the prevailing winds exposed them to additional chloride contamination picked up from a nearby river estuary. A detailed knowledge of both the macro- and microenvironmental conditions to be encountered is thus seen to be essential if the best choice of coating is to be made, and it is often desirable to make site inspections before recommending a coating system for a particular application.

When the corrosive environment consists of water or other liquids, the effect of the presence of minor constituents in the liquid as well as the degree of aeration and rate of flow must be taken into account.

4.04.3.2 Practicability of Application

It is essential to choose a material and a method of application that will provide a coating of adequate thickness with good coverage and distribution over the surface of the article.

Hot-dipped tin coatings are difficult to apply outside the thickness range of 8–38 mm,[10] and hot-dipped zinc coatings do not normally greatly exceed 50 mm in thickness. Hollow sections and excessively large articles may be impractical to handle by the hot-dipping process, and very thin sections may be subject to much distortion.

Electrodeposited coatings may range in thickness from about 0.1 mm to about 25 mm for decorative and protective purposes, though considerably greater thicknesses may be applied in the case of coatings for wear resistance purposes. The shape of the article to be plated greatly influences the thickness and coverage of the electrodeposit. Copper and nickel deposits cover well and throw well into recesses, and leveling can be obtained during electrodeposition. Zinc gives good coverage but poor leveling, and chromium has a very poor throwing power leading to bare areas in deep recesses of the plated article. Precious metals, because of cost, tend to be electrodeposited in thicknesses of less than 1 mm, and at these thicknesses, porosity of the electrodeposit is a significant factor; acid gold electrodeposits tend to be less porous than the deposits from alkaline baths.

Sprayed metal coatings may be applied without limitations of size of the article to be processed such as may apply for hot-dipping processes, and the thickness and coverage of the coating can be readily controlled during application. Problems can arise, however, with applications involving complex shapes or hollow sections. Coating thicknesses are normally in the range 50–250 mm but considerably greater thicknesses may be built up for applications involving wear resistance, and diffusion heat-treatments may be subsequently applied in order to improve the resistance further. Sprayed metal coatings are of a porous nature and contain a high proportion of oxides produced by the method of application. In service, corrosion products may build up in the pores of the coating which can contribute materially to a stifling of the corrosion reaction, but even so, sacrificial protection of the substrate exposed at any coating discontinuities may still be maintained.

Cladding by pressing, rolling or extrusion can produce a coating in which the thickness and distribution can be readily controlled over wide ranges, and the coatings so produced will be completely free from porosity. Although there is very little practical limit to the thickness of coatings that can be produced in this way, the application of the process is limited to comparatively simple-shaped articles that do not require much subsequent mechanical deformation. Among the principal uses are lead and aluminum sheathing for cables, lead-sheathed sheets for architectural applications and composite extruded tubes for heat exchangers.

4.04.3.3 Compatibility of Galvanic Coupling

Most of the published data on galvanic corrosion concern solid metal couples rather than bimetallic coating systems, and it is important to bear in mind that the same galvanic relationships do not necessarily apply in both cases; nevertheless, useful guidance can be obtained from the data for the solid-couple systems exposed to suitable environments. Data have been reported[11] for combinations of metals commonly used in the electrical industry; couples involving plated brass, copper, and aluminum were exposed to a 1% salt spray and the corrosion currents (mA) were measured over a 1-week test period. The relative ratings in this test are shown in **Table 1**, and items of particular interest in this table are coatings of aluminum on either brass or copper that are unsatisfactory because of the active galvanic corrosion that occurs at discontinuities. If tin plating is used as an undercoat to the aluminum, corrosion of the substrate is prevented, but if tin is applied as a topcoat over the aluminum (particularly by means of the conventional zincate process) it is sufficiently porous to allow the aluminum to continue to function as an active anode and corrosion can continue.

Table 1 Performance of various crimped metallic couples in 1% salt spray

A. Completely Satisfactory Combinations
Copper/nickel-plated copper
Copper/gold-plated copper
Tin-plated copper/aluminum
Tin-plated copper/nickel-plated copper
Tin-plated copper/solder-dipped copper
Tin-plated brass/aluminum
Solder-dipped copper/nickel-plated copper
Nickel-plated copper/gold-plated copper
Nickel-plated copper/silver-plated copper
Gold-plated copper/silver-plated copper
Aluminum/tin-plated aluminum (no copper undercoat)
B. Satisfactory Combinations, Slight Galvanic Corrosion
Copper/silver-plated copper
Solder-dipped copper/tin-plated aluminum
Copper/tin-plated copper
Copper/solder-dipped copper
Copper/reflowed tinned copper
Silver-plated copper/tin-plated copper
Silver-plated copper/solder-dipped copper
Gold-plated copper/tin-plated copper
Aluminum/tin-plated aluminum (zincate process)
C. Borderline, Moderate Galvanic Corrosion
Gold-plated copper/solder-dipped copper
Tin-plated aluminum/nickel-plated copper
Aluminum/solder-dipped aluminum
D. Unsatisfactory, Severe Galvanic Corrosion
Aluminum/brass
Aluminum/copper
Tin-plated aluminum/copper
Aluminum/nickel-plated copper
Aluminum/nickel-plated brass
Aluminum/silver-plated copper
Tin-plated aluminum/silver-plated copper
Aluminum/gold-plated copper
Tin-plated aluminum/gold-plated copper

The relationships given in Table 1 apply to the specific environment quoted, and it must always be remembered that if the conditions are varied, even to only a small extent, different galvanic effects may be produced.

4.04.3.4 Effect of Coating Process on Substrate Properties

The application of any coating process may affect the physical or mechanical properties of the substrate material and any such effects should be considered when choosing the type of coating to be used and its method of application.

With hot-dipping processes, apart from the risk of distortion previously mentioned, the high temperatures involved can produce annealing, for example, softening of brass and copper during hot-tinning. Furthermore, hard and brittle intermetallic-alloy zones are produced during hot-dipping as a result of diffusion of the liquid coating metal into the solid basis metal, for example, $FeSn_2$ in the tinning of steel, Cu_6Sn_5, and Cu_2Sn in the tinning of copper – the extent and depth of the alloy formation depending on temperature and time of dipping. Thus, too long a dipping time in hot-dip galvanizing can lead to flaking during subsequent mechanical deformation.[12,13]

Evolution of hydrogen during some electrodeposition processes can cause embrittlement if it diffuses into the substrate; the effect has been reported for chromium and cadmium plating of high-strength steels,[14] and provision is made in relevant standards[15,16] for diffusion heat-treatments after plating to reduce the hazard. Alternatively, zinc or cadmium coatings may be applied by vacuum deposition, thus avoiding any embrittlement of the steel – a process of this nature having been developed by the Royal Aircraft Establishment, Farnborough. Cases have also occurred where cracks in a highly stressed electrodeposit have acted as stress-raisers, which initiate stress-corrosion of susceptible substrate metals.

Although the annealing effects of overheating are avoided when coatings are applied by metal spraying processes – provided that those processes are properly applied – it has been reported[17] that compressive stresses imparted to the substrate by the grit-blasting pretreatment can alter the fatigue properties of the material. Cladding involves extensive cold-working, which may necessitate annealing of the composite material before use.

4.04.3.5 Coating Properties

A number of physical and mechanical properties of coating metals need to be considered when making a choice of metal to be used in a particular application.

Appearance, color, and brightness are important in decorative applications. Copper, zinc, cadmium, nickel, silver, and gold can be readily plated in a bright condition, while tin normally plates as a dull deposit but may be brightened by flash-melting after electroplating (flow brightening process). Aluminum and lead deposits are always dull, but reflective aluminum coatings can be produced by roll-cladding using highly polished rolls. Colors may range from the blue-white of chromium through yellows for gold or brass to the reds of bronzes. Reflectivity after polishing also varies with the coating metal, being very high for silver and rhodium and progressively decreasing in the order aluminum and palladium, tin, zinc, gold, iron, and lead.

Hardness, strength, and wear resistance are prime properties, not necessarily interrelated. For example, rubbing contact between two hard surfaces may produce more wear than with two soft surfaces, though, in general, rubbing contact between one hard and one soft surface causes wear in the softer material. However, mechanical design factors can alter this wear relationship so that the harder material wears to a greater extent, for example, the case of the rapid wear imposed on a steel record needle rubbing against a vinyl record surface. In general, the hardest deposits are those of chromium, nickel and rhodium; with iron, copper, zinc, cadmium, and silver in an intermediate hardness group; with tin, lead, gold, and indium being relatively soft.

Temperature resistance, that is, a combination of melting point and oxidation resistance, may be of prime importance. A general correlation exists between melting point and hardness since both reflect the bond strength of the atoms in the crystal lattice, and the preferred order of coating metals for use in high temperature applications as temperature is increased is silver, aluminum, nickel, rhenium, chromium, palladium, platinum, and rhodium.

The electrical conductivity of coatings is often of secondary importance since they are of thin section and are in parallel with a metallic substrate of larger cross section, which is generally a good electrical conductor. A more important property for coatings used as electrical contacts is surface hardness and the ability to remain free from oxide and tarnish films.

Thus, although aluminum has almost four times the conductivity of tin, it is often tin-plated to improve its electrical contact properties. Other coating metals commonly used for low-voltage applications are gold, tin/lead, silver, palladium, copper, rhodium, and nickel.

4.04.3.6 Economics

Economic factors are obviously of prime importance when choosing both the coating material and its method of application. Individual items in the economic balance sheet will vary not only with the material and the process but also with availability, local labor costs and factors unique to the design and use of the articles concerned. A further factor that frequently does not receive adequate importance in costing is the ease or otherwise of maintaining the finish to ensure an adequate and efficient service life for the component. In general, though with many exceptions, processing costs may range in ascending order from hot-dipping to plating, spraying, and cladding. The lowest cost group of metals includes zinc, copper, iron, and lead; the intermediate group contains nickel, tin, tin/lead, cadmium, and aluminum; and the highest cost group comprises silver, palladium, gold, and rhodium, though cost relationships may vary from time to time as a result of price fluctuations in response to supply and demand.

Experience in the application of metal-coating processes can materially affect economics. Thus, although it is possible to apply aluminum by electrodeposition, the process is difficult to operate and few metal finishers apply the process; the application of aluminum coatings by hot-dipping or by metal spraying is much more readily accomplished, and more of these types of installations are becoming available on the metal-finishing market.

4.04.4 Coatings in Practical Use – Overview

In modern coating technology, the range of materials used is ever increasing and specific coatings may be chosen and applied, often by specially designed techniques, for particular applications. Details of the behavior of various specific metal coatings are given elsewhere in this book, but some general information on a number of the more commonly applied coating metals is as follows.

4.04.4.1 Zinc

This is an anodic coating material that may be applied by hot-dipping, metal spraying or electrodeposition, with a good corrosion resistance to most neutral environments, particularly when used in combination with chromate or phosphate passivation treatments. In most cases of atmospheric exposure, zinc will provide good protection to steel, particularly where any sulfur pollution is present, but in rural and pure marine environments the conditions of humidity and chloride pollution level can reduce the effectiveness of zinc coatings and make the use of cadmium more suitable, though the same degree of protection may often be achieved at lower cost by increasing the thickness of the zinc coating. Zinc is the preferred coating for steel used under immersed conditions in scale-forming waters or sea-water and, since it is less toxic than cadmium, it should be used in applications involving welding.

The life of zinc coatings is generally proportional to thickness and independent of the method of application, though it has been reported[18,19] that zinc electrodeposited from the sulfate bath gives a better performance than when deposited from the cyanide bath. Hudson[20] has reported lives for 42-mm-thick zinc coatings on steel ranging from 3½ years in a severe industrial environment (Sheffield) to more than 10 years in a rural environment (Llanwrtyd Wells), and Gilbert[21] quotes lives of 4–5 years in London, 9 years in Cambridge, and 18 years in Brixham.

4.04.4.2 Cadmium

Cadmium also provides a sacrificial coating to steel and gives better protection than zinc in applications where strong acids and alkalis may be encountered and those involving immersion in stagnant or soft neutral waters. It should be used in applications involving bimetallic contact with aluminum and in electrical applications where ease of solderability is important. Cadmium has a low torque resistance and should be used as a coating material in cases where bolted assemblies have to be frequently dismantled. It also provides better protection than zinc in enclosed spaces where condensation can occur, particularly when there is contamination by organic vapors.

Cadmium is more expensive than zinc. It is usually applied by electrodeposition in thicknesses up to about 25 mm and has a superior tarnish and stain resistance to that of zinc. As with zinc, the life of cadmium coatings is proportional to thickness; Hudson[20] quotes a life of only 9 months at Sheffield for a 25-mm-thick coating and ~8 years for a 42-mm-thick coating exposed to a marine environment at Calshot.

4.04.4.3 Tin

Tin is applied by hot-dipping or electrodeposition and has a similar corrosion behavior as that of zinc. Coating thicknesses are usually in the range 12–50 mm, and in the lower portion of this range coating porosity can be a factor to be taken into account (see discussions by Kochergin,[22] and Gonser and Strader[23]).

Tin coatings are widely used in the electrical industry because of their good contact properties and in the food industry because of low toxicity. In addition to pure tin coatings, a number of alloy coatings have been developed for special applications, for example, tin–lead (terne plate), tin–zinc, tin–cadmium, tin–bronze, and tin–nickel. Reference should be made to the relevant chapter in this book and to the publication by Britton[24] for data on the corrosion of tin and its alloys.

4.04.4.4 Aluminum

Aluminum may be applied as coatings by metal spraying, cladding, hot-dipping and electrodeposition, though the last-named process is difficult to apply, and by far, the largest proportion of aluminum-coated metals are produced by the first two methods.

In atmospheric exposure to industrial environments, its corrosion rate is only about one-third that of zinc and the corrosion reaction is stifled by the tenacious oxide which is produced; nevertheless, it can frequently function as an anodic coating both for steel and for the less corrosion-resistant aluminum alloys.

Hudson[20] reported lives of about 4½ years for 38-mm-thick metal-sprayed aluminum coatings on steel exposed at Sheffield, and more than 11½ years for coatings 75 mm thick. Sprayed aluminum coatings (~125 mm thick) have also provided complete protection against exfoliation and stress corrosion to aluminum–copper–magnesium (HE15) and aluminum–zinc–magnesium (DTD 683) alloys in tests lasting up to 10 years in industrial and marine environments.[25,26]

4.04.4.5 Nickel

Nickel has an inherently high corrosion resistance, particularly in chloride-free atmospheres, and is widely used as a coating material in the chemical industry. When exposed to the atmosphere, rapid tarnishing and slow superficial corrosion occur; for this reason, nickel coatings are seldom used alone, but they are widely used as undercoats beneath bright chromium to give decorative and protective schemes for steel, zinc-alloy and copper-alloy consumer goods notably in the automobile and domestic hardware industries. Used in this way, corrosion of the nickel undercoat is confined to localized pitting that develops at discontinuities in the chromium layer and which will eventually penetrate into the substrate. Many special processing variations have been developed to improve the corrosion resistance of these composite coatings, and recommended systems are detailed in standards documents such as BS 1224 (1970).[16]

4.04.4.6 Lead

Lead coatings are mainly applied by cladding and find principal use in the chemical industry for resistance to sulfuric acid, for cable sheathing resistant to attack by soils and in architectural applications where resistance to industrial atmospheres is particularly good. They rely for their protective action on the formation of insoluble corrosion products that stifle the corrosion reaction and lead to very long service lives, but the corrosion resistance is impaired when chlorides are present.

4.04.4.7 Copper

Except in the case of certain decorative and electrical applications, copper is seldom used as a coating material in its own right owing to the rapidity with which it tarnishes, particularly in sulfur-polluted environments. Nevertheless, its atmospheric corrosion resistance is good owing to the development of the well-known green patina of basic copper salts, which give protection against further corrosion of the metal. When copper coatings are used for their decorative effect, the high luster and distinctive color are retained by applying a protective coating of transparent lacquer which may contain an inhibitor, for example, benzotriazole.

By far, the largest use of copper as a coating metal is in the form of undercoats to other protective schemes, such as the nickel plus chromium systems, where they offer great benefit by leveling the surface to improve the brightness of the finished article. Their role in the corrosion protection of the substrates is complex; they are themselves often preferentially attacked when overlay coatings are penetrated by corrosion, and can stimulate enhanced corrosion of the substrate when penetration through their thickness occurs. On the other hand, however, in the case of coatings of bright nickel plus microdiscontinuous chromium, the use of a copper undercoat is known to improve corrosion resistance and to extend the period of protection of the substrate.[27]

4.04.4.8 Chromium

Chromium is highly resistant to atmospheric corrosion, being almost inert in most atmospheres, and is therefore used as a thin, bright overlay to other coatings to retain decorative appeal for long periods. The thickness of these coatings, applied by electrodeposition, is normally in the range 0.3–1.3 mm. In the lower thickness range, the coating contains minute discontinuities which cannot be eliminated by increasing the thickness, since spontaneous cracking of the deposit occurs as the thickness builds up. The tendency to cracking of chromium electrodeposits is encouraged and put to good use by inducing cracking on a microscale by processing modifications. When this is done, the microcracked deposits so produced provide greater protection to nickel-plated steel and zinc-alloy substrates exposed to the atmosphere by increasing the area of nickel exposed at the microdiscontinuities, and thereby reducing the corrosion current density at individual corrosion sites with a consequent reduction in the rate of penetration through the nickel layer.

Chromium is also a very hard metal with excellent wear resistance, and so is widely used as a coating material for engineering applications. For these purposes, coatings are applied by electrodeposition which may be several millimeters thick. These hard engineering chromium coatings invariably contain fine cracks and fissures which can allow corrodents to attack the substrate, but this is not often a hazard in service and in many cases they are advantageous in providing a means of retaining lubricant on the working surface during use.

4.04.4.9 Precious Metals

Gold and platinum, being highly noble metals, can provide highly corrosion-resistant coatings, but are rarely used for this application alone because of cost. Silver, though cheaper than gold or platinum, has a somewhat lower corrosion resistance since it is very prone to attack by sulfides, which cause dark tarnishing.

The principal use of gold is as a very thin coating about 0.05 mm thick for electrical and electronic applications. Because of the thinness of gold electrodeposits, porosity must be very carefully controlled since seepage of corrosion products from substrate or undercoat exposed at these pores can have serious adverse effects on both appearance and electrical properties of the composite. The porosity can vary with the thickness of the deposit (Figure 1), and with the type of plating bath and with its method of operation (Figure 2), and the phenomenon has been extensively studied by Clarke and many others.

4.04.5 Recent Developments

The general principles of protection of metal substrates by metallic coatings are, of course, clear. Nevertheless, detailed considerations and particular aspects have received continued attention and some

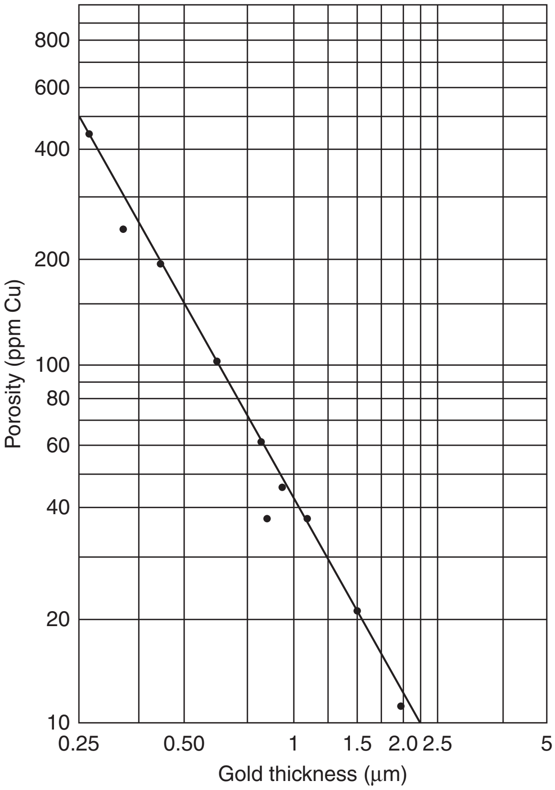

Figure 1 Log–log plot of gold-plate porosity against thickness for the conventional hot-cyanide gold-plating bath on copper substrate. The porosity was determined by the amount of copper (ppm) dissolved under standard conditions by an ammonia–ammonium persulfate test solution.

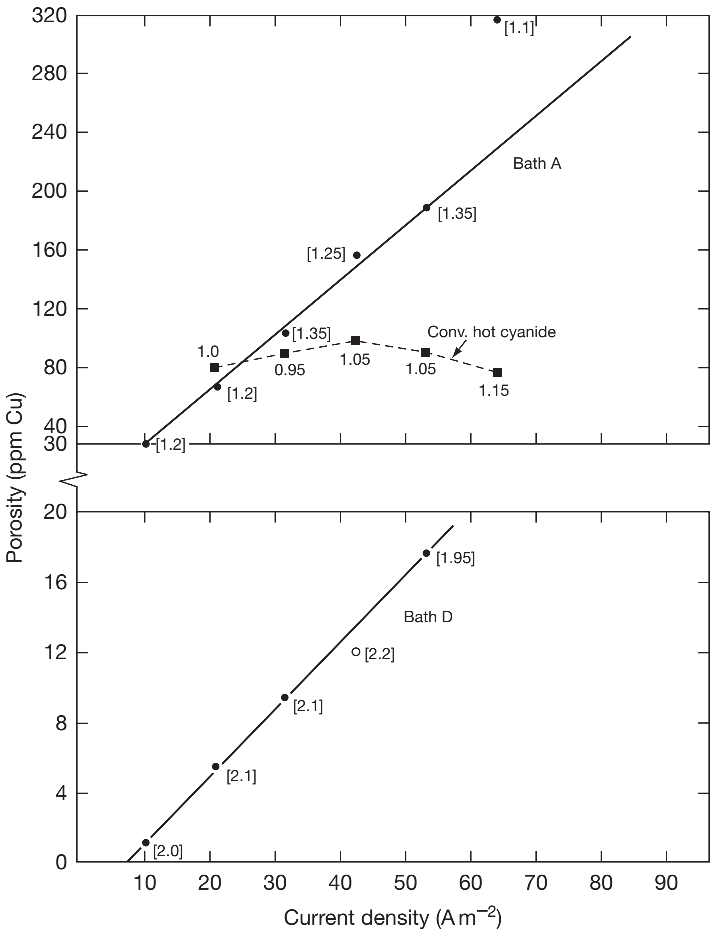

Figure 2 Linear plots of the effect of current density on the porosity, expressed as ppm Cu, for three different gold-plating baths. The numbers next to each point show the actual average thickness (in mm) for each test. Bath A was a proprietary alkaline cyanide bath using silver as a brightener. Bath D was an acid gold bath containing cobalt and an ethylenediaminetetraacetic acid (EDTA) gold complex.

of these developments can be highlighted. Among general treatments, several books may be noted dealing with the coating spectrum and the theory of protection,[28–30] and a book on the testing of such coatings for product performance assessment in relation to quality assurance is also available.[31]

4.04.5.1 Galvanic Coupling

This particular topic remains vital but often controversial especially when attempts are made to codify practice and opinion. The British Standards Institution have published a 'Commentary on corrosion at bimetallic contacts and its alleviation,'[32] which represents an important first attempt to produce such a code. It lists 23 metals and alloys coupled to each other in three atmospheric and two immersed environments using a four-point subjective scale to describe behavior.

The shortcomings of such a code are mainly attributable to the limited number of environments considered because specific behavior is generally related to specific metal–electrolyte behavior which can result in substantial potential changes or even polarity reversals. A polarity reversal implies a large potential at one or both metal electrodes and may be attributed to two main factors:

1. onset of passivity on the more base (negative) metal, thereby raising its surface potential to more noble values;
2. solution complexants reacting with free metal ions of the corroding metal thereby lowering that metal's corrosion potential.

The features of instances of such potential reversals have been described[33] and include tin coatings on steel in various foodstuffs, particularly acid fruits,[34,35] cadmium coatings on steel in hard waters,[36] and zinc and aluminum for cathodic protection of steel in natural groundwaters.[37,38]

4.04.5.2 Porosity

The study of coating porosity and its effect on corrosion rates continues to be an important subject and is generally directed at establishing the minimum thickness that can be allowed in a specification, related of course to a test/service corrosion environment. Porosity usually decreases exponentially with coating thickness (**Figure 1** represents a relationship for part of the range only) and the minimum acceptable thickness can be defined according to 0, 0.5, 1.0%, etc. porosity level or to a threshold corrosion rate. The ability to measure porosity rapidly and precisely is therefore of importance and the whole subject has been critically reviewed by Clarke.[39] In many cases, the purpose of such testing is to separate effects on porosity of the coating process itself and the substrate preparation and roughness; the latter is often the aspect most susceptible to improvement.

The comparative tests for porosity are not very accurate or susceptible to statistical analysis. A number of electrochemical tests have been devised that are more sensitive and give better numerical data; such tests depend upon selection of a suitable solution for each coating–substrate combination but have shown considerable promise and commercial instruments have been marketed.[40–42]

4.04.5.3 Environment Classification

All testing has to be related to environmental conditions whose characteristics must be defined. The relation of accelerated corrosion test condition to real service conditions is one aspect, while another is defining classes of environment and relating them to characteristic corrosion performance in order to produce useful specification guidelines. BS5493:1977 is an attempt to do this using four categories appropriate primarily to the United Kingdom (**Table 2**). Such a classification is clearly an oversimplification, but represents an important step in this particular direction.

Table 2 Atmospheric corrosion environments[a]

Type 1	Nonpolluted inland	Rural areas, town suburbs
Type 2	Polluted inland	Industrial towns and cities
Type 3	Nonpolluted coastal	Type 1 but with marine spray
Type 4	Polluted coastal	Type 2 but with marine spray

[a] BS 5493:1977.

4.04.6 Alternative Coating Systems

The drive of financial economy has been manifest in terms of the need to establish alternative coating systems for particular applications based not on technical performance alone but also on cost saving and sometimes environmental or ecological considerations. Thus expensive metals may be challenged by cheaper metals and alloys, and cheap metals by nonmetals. Every coating is under such economic pressure; some have withstood by reducing thickness, improving quality, and maintaining performance, but some have succumbed to the competition. Gold in particular has faced competition from brass electrodeposits in the cheap market, titanium carbonitride (CVD produced) for wear-resistant applications and Pd-Ni alloy electrodeposit for electrical connectors and contacts, each representing cost saving and improvement in selected properties.[40–42]

The desire to replace cadmium is generally attributed to its toxicity, both in terms of process pollution and product corrosion, and several alternatives are feasible: thicker zinc, tin–zinc alloy or tin–nickel alloy depending upon the precise application.[43] The demise of decorative nickel–chrome systems in the automotive industries of the world is partly due to cost and partly to market image, and not to technical performance where major improvements took place in the period 1960–1975 through the establishment of duplex nickel underlayers and microdiscontinuous chromium top layers. In the 1980s, the trend has been towards black finishes produced generally by powder-applied epoxy polymers.

A recent publication by Dini[47] provides a relatively novel text covering the material science of coatings and substrates.

4.04.7 Multilayer Coatings

The use of layered electrodeposits has been practiced since the 1800s and has continued to the present day. The usual reason is for the use of a thick functional underlayer with a thin decorative or cosmetic top layer; cost of a top layer such as gold is clearly an important factor. In the case of chromium, which is stressed and liable to cracking in service, the underlayers of nickel provide both protection against corrosion and resistance against crack continuation to the substrate. Nickel has been a common underlayer but recently concerns of nickel allergy with consumer–jewellery products have led to nickel-free underlayers, for example, Cu–Sn–Zn, being used. Such underlayers are usually of 1–20 µm thickness, the top layer being 0.1–2 µm thick. The history and wider development of such layered systems have been reviewed elsewhere.[48–50]

Underlayers for electrodeposits are deliberately added and are now an integral part of the coating specification. The origin has clearly been the need to increase corrosion resistance with a vulnerable top layer. The logic has been that if one layer can have a dramatic effect, perhaps many layers will continue the trend. The technique has been to use pulse techniques with specially formulated solutions and often potential, not current, control. In this way, an alloy plating solution of A and B can be pulsed to yield alternate layers of A-rich and B-rich layers. The length of the current pulses determines the layer thickness by a Faraday–Coulomb calculation. A number of layered electrodeposits have been studied, for example, Zn–Ni, Zn–Co, Zn–Fe, and enhanced corrosion resisting performance has been reported using layer thicknesses of ∼1 µm. It has been noted that for steel, it is generally better to use an initial layer rich in zinc, and total thicknesses up to 50 µm have been produced. (It should be noted that the alternative production technique of using two solutions with the substrate being moved from solution to solution is possible but is much less elegant because of the need to rinse between plating stations and the risk of passivation during the transfer.) Similarly, pumping alternate solutions and rinses through a fixed cell is possible but again rather inconvenient.

The ideal alloy system has often been stated to be Cu–Ni, as the alloy is one continuous FCC phase. This has also been well studied but for enhanced magnetic characteristics (giant magnetoresistive (GMR) applications). The solution requires a mild complexant, typically citrate or tartrate, in a simple acid formulation to be most effective.

The same principles have been adapted to attain enhanced coating hardness or strength for which thicknesses in the nanometer range are needed, and some promising results have been achieved. The nanometer thickness appears to exploit the grain interfaces as dislocation ‘wave’ guides, thereby restricting ductility in depth direction.

These layering techniques have long been recognized as coating design opportunities and should always be part of any specification. Substantial development can be expected leading to more widespread incorporation into standard specifications.[48–50]

4.04.8 Metal Whiskers

Metal whiskers are primarily, but not exclusively, found on electrodeposited coatings during product storage generally over relatively long periods of time. The phenomenon of such spontaneous metallic whisker growth can be identified, commonly, for metals such as tin, zinc, and cadmium. The first real documented evidence is from such growths emanating from cadmium-electroplated surfaces in capacitors in aircraft radios during the Second World War.[51] It soon became evident that such growths were more problematic on tin and perhaps, to a lesser extent, zinc surfaces. Whisker growths can vary in their morphology, with filamentous and nodular outcrops being the most common. Long filaments often pose the biggest potential problems because of their size and propensity and becoming detached from the metal surface from which they are growing. With tin finishes widely utilized in electronics, the chances of such growths causing reliability issues are obvious.

A single mechanism for whisker growth still eludes researchers. Many attempts have been made to provide such a theory: well known mechanisms include dislocation theories involving Frank–Read sources,[52] recrystallization,[53] two-stage dislocation involving climbing and gliding of dislocation loops,[54] and a cracked oxide theory.[55] With electronic devices reducing in size and intercomponent spacing becoming commensurately less, the threat from failures, particularly ‘shorting,’ is ever present. Until recently, one way of reducing the negative effects of tin whiskers was through alloying the metal with lead. However, with the advent of environmental concerns over the use of lead in electronics (and elsewhere) and the implementation of the so-called Pb-free solders, the occurrence of tin whisker growth may become more problematic. The continued use of tin finishes (particularly bright tin) is also problematic from a whisker growth viewpoint.

Recent investigations[56] have suggested that electrodeposited Sn–Mn alloys are capable of producing

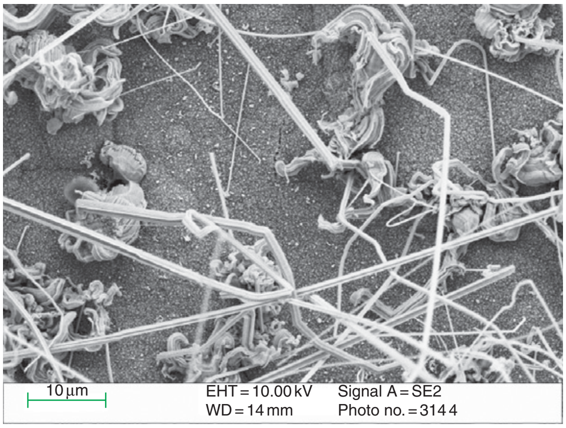

Figure 3 Scanning electron micrograph of tin whisker growth on an electrodeposited tin–manganese alloy coating.[57]

whisker growth after only a few hours at room temperature following coating formation (see Figure 3). Subsequent whisker growth was rapid and profuse.

Although the occurrence of cadmium whiskers may not be a major cause for concern due to its reduced usage (due to a poor environmental status), zinc whisker growth has come into prominence in recent years due to the metal's use as a protective coating in raised flooring in computer rooms. One particular incident in the United States involving computers in the Colorado Department of State's data center failing has been highlighted as a serious concern.[58] The occurrence of zinc-electroplated finishes in the vicinity of electronic components (e.g., on steel casings) must also be a cause for concern. The recent discovery of zinc whiskers on hot dip-galvanized surfaces[59] is a further indication of the potential size of the problem.

The perceived future problems associated with metal whisker growth, particularly on tin and zinc coated surfaces, are a cause for concern. The reasons for the occurrence of these types of growth need to be understood. At present, mitigation strategies are mainly based around the use of polymeric conformal coatings on areas of concern. The coatings do not preclude whisker growth underneath and, depending on the coating type and thickness, actual breaches of the coating layers have been reported.

For those wanting more information on whisker growth, a NASA website exists that is generally regarded as an excellent and comprehensive source of information.[60]

References

1. Layton, D. N. *Trans. I.M.F.* **1965**, *43*(14), 153.
2. Hoar, T. P. *Trans. Faraday Soc.* **1934**, *30*, 472.
3. Koehler, E. L. *J. Electrochem. Soc.* **1956**, *103*, 486.
4. La Que, F. L. *Corrosion, News Section* 8(1), April **1952**.
5. Compton, K. G.; Mendizza, A.; Bradley, W. W. *Corrosion* **1955**, *11*, 35.
6. La Que, F. L.; Cox, G. L. *Proc. Am. Soc. Test. Mat.* **1940**, *40*, 670.
7. Evans, U. R.; Rance, V. E. *Corrosion and its Prevention at Bimetallic Contacts*; HMSO: London, 1958.
8. McKay, R. J.; Worthington, R. *Corrosion Resistance of Metals and Alloys*; ACS Monograph Series, 1936.
9. *Metal Corrosion in the Atmosphere*; A.S.T.M. Special Technical Publication No. 435, 1968.
10. Hoare, W. E. *Hot Tinning*; Tin Research Institute: Perivale, Middlesex, 1947; p 7.
11. Frant, M. S. *Electron. Des.* **1961**, *20*, 112.
12. Mathewson, C. H. *Zinc*; Reinhold: New York, 1959; pp 462–465.
13. Spencer, L. F. *Metal Prod. Manuf.* **1960**, *17*, 27.
14. Cotton, W. L. *Plating* **1960**, *47*, 169.
15. BS EN12329-30:2000 – Electroplated Coatings of Cadmium and Zinc on Iron and Steel (formerly BS 1706).
16. BS EN12540:2000 – Electroplated Coatings of Nickel and Chromium (formerly BS 1224).
17. Whittaker, J. A.; King, H.; Liddiard, E. A. G. In Proceedings of the 2nd International Congress on Metallic Corrosion, 1966, pp 229–235.
18. Hippensteel, C. L., Borgmann, C. W. *Trans. Am. Electrochem. Soc.* **1930**, *58*, 23.
19. Biestek, T. *Met. Finish.* **1970**, *68*(4), 48.
20. Hudson, J. C.; Stanners, J. E. *J. Iron and Steel Inst.* **1953**, *175*, 381.
21. Gilbert, P. T. *J. Appl. Chem.* **1953**, *3*, 174.
22. Kochergin, V. P. K.; Prostkov, M. F.; Nimvitskaya, T. A. *Konserv. Ovoshchesushil. Prom.* **1959**, *14*, 22.
23. Gonser, B. W.; Strader, J. E. In *The Corrosion Handbook*; Uhlig, H. H., Ed.; Wiley: New York, 1948.
24. Britton, S. C. *The Corrosion Resistance of Tin and Tin Alloys*; Tin Research Institute: Perivale, Middlesex, 1951.
25. Carter, V. E.; Campbell, H. S. *J. Inst. Met.* **1960**, *89*, 472.
26. Carter, V. E.; Campbell, H. S. *Br. Corros. J.* **1969**, *4*(1), 15.
27. Clauss, R. J.; Klein, R. W. In Proceedings of the 7th International Metal Finishing Conference, Hanover (Interfinish 68), **1968**, p 124.
28. Carter, V. E. *Metallic Coatings for Corrosion Control*; Newnes-Butterworths, 1977.
29. Gabe, D. R., *Principles of Metal Surface Treatment and Protection*, 2nd ed.; Pergamon, 1978.
30. Gabe, D. R. Ed. *Coatings for Protection*; Inst. Prod. Eng.: London, 1983.
31. Carter, V. E. *Corrosion Testing for Metal Finishing*; Butterworths, 1982.
32. PD6484: 1979, British Standards Institution, London.
33. Gabe, D. R. *Bull. Inst. Corros. Sci. Technol.* **1981**, *19*(3), 2–4.
34. Willey, A. R. *Brit. Corros. J.* **1972**, *7*, 29–35.
35. Sherlock, J. C.; Britton, S. C. *Brit. Corros. J.* **1972**, *7*, 180–183.
36. Zanker, L.; Yahalom, J. *Corros. Sci.* **1969**, *9*, 157–167.
37. Ashworth, V.; Fairhurst, D. *Corros. Sci.* **1975**, *15*, 669–686.
38. Gabe, D. R.; Shirkhanzadeh, M. *Brit. Corros. J.* **1980**, *15*, 216–221.
39. Clarke, M. In *Properties of Electrodeposits: Their Measurement and Significance*; Sard, R., Leidheiser, H., Ogburn, F., Eds.; Electrochemical Society: USA, 1975.

40. Notter, I. M.; Gabe, D. R. *Corros. Rev.* **1992**, *10*, 217.
41. Notter, I. M.; Gabe, D. R. *Trans. I.M.F.* **1990**, *68*, 59.
42. Notter, I. M.; Gabe, D. R. *Corros. Sci.* **1993**, *10*, 217.
43. Stevenson, J. S. *Trans. I.M.F.* **1981**, *59*, 113–117.
44. Whitlaw, K. J. *Trans. I.M.F.* **1982**, *60*, 141–146.
45. Graham, A. H.; Pike-Biegunski, M. J.; Updegraff, S. W. *Plating Surf. Finish.* **1983**, *70*(11), 52–57.
46. Carter, V. E. *Met. Finish. J.* **1972**, *18*, 304–309.
47. Dini, J. W. *Electrodeposition: The Material Science of Coatings and Substrates*; Noyes Publications: Park Ridge, NJ, 1993.
48. Gabe, D. R. *Electrochim. Acta* **1994**, *39*, 115.
49. Gabe, D. R. *J. Korean Inst. Surf. Eng.* **1999**, *32*, 195.
50. Gabe, D. R.; Wilcox, G. D. *Met. Finish. (USA)* **2002**, *100*(4), 18.
51. Reported in Cobb, H. L. *Monthly Rev. Am. Electroplaters Soc.* **1946**, *33*(28), 28.
52. Eshelby, J. A. *Phys. Rev.* **1953**, *91*, 755.
53. Ellis, W. C.; Gibbons, D. F.; Treuting, T. C. In *Growth and Perfection of Crystals*; Doremus, R. H., Roberts, B. W., Turnbull, D., Eds.; Wiley: New York, 1958; p 102.
54. Lindborg, U. *Acta Metall.* **1976**, *24*, 181.
55. Tu, K. N. *Phys. Rev. B* **1994**, *49*, 2030.
56. Chen, K.; Wilcox, G. D. *Phys. Rev. Lett.* **2005**, *94*, 066104.
57. Lu, D.; Chen, K.; Wilcox, G. D. Unpublished work.
58. Svaldi, A. *The Denver Post*, Denver, CO, USA, 2004; p C01 1 July.
59. Lahtinen, R.; Gustafsson, T. E. *J. Appl. Surf. Finish* **2007**, *2*(1), 15.
60. NASA Goddard Space Flight Centre. http://nepp.nasa.gov/whisker

4.05 Diffusion Coatings

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Abbreviations

APS Air plasma spray
CVD Chemical vapour deposition
DBTT Ductile to brittle transition temperature
EB-PVD Electron beam physical vapour deposition
FBR-CVD Fluidized bed reactor-chemical vapour deposition
HTLA High temperature, low activity – referring to Al activity in the CVD process
HVOF High velocity oxy-fuel
LTHA Low temperature, high activity – referring to Al activity in the CVD process
MCFC Molten carbonate fuel cell
PVD Physical vapour deposition
TCP Topological close packed
TMF Thermo-mechanical fatigue
VPS Vacuum plasma spray

4.05.1 Introduction

Diffusion coating processes have been applied for more than half a century as a cost-effective method of improving the environmental resistance of a base alloy by enriching the surface in Al, Cr, Si, B, Ti, Zn, etc. The choice of surfacing material to be used depends on the base alloy and the final application of the component once surface-treated. For example, bolt stock are widely available zinc-coated using the sheradizing process to resist atmospheric and aqueous corrosion, while for high temperature applications, similar bolt materials could be chromized, that is, surface-enriched in chromium to produce a stainless steel surface layer. Probably the most exotic of these is the current practice to plate turbine blades with 5–10 μm of platinum, diffuse and then vapor-aluminize to produce a platinum aluminide, a high temperature oxidation-resistant coating that may be also used as a bondcoat for thermal barrier coatings for first-stage turbine blades in aero and industrial gas turbines.

Advanced applications include the surface engineering of materials and components for aerogas turbines, industrial gas turbines, medium speed diesels, automotive petrol engines, steam turbines, various power plant components, heat exchanges as well as catalytic reactors in chemical and petrochemical process plant. These illustrate the breadth of diffusion-coating applications.

From a surface engineering perspective, the final selection of the most suitable surface treatments/coatings must consider the following:

(i) the operating temperature, both of the component in service and the part/component during coating manufacture and heat treatment;
(ii) the service environment, duty cycle, and load-bearing capability of the treated components;
(iii) the desired design life and the influence of the service temperature and duty cycle on long-term metallurgical stability, with respect to oxidation, corrosion and interdiffusion with the substrate;
(iv) ease of manufacture, reproducibility, and the unit cost of the coating, compared to other manufacturing routes that may involve more costly corrosion-resistant alloys.

Obviously, loss of surface protection (passivation) can result in very high rates of attack to the substrate. In many cases, failure of a surface coating could make substrate attack worse, and may, on occasions, lead to catastrophic component failure. Even when not catastrophic, it is bound to be costly as a result of unplanned outage, downtime, and loss of production. Hence, the principal reason for applying a surface treatment of coating is to ensure that the coating is capable of operating efficiently throughout its design life. Diffusion coatings often are proven to be a cost-effective solution in this respect. Many diffusion-coating processes are so well established that international standards exist for their manufacture: for example, ASTM B 874-96 (2008) 'Standard specification for chromium diffusion coating applied by pack cementation'[1]; ASTM B 875-96 (2008) 'Standard specification for aluminum diffusion coating applied by pack cementation'[2]; and British Standard BS 4921 'zinc deposition using the "sherardising" process.'[3]

Pack-chromizing was in widespread use in the early 1950s[4] to increase the oxidation/corrosion resistance of low alloy steels. In the late 1960s, aluminizing was first used for the protection of superalloy gas turbine aerofoils.[5–7] Aluminide diffusion coatings are now routinely applied to nickel-base superalloy blades and vanes used in the hot sections of gas turbines to enhance their resistance to high temperature oxidation and hot corrosion. Plain aluminides have provided cheap and cost-effective solutions to protect superalloy components within the high-pressure turbine of both aero and industrial gas turbines. As such, they are probably the most widely used coatings in service within the gas-turbine industry. There was renewed interest in siliconizing and silicon-modified aluminide diffusion coatings for high temperature service in the early 1970s[8–11] when novel solutions to the low-temperature hot corrosion problems associated with contaminants in marine turbine plants burning impure fuels were required. This interest continues with development of multifuel-capable plants that may be fired on gasified coal, biomass, or waste-derived fuels[12] and as coating methods to coat the internal cooling passages of turbine blades.[13,14]

These aluminizing, chromizing, and siliconizing processes result in enhanced corrosion resistance through the formation of protective thermally grown oxides of Al_2O_3, Cr_2O_3, and SiO_2 as discussed elsewhere in this book. It is also possible to produce diffusion coatings containing a combination of aluminum and chromium (chromaluminizing)[15–26] or aluminum and silicon[8–13] plus modified aluminides containing precious metals (Pt, Pd)[6,27–34] or reactive elements (Y, Hf and Zr).[35–45] The performance of these modified aluminide coatings will be discussed later in this chapter.

Diffusion coatings can be applied to hot gas components using a variety of techniques including pack cementation, slurry cementation, and metallizing. Comprehensive reviews of the methods of deposition of diffusion coatings are given in Goward *et al.*,[5] Goward and Boone,[6] Grisaffe,[7] Streiff and Boone,[30] Meier and Pettit,[31] Pichoir,[46] Goward,[47] Goward and Cannon,[48] Mevrel,[49] Nicholls,[50,51] and Pomeroy.[52] All diffusion coatings, whether depositing zinc vapor onto steels (sheradizing) for aqueous/atmospheric corrosion protection, or forming high temperature oxidation-resistant nickel or platinum aluminides, are formed as a result of two distinctly similar process steps, no matter what the manufacturing method used.

1. *The solute elements must be brought into contact with surface to be coated* In the sheradizing process (zinc deposition), the vapor pressure of zinc within the pack (it is a pack cementation-based process) is sufficiently high that no vapor-phase activator is

required; thus, zinc vapor generated in the pack directly deposits onto the component surface, ready for step 2, which is the 'diffusion' process. However, for most metallic systems, this is not the case; instead, an intermediate step is required, which is the production of a vapor species with a high solute metal content. This is most commonly achieved through the use of a halide salt, or salt mix, which may involve fluoride, chloride, or iodide species. Bromide species are almost never used for health reasons, although thermodynamically there is no reason why they should not be used. These halide additions are known as 'halide activators' in the industry.

2. *The solute diffuses into the component surface* Step 2 is a key stage in the manufacture of a diffusion coating. This diffusion step forms the surface alloy or intermetallic compound. The process temperature influences the rate of diffusion, which species may diffuse and the metallurgy of the surface compound that may form and is, therefore, a critical parameter in the processing and manufacture of diffusion coatings. This aspect will be explained in more detail using the 'pack-aluminizing' process as a case study (see Section 4.05.2.1). As well, time at temperature defines the thickness of the coating formed during this diffusion step.

Thus, the main differences between diffusion-coating process routes reflect the method by which solute and substrate are brought into contact. The time at temperature controls the degree of interdiffusion, establishes the concentration gradients that will develop from the surface to the interior of the coating and defines the various layers that may form as dictated by thermodynamic and kinetic considerations.

Table 1 summarizes the currently available diffusion-coating process routes, together with a selection of elements that may be enriched into the substrate surface using these methods. Each of these process routes will be briefly reviewed.

4.05.2 The Pack Cementation Process

Pack cementation is still the traditional route used to apply diffusion coatings, with standard procedures established for chromium,[1] aluminum,[2] and zinc deposition.[3] For example, within the gas turbine industry, pack cementation was introduced into aero-engine service in 1957[48] and has been widely used to coat turbine components since the mid-1960s.[6,46–48] The coatings produced were based on the formation of nickel or cobalt aluminides and this class of coating is still extensively used, probably satisfying some 75–80% of the current world market, for protecting turbine blades under aero, marine, and industrial turbine service.

In this process, the components to be coated are buried in a 'pack,' contained in a sealed retort. Figure 1 shows a schematic diagram of a typical retort used to produce diffusion coatings, and Figure 2 shows a photograph of the quarter-size commercial production facility at Cranfield University.

The retort is heated to the desired processing temperature under either an inert gas or hydrogen atmosphere to prevent oxidation. The exact process cycle, time, and temperature are dependent on the required coating, coating thickness and the subsequent substrate heat treatment. The pack contains a donor alloy that releases solute material at a known rate and hence determines the pack activity, a halide activator that dissociates during the process cycle and acts to transport the solute material from the pack to the component to be coated and an inert oxide diluent to prevent pack sintering.

Typical pack compositions used to produce a range of metallic coatings are given in Table 2. Of these, the three diffusion-coating processes that are most widely used are: 'sheradizing' to zinc-alloy coat many small steel parts in a wide range of manufacturing sectors from the building industries, through domestic white goods to many automotive parts to impart corrosion resistance[3]; 'chromizing' which may be used to coat a wide range of steel, stainless steel and nickel or cobalt-based superalloys to impart improved corrosion resistance for temperatures up to and sometimes in excess of 800 °C[1]; and 'aluminizing' which is widely used in the aero and industrial gas turbine sector to develop intermetallic surface layers that impart enhanced corrosion resistance, thermal stability and, for some applications, wear-resistant properties. The pack aluminizing process will be used as an example. The formation of aluminide coatings by pack cementation has been extensively studied, and details of the process and characteristics of the coating are well documented in the literature.[3,5,6,15–18,20–31,35–42,46–52]

4.05.2.1 The Pack Aluminide Process

During the aluminizing process, material from the pack is transferred to the component surface through the formation of intermediate volatile aluminum

Table 1 Diffusion coating process routes

Process route	*Process characteristics*	*Diffusion coatings that may be produced on ferrous materials and superalloys*												
		Al	*B*	*C*	*Cr*	*Cu*	*Mo*	*N*	*Nb*	*Si*	*Ta*	*Ti*	*V*	*Zn*
Pack cementation	● Gas phase transport # source material as a powder # halide activator # 700–1200 °C	■	■	■	■	■	■		■	■	■	■	■	■
	● Solid state diffusion # source material as a fine powder # temperature below the alloy melting point # no activator			■										■
Slurry cementation	● Spray or dip coat application # coating material, halide activator and organic binder prepared as a paint or slurry # heat treated after coating 700–1200 °C	■			■					■				
Fluidized bed methods	● Activated gas fluidization # the halide activator is incorporated in the fluidizing gas # the coating material is in the fluidizing bed # 500–1100 °C	■		■	■					■		■		
Molten salt bath processes	● Direct thermochemical processing # 500–900 °C		■	■	■			■						
	● Metallizing # an electrolytic process in alkali fluoride solvents # 500–1200 °C	■				■		■						
Gas or vapor phase processes	● Over pack process # similar to pack process, but components processed in the gas above the pack # 900–1200 °C	■			■									
	● Vapor phase sources # Halide vapor phase sources generated in a separate vapor generator # 900–1200 °C	■		■	■			■						

monohalide gas, and as such the coating process is probably more accurately described as a chemical vapor deposition (CVD) process. Interdiffusion between the depositing aluminum and the substrate alloy results in the formation of the intermetallic coating, primarily NiAl, CoAl, FeAl, or TiAl depending on the alloy base, but containing, to a degree, most of the elements present in the base alloy, either in solution or as dispersed phases.

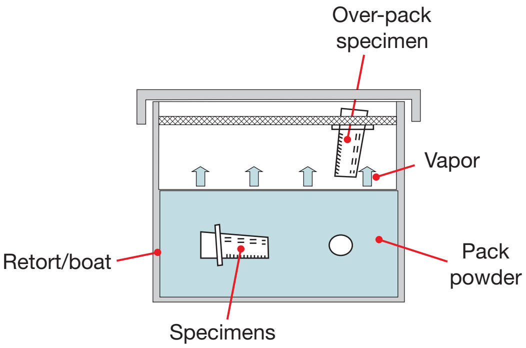


Figure 1 Schematic of a pack cementation facility.

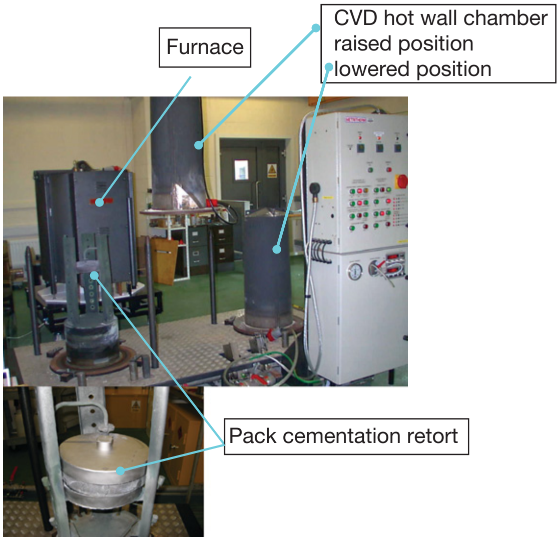


Figure 2 Pack cementation facility at Cranfield University: this is quarter size of an industrial production facility.

The CVD aluminizing process is best illustrated and described by the schematic in Figure 3, which describes the various chemistries involved during aluminum deposition and the formation of a nickel aluminide coating from an aluminizing pack. The processes involved in diffusion coating are complicated even when only nickel and aluminum are considered, as illustrated schematically in Figure 3. This behavior reflects the thermodynamic stability of the various phases in the nickel–aluminum binary system; the range of compositions for which each nickel aluminide phase is stable (which varies with process temperature); and the dominant diffusion processes in the newly (near surface) formed alloy due to the interdiffusion processes (which also depends on alloy composition).

The deposition rate and morphology of the coating depend on pack activity, process time and temperature. Table 3 presents two pack compositions used in research at Cranfield to produce nickel aluminide coatings described in this section and illustrated in Figures 4 and 5. Coatings are classified as either ‘high activity,’ when inward diffusion of aluminum occurs or ‘low activity,’ when outward diffusion of nickel occurs. Thus the first pack composition in Table 3, with a higher aluminum content, is used at lower temperatures, 700–950 °C. This forms ‘low-temperature high-activity (LTHA)’ nickel aluminide coatings. (See Figure 4 for a sample micrograph of this coating produced on the nickel-based superalloy CMSX4.) For this case, a surface layer of Ni_2Al_3 forms and a further heat treatment is required to convert this brittle surface layer to NiAl. This step is usually combined with the heat treatment required

Table 2 Typical compositions and deposition temperatures for halide activated pack cementation

Coating	*Pack composition (wt%)*	*Deposition temperature (°C)*
Al	1.2–2.7% Al, 0.8–1.2% NaF, bal. Al_2O_3	900
B	80% B, 16% $Na_2B_4O_7$, $4KBF_4$	900
Cr	48%Cr, 48% Al_2O_3, $4NH_4Cl$	850–1050
Cu	50% CuO, 50% NH_4Cl	–
Mo	75% Mo, 6% Mg, 18% TiO_2, 1% NH_4Cl	–
Nb	NbFe, Al_2O_3, NH_4Cl	1000–1100
Ti	77% Ti, 20% TiO_2, 3% NH_4Cl	–
V	40–50% FeV, 2% NH_4Cl bal. Al_2O_3	900–1200
Zn	37.5% Zn, 43.5% $ZnCl_2$, 19% KCl	300–350

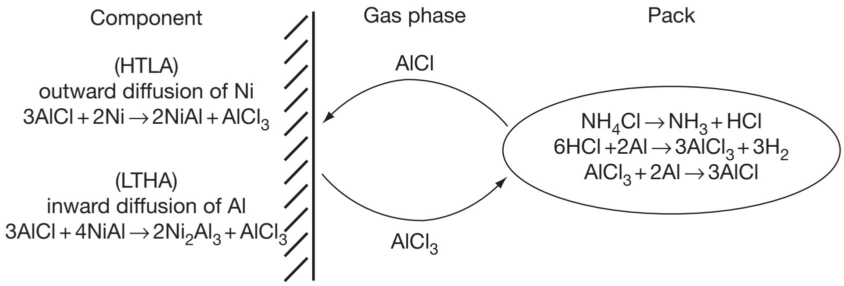


Figure 3 Schematic illustration of the chemistry involved in the 'pack aluminizing' process.

Table 3 Example aluminide pack compositions

Pack Constituent	*Low-temperature high-activity (LTHA) pack*	*High temperature low-activity (HTLA) pack*
Process temperature	700–950 °C	950–1100 °C
Aluminum flake: (to BS 388)[40]	1.7–2.7 wt%	1.2–1.5 wt%
Activator		
NaF	0.8–1.2 wt%	0.8–1.2 wt%
KHF	0.05–0.15 wt%	0.05–0.15 wt%
NH_4Cl	0.1–0.2 wt%	0.1–0.2 wt%
AlF_3	Trace	Trace
Alumina	Balance	Balance
Uncombined water	<0.3 wt%	<0.3 wt%

to recover substrate properties. This coating was deposited using an aluminiding pack containing 2% Al at 900 °C, and was heat-treated for 2 h at 1120 °C and then for 24 h at 845 °C. Figure 5 illustrates, similarly, a nickel aluminide coating produced using a high temperature low-activity (HTLA) process. The HTLA process results in the outward diffusion of nickel from the superalloy to react with the depositing aluminum to form a monophase β-NiAl intermetallic surface layer. The pack composition (Table 3) used to deposit this coating has a lower aluminum content but is processed at high temperatures, 950–1100 °C.

From this simple illustration, it is clear that the properties and performance of an aluminide coating (or for that matter any diffusion coating) will depend upon the process methodology used, the substrate temperature and the subsequent heat treatment. For aluminide coating (also modified aluminizing coatings such as platinum aluminides, see Section 4.05.4.1), the critical difference in the processes reflects whether the coating is formed by inward aluminum diffusion, that is, inward grown diffusion coatings, or outward nickel diffusion, that is, outward grown diffusion coatings.

4.05.2.2 Inward Growth Diffusion Coatings

When the aluminizing process parameters are chosen such that the aluminum activity at the component surface is high, then reaction between the nickel-based superalloy (γ-Ni + γ'-Ni_3Al matrix) and the depositing aluminum forms a surface layer of δ-Ni_2Al_3, over a subsurface layer of β-NiAl. This reaction is evident in the simple Ni–Al binary phase diagram, for process temperatures between 854 and 1133 °C (Figure 6), but may be further complicated by the addition of tertiary and quaternary elements which may modify the equilibrium phase structures.

In δ-Ni_2Al_3, the diffusivity of nickel is near zero when compared to aluminum, which diffuses rapidly (Janseen and Rieck measured this diffusion rate as 1.8×10^{-8} cm^2 s^{-1} at 600 °C)[53]; thus, the formation of a surface layer of δ-Ni_2Al_3 ensures that the coating growth results from the inward diffusion of aluminum. Phase equilibria require that beneath this layer β-NiAl is formed to accommodate the aluminum flux. This β-NiAl phase can react further with the inward diffusing aluminum to form more δ-Ni_2Al_3.

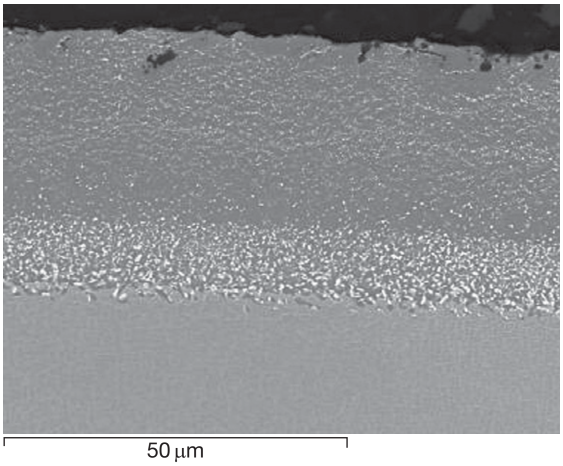


Figure 4 A nickel aluminide diffusion coating produced using a low-temperature high-activity (LTHA) pack cementation process.

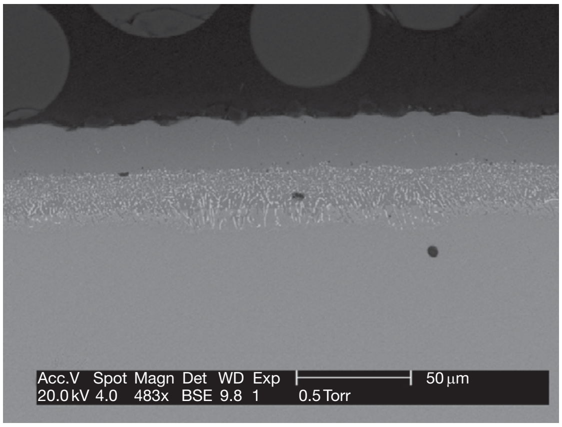


Figure 5 A nickel aluminide diffusion coating produced using a high temperature low-activity (HTLA) pack cementation process.

$$2\mathrm{NiAl} + \mathrm{Al} \rightarrow \mathrm{Ni_2Al_3}$$

As a consequence of this inward growth process, slowly diffusing alloying elements within the substrate can be entrapped in the inwardly growing aluminide coating. Thus, a high-activity aluminide coating contains precipitates that are rich in W, Mo, Ta, Re, and Cr within the β-NiAl phase.

After aluminizing, the coated material is given a high temperature heat treatment (usually linked to the heat treatment necessary to recover the base alloys' mechanical properties). During this heat treatment, nickel is able to diffuse outward from the substrate, which results in the transformation of the brittle δ-$\mathrm{Ni_2Al_3}$ phase into an aluminum-rich β-NiAl (β-NiAl has a wide solubility range for nickel and aluminum, from 46 to 74 at% Ni, 36 to 54 at% Al measured at 1100 °C).

4.05.2.3 Outward Grown Diffusion Coatings

When the aluminizing process parameters are selected such that the aluminum activity at the component surface is low (low aluminum content in the pack, high process temperatures), then aluminum is deposited on the surface, but at a reduced rate, and nickel simultaneously diffuses outward to the surface. A β-NiAl surface layer now forms. For stoichiometric and substoichiometric NiAl (Al contents less than 51 at%),[55] the diffusivity of nickel in β-NiAl is much higher than that of aluminum. Figure 7 presents the variation in nickel to aluminum diffusivity at 1100 °C as a function of the aluminum content of the β-NiAl phase.[55] Thus, this rapid nickel diffusion to the surface, coupled with the low aluminum activity at the surface, effectively holds the surface aluminum content at 51 at%. Hence, HTLA coatings are near-stochiometric at the surface and nickel-rich within the subsurface β-NiAl phase that has formed. This structure ensures outward nickel transport and the outward growth of the coating microstructure. Another important outcome of this outward diffusion process is that slowly diffusing elements from the substrate are unable to diffuse to form significant concentration levels in the outwardly growing β-NiAl. The outer zone of this coating therefore appears much 'cleaner' and is free from such precipitates as observed in the inwardly grown, aluminum-rich coating formed at lower temperatures and higher aluminum activities.

4.05.3 Other Process Methods to Form Diffusion Coatings

4.05.3.1 Slurry Cementation

Slurry-based diffusion coatings are commercially available, offering similar chemistries to those found in conventional pack cementation aluminide coatings. In slurry cementation, the coating materials and halide activator are blended as a slurry or particle-loaded paint system, using either an organic binder or a water-based emulsion. The slurry/paint system can be applied to the part to be coated through dipping or spraying at or near room temperature. The slurry spray is then cured onto the part through a low-temperature thermal treatment, typically around 200 °C. The cured pre-diffusion coating

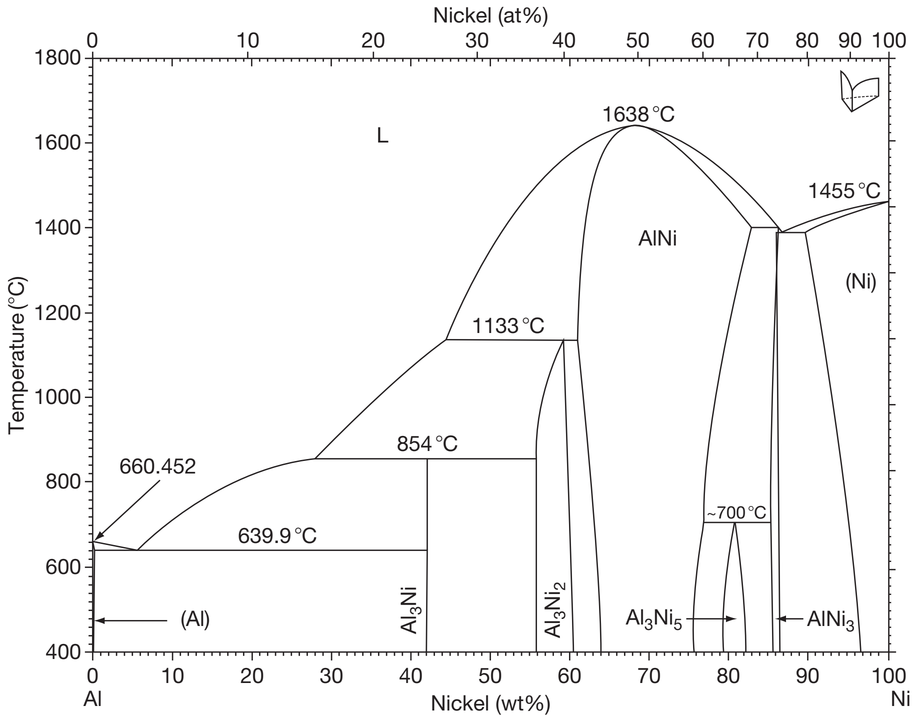


Figure 6 The Ni–Al binary phase diagram. Reproduced from Singleton, M. F.; Murray, J. L.; Nash, P. In *Binary Alloy Phase Diagrams*; Massalski, T. B., Ed.; ASM Materials Park: OH, 1990; Vol. 1, p 142.[54]

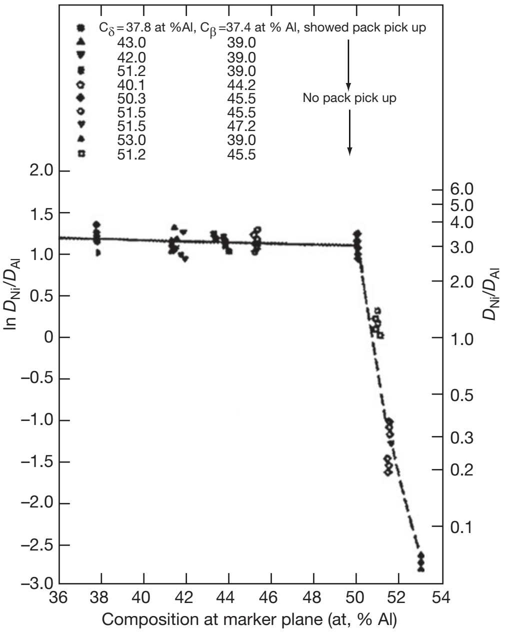


Figure 7 Variation of D_{Ni}/D_{Al} with composition in β-NiAl at 1100 °C. Reproduced from Shanker, S.; Siegle, L. L. *Met. Trans.* **1978**, *9A*, 1467.

may contain only aluminum, aluminum + chromium, aluminum + silicon, or aluminum + chromium + silicon, depending on the final service conditions envisaged. After this overlay of binder, activator and reactive metals has been built up, the aluminum, silicon and other additions are diffused into the substrate by heating the precoated parts in a furnace at temperatures between 650 and 1100 °C depending on the substrate to be coated and its final application. The temperature is chosen such that the coating material contained in the slurry reacts and interdiffuses with the substrate to form the final intermetallic coating. Reaction temperatures and the reaction chemistries are similar to those for pack cementation for halide-activated slurry systems. For systems not involving halide activation, diffusion occurs through direct contact between the molten aluminum or aluminum-silicon particles in the precured cement and the substrate to be coated.

Sermatech was an early protagonist of this form of coating, with SermaLoy J (Figure 8) – one of the first widely adopted slurry aluminide coatings – providing outstanding resistance to type II hot corrosion.[56–58]

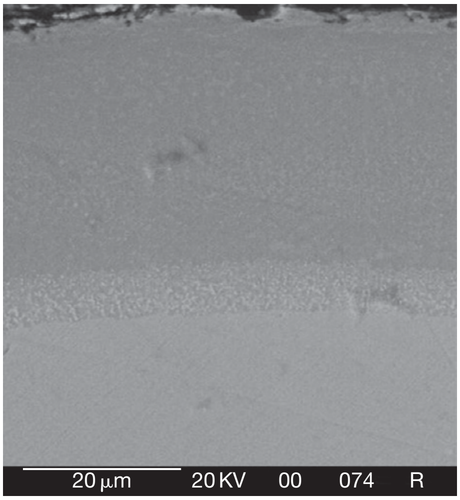


Figure 8 Micrograph of SermaLoy J.

This slurry aluminide coating forms a silicon-enriched outer layer containing Cr_2Si phases in β-NiAl, and provides oxidation and corrosion protection up to 1000 °C.[56–58] Later, as engine technologies advanced and directional solidified or single-crystal alloys were more widely adopted, less chromium was available within the alloy to form $CrSi_2$ (a critical phase within SermaLoy J)[56]; thus, joint research between Sermatech and Rolls Royce led to the development of SermaLoy 1515,[59] a multilayered structure slurry aluminide coating containing bands of $CrSi_2$. This variant is capable of providing hot corrosion protection to low-chromium-containing single-crystal alloys.[58,59] Other variants of the slurry aluminide process are now available commercially, including IP1041 developed by Indestructible Paints in the UK, and Ceral 10 by BWD Turbines Ltd. The latter uses a water-based slurry process to deposit the prediffused overlay coating prior to heat treatment and reaction to form the Si-containing aluminide coating. Most recently, slurry aluminide coating methods have been researched as a potential method for providing oxidation protection of Fe–Cr ferritic steels for steam power plants,[60–62] where the ability to form an iron aluminum oxidation-resistant coating at temperatures as low as 650 °C, coupled with the capability to coat large steam turbine components at reasonable costs, makes the process commercially competitive.

4.05.3.2 Fluidized Bed Techniques

Fluidized bed reactor-chemical vapor deposition (FBR-CVD) offers a cross between pack cementation and CVD processes. In addition, because of the excellent mixing and dispersion within the bed, efficient heat and mass exchange is ensured, giving uniform coatings on complex-shaped parts.[63–65] This allows uniform aluminide coatings to be produced on ferritic steels in relatively short times at temperatures below 700 °C.[66,67] For FBR-CVD, the fluidized bed (**Figure 9**) consists of a mixture of the material to be deposited and an inert diluent, which forms the bulk of the fluidized bed and is most often alumina or silica. The halide activator is carried in vapor form by the fluidizing gas and is introduced into the fluidizing gas usually from a separate vapor generator or directly as HCl gas. This latter process is widely used in laboratory-scale systems by fluidizing the bed in a once-through cycle with HCl in the fluidizing gas.[66,68] In more commercial-size plants, the fluidizing gas is recirculated and the level of HCl to H_2 in the feed gas adjusted to control the generation of the precursor vapor species. Also, when a vapor generator is used, it is possible to control the chemical activity of the active vapor supply to the fluidized bed reactor.

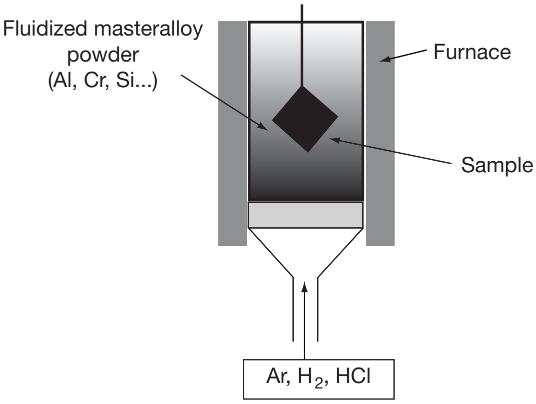


Figure 9 Schematic of a fluidized bed chemical vapor deposition system.

Components to be coated can be hung in the fluidized bed or supported on custom-designed fixtures, depending on their size. The chemistries in FBR-CVD has been extensively studied[60–68] and is similar to the LTHA aluminizing process of the pack cementation method, when aluminum powder is part of the fluidized bed medium. The primary differences are that the halide vapors are flowing, rather than diffusing, and that the carrier particle density is much lower in the fluidized bed than in the pack. Specifically, the gas flow rate must be greater than the minimum fluidization velocity; for a small laboratory experimental system, this would require argon gas flow rates between 0.35 and 1.1 l min^{-1}, with the fluidizing gas containing 5–30 vol% H_2 and 0.5–3 vol% HCl.[66,68] Given a reactor tube diameter of 3.5 cm in this laboratory scale system,[66] this equates to a linear fluidization velocity between 0.6 and 2.0 cm s^{-1} when the fluidized bed has a height of 3 cm. Scaling to large fluidizing vessel sizes, therefore, requires high gas flows; for example, for a once-through cycle, a 35-cm-diameter bed would require gas flows in excess of 100 l min^{-1}. Thus, large quantities of activator (HCl) and reactive gas ($AlCl_3$ in the case of aluminizing) would be lost to the scrubbing system. For these reasons, commercial fluidized bed systems use recirculating fluidizing gases, but this requires that the pumps, pipework and flow control equipment are designed for HCl service.

However, the benefits are that the use of a fluidized bed reactor for CVD deposition offers rapid and uniform heating of parts to be coated and good long-term stability (typically ± 0.5% variation in bed temperature, even when the bed is 15 m in diameter). These properties reflect the high heat and mass transport rates reported for fluidized bed systems,[63,64] improved process flexibility, lower capital and operating costs, precise process control, better environmental control, and the ability to automate the coating process.[67] Thus, in addition to aluminizing, fluidized bed systems have been proposed for chromizing, boronizing, nitriding, and carburizing.[68–72]

4.05.3.3 Metalliding

Metalliding uses molten alkali and alkaline-earth fluorides as solvents for the electrolytic deposition of diffusion coatings. This process is well documented for the formation of alloy and intermetallic coatings following high temperature electrolysis in these molten salts.[73–78] The process is usually carried out at temperatures in the range 500–1200 °C in metallic vessels under inert gas, principally argon. The metalliding process is a specific method to deposit highly reactive metals that cannot be normally plated from aqueous solutions. Thus, aluminum, various refractory metals, the actinides, and many rare-earth metals can be deposited using the metalliding process. This capability to deposit refractory metals means that the metalliding process provides a coating route for niche-market applications. It has been used to manufacture protective refractory metal carbide coatings to protect components in contact with nuclear fuel[73] and to manufacture protective coatings for nickel cathodes (Ni_3Nb) for use in molten carbonate fuel cells (MCFCs).[76]

The metalliding process was patented by N.C. Cook in the 1960s,[79,80] then at General Electric, to manufacture alloy and intermetallic coatings. Although process temperatures between 500 and 1200 °C are quoted, it is now acknowledged that many of the surface layers that are formed are thin unless processed above 800 °C.[73] The process consists of a galvanic cell where the anode is the reactive metal to be deposited and the cathode is the component to be coated.[79–81] Three modes of coating manufacture are now cited[81]:

1. Electrodeposition of a pure reactive metal onto the cathode, followed by interdiffusion of the metallic layers to form the alloy or intermetallic coating.
2. Metalliding, using a galvanic cell, as originally proposed by Cook.[79,80] In this metalliding process, interdiffusion occurs alongside the electrodeposition to form the alloy or intermetallic coating.
3. Thus, mode 1 can be used to deposit a surface coating from a molten salt in the temperature range 500–800 °C, which is subsequently diffused at higher temperatures or for longer times at the deposition temperature, whereas mode 2, the original patented metalliding process, requires higher process temperatures, in excess of 800 °C.
4. The third mode is similar to mode 1 but involves deposition of the coating at the ‘under potential’ for the alloy formation, following some interdiffusion process.[81]

In general, the purity of the fluoride solvents must be very high if a good and reproducible diffusion coating is to be formed. Any impurity cations in the melt will be codeposited.

Since metalliding reagents are electrochemically more reactive than the components to be coated, each coating material can only be deposited onto a specific group of metals to produce diffusion coatings. The more active the metal, the larger the scope of metallic substrates that can be coated. The most useful metalliding reactions include boriding, aluminiding, siliciding, titaniding, chromiding, zirconiding, and most recently the deposition of niobium and tantalum intermetallic coatings ‘niobiding’ and ‘tantaliding’ for the niche metal carbonate fuel cell markets.[73,76]

4.05.3.4 Molten Salt Baths

Molten salt baths have been widely used for the direct thermochemical formation of diffusion coatings.

The formation of chromized coatings for corrosion protection and chromized, carburized, carbo-nitrided, nitrided, and borided diffusion coatings for wear protection are classic commercial examples of this form of diffusion coating manufacture.

In this process, components are treated in a bath containing a molten salt of the species to be deposited, which is then diffused into the component surface. For example, a mixture of chromous and chromic chlorides is used to form a 'chromized' diffusion coating.

Sodium and potassium cyanides are used in the salt baths for carburizing, carbonitriding, and nitriding. At a given temperature, the percentage of sodium or potassium cyanate generated in the bath determines whether a carburized or nitrided surface is produced. For low cyanate and high cyanide concentrations, carburization of the component surface occurs. At cyanate concentration around 10% and for temperatures between 750 and 900 °C, mixed carbonitride surface coatings are produced. Increasing the cyanate concentration to around 25% at temperatures between 500 and 750 °C results in the formation of a nitride-rich surface layer (all salt bath nitriding processes produce iron carbides as well as iron nitrides).

Thermochemical liquid-phase boriding processes are based on molten borax to which reducing agents such as ferroboron or boron carbide are added.

4.05.3.5 Gas and Vapor Phase Chemical Vapor Deposition Processes

Gas and vapor phase processes offer the most diverse range of diffusion/chemical conversion coatings. The largest volume production of coatings based on gas and vapor phase CVD is used to combat wear. Pyrolysis of hydrocarbon gases, such as methane and propane, is used to carburize metal components. This method is generally cheaper to operate and more widely used for high-volume production than any other method aimed at producing a carburized surface treatment. The addition of ammonia to the hydrocarbon gas results in the formation of carbon nitride coatings; while pyrolysis of ammonia at temperatures between 500 and 525 °C produces a nitrided surface.

Chromized, boronized, siliconized, and aluminized diffusion coatings can also be produced by vapor decompositions but not generally at the commercial scale used for carburized and nitrided surface treatments.

In the corrosion field, especially high temperature oxidation and corrosion, chromizing and aluminizing are the most widely applied CVD coatings. Although, pack cementation (**Section 4.05.2**) is probably the most versatile and easiest-to-install small-batch process, the better process control of CVD – particularly the ability to codeposit metals and add small reactive element additions (see **Section 4.05.4.4**) – has seen an increased use of CVD and vapor phase coating routes to deposit high temperature corrosion-resistant coatings. A further advantage of these purely gas phase processes is the ability to coat internal cooling passages of the gas turbine blades, by directly feeding the vapor species into the existing cooling passages cast into the turbine blades.[13,14,43,44] Pressure 'pulse aluminizing'[82] can also be used to aid vapor transport into these narrow internal cooling passages.

(a) *The out-of-pack or over-pack process* operates in a manner very similar to pack cementation, except that the parts to be coated are suspended either above the pack or downstream from the pack (vapor generating) retort. The coating vapors (AlCl and $AlCl_3$, if aluminizing, depending on temperature and aluminum activity) are transported to the parts to be coated by an inert carrier gas. This approach results in a much cleaner coating, with no entrapped bed particles, but because of the longer path lengths for vapor transport, out-of-pack processes favor a low activity-type process, with outward coating growth and reduced coating deposition rates and thus longer processing times at any given temperature.

Figure 10, illustrates the modified retort used at Cranfield University to provide vapor phase coating deposition using an over-source deposition process. The process is entirely vapor phase using a process very similar to the Snecma vapor phase aluminizing process.[83] No longer is a powder pack required as a vapor source; instead, the source material is a crushed Cr–Al intermetallic alloy, which plays two roles: it lowers the aluminum activity creating a low-activity, outwardly grown aluminide coating, but does not melt at the desired processing temperatures. This means that it is no longer necessary to blend pack composition, and activation of the process only requires addition of the halide activator salt. **Figure 11** illustrates a micrograph of the nickel aluminide coating produced using this vapor phase route, using NaF as the activator and a deposition temperature of 1050 °C.

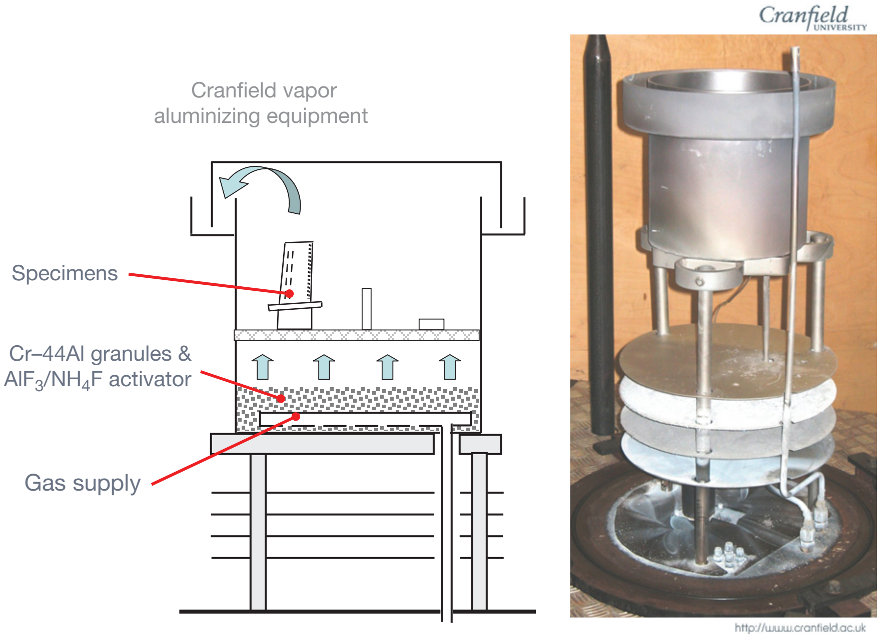


Figure 10 Modified retort to permit vapor phase aluminizing using an 'over-source' process.

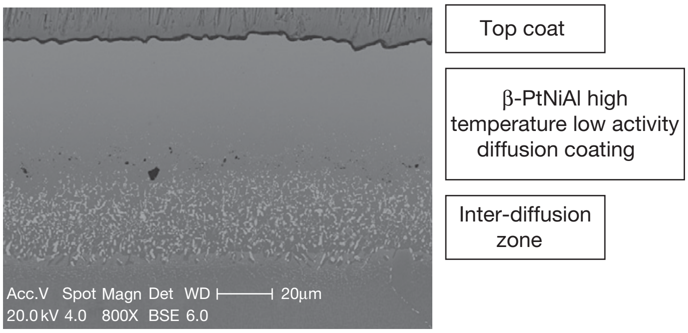


Figure 11 Micrograph of a nickel aluminide coating produced by the Cranfield vapor aluminizing process at a deposition temperature of 1050 °C.

(b) Gas phase chemical vapor deposition process reaction gases are metered into the reaction vessel from external sources, see Figure 12. Thus, the aluminum halide source gas is generated in an external vaporizer prior to being introduced into the reaction chamber. This enables better control over the reaction, since temperature, pressure, chemical activity and the flow path of the active gas can all be controlled independently. Further, separate vapor sources can be used for the external and internal aerofoil vapor circuits, permitting the outer gas-washed surface and the internal cooling passages to be coated with different compositions/thicknesses. With recent interest in adding active elements (see Section 4.05.4.4) and modifying coating compositions through codeposition, the ability to use a number of separated, controllable vapor sources permits more repeatable and reliable manufacture of the more complex coating formulations. Recent patents by Howmet have identified this approach as a method to ensure cleaner 'diffusion coatings.'[84,85]

4.05.4 Modified Aluminide Coatings

From the foregoing, it is clear that the properties of an aluminum coating (or for that matter any diffusion coating) depend on the process methodologies used to deposit the coating, the substrate composition,

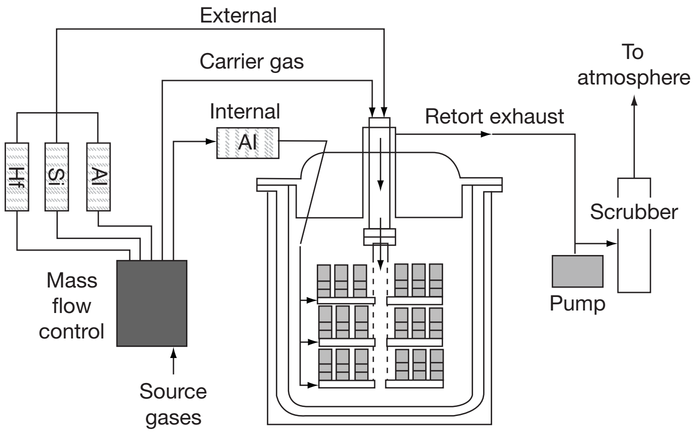


Figure 12 Schematic diagram of Howmet's vapor aluminizing process using gas phase CVD. Reproduced from Warnes, B. M.; Punola, D. C. *Surf. Coat. Technol.* **1997**, *94–95*, 1–6.

and the subsequent heat treatment. Thus, coatings produced by 'pack cementation,' 'out-of-pack' processes or 'chemical vapor deposition' will all differ in performance as discussed later in Section 4.05.4.2. Similarly, a 'pack aluminide' coating whether a simple aluminide or modified aluminide on IN100,[83,86,87] IN738,[84,88–91] IN792,[34] CMSX4,[31–34,52] AM1,[83] Rene 80,[31] or PWA 1480[31] would all be expected to behave differently. Typically, a 'high activity' pack aluminide coating (e.g., PWA73) would be 50 μm thick (65 μm including the interdiffusion zone), with an aluminum content in excess of 30 wt% in the near-surface region of the diffusion coating.[33,34] Such pack aluminide coatings offer satisfactory performance for many aviation, industrial and marine applications and provide satisfactory performance at relatively low cost. It is a mature technology first patented in 1961 and in wide service for protecting turbine blades and vanes since 1970 (as cited by Goward[48] while reviewing the historical perspective of high temperature coatings). However, at temperatures above 1050 °C, especially under cyclic conditions, or under severe hot corrosion, these simple aluminide coatings offer limited protection. Thus, from the 1970s onwards, developments in diffusion coating technologies included modification of the aluminide coatings.

Modified aluminides have been fabricated using one of the following techniques:

1. codeposition of elements from the same pack;
2. codeposition from two separate vapor sources (generated using the over-pack process or by CVD);
3. pretreatment of the superalloy before pack-aluminizing (or vapor phase aluminizing), for example, chromizing a part prior to aluminum;
4. deposition of a metallic layer, using electroplating or PVD (physical vapor deposition) techniques, prior to aluminizing, for example, a platinum-aluminide coating produced by depositing platinum onto the superalloy prior to the aluminizing treatment.

Alloy additions may include chromium,[15–26,92–97] silicon,[8–13,56–58] platinum,[6,27–34,50,93,100–113] and, most recently, various reactive element additions, including Hf, Zr, Ce, and Y.[35–45] Probably the most significant advance in this area was the development of the platinum-modified aluminum class of coating. The first commercial coating in this class was designated LDC-2 and was produced by electrodepositing a thin layer of Pt, followed by a pack-aluminizing treatment at 1100 °C.[84] Since 1970, this process has been licensed to many manufacturers who produce their own variants of this basic coating design, see Figures 14–16 for examples. Platinum aluminide coatings have much improved high temperature performance over diffusion aluminides. Although typically 2–3 times costlier than a conventional pack aluminide coating, they may last up to 3 times longer, depending on the service environment and duty cycle. Much of this most recent work results from the recognition in the 1990s that platinum-modified aluminide coatings develop stable alumina scales and hence perform as a useful bondcoat for EB-PVD thermal barrier coatings (see Section 4.05.4.1).

4.05.4.1 Platinum Aluminide Coatings and Bondcoats

Most commercial platinum aluminide coatings are manufactured by first electroplating typically 5–7 μm of platinum onto the component surface, and then heat-treating the platinum-plated component to diffuse the platinum into the nickel-based superalloy surface, prior to aluminizing. The quantity of platinum varies from one manufacturer to another, with between 2 and 10 μm in common usage. There is a commercial drive to reduce the platinum thickness to produce platinum-lean platinum aluminides with the performance enhanced by adding various reactive elements[114] (see **Section 4.05.4.4**). Equally, platinum need not be electroplated, and in a drive to develop 'clean' coating methods, alternative routes involving the PVD (physical vapor deposition) of platinum have been investigated, although electroplating methods are still the most widely used in industry.

Both high-activity and low-activity aluminizing may be used following platinum plating and its partial diffusion into the component surface. Thus, platinum aluminide coatings have been produced commercially using pack cementation, out-of-pack or over-pack processes and gas phase CVD (Warnes and Punola[84] provides a comparison of pack cementation and gas phases CVD for the production of platinum aluminum coatings, and will be discussed in more detail in **Section 4.05.4.2** on the role the coating process has on introducing impurities into the coating). Depending on the initial Pt thickness, its diffusion heat treatment and the mode of aluminizing, together with aluminizing parameters, a range of microstructures can be produced. The four most widely found structures are illustrated schematically in **Figure 13**. Thus the platinum aluminide coating can be single-phase (β-PtNiAl) platinum aluminide, for example, MDC150, MDC150L, or CN91 (see **Figure 14** for example), or a two-phase platinum aluminide, classified into one of three microstructures: an outer zone consisting of a two-phase β-PtNiAl + $PtAl_2$ over an inner β-phase NiPtAl layer (an RT22 type), an outer zone of $PtAl_2$ over an NiPtAl β phase and a structure that is a mix of both these morphologies, consisting on an outer $PtAl_2$ layer, a middle zone of $PtAl_2$ + β PtNiAl, and an inner layer of β-NiPtAl.

Figure 15 illustrates the single phase β-PtNiAl microstructure manufactured using the coating facilities at Cranfield to produce a microstructure similar to CN91. The coating was produced by PVD

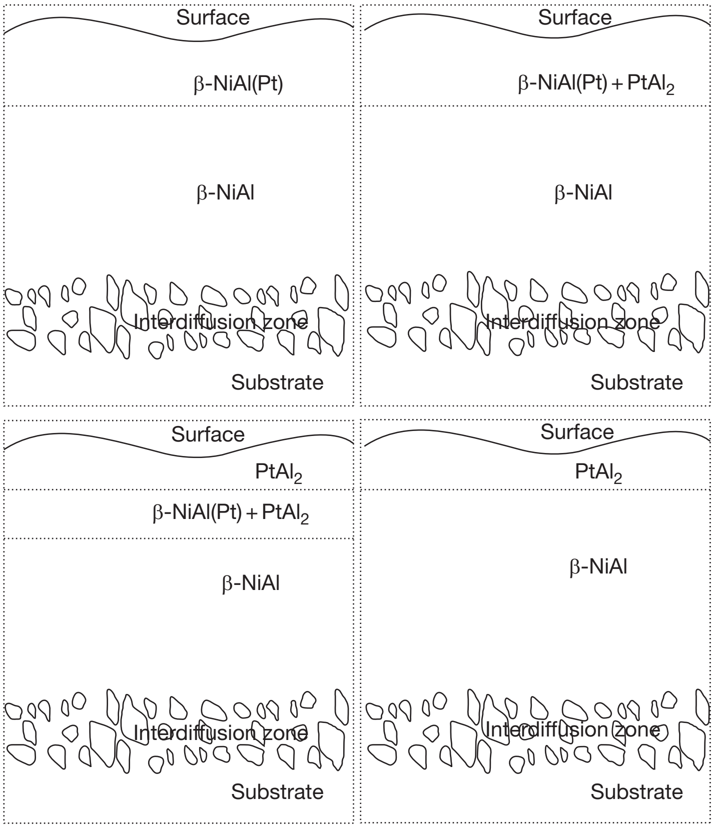


Figure 13 Schematic microstructures of platinum-modified diffusion coatings.

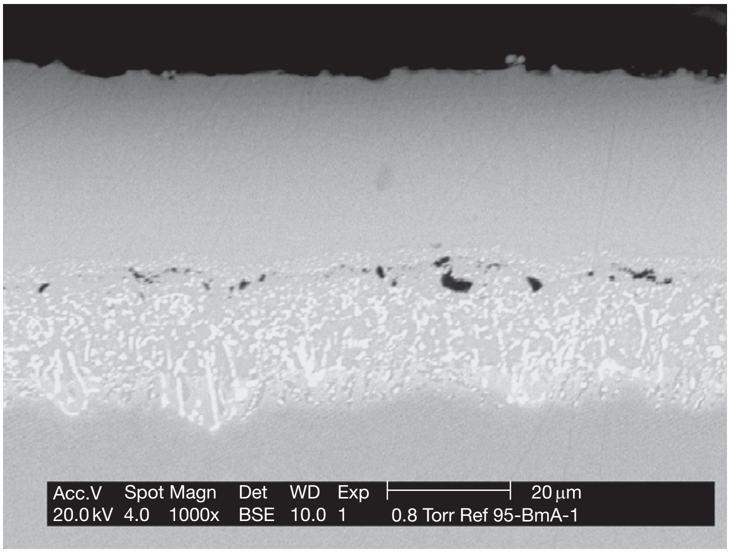


Figure 14 Micrograph of MDC150L platinum aluminide coating, produced by a gas-phase CVD process.

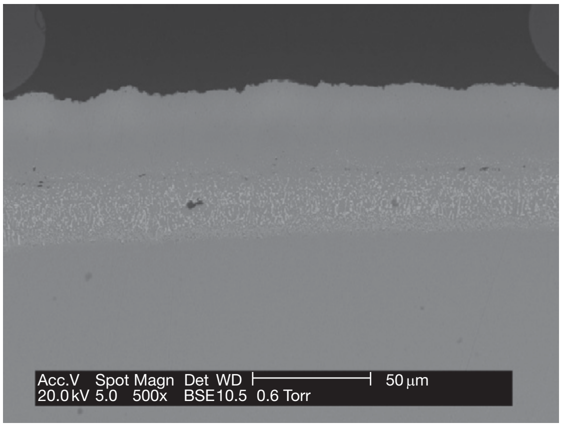


Figure 15 Single-phase platinum aluminide coating (CN91 type).

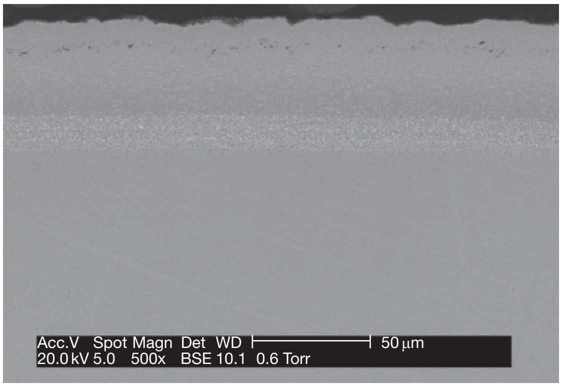


Figure 16 Two-phase platinum aluminide coating (RT22 type).

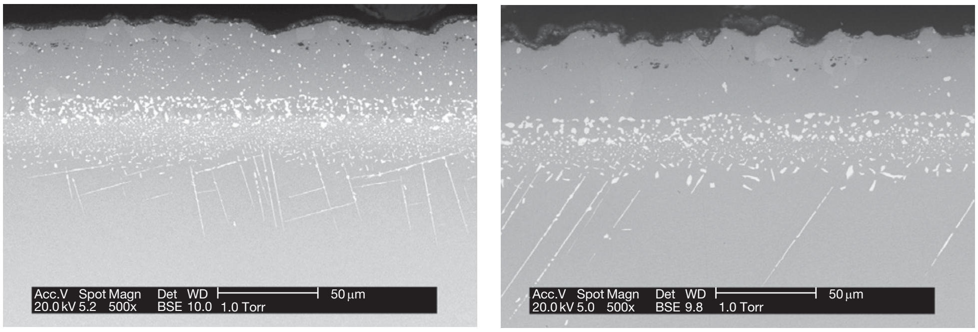
deposition of platinum to a thickness of 7 μm, heat-treated, then over-pack aluminized at 1080 °C using a HTLA process.

Figure 16 illustrates a two-phase $PtAl_2 + \beta$-PtNiAl microstructure manufactured at Cranfield. The platinum layer was again 7 μm by PVD and heat-treated, but the aluminizing treatment was a high-activity pack aluminizing process at 970 °C.

During service at elevated temperatures (above 850 °C), the microstructure of the coating continuously evolves with time and temperature. The effect of ageing up to 4000 h at 1000 °C and 1050 °C on the microstructure of RT22 is illustrated in Figure 17, which demonstrates the effect of platinum diffusion into the substrate: aluminum consumption by interdiffusion, oxidation, and the formation of various TCP precipitate phases containing refractory metals that have diffused into the platinum aluminide coating from the substrate.

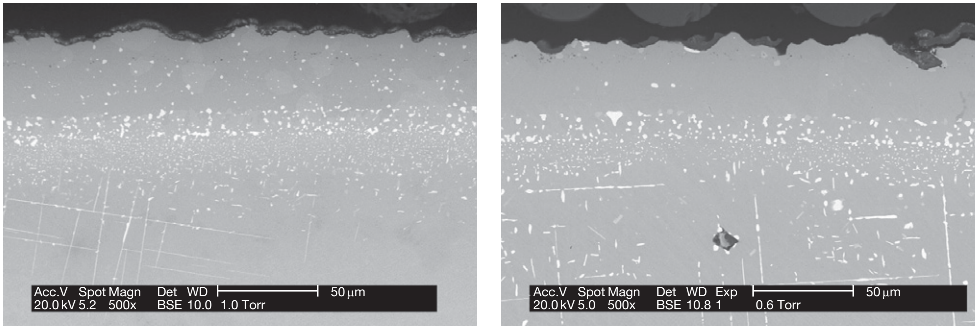
4.05.4.2 The Role of Impurities Introduced in Coating Manufacture

As discussed above, the way the coating is made as well as its final microstructure and composition can have a major influence on its performance and lifetime. With the aim of increasing oxidation life, Howmet[84] undertook a research program on the role of tramp impurities, introduced through the manufacturing process, on the cyclic oxidation lifetime of platinum aluminide coatings.



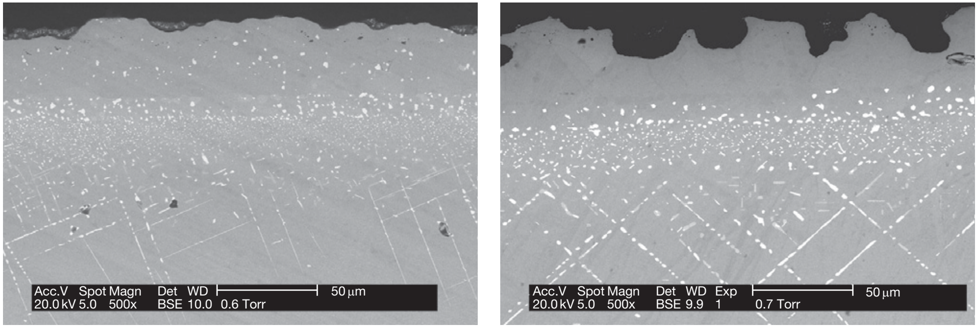
RT22 – 1000 °C, 1000 h

RT22 – 1050 °C, 1000 h



RT22 – 1000 °C, 2000 h

RT22 – 1050 °C, 2000 h



RT22 – 1000 °C, 4000 h

RT22 – 1050 °C, 4000 h

Figure 17 Influence of long-term exposure on the microstructured degradation of the platinum aluminide coating RT22 at 1000 °C and 1050 °C.

This research investigated three alternative routes to manufacture a platinum aluminide coating deposited onto an IN738 nickel-based superalloy substrate. A common platinum plating method was used for all three platinum aluminides with difference only in the method of undertaking the aluminizing process. The processes were:

(a) LDC2E: a high aluminum activity pack cementation process, resulting in inward aluminum diffusion.
(b) MDC-150: a high aluminum activity, gas phase CVD process. An inwardly grown aluminide coating activated by $AlCl_3$ generated external to the CVD retort.
(c) MDC-150L: a low-activity aluminide coating formed by outward nickel diffusion using the gas phase, and external $AlCl_3$ vapor source used to manufacture the MDC-150 coating.

Four tramp impurity levels were studied: B, P, S, and W. Three of these perceived harmful impurities come from the IN738 substrate alloy, namely B, S, and W, while the fourth (P) comes from the electroplating of platinum. Table 4 illustrates the chemical analysis results.[84]

The four elements were selected because they could be introduced into the coating from three potential sources:

(a) the superalloy substate: W, S, P, and B;
(b) the platinum plating process: P;
(c) the aluminizing process: S and B.

Table 4 Bulk chemical analysis of coated IN738 foils

Element	*As platinum plated*	*LDC2E coated*	*MDC 150 coated*	*MDC 150L coated*
B	120	140	150	50
P	450	440	390	140
S	6	7	8	5
W	23 900	23 000	5700	1300

All concentrations are in parts per million by weight (ppm).
Source: Warnes, B. M.; Punola, D. C. *Surf. Coat. Technol.* **1997**, *94–95*, 1–6.

Bulk chemical analysis of the coated foils reveals some interesting results. First, the 'low activity' CVD aluminizing process is able to 'clean up' the coating with respect to these tramp additions, reducing significantly the level of each tramp element addition. Second, the high-activity aluminide processes increase the level of B and S in the coating over that of the 'as-plated' condition. For the pack aluminide process (LDC 2E) this was thought to be due to transfer of S and B from the source alloy (analysis of the aluminum–chromium source gave 22 ppmw S and 310 ppmw B); however, the high-activity vapor aluminizing process used 99.999 wt% Al as a source in the $AlCl_3$ vapor generator.

Further microprobe studies showed that in the MDC150L coating, where the low activity aluminide appeared to clean the process, concentrations of impurities peaked in the interdiffusion zone and dropped in the diffusion coating surface, with levels at the surface significantly below that found in the IN738 substrate. Such behavior is consistent with the aluminizing process removing contaminants from the surface as a result of a gas–solid surface reaction.[84] In the 'as-coated' condition, both 'high activity' processes (LDC-2E and MDC-150) had a two-phase ($NiPtAl + PtAl_2$) microstructure, while the MDC-150L had a single-phase NiPtAl microstructure. After solution heat-treatment of the IN738, all of the coatings were single phase, but varied in thickness and surface aluminum and platinum contents: LDC-2E 74 μm thick, 20.0 wt% Al, 30.6 wt% Pt; MDC150 88 μm thick, 23.2 wt% Al, 22.6 wt% Pt; MDC-150L 77.5 μm thick, 19.5 wt% Al, 19.0 wt% Pt (the quoted thickness included the coating and interdiffusion zone).

Cyclic oxidation tests at 1100 °C (50 min at temperature, 10 min cooling) on these three coating variants (**Figure 18**) showed that the MDC150L (low-activity aluminide, formed by outward nickel diffusion) had a significantly longer life. The lifetime was defined as the time to 'zero crossover' (see **Figure 21** to illustrate this definition).

A very important conclusion from this study is that minor tramp element contaminants can influence the oxidation cyclic life, with higher contaminant levels lowering the life. Even more important is the fact that the choice of processing route can influence the level of tramp contaminants in the coating and that through a correct choice of processing it is possible to 'clean up' the coating, thereby, giving between 20% and 40% improvement in lifetime, using rounded numbers.

4.05.4.3 Chromium- and Silicon-Modified Aluminides

To combat hot corrosion, additions of chromium[56,57,92–97] and silicon[98–100,103] were extensively researched in the 1970s and 1980s. Research into the influence of these additions still continues as additions to both standard aluminides and platinum-modified aluminides, especially when considering coating on the latest third- and fourth-generation low-chromium-containing single-crystal alloys.

This early research plus service experience has shown that chromium additions to aluminide coatings offer little advantage over standard aluminide coatings under high temperature oxidation conditions. However, chromium additions are found to be beneficial and offer improved performance in industrial and marine turbine applications burning high-sulfur fuels.[15,19,20,46,49,94,97]

Additions of silicon are also known to improve hot corrosion resistance, but may also benefit the high temperature oxidation performance of aluminide coatings. Since the early work in the late 1970s and early 1980s, a number of researchers have investigated the role of Si, both for high temperature oxidation resistance and hot corrosion resistance, in diffusion aluminide coatings.[10,56–114] The possibility of using silicon aluminides for protecting internal cooling passages has also been investigated.[14,115]

The most commonly used silicon aluminide is the commercial coating SermaLoy J, a $CrSi_2$-dispersed

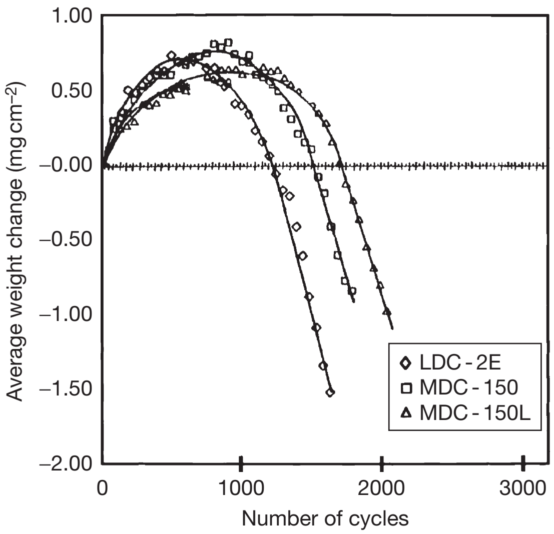


Figure 18 Cyclic oxidation lifetimes for various platinum aluminide coatings on IN738 at 1100 °C: The cycle is 50 min at temperature, 10 min cool, cycled hourly, with failure defined as the time to zero mass gain cross over (the cyclic lives were calculated from data present in Warnes and Punola).[84]

β-NiAl diffusion coating.[11,56–58,100] The microstructure of this coating is illustrated in Figure 8. SermaLoy J is manufactured using a slurry aluminizing process route. At about 10 wt% silicon in a diffusion aluminide coating, the silicon aluminide coating provides unsurpassed resistance to type I and II hot corrosion.[11,58,100] It is, however, somewhat brittle and this limits its use for internal cooling passage applications at this level of silicon content. Later, as engine technologies advanced and single-crystal alloys were widely adopted, with lower chromium contents, there was less chromium available within the alloy to form the $CrSi_2$ precipitates – a critical component of SermaLoy J[56–58] – thus a research program between Sermatech and Rolls Royce led to the development of SermaLoy 1515. SermaLoy 1515 is a layer-structured slurry aluminide diffusion coating containing bands of $CrSi_2$ precipitates as illustrated in Figure 19. SermaLoy 1515 is, thus, specifically designed to provide hot corrosion resistance on low-chromium-containing single-crystal alloys.[56,58,59]

For cooling passage applications,[115,116] this silicon content of the aluminide has to be reduced such that is does not impact on the alloy mechanical performance but must be sufficiently high to confer good oxidation and hot corrosion protection. Reducing the silicon level to between 1 and 2 wt% meets this criteria. Testing coatings with silicon levels in this range under Cyclic oxidation at 1100 °C and 1 h hot dwell cycles gives a lifetime of 280–320 cycles.[116] A result superior to that of a standard aluminide (HTLA aluminide) was obtained, for which the cyclic lifetime varied between 25 and 120 cycles, but was inferior to a platinum aluminide. The worst of the platinum aluminides in Figure 18 gave a lifetime of 1174 cycles under similar test conditions.

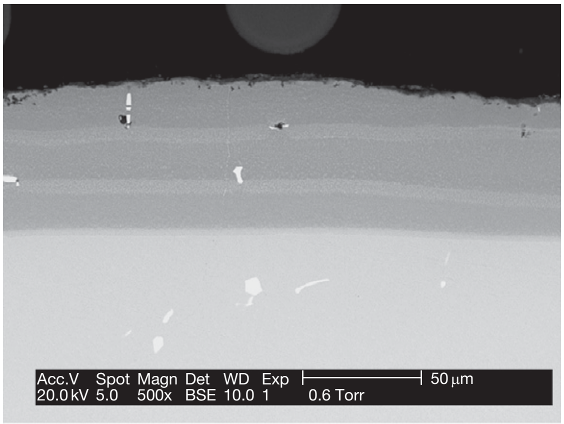


Figure 19 SermaLoy 1515 silicon aluminide coating on IN738 produced by a repeat slurry aluminizing process route.

Under hot corrosion conditions, both type I and type II, this coating with 1–2% silicon addition was superior to a conventional aluminide, lasting approximately twice as long to through coating penetration, but was inferior to the performance of Sermaloy J containing a higher silicon content.

4.05.4.4 Reactive Element-Modified Aluminide Coatings

There has been continued interest in the ability to incorporate active elements in β-NiAl to improve cyclic oxidation resistance through enhanced scale adherence. The benefits of oxygen-active elements are well documented in the literature; for example, yttrium levels below 0.5 wt% are widely added to commercial overlay coatings to reduce oxidation rates and improve scale adhesion. Even in the development of the earliest MCrAlY coatings this was recognized.[48] The most recent MCrAlY overlays are far more complex and may contain multiple active elements, including Y, Si, Hf, Zr, Ta, etc.[11,28,99,117–120] and even minor addition of precious metals.[31,104–106,117]

For systems based on β-NiAl, the systems are far less advanced, with few reactive-element-modified diffusion coatings commercially available.[43,44] Most of the research has been on model alloys[36,121–125] and

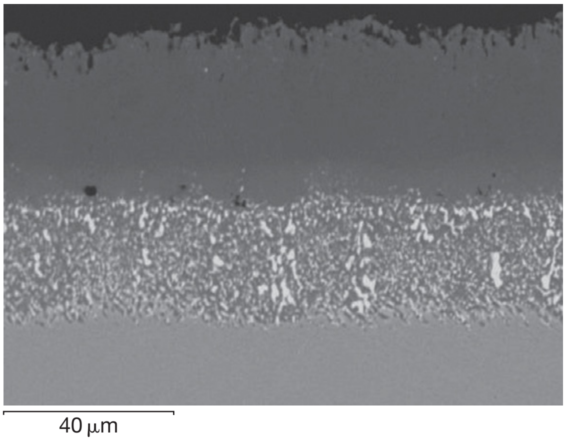


Figure 20 Yttrium-modified aluminide 'over pack' CVD coating.

in particular on the roles of hafnium, zirconium, and yttrium. Some research papers have considered the incorporation of reactive elements as part of the CVD process.[35–44] Early published work by Bianco and Rapp[35–37] introduced reactive elements into the CVD process such that codeposition of the reactive element with the aluminide occurred. This approach has also been adopted in the one published commercial application in which Howmet used multiple vapor sources to blend the vapor phase environment from which the codeposited active-element-modified aluminide is formed.[84,114] In the work of Kim *et al.*,[42] a yttrium-modified aluminide was formed by first pack-aluminizing the substrate alloy (in this case IN738) and then depositing a thin layer of yttrium by electron beam evaporation, prior to heat treatment to interdiffuse the coating. It is only recently that yttrium-modified aluminide has been able to be produced using a simple pack cementation or the 'over-pack' CVD process.[126] Figure 20 illustrates a micrograph of a yttrium-modified aluminide using the 'over-pack' CVD process developed at Cranfield. Figure 21 compares the cyclic oxidation performance (1100 °C, 1 h hot dwell) of various aluminide and modified aluminide coatings produced using facilities at Cranfield University on an IN738 substrate alloy. The improvement in performance of the modified aluminides can be seen relative to that for an uncoated IN738 alloy and IN738 aluminized using a high-activity aluminide process. The uncoated alloy failed (zero net mass gain crossover point) at 30 × 1 h cycles and the high-activity aluminide failed at 620 × 1 h cycles, while the monophase (high temperature, low activity) platinum aluminide and the yttrium-modified aluminide did not fail (zero net mass gain crossover) at the end of the test (900 × 1 h cycles at 1100 °C). Extrapolation of the oxide spalling regime leads to an estimated life of 1000 × 1 h cycles for both the platinum aluminide coating and the yttrium aluminide coating, based on the zero net mass gain crossover point. However, whereas the platinum aluminide coating started to spall at 170 × 1 h hot cycles, the yttrium aluminide did not start to spall until 800 × 1 h hot cycles at 1100 °C.

4.05.5 Mitigating Substrate Alloy Interdiffusion Effects

As is evident from the earlier sections reviewing diffusion coating manufacture, all diffusion coatings must involve an underlying material, usually the substrate alloy, as part of the coating manufacturing process. It is for this reason that similar diffusion coating processes but on different substrate alloys produce different coating systems, and hence the lifetimes of such coatings, be it oxidation, cyclic oxidation or high temperature corrosion, will be influenced by alloying additions diffusing out from the substrate into the coating. Some elements can be beneficial, for example Cr, Si, Hf, Y, etc., while others are clearly detrimental, such as W, Mo, V, possibly Ru, either to the cyclic oxidation or hot corrosion performance of the coating.

One of the benefits of the high temperature low-activity aluminizing processes is the reduction of refractory metals, such as W and Mo, that move outward from the substrate into the coating owing to the fact that the coating is formed as a result of outward nickel transport, and the refractory metals diffuse outward much more slowly than nickel. This observation highlights one way of mitigating the detrimental effects of alloy additions and tramp elements moving from the substrate into the coating during manufacture: that is, to precoat the alloy with some form of temporary or partial barrier (nickel plating the substrate, for example, in its simplest form) prior to aluminizing. A second is to deposit an MCrAlY overlay coating as a partial diffusion barrier and then aluminize the MCrAlY overlay coating.

Commercially, variants on this approach have been used. General Electric has a patented process for over-aluminizing an MCrAlY coating, previously sprayed or EB-PVD-deposited onto the alloys surface. GT29+ and GT33+ are examples of the 'over-aluminized' version of GT29 (Co28Cr6Al0.5Y) and

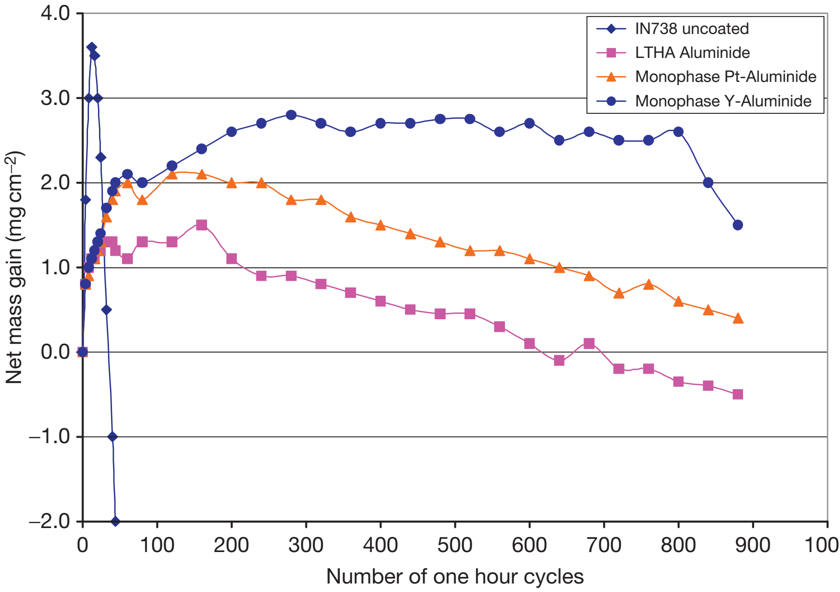


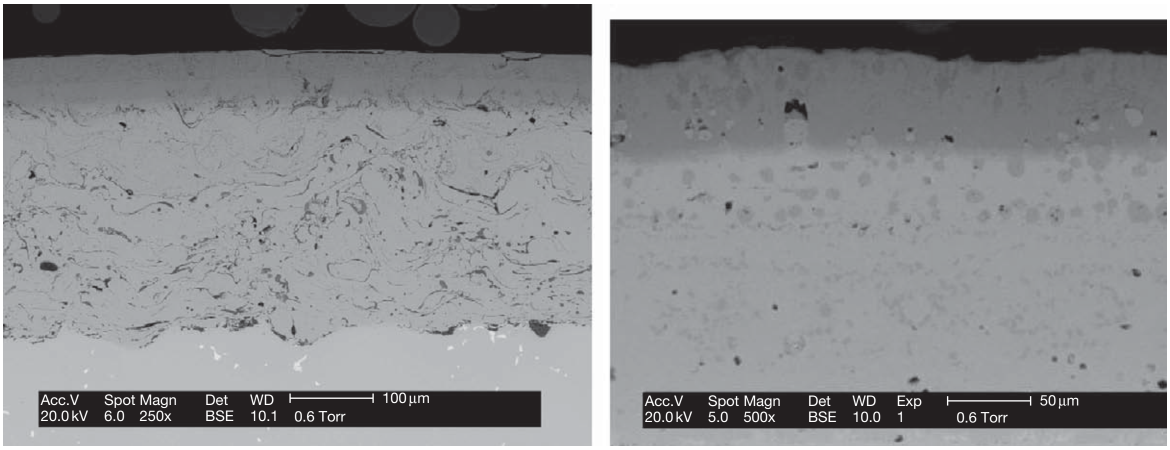
Figure 21 Cyclic oxidation performance of modified aluminide coatings, produced at Cranfield University: 1100 °C, 1 h hot dwell cycles (data from Long and Nicholls and Nicholls and Wing).[116,126] (Note: ↑ equals point of zero crossover for a LTHA aluminide.)

GT33 (Ni22Cr9Al0.5Y). These coatings are used on blades and vanes of GE industrial engines, models 7/9EA and 7/9FA/FA+,[127] making the performance of the coating less dependent on the substrate alloy chemistry from an oxidation and/or corrosion perspective. These dual-layered over-aluminized MCrAlY alloys provide surface layers with up to 25 wt% Al for good oxidation resistance, while the MCrAlY base confers better hot corrosion resistance because of the higher levels of Co and Cr.[127] Additionally, the incorporation of Y from the MCrAlY into the surface aluminide layer confers improved scale adhesion to the alumina scale, improving the cyclic oxidation resistance of this dual layer coating. The surface aluminide layer is brittle, however, and the higher ductile to brittle transition temperature (DBTT) makes the surface layer prone to thermo-mechanical fatigue (TMF) cracking during start/stop cycling. The more ductile MCrAlY underlayer can blunt these cracks, thereby, limiting their propagation into the substrate. The presence of an outer aluminide layer on a CoNiCrAlY basecoat (GT33+ compared to GT33) can lower the TMF life by a factor of 2.5 at high strain ranges, while at low strain ranges (0.45%ε), the TMF lives are comparable.[127]

Howmet now also offers these duplex MCrAlY + aluminide coatings.[128] However, they claim that by using low-activity aluminizing in addition to the MCrAlY alloy, they can further improve the oxidation performance when compared to a similar coating made by pack cementation.

4.05.5.1 Smart Coating Concepts

Smart overlay coatings[129–131] are functionally gradient coating systems designed to provide high temperature oxidation and corrosion protection over a wide range of operating conditions. The SMARTCOAT concept is a natural extension of the ideas embodied in GT29+ and GT33+, the over-aluminized MCrAlYs, which involves surface-treating a base overlay coating using diffusion coating processes to obtain improved performance and durability, but now extended to produce a chemically graded structure that can provide both high temperature oxidation protection as well as more optimized protection to type I and II corrosion. Thus, the SMARTCOAT design consists of an MCrAlY base coating, which can be deposited by any spray deposition method (air plasma spray (APS), Vacuum plasma spray (VPS), and high velocity oxy-fuel (HVOF)), by occluded electroplating or by EB-PVD, which is overcoated with successive layers to produce the chemical gradient structure. A second layer, enriched in chromium and/or silicon, is then deposited prior to surface aluminizing, which then generates the required gradient chemical structure.



(a) SmC155 (b) SmC253E

Figure 22 Micrographs of two SMARTCOAT structures: (a) SmC155, showing the three-layered structure characteristic of SMARTCOAT, but produced using air plasma spraying; (b) SmC253E, produced by occluded electroplating of the basecoat and chromium-rich interlayer.

Figures 22(a) and 22(b) illustrates two variants of this SMARTCOAT design. SmC155 (Figure 22(a)) is produced by surface-treating an Amdry 995 basecoat that has been deposited by air plasma spraying. The chromium-rich interlayer is also deposited by air plasma spraying before the bi-layer structure is aluminized to give the final SMARTCOAT design. The composition of the three-layered microstructure critically affects performance. The outer aluminide layer varies in composition between those of Ni–15Cr–32Al and Ni–10Cr–21Al, with small additions of Y as a result of the aluminizing of an MCrAlY base alloy, and is designed to produce a protective alumina scale for oxidation- and cyclic-oxidation-protection at temperatures above 900 °C. However, at lower temperatures, this alumina scale does not reform fast enough to confer a protection under type II hot corrosion conditions. SMARTCOAT is, therefore, designed with an intermediate chromium-rich layer, which permits the rapid formation of chromia, which are healing areas of type II corrosion damage. Research into optimum corrosion-resistant alloy compositions[132,133] defined the useful composition range of this interlayer, in the final chemical gradient structure, between Ni–60Cr–20Al and Ni–35Cr–40Al, adding tantalum may be beneficial. The basecoat may be any MCrAlY alloy, Amdry 995 (Co–32Ni–21Cr–8Al–0.5Y) for the SmC155 variant of SMARTCOAT.

Figure 22(b), a second variant of SMARTCOAT, is produced using occluded electroplating[134] to deposit the basecoat and interlayer. Ghost images of the original particles in the occluded electroplate can still be seen. The base alloy is Amdry 963: a NiCrAlY alloy; otherwise the coating procedure matches that of the aluminized, plasma-sprayed MCrAlY, but with the difference that the basecoat and interlayer were deposited by electroplating.

Figure 23 illustrates the comparative performance of three variants of SMARTCOAT, when compared to two platinum aluminide coatings RT22 and CN91, and an over-aluminized CoNiCrAlY – a similar process and structure to that of GT29+, a General Electric proprietary coating. For each coating system, the substrate was IN738. The hot corrosion tests were of 500 h duration and conducted at 700 and 800 °C, using a salt recoat test procedure with daily replenishment of an 80% Na_2SO_4/20% K_2SO_4 salt mix at an equivalent salt deposition flux of 0.015mg cm^{-2} h^{-1}. The test was conducted in an air +300 vpm SO_2/SO_3 gaseous environment.

Under hot corrosion conditions, only the outer aluminide region of the smart coatings was attacked. The corrosion front effectively stopped at the chromium-rich interlayer, whereas the platinum aluminide coating was consumed down to the interdiffusion zone at 700 °C and completely penetrated at 800 °C. For the over-aluminized CoNiCrAlY, the worst attack was observed at 700 °C, as a result of severe type II pitting of the Co,Ni aluminide, and the underlying CoNiCrAlY basecoat layer.

4.05.6 Summary and Conclusions

This chapter reviewed the methods and applications of diffusion coatings. Diffusion coatings can offer a

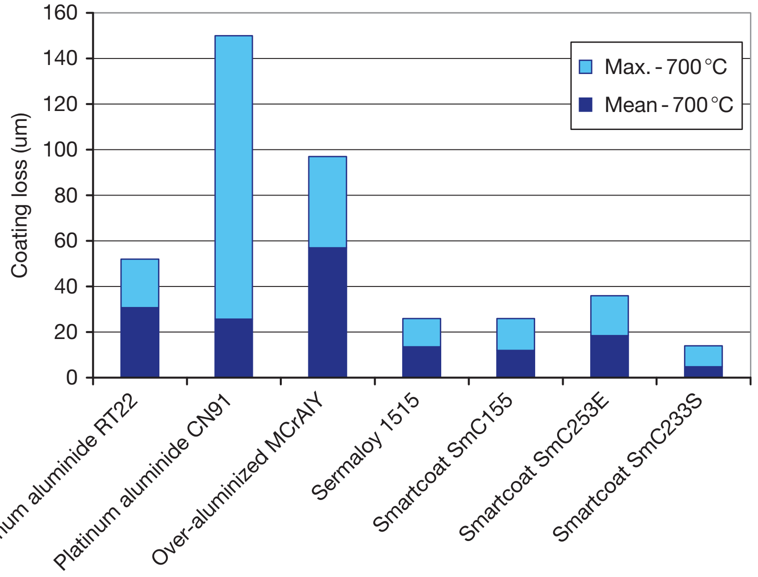


Figure 23 Hot corrosion performance of SMARTCOAT SmC155 and SmC253E, relative to an over-aluminized CoNiCrAlY and platinum aluminide coatings (RT22 and CN91) at 700 °C.

low-cost solution for providing environmental protection, or can be a part manufacture of more sophisticated custom-designed coatings.

Applications may vary from aqueous corrosion protection through to high temperature oxidation and hot corrosion environments, and can encompass industries as diverse as aerospace, motor sports, petrochemical processes, chemical industries, steam turbines and advanced combined-cycle power generation plants.

Coating solutions vary from the low-cost aluminide diffusion coatings, first introduced into gas turbine service in 1957, through to platinum aluminide bondcoats for thermal barrier coatings.

To the future, one can foresee the development of 'custom surface engineering' solutions, where the component and coating are designed as a material system. SMARTCOAT is one such design for high temperature aggressive service condition, and there are many others. CVD and diffusion coating processes will form an important part of such functional surface engineering solutions.

References

1. ASTM 874-96. Standard specification for chromium diffusion coating applied by pack cementation, 2008.
2. ASTM B 875-96. Standard specification for aluminium diffusion coating applied by pack cementation, 2008.
3. BS4921: The sherardizing process, 1973.
4. Samuel, R. L.; Lockington, N. A. *Met. Treat. Drop Forging* **1951**, *18*, 354–359, 407–415, 440–444, 495–502, 506.
5. Goward, G. W.; Boone, D. H.; Giggins, C. S. *Trans. ASM* **1967**, *60*, 228–241.
6. Goward, G. W.; Boone, D. H. *Oxid. Met.* **1971**, *3*, 475–495.
7. Grisaffe, S. J. In *The Superalloys*; Sims, C. T., Hagel, W. C., Eds.; Wiley: New York, 1972; p 341.
8. Felix, P.; Erdos, E. *Werkst. Korros.* **1972**, *23*, 626–636.
9. Fitzer, F.; Schlichting, J. In *High Temperature Corrosion*; Rapp, R. A., Ed.; NACE: Houston, TX, 1983; pp 604–614.
10. Grünling, H. W.; Bauer, W. *Thin Solid Films* **1982**, *95*, 3.
11. Van Roode, M.; Hsu, L. *Surf. Coat. Technol.* **1989**, *37*, 461–481.
12. Agüero, A.; Muelas, R.; Scarlin, B. In *Materials for Advanced Power Engineering*; Lecomte-Beckers, J., *et al.*, Eds.; Forschungzentrum Julich 21 (II), 1143–1157 (2002).
13. Long, K. Ph.D. Thesis, Cranfield University, 2004.
14. Kohlsheen, J.; Stock, H. R. *Surf. Coat. Technol.* **2008**, *203*, 476–479.
15. Pichoir, R. In *High Temperature Alloys for Gas Turbines*; Coutsouradis, D., *et al.* Eds.; Applied Science: London, 1978; pp 191–208.
16. Gupta, B. K.; Seigle, L. L. *Thin Solid Films* **1980**, *73*, 365–371.
17. Malik, M.; Morbioli, R.; Huber, P. In *Proceedings of the High Temperature Alloys for Gas Turbines*; Brunetaud, R., *et al.* Eds.; D. Reidel: Dordrecht, 1982; pp 87–98.
18. Duret, C.; Davin, A.; Marrijnissen, G.; Pichoir, R. In *Proceedings of the High Temperature Alloys for Gas Turbines*; Brunetaud, R., *et al.* Eds.; D. Reidel: Dordrecht, 1982; pp 83–87.
19. Restall, J. E.; Malik, M.; Singheiser, L. In *Proceedings of the Conference on High Temperature Alloys for Gas Turbines and Other Applications 1986*; Betz, W., *et al.* Eds.; D. Reidel: Dordrecht, 1986; pp 357–404.

20. Mevrel, R.; Duret, C.; Pichoir, R. *Mater. Sci. Technol.* **1986**, *2*(3), 201–206.
21. Luthra, K. L.; LeBlanc, O. H. *Mater. Sci. Eng.* **1987**, *88*, 329.
22. Choquet, P. A.; Naylor, E. R.; Rapp, R. A. *Mater. Sci. Eng. A* **1989**, *121*, 413–418.
23. Geib, F. D.; Rapp, R. A. *Oxid. Met.* **1993**, *40*, 213–228.
24. Da Costa, W.; Gleeson, B.; Young, D. *J. Electrochem. Soc.* **1994**, *141*, 1464–1471.
25. Da Costa, W.; Gleeson, B.; Young, D. *J. Electrochem. Soc.* **1994**, *141*, 2690–2697.
26. Da Costa, W.; Gleeson, B.; Young, D. *Surf. Coat. Technol.* **1996**, *88*, 165–171.
27. Lehnert, G.; Meinhardt, H. W. *Electrodepost. Surf. Treat.* **1972**, *1*, 189.
28. Levin, S. R.; Caves, R. M. *J. Electrochem. Soc.* **1973**, *120*, C232.
29. Pint, B. A. *Mater. Sci. Forum* **1997**, *251–254*, 397.
30. Streiff, R.; Boone, D. J. *Mater. Eng.* **1988**, *10*, 15.
31. Meier, G. H.; Pettit, F. S. *Surf. Coat Technol.* **1989**, *39–40*, 1.
32. Angenete, J.; Stiller, K. *Mater. High Temp.* **2000**, *17*, 179.
33. Angenete, J.; Stiller, K. *Surf. Coat. Technol.* **2002**, *150*, 107.
34. Vialas, N.; Monceau, D. *Surf. Coat. Technol.* **2006**, *201*, 3846–3851.
35. Bianco, R.; Rapp, R. A. *Oxid. Met.* **1992**, *38*, 33–43.
36. Bianco, R.; Rapp, R. A. *J. Electrochem. Soc.* **1993**, *140*, 1181–1190.
37. Bianco, R.; Rapp, R. A.; Smialek, J. L. *J. Electrochem. Soc.* **1993**, *140*, 1191–1203.
38. Xiang, Z. D.; Datta, P. K. *Mater. Sci. Eng. A* **2003**, *363*, 185–192.
39. Quraishi, M. A.; Sharma, H. S. *Anti-corros. Meth. Mater.* **2004**, *51*, 41.
40. Haynes, J. A.; Pint, B. A.; Moore, K. L.; Zhang, Y.; Wright, I. G. *Oxid. Met.* **2002**, *58*, 513–544.
41. Nicholls, J. R.; Wing, R. In *Materials for Advanced Power Engineering 2002*; Lecomte-Beckers, J., *et al.* Eds.; Forschungzentrum Julich: Germany, 2002; Part 1, pp 57–71.
42. Kim, K. Y.; Jun, J. H.; Lee, J. K. *J. Phys. IV* **1993**, *3*, 521–529.
43. Warnes, B. M.; Punola, D. C.; Smith, J. S.; Daniel, N. L. *U.S. Patent 6* **2004**, *689*, 422.
44. Warnes, B. M. *Surf. Coat. Technol.* **2001**, *146–147*, 7–12.
45. Nicholls, J. R.; Bordenet, B. In *Materials for Advanced Power Engineering 2006*; Lecomte-Beckers, J., *et al.* Eds.; Forschungzentrum Julich: Germany, 2006; Part 111, p 1696.
46. Pichoir, R. In *Materials and Coatings to Resist High Temperature Corrosion*; Holmes, D. R., Rahmel, A., Eds.; Applied Science: London, 1978; pp 271–291.
47. Goward, G. W. *Surf. Coat. Technol.* **1998**, *108–109*, 73.
48. Goward, G. W.; Cannon, L. W. ASME Paper 87-GT-50 American Society of Mechanical Engineers: New York, 1988.
49. Mevrel, R. *Mater. Sci. Eng. A* **1989**, *120*, 13–24.
50. Nicholls, J. R. *J. Met.* **2000**, *52*, 28.
51. Nicholls, J. R. *MRS Bull.* **2003**, *28*(9), 659–670.
52. Pomeroy, M. J. *Mater. Des.* **2005**, *26*, 223–231.
53. Janssen, M. M. P.; Rieck, G. D. *Trans. Met. Soc. AIME* **1967**, *239*, 1372.
54. Singleton, M. F.; Murray, J. L.; Nash, P. In *Binary Alloy Phase Diagrams*; Massalski, T. B., Ed.; ASM Materials Park: OH, 1990; Vol. 1, p 142.
55. Shanker, S.; Siegle, L. L. *Met. Trans.* **1978**, *9A*, 1467.
56. McMordie, B. G.; Weatherill, A. *In Proceedings of the Turbine Forum*; Nice: France, 2002.
57. Meelu, M. C.; McMordie, B. G.; Loretto, M. H.; Jones, A. In *The Processing, Properties and Application of Metallic and Ceramic Materials*; Loretto, M. H., Beevers, C. J., Eds.; EMAS Publishing: Washington, 1992; Vol. II, p 1250.
58. Berry, D.; Meelu, M. C.; McMordie, B. G.; Kircher, J. A. ASME Pub. 95-GT-359, 1995.
59. SermaLoy 1515, U.S. Patent 5,547,700.
60. Scheefer, M.; Knodler, R.; Scarlin, B.; Bruna, A. A.; Tsipas, D. N. *Mater. Corros.* **2005**, *56*, 907–915.
61. Aguero, A.; Muelas, R.; Gutierrez, M.; Van Vulpen, R.; Osgerby, S.; Banks, J. P. *Surf. Coat. Technol.* **2007**, *201*, 6253–6260.
62. Aguero, A. *Mater. High Temp.* **2008**, *25*, 257–265.
63. Sanjuro, A.; Lau, K.; Wood, B. *Surf. Coat. Technol.* **1992**, *54–55*, 219–223.
64. Tsipas, D. N.; Anthymidis, K. G.; Flitris, Y. J. *Mater. Process Technol.* **2003**, *134*, 145–152.
65. Kinkel, S.; Angelopoulos, G. N.; Dahl, W. *Surf. Coat. Technol.* **1994**, *64*, 234–240.
66. Perez, F. J.; Hierro, M. P.; Trilleros, J. A.; Carpintero, M. C.; Sanchez, L.; Brossard, J. M.; Bolivar, F. J. *Intermetallic* **2006**, *14*, 811–817.
67. Lau, K. H.; Sanjurgo, A.; Wood, B. J. *Surf. Coat. Technol.* **1992**, *54–55*, 234–240.
68. Perez, F. J.; Hierro, M. P.; Pedraza, F.; Gomez, C.; Carpintero, M. C.; Trilleros, J. A. *Surf. Coat Technol.* **1999**, *122*, 281–289.
69. Anthymidis, K. G.; Stergioudis, G.; Tsipas, D. N. *Mater. Lett.* **2001**, *51*, 156–160.
70. Anthymidis, K. G.; Sterigioudis, G.; Tspias, D. N. *Sci. Tech. Adv. Mater.* **2002**, *3*, 303–311.
71. Anthymidis, K. G.; Maragoudakis, N.; Stergioudis, G.; Haidar, O.; Tspias, D. N. *Mater. Lett.* **2003**, *57*, 2399–2403.
72. Reynoldson, R. W. *Heat Treatment in Fluidised Bed Furnaces*; ASM International: Ohio, USA, 1993; p 111.
73. Taxil, P.; Chamelot, P.; Massot, L.; Hamel, C. *J. Mining Metallurgy* **2003**, *39*, 177–200.
74. Trusov, G. N.; Goliasheva, E. P.; Gorachenko, B. A.; Mikheev, V. S. Cited in Ref. 73.
75. Taxil, P. *Appl. J. Electrochem.* **1985**, *17*, 261.
76. Fang, B.; Zhou, C.; Liu, X.; Duan, S. *Appl. J. Electrochem.* **2001**, *31*, 201.
77. Comninellis, Ch.; Vercesi, G. P. *Appl. J. Electrochem.* **1991**, *21*, 335.
78. Cardarelli, F.; Taxil, P.; Savall, A. *Appl. J. Electrochem.* **1998**, *28*, 245.
79. Cook, N. C. U.S. Patents 2,970,091, 1961; 3,024,176, 1962; 3024b117, 1966: 30,232,853, 1966.
80. Cook, N. C. *Sci. Am.* **1969**, *221*, 38.
81. Taxil, P.; Qiao, Z. Y. *Molten Salts Chemistry-Principle and Applications*; The Metallurgical Industry Press: Beijing, 1987.
82. Restall, J. E.; Hayman, C. In *Proceedings of the Workshop on Coatings for Heat Engines*; Clarke, R. L., *et al.* Eds.; US Department of Energy: Washington DC, 1984; pp 347–357.
83. Benoist, J.; Badawa, K. F.; Malie, A.; Ramade, C. *Surf. Coat. Technol.* **2004**, *182*, 14–23.
84. Warnes, B. M.; Punola, D. C. *Surf. Coat. Technol.* **1997**, *94–95*, 1–6.
85. Warnes, B. M. *Surf. Coat. Technol.* **2003**, *163–164*, 106–111.
86. Lindblad, N. R. *Oxid. Met.* **1969**, *1*, 143.
87. Sivakumar, R. *Oxid. Met.* **1982**, *17*, 27.
88. Jackson, M. R.; Rairden, J. R. *Met. Trans. A* **1977**, *8*, 1697.
89. Niu, Y.; Wu, W. T.; Boone, D. H.; Smith, J. S.; Zhang, J. Q.; Zhen, C. L. *J. Phys. IV* **1993**, *3*, 511.

90. Calliari, I.; Dabala, M.; Zambon, A. *J. Mater. Eng. Perform.* **2001**, *10*, 258.
91. Elsawy, A.; Soda, H.; McLean, A. *Mater. Corros.* **2005**, *56*, 669.
92. Nicholls, J. R.; Hancock, P. *Ind. Corros.* **1987**, *5*(4), 8–18.
93. Goward, G. W. In *Proceedings of the Conference on High Temperature Corrosion, NACE-6*; Rapp, R. A., Ed.; NACE: Houston, TX, 1983; pp 553–560.
94. Nicholls, J. R.; Saunders, S. R. J. In *High Temperature Materials for Power Engineering*; Bachelet, E., *et al.* Eds.; Kluwer Academic Publishers: Dordrecht, 1990; pp 865–875.
95. Mom, A. J. A. NLR Report MP 81003U, Amsterdam, 1981.
96. Novak, R. C. Cited in Coatings for High Temperature Structural Materials, National Materials Advisory Board Report; National Academy Press: Washington, DC, 1996.
97. Luthra, K. L.; LeBlanc, O. H. *Mater. Sci. Eng.* **1987**, *88*, 329.
98. Fitzer, F.; Schlichting, J. In *High Temperature Corrosion, NACE-6,* 1984; pp 604–614.
99. Davis, F. N.; Grinell, C. E. ASME Pub. 82-GT-244 1982.
100. Stringer, J.; Viswanathan, R. In *Advanced Materials and Coatings for Combustion Turbines*; Swaninathan, V. P., Cheruvu, N. S., Eds.; ASM, 1994; p 6.
101. Stringer, J.; Viswanathan, R. In Proceedings of ASM 1993 Materials Congress Materials Week'93, Pittsburgh, Pennsylvannia, October 17–21; ASM International: Materials Park, OH, 1993; pp 1–21.
102. Czech, N.; Schmitz, F.; Stamm, W. *Surf. Coat. Technol.* **1994**, *68–69*, 17–21.
103. Pint, B. A. *Oxid. Met.* **1997**, *48*, 303–333.
104. Pint, B. A.; Wright, I. G.; Lee, W. Y.; Zhang, Y.; Prüssner, K.; Alexander, K. B. *Mater. Sci. Eng. A* **1998**, *245*, 201–211.
105. Tawancy, H. M.; Abbas, N. M.; Rhys Jones, T. N. *Surf. Coat. Technol.* **1992**, *54–55*, 1.
106. Tawancy, H. M.; Sridhar, N.; Abbas, N. M.; Rickerby, D. S. *Scr. Metall. Mater.* **1995**, *33*, 1431.
107. Felten, E. J. *Oxid. Met.* **1976**, *10*, 23–28.
108. Felten, E. J.; Pettit, F. S. *Oxid. Met.* **1976**, *10*, 189–223.
109. Fountain, J. G.; Golightly, F. A.; Stott, F. S.; Wood, G. C. *Oxid. Met.* **1976**, *10*, 341–345.
110. Allam, I. M.; Akuezlte, H. C.; Whittle, D. P. *Oxid. Met.* **1980**, *14*, 517–530.
111. Vogel, D.; Newman, L.; Deb, P.; Boone, D. H. *Mater. Sci. Eng.* **1987**, *88*, 227.
112. Malik, M.; Morbioli, R.; Huber, P. In *Proceedings of the Conference on High Temperature Alloys for Gas Turbines*; Brunetaud, R., *et al.* Eds.; D. Reidel: Dordrecht, 1982; pp 87–98.
113. Nicholls, J. R.; Stephenson, D. J.; Hancock, P.; Wood, M. I.; Restall, J. E. *Proceedings of the Workshop on Gas Turbine Materials in a Marine Environment* 1984; Paper 7.
114. Warnes, B. M. *Surf. Coat. Technol.* **2001**, *146–147*, 7–12.
115. Michels, H. T.; Friend, W. Z. *Corrosion of Nickel and Nickel*; Electrochemical Society, 1980; p 49.
116. Long, K.; Nicholls, J. R. in press.
117. Zhang, Y.; Haynes, J.; Lee, W. Y.; Wright, I. G.; Pint, B. A.; Cooley, K. M.; Laiw, P. K. *Metall. Mater. Trans. A* **2001**, *32*, 1727.
118. de Wit, J. H. W.; Van Manen, P. A. *Mater. Sci. Forum* **1994**, *154*, 109.
119. Dickey, E. C.; Pint, B. A.; Alexander, K. B.; Wright, I. G. In *High Temperature Surface Engineering*; Nicholls, J. R., Rickerby, D. S., Eds.; IoM Communications: London, 2000; pp 115–128.
120. Fisher, G.; Datta, P. K.; Burnell-Gray, J. S.; Chan, W. Y.; Wing, R. In *High Temperature Surface Engineering*; Nicholls, J. R., Rickerby, D. S., Eds.; IoM Communications: London, 2000; pp 1–11.
121. Pint, B. A.; More, K. L.; Wright, I. G. *Mater. High Temp.* **2003**, *20*, 375–386.
122. Bennett, I. J.; Sloof, W. G. *Mater. High Temp.* **2002**, *20*, 395–403.
123. Schumann, E.; Yang, J. C.; Graham, M. J.; Ruhle, M. *Mater. Corros.* **1996**, *47*, 631–632.
124. Pint, B. A.; Garrett-Reed, A. J.; Hobbs, L. W. *Microsc. Oxid.* **1993**, *2*, 463–475.
125. Pint, B. A.; Wright, I. G.; Lee, W. Y.; Zhang, Y.; Prussner, K.; Alexander, K. B. *Mater. Sci. Eng. A* **1998**, *245*, 201.
126. Nicholls, J. R.; Wing, R. In *Materials for Advanced Power Engineering 2002*; Lecomte-Beckers, J., *et al.* Eds.; Forschungzentrum Julich: Germany, 2002; Part 1, pp 57–71.
127. Cheruvu, N. S.; Chan, K. S.; Viswanathan, R. *Energy Mater.* **2006**, *1*, 33–47.
128. Warnes, B. M. *Surf. Coat. Technol.* **2003**, *163–164*, 106–111.
129. Nicholls, J. R.; Simms, N. J.; Chan, W. Y.; Evans, H. E. *Surf. Coat. Technol.* **1992**, *149*, 236.
130. Nicholls, J. R.; Simms, N. J.; Neseyif, S.; Evans, H. E.; Ponton, C.; Taylor, M. *J. Electrochem Soc.* **2002**, *99*(38), 305–316.
131. Nicholls, J. R.; Simms, N. J.; Taylor, M.; Evans, H. E. *Proceedings of the Turbine Forum*; Nice, France, 2002.
132. Nicholls, J. R.; Hancock, P.; Al Yasiri, L. H. *Mater. Sci. Technol.* **1989**, *5*, 799–805.
133. Nicholls, J. R.; Lawson, K. J.; Al Yasiri, L. H.; Hancock, P. *Corros. Sci.* **1993**, *35*(5–8), 1209–1223.
134. Honey, F. J.; Kedward, E. C.; Wride, V. *J. Vac. Sci. Technol A* **1986**, *4*, 2593–2597.

4.06 Hot Dipped Coatings

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4.06.1 Introduction

Hot-dipped coatings are prepared by cleaning a metal substrate, usually steel, and also other metals such as copper, and immersing it in a bath of molten (lower melting point) metal. During dipping, a reaction takes place to form a metallurgically bonded coating. The most widely used hot dip coating is zinc or alloys of zinc with other metals, followed by aluminum and tin coatings. Typical thicknesses of hot dip zinc coatings on steel depend upon the application process. Prefabricated steel articles, such as structurals, dipped in zinc have coatings between 85 and 250-μm thick, continuous galvanized sheet have between 10 and 20 μm thick, and fasteners that are hot dip galvanized and then centrifuged have coatings around 50 μm thick. Zinc–aluminum coatings are normally between 5 and 33 μm thick. Aluminum–silicon coatings on steel sheet are most often supplied between 6 and 33 μm of thickness. The hot dip zinc coating not only serves as a protective barrier coating for iron and steel, with a generally much lower rate of corrosion than steel in the application environment, but is also electronegative to iron and protects it sacrificially.[1] Aluminum coatings also serve as barrier coatings, and provide sacrificial protection of steel in chloride-bearing environments. Tin coatings serve as barrier coatings, but are generally cathodic to steel in many environments and thus derive their utility from their corrosion resistance in selected application environments, such as food canning, together with other processability attributes.[2] The metallurgical reaction during hot dipping results in coatings that have two components: a reaction layer of intermetallic compound that is formed on the base of the steel, and an overlay of the molten coating bath that solidifies on top of this reaction layer and can be controlled to desired thicknesses during the hot dipping operation. The reaction layer thickness and character varies widely with the type of hot dip coating, for example, in the Zn–5% Al continuous galvanized coating, it is on the scale of nanometers, while after fabrication, galvanizing of reactive steels can give reaction layer thicknesses in excess of 60 μm.[3,4] Both the overlay and reaction layers are important components in the ability of the hot dip coating to protect the substrate to which it is applied. Pure zinc is mostly used for general galvanizing, while zinc alloyed with about 0.2% aluminum is generally used for continuous galvanized sheet. In recent years, new alloy coatings have entered both sectors to improve either processability or corrosion resistance.[5]

In many cases, the hot dip coating is also given a surface treatment, either a chemical conversion layer such as chromate or an organic layer such as paint. A wide range of paints, meeting different demands for formability, weathering resistance, and appearance are available for galvanized steel. Aluminized steels are generally chromated but occasionally painted, while tin coatings can be lacquered if required.

4.06.2 Corrosion Characteristics of Zinc

4.06.2.1 General Considerations

Zinc coatings generally corrode as a result of the slow general dissolution of zinc from the surface. Zinc has the ability to form protective layers comprising basic carbonates, oxides, or hydrated sulfates, depending upon the nature of the environment. When protective layers have formed and completely covered the surface of the coating, corrosion proceeds at a greatly reduced rate. Localized pitting occurs only under special conditions, for example, in waters where a calcareous scale may crack locally, exposing a small area of zinc. Provided that specifications are adhered to, intergranular corrosion of zinc is not a problem; however, certain impurities, especially in zinc aluminum alloy coatings, can cause intergranular corrosion. By its very nature, the protection of galvanized steel by zinc can result in bimetallic corrosion when steel surfaces are exposed, such as at cut edges, drilled holes, or when uncoated fasteners are inserted into structural items. Good design will minimize the amount of steel that is exposed to the environment and therefore minimize metallic corrosion.

The ability of zinc to maintain a protective layer is mainly determined by the pH of the environment, especially acidic pollutants. Because zinc forms an amphoteric oxide, strong alkalinity can also adversely effect zinc's corrosion behavior by interfering with the formation of protective layers. Figure 1 shows that the corrosion rate of zinc varies with pH and shows that attack is most severe at pH values below 6 and above 12.5, while within this range, corrosion is

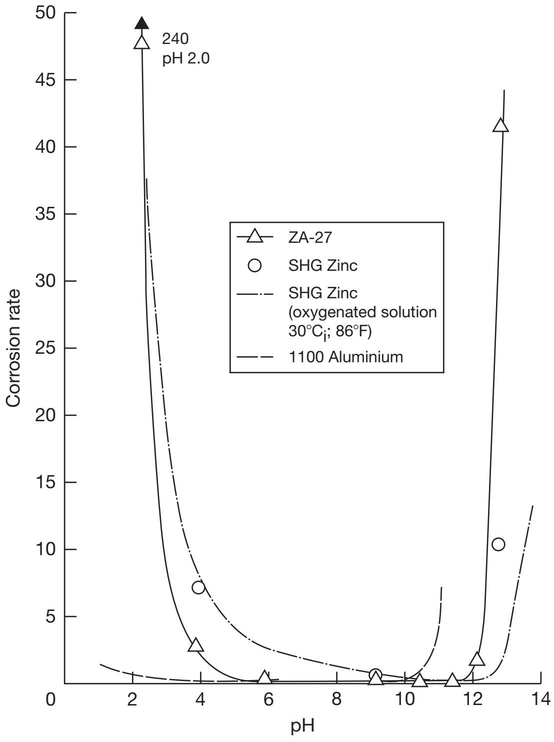

Figure 1 Variation of corrosion rate with pH. Based on Noranda, *Designing zinc castings for corrosion resistance*; 1993; 24, and earlier data.

very slow. The actual rates of corrosion shown in this figure are not of direct relevance in any particular application, but mainly serve as a guide to the relative severity of corrosion.

Aluminum is particularly beneficial in zinc coatings and has resulted in development of trade name products such as Microzinc D4 (Zn–>3%Al), Zinkopal (Zn–5% Al), Supergalva (Zn–5%Al), Galfan (Zn–5% Al), and Galvalume (Zn–55%Al). In these coatings with 5 and 55% aluminum, respectively, the surface is made up of mixed compounds of zinc and aluminum, which increase corrosion performance in many applications. Figure 2 shows the effect of aluminum content on the corrosion resistance of Al–Zn coatings.

Zinc–iron alloys are present in a reactive layer formed on coatings prepared by dipping prefabricated steel in nearly pure zinc baths and also in the continuous galvanized sheet product termed 'galvanneal.' When coatings on prefabricated items are exposed for a sufficient time, the pure zinc overlay coating will be removed and expose the underlying zinc–iron reaction layer, causing a red staining. This is often confused with attack of the underlying steel; however, in many cases, this intermetallic layer, which contains in excess of 85% zinc, is capable of protecting the underlying steel for many additional years. The galvanneal coating produced on continuous galvanized sheet is a fully alloyed coating with no zinc overlay. Its rough surface makes it particularly useful as a substrate for application of paints, while the ∼85% zinc content of this intermetallic layer provides good protection to the steel substrate. Painted galvanneal has found widespread applications in automobile bodies and structures.

4.06.2.2 Atmospheric Corrosion

Zinc and zinc alloy coatings have good resistance to atmospheric corrosion. Atmospheres are usually classified subjectively as industrial, urban, rural, or marine. In the first three classifications, the severity of corrosion is usually related to the amount of sulfur dioxide in the atmosphere, whereas in the latter the presence of chloride is an important determinator of corrosion rate. Guidelines for life expectancies of zinc coatings exposed to different atmospheres are shown in Table 1. The corrosion rate of zinc coatings is approximately linear with time in most aggressive atmospheres. Milder atmospheres allow the protective films formed on zinc to enable a decrease

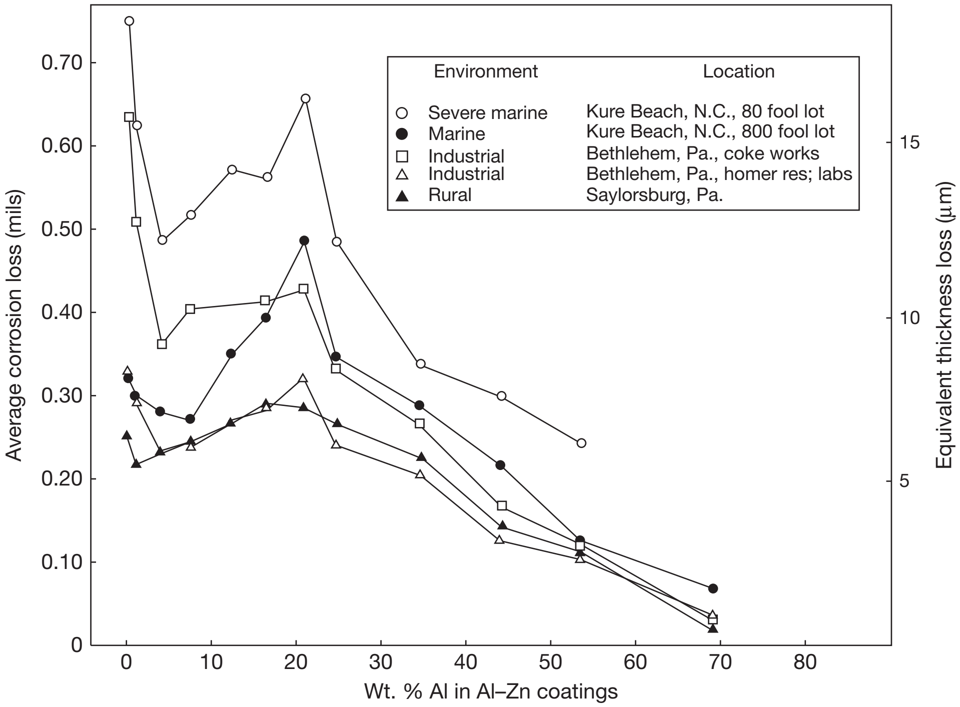

Figure 2 Five-year corrosion tests on early zinc–aluminum alloys; effect of aluminum content on corrosion performance of aluminum–zinc alloy coatings after exposure in various atmospheres: 1 mm = 25.4 μm, 1 ft = ∼0.035 m. Zoccola, J. C.; Townsend, H. E.; Borzillo, A. R. and Horton, J. B. In *Atmospheric Factors Affecting the Corrosion of Engineering Metals*, STP 646, Coburn, S. K. Ed.; American Society for Testing and Materials: Philadelphia, PA, 1978; pp 165–184.

Table 1 Description of typical atmospheric environments related to the estimation of corrosivity categories and average corrosion rates for zinc

Corrosivity category (C), Corrosion rate (based upon one year exposures), r_{corr} (m per annum), and corrosion level	*Typical environments (examples)*	
	Indoor	*Outdoor*
C1 $r_{corr} \leq 0.1$ Very low	Heated spaces with low relative humidity and insignificant pollution, e.g., offices, schools, museums	Dry or cold zone, atmospheric environment with very low pollution and time of wetness, e.g., certain deserts, central Arctic/Antarctica
C2 $0.1 < r_{corr} \leq 0.7$ Low	Unheated spaces with varying temperature and relative humidity. Low frequency of condensation and low pollution, e.g., storage, sport halls	Temperate zone, atmospheric environment with low pollution (SO_2 $< 5\mu g\ m^{-3}$), e.g., rural areas, small towns. Dry or cold zone, atmospheric environment with short time of wetness, e.g., deserts, subarctic areas
C3 $0.7 < r_{corr} \leq 2$ Medium	Spaces with moderate frequency of condensation and moderate pollution from production process, e.g., food-processing plants, laundries, breweries, dairies	Temperate zone, atmospheric environment with medium pollution (SO_2: 5–30$\mu g\ m^{-3}$) or some effect of chlorides, e.g., urban areas, coastal areas with low deposition of chlorides, e.g., Subtropical and tropical zone, atmosphere with low pollution
C4 $2 < r_{corr} \leq 4$ High	Spaces with high frequency of condensation and high pollution from production process, e.g., industrial processing plants, swimming pools	Temperate zone, atmospheric environment with high pollution (SO_2: 30–90$\mu g\ m^{-3}$) or substantial effect of chlorides, e.g., polluted urban areas, industrial areas, coastal areas, without spray of salt water, exposure to strong effect of deicing salts, e.g., subtropical and tropical zone, atmosphere with medium pollution
C5 $4 < r_{corr} \leq 8$ Very high	Spaces with very high frequency of condensation and/or with high pollution from production process, e.g., mines, caverns for industrial purposes, unventilated sheds in subtropical and tropical zones	Temperate and subtropical zone, atmospheric environment with very high pollution (SO_2: 90–250$\mu g\ m^{-3}$) and/or important effect of chlorides, e.g., industrial areas, coastal areas, shelter positions at coastline
CX $8 < r_{corr} \leq 25$ Extreme	Spaces with almost permanent condensation or extensive periods of exposure to extreme humidity effects and/or with high pollution from production process, e.g., unventilated sheds in humid tropical zones with penetration of outdoor pollution including airborne chlorides and corrosion stimulating particulate matter	Subtropical and tropical zone (very high time of wetness), atmospheric environment with very high pollution SO_2 ($>250\mu g\ m^{-3}$) including production and industrial zones and/or strong effect of chlorides, e.g. extreme industrial areas, coastal and off shore areas, occasionally contact with salt spray

Proposal for update to EN ISO 14713: 1999 incorporating corrosion rates for zinc set out in ISO 9223, UK Galvanizers Association, 2006.

in corrosion rate with time. Therefore, a straight line relationship will have a substantial safety margin in milder atmospheres. Corrosion rates increase as the amount of sulfur deposition in the atmosphere increases. Chlorides and nitrogen oxides usually are not as significant in determining corrosion resistance as sulfur compounds, but, in combination with sulfur, can significantly increase corrosion rates. Corrosion resistance also increases with time of wetness. Therefore, the relative humidity and the amount of rainfall both influence the observed corrosion rate. Table 2 gives the results from the ISOCORRAG

Table 2 Zinc 1-year corrosion rates and ratio of steel corrosion and site atmospheric characteristics to zinc corrosion[a]

Test site	*Code*	*Zinc corrosion 1-year results (μm)*		*Steel/zinc ratio (mean) 1-year results*		*Environmental characteristics*[b]		
		Flat	*Helix of wire*	*Flat*	*Helix*	*Cl^- mean ($mg\ m^{-2}$)*	*SO_2 mean ($\mu g\ m^{-3}$)*	*Time of wetness (TOW), mean (h per annum)*
Iguazu	ARG1	1.6		4		Semiarid, wet, rural		5680
Camet	ARG2	1.3		28		Subtropical, marine, wet		6088
Buenos Aires	ARG3	1.0		16		Subtropical, marine, wet		4645
San Juan	ARG4	0.2		23		Subtropical, dry, rural		855
Yubany Base	ARG5	1.9		19		Antarctic, desert		2693
Boucherville	CND1	1.4	2.0	17	14	59	16	1396
Kasp Hory	CS1	1.9	2.2	14	22	Rural	17	3206
Praha-Bechov	CS2	2.8	3.3	17	21	Urban	67	2991
Kopisty	CS3	3.5	4.8	20	23	Industrial	90	2444
Helsinki	SF1	1.3	2.6	26	16	4	19	3578
Otaniemi	SF2	0.9	1.8	28	21	3	15	3256
Athari	SF3	0.7	1.2	18	13	Rural	4	3105
St. Denis, Paris	F1	1.5	3.6	25	14	28	50	4268
Ponteau Mart	F2	2.6	13.4	28	9	241	87	3846
Picherande	F3	0.9	2.2	18	10	7	9	4171
St. Remy	F4	1.5	4.2	29	23	378	30	6310
Salin de Gir	F5	4.6	5.7	16	23	184	20	3311
Ostende (Belgium)	F6	5.1	10.6	19	12	173	24	6083
Paris	F7	3.0	2.8	14	18	Urban	53	3189
Auby	F8	5.6	8.5	19	17	16	188	4571
Biarritz	F9	4.3	8.2	20	8	193		
Bergisch Glad	D1	1.6	1.8	23	29	Urban	18	4267
Choshi	J1	1.4	2.8	31	33	56	8	5704
Tokyo	J2	1.5	1.5	26	26	4	15	2173

Okinawa	J3	3.4	8.8	22	12	97	11	3852
Judgeford, Wellington	NZ1	0.7	1.2	29	30	Rural-marine		
Oslo	N1	1.3	1.8	19	19	2	14	2641
Borregaard	N2	3.8	5.7	16	16	9	44	3339
Birkenes	N3	2.3	2.0	9	14	Acid rain	1	4138
Tananger	N4	3.0	3.3	20	22	308	4	4583
Bergen	N5	2.1	2.2	13	15	7	9	4439
Svanvik	N6	0.8	1.4	25	21	1	17	2605
Murmansk	SU1	1.1	2.1	28	25	19	5	3227
Batum	SU2	1.6	2.0	18	14	1	26	3216
Vladivostok	SU3	2.3	3.1	11	22	18	29	3920
Oymyakon	SU4	0.4	0.6	2	3	Cold	5	381
Madrid	E1	0.6	1.6	46	18	Urban	44	2060
El Prado	E2	0.5	1.2	31	18	Urban	5	3223
Lagoas-Vigo	E3	1.0	2.5	27	14	29	49	2840
Baracaldo-Vizcaya	E4	1.2	2.6	37	22	25	32	4375
Stockholm Vana	S1	0.6	1.5	41	28	Urban	10	
Kattesand	S2	1.5	2.8	23	22	76	5	
Kvarnvik	S3	1.8	3.5	34	19	650	5	
Stratford	UK1	1.7	1.5	23	34	Industry	20	5783
Crowthorne	UK2	1.1	1.2	34	48	Rural		
Rye	UK3	2.5	2.0	23	46	Marine	21	
Fleet Hall	UK4	1.3	2.3	29	25	Urban		
Kure Beach	US1	2.0	3.9	19	21	102	10	4289
Newark	US2	2.0	2.2	13	12	Industrial		
Panama CZ	US3	17.5	7.6	21	39	619[c]	52	7598
Research Triangle	US4	0.8		28		Urban		
Point Reyes	US5	1.7	3.5	23	42	Marine		
Los Angeles	US6	1.1	1.8	20	11	Urban, marine	20	4003

[a] The zinc corrosion results are normally the mean of 18 determinations (3 replicates for 6 1-year exposures) starting in spring and autumn for 3 years.

[b] Where no atmospheric data are available, a qualitative description of the site is given.

[c] Marine, splash zone.

Source: Knotkova, D. Atmospheric Corrosivity Classification. Results of the International Testing Programme ISOCORRAG, In International Corrosion Conference, Houston, TX, USA, 1993; 16 pp.

tests for a 3-year period in many locations around the world.[6] The ISOCORRAG severity classification is given. The steel/zinc ratio is shown for both flat and helical-shaped samples together with environmental characteristics that govern atmospheric corrosion.

4.06.2.3 Water Corrosion

Zinc coatings provide good protection for steel in hard waters, where the scale forming ability of the hardness salts allow for development of passive layers. Less favorable corrosion resistance is seen in distilled and soft waters. Zinc, being an amphoteric metal, exhibits good corrosion resistance in water having a pH near neutral. The corrosion rates of both galvanized and aluminized steels in four potable waters in the Soviet Union are shown in Table 3. The normal application of galvanized steel with potable water is in the form of supply pipes.

Seawater corrosion of galvanized steel is moderate in temperate climates, but more severe in the tropics. In temperate seawater, magnesium salts are sufficient to act as inhibitors. Typical corrosion rates are 25 µm year^{-1} in the tropics and half that in the temperate seas such as the North Atlantic. In tidal areas, in which twice daily immersion occurs, or in areas splashed by waves, the corrosion rate is typically twice as great as that for completely immersed areas.

4.06.2.4 Soil Corrosion

There is a wide variation and composition of natural soils, and therefore, a wide range of corrosion rates that can be expected from galvanized steel, but sandy, well aerated soils with neutral or slightly alkaline pH are likely to cause only limited corrosion of zinc-coated steel. Zinc coatings prevent pitting of steel in soil, and even when the zinc coating is destroyed, the coated steel corrodes much less than do the bare specimens. The controlled use of backfilled materials can allow for satisfactory use of zinc-coated steel in soil contact applications. Typical corrosion rates of galvanized steel pipe in contact with a variety of soils in the United States are shown in Table 4. Here, it is indicated that inorganic oxidizing soils should allow an 85 µm coating to provide at least 10 years of protection. In most inorganic reducing soils, a 130-µm coating should give 10 years of life; however, this thickness would not be sufficient to protect steel in soils containing highly reducing organic or inorganic matter, or in cinders.[7]

4.06.2.5 Other Corrosion Media

Alkaline solutions of ordinary laundry soaps develop a protective coating when in contact with zinc coatings. Satisfactory corrosion rates are observed with both warm and cold applications. Detergent solutions are more corrosive; however, the better grades include inhibitors that reduce corrosion and allow the use of zinc-coated containers. Strong alkalis will result in excessive corrosion.

Many inorganic chemicals may be used in contact with zinc; however, in the presence of moisture, or with water in solution, many inorganic chemicals react with zinc. Mixtures of chemicals can sometimes be more corrosive than the sum of their separate effects, but in many cases, there are often inhibitors present that

Table 3 Corrosion rates for galvanized and aluminized steel in four waters of the Soviet Union

Rate of Corrosion (µm per annum)

Water	*Duration of testing (h)*		*Galvanized Specimens*			
	Total	*Actual (in the given regime)*	*Of Steel Specimens (uncoated)*	*Specimens galvanized with additions of 0.11–0.15% Al*	*Galvanized specimens subsequently heat-treated at 500 °C for 10 min*	*Aluminized specimens (coated in a bath of molten Al)*
Dnieprovsk	8 000	3000	0.460	0.042	0.011	0.003
Moskovorents	24 300	3000	0.207	0.017	0.009	0.016
Volzhsk	24 300	3000	0.280	0.028	0.020	0.180
Nevsk	24 300	3000	1.01	Pitting corrosion of the coating		0.100[a]

[a] Total duration of testing 10 800 h; actual duration, 2000 h.

Source: Proskurkin, E. V.; Bakalyuk, Ya. K. L.; Zholudev, M. D.; *et al. Water. Supply Sanit. Technol.* 1981, *10*, 16–18.

Table 4 Corrosion of galvanized steel pipe in contact with a variety of soils in the United States

Weight loss (g m^{-2})[a] and maximum pit depth (mm) after burial for years stated

Soil type	*Loss after 2.1 years*	*Max. pit depth*	*Loss after 4.0 years*	*Max. pit depth*	*Loss after 9.0 years*	*Max. pit depth*	*Loss after 12.7 years*	*Max. pit depth*
Inorganic oxidizing acid soils								
Cecil clay loam	90	0.23	430	0.15	180	<0.15	180	<0.15
Hagerstown loam	90	<0.15	300	0.20	210	0.15	180	<0.15
Susquehanna clay	300	0.23	700	0.23	270	<0.15	240	<0.15
Inorganic oxidizing alkaline soils								
Chino silt loam	330	<0.15	700	0.15	490	<0.15	330	<0.15
Mojave fine gravelly loam	480	0.15	1000	0.20	330	<0.15	330	<0.15
Inorganic reducing acid soils								
Sharkey clay	180	0.15	460	0.30	210	<0.15	330	0.15
Acadia clay	1000	0.15			1460	0.20		
Inorganic reducing alkaline soils								
Docas clay	980	0.20	490	0.23	490	0.25	490	<0.15
Merced silt loam	640	0.20	130	0.30	30	0.15	400	0.20
Lake Charles clay	1130	0.13	1190	0.18	1680	0.33	4210	1.68
Organic reducing acid soils								
Carlisle muck	360	0.20	1040	0.28	915	0.20	1040	<0.15
Tidal marsh	360	<0.15	640	0.25	610	0.20	1460	1.32
Muck	1310	0.33	1650	0.53	2750	1.63	3260	1.93
Rifle peat	1310	0.25	2200	0.30	5980	2.11	5950	2.23
Cinders								
Cinders	2040	1.57	1650	1.14	1710	0.53	3630	1.22

[a] To obtain weight loss in micrometers, divide g m^{-2} result by 7.2.

Normal mass coating, 915 g m^{-2} of exposed area, is the mass of coating on one side of the pipe; 915 g m^{-2} is equivalent to approximately 0.13 mm thickness of coating.

Source: Romanoff, M. *Underground Corrosion*; National Association of Corrosion Engineers (NACE): Houston, TX, 1989. (Originally Issued by the National Bureau of Standards, Circular 579, 1957).

give a net beneficial effect. A short immersion trial is desired for water-based solutions, from which results can be linearly extrapolated to give the worse possibility, because attack often reduces with time.

Many organic chemicals can be used with zinc-coated steel, and many of these organic liquids are inert in contact with zinc. Air entrapped during encapsulation and vapor from polymeric materials such as epoxy resin can cause corrosion. When 85–90% humidity is present, zinc can deteriorate in contact with several synthetic organic chemicals.

Zinc-coated steel is not highly corroded when it is placed in contact with pure fuels, but sulfur or water in ordinary fuels may form compounds with zinc that can both cause high corrosion rates and also form compounds that can clog small orifices. Surface treatments that provide resistance to sulfur or moisture impurities are recommended in this application.

Many lubricants, when in contact with galvanized steel, produce a smooth lightly etched surface, and therefore, form a natural protective coating. Lubricants should be stable and free from acidity. Lubricants of mineral origin are completely satisfactory, while those containing animal or vegetable oils or fats should be avoided.

Chromated zinc coatings are widely used in contact with concrete in reinforced concrete applications. Galvanized reinforcing bar in concrete has a much higher tolerance for chloride contamination of the concrete resulting from marine exposure or contact with deicing salts. Zinc corrosion products are much less expansive than are iron corrosion products, greatly reducing the risk of cracking, rust staining, and spalling of concrete. Static strength and bond strength of the reinforcement in concrete is not affected by the presence of the coating.

One form of general corrosion that is not protective is ‘white rust,’ more properly called wet storage stain. This corrosion occurs when there is access for water but limited supply of oxygen and carbon dioxide. The presence of chlorides and sulfates accelerates wet storage stain formation. White rust is particularly found in newly galvanized, bright surfaces, and especially in crevices between closely packed galvanized articles. In such cases, the surfaces come into contact with moisture, and it cannot dry quickly. Zinc surfaces that already have a normal protective layer of corrosion products are seldom attacked. The presence of white rust does not affect the functional corrosion resistance of the zinc coating. Short-term protection against white rust is attained by chromating or phosphating. Freshly galvanized work should always be stored, so that all surfaces are well ventilated and water allowed to easily run off the surfaces.

4.06.3 Corrosion Characteristics of Aluminum

Low corrosion rates are seen with aluminum-coated steel between pH levels of 5 and 8.5. Like zinc, aluminum is amphoteric and its corrosion dependence on pH of several media is shown in Figure 3. Aluminum corrodes under both acidic and alkaline conditions; however, when the corrosive environment is highly oxidizing, the aluminum oxide film will be more protective. Also, in several specific cases, the oxide film is not soluble in acidic or alkaline solutions. Two notable examples are acetic acid and sodium disilicate, which are shown in Figure 3. Ammonium hydroxide with >30% concentration by weight, nitric acid at >80% weight concentration, and sulfuric acid of 98–100% concentration are also exceptions. There is no general relationship between pH level and the rate of attack, because specific ions largely regulate corrosive behavior. Aluminum coatings are inert to strong nitric or acetic acid solutions, but are easily attacked in dilute nitric, sulfuric, or hydrochloric acid solutions. Similarly, solutions with a pH as high as 11.7 may not attack aluminum alloys, provided silicate inhibitors are present, but in the absence of silicates, appreciable attack may occur at pH levels as low as 9.0. Generally, less corrosion occurs in the near-neutral pH range of chloride-containing solutions, 5.5–8.5, than in more distinctly acid or alkaline solutions.

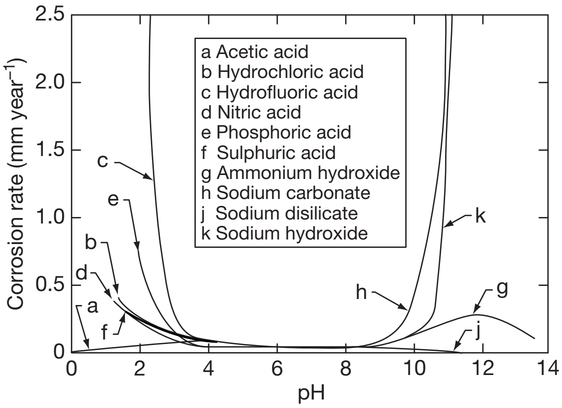

Figure 3 Relation to pH of the corrosivities towards 1100-H14 alloy sheet of various chemical solutions. Revie, W. R. *Uhlig's Corrosion Handbook*, 2nd ed.; Wiley, 2000; Chapter 40, pp 677–714.

Aluminum coatings are not appreciably corroded by distilled water even at temperatures up to 180 °C. For this reason, aluminum-coated steel can be used in many distilled water storage and handling applications, provided the coating is continuous, so that the underlying steel is not exposed. Freshwaters vary widely in their composition, and in many cases, the use of aluminum-coated steel in contact with many freshwaters will be satisfactory. However, certain waters may cause severe localized attack or pitting. Pitting is of special importance when coatings are thin. However, aluminized culvert is widely used for freshwater drainage applications. In this case, the greater hardness of aluminized coatings provides better abrasion resistance compared with zinc, even though the aluminized coating provides only barrier, and not sacrificial protection of the steel.

Corrosion of aluminum coatings in seawater is mainly characterized by pitting. Rates of pitting usually range from 3 to 6 μm year^{-1} during the first year and from 0.8 to 1.5 μm year^{-1} after that.

4.06.4 Corrosion Characteristics of Tin

As with other metal coatings, the corrosion rate of tin in the atmosphere is highly influenced by moisture. In dry conditions, slow growth of tin oxide is expected; however, in wet conditions, tin coatings behave in a manner similar to that of steel. In wet conditions, tin behaves as a cathode for steel, being more noble than steel in the electromotive series. The only barrier offered by tin to steel under such conditions is as a physical barrier.[2]

Liquid phase corrosion of tin has been extensively studied because of the use of tin steel in food-containment applications. However, the necessary control of process temperatures and times of cooling to ensure product safety, usually results in the avoidance of tin corrosion problems. However, poor drying of cans may initiate corrosion that is only observed later. Also, poor practice regarding external packaging, such as shrink wrapping of wet cans may trap water and cause noticeable tin corrosion. Uptake of chloride from cardboard in contact with food cans may also cause local attack.

Within tin cans, the corrosion of tin is largely affected by the character of the contained food or other substances such as beverages, domestic cleaners, paints, and decorative materials, together with a wide variety of other materials that are stored or transported in tin cans. Organic complexes such as citrate or tartrates can result in conditions that influence the nature of tin corrosion. Pesticide residues or the residues from nitrate fertilizers may also be present. Some foods and beverages are themselves likely to attack steel. Thus, cola-type drinks having phosphate as well as citrate ions and low pH tend to be iron dissolvers. As these products are normally packed in lacquered cans, the potential effects of a large tin cathode are minimized and hence perforation is uncommon. Tinned meats, fish, and vegetables (such as peas) can contain sulfur-bonded protein species. During processing, these may breakdown to yield hydrogen sulfide, which can react readily with both tin and steel. Although they offer no food contamination problems because of the low solubility, they are unsightly. This can be controlled by using internal lacquers pigmented with zinc carbonate or oxide. The sulfide reacts with these pigments, but the resulting zinc compound is off-white and causes no concern to the customer.

4.06.5 Applying Coatings by Hot Dipping

4.06.5.1 Introduction

Dipping of metals into molten lower melting point metals is the oldest, simplest, and generally, the cheapest method of forming a surface coating. The base metal must withstand the dipping temperature without undesirable changes in properties. To obtain a coating, the coating metal must be wetted and alloyed with the substrate. The coating metal, in addition to having a lower melting point, must be inexpensive and must confer the desired properties: corrosion resistance is the most important, but often the coated product is required to be formed and must have reasonable abrasion resistance. Commercial coating of zinc, aluminum, tin, and their alloys are most important. Steel is by far the most important metal that is coated by hot dipping. Cast irons are also coated by hot dipping and some copper is coated with tin or tin alloys. Stainless steel is hot dip coated with aluminum, mainly for use in automotive exhaust systems. Other hot dip coatings are only applied for special purposes.

The dipping processes are of three basic types: (1) continuous lengths of strip, wire, or tube pass through the molten coating metal; (2) semimanufactured products (such as cut tube lengths or sheets) are dipped into the molten metal in batches in specially designed and automatically operated plants; and (3) fabricated products are dipped into the molten metal.

The coatings produced are designed to differ because with most semifabricated materials, such as sheet, the final coating needs to be formed as easily as the base metal, whereas on fabricated products this does not apply and thicker coatings with better corrosion resistance are provided. The vast majority of coatings are zinc based: more than 20 times as much zinc is used for hot dip coatings as the total of all other hot dip metallic coatings. All three types of processes apply for hot dip zinc (galvanizing) and zinc–5% aluminum coatings. Hot dip aluminum coatings (aluminizing), while used in the past on fabricated products, are now expanding for continuously coated strip and also for wire. The 55% aluminum–43.5% zinc–1.5% silicon coating (Galvalume type) and Zn–Al–Mg coatings are used similarly for continuous coating of strips where the coating operation can be in a controlled atmosphere. Hot tinning is used to protect food containers and also to facilitate the soldering of steel, copper, brass, and other metals, for example, copper wire is often tinned. With continuously coated steel sheet and wire, in addition to thin coatings, the ‘terne’ coating, an alloy of lead usually with 2–25% tin, continues in industrial use as a coating for steel sheet and wire, although because of environmental concerns, it has largely been replaced by lead-free materials.

4.06.5.2 Principles of the Hot Dipping Operation

Most of the principles of hot dipping are common to galvanizing, tinning, terne coating, and aluminizing.

4.06.5.2.1 Cleaning

The surface must be cleaned of oil, grease, and other surface contaminants and also scale and oxide, using degreasing and/or pickling treatments as required. The original Sendzimir pretreatment of steel strip by oxidation followed by reduction at high temperature or other high temperature gaseous treatments, developed more recently, eliminates the necessity for these operations and also for fluxing, although electrolytic cleaning can be used before the gaseous treatment processes, to obtain the highest quality hot dip coatings on strip.

Keeping the material in a controlled atmosphere is often sufficient to retain a clean surface until coating takes place, but where exposure to air occurs (as with most coating of fabricated articles), a flux coating is usually applied to keep the surface clean and free from oxide. Fluxing may be by immersion in an aqueous prefluxing bath, followed by drying, or by passing through the molten flux floating on the bath of molten metal, or both of these. Molten flux attacks the surface, cleaning it and promoting the wetting of the base metal by the molten metal in which it is dipped.

4.06.5.2.2 Dipping

Strip or wire is coated continuously, up to 4 m s^{-1} in speed. Continuous coating plants in which the sheet is continuously uncoiled, passed through the coating equipment, and then recoiled have largely replaced cut sheet plants, except in developing countries. Fabricated articles are either dipped in batches, mounted on suitable jigs if small, or singly if large, and the operation may be mechanized. Small articles and threaded work are dipped in perforated baskets suitable for subsequent centrifuging before the coating solidifies. Assuming that the articles to be coated have been properly cleaned and fluxed, the base metal and the molten coating metal interact on dipping, producing an alloy layer. If the article is colder on entry than the melting point of the coating metal, there may be a short intermediate stage where a solid skin forms around the article. Frequently, the base metal (or article) is preheated to avoid this.

For any given pair of metals, the total amount of alloy increases with the duration of immersion and is also affected by the temperature of the bath.

The amount and nature of the alloy layer may also be profoundly affected by additions to the molten bath, such as silicon to an aluminum bath or aluminum to a galvanizing bath. The change in the composition of the base metal may also have a marked effect, for example, mild steel containing a little silicon continues to react with zinc at a steady state throughout immersion, whereas with steel without silicon, the reaction rate decreases with time. Although the alloy layer is always referred to as if it were a single layer, it is usually made up of two or more layers, corresponding to known metallurgical phases. Reaction can occur after the work has left the molten metal bath while the coating is solidifying and cooling.

4.06.5.2.3 After treatments

These include processes intended to produce one or more of the following results:

(a) Reduction of coating thickness by reducing the amount of molten metal adhering to a substrate as it leaves the bath. Air or gaseous jets are used for control of the coating thickness of continuous sheet and wire and tubes. For fabricated articles, this is done by centrifuging while the coating is still molten.
(b) Improvement of the properties or appearance of the coating for substrates. Such improvements include quenching (to avoid unwanted alloy growth), chromating and phosphating, and special treatments in both chemical and mechanical types for sheet such as temper rolling and stretch leveling.
(c) Change in the character of the coating – as distinct from the more superficial treatments listed under (b). Hot-dipped zinc coatings are sometimes annealed to covert the whole of the coating into alloy as are aluminum coatings intended for heat resistance.

4.06.6 Hot Dip Galvanizing

4.06.6.1 Introduction

Large tonnages of fabricated steelwork are hot dip galvanized each year. Over 6 million tons of steel were hot dip galvanized within the European Union in 2006.[8] The principles of hot dip galvanizing have remained unchanged for 150 years; however, a vast amount of research has enabled the industry to become technically advanced over this period. Many changes to plant configuration have also been brought about in response to modern national and European environmental and health and safety legislation. The hot dip galvanizing process essentially consists of cleaning the articles (degreasing and pickling), fluxing the work, and then immersing the work in a bath of molten zinc. Coated work can then be either quenched or allowed to air cool.

4.06.6.2 Design for Hot Dip Galvanizing

Steelwork intended for processing should ideally be designed with the coating process in mind.[9] When an article is received for hot dip galvanizing it is assessed for suitability for further processing. It should be free from contamination, which would not be removed in the normal pretreatment process prior to galvanizing. It is important that the design allows adequate handling through the process and for the access and egress of all pretreatment solutions and molten zinc. Articles containing sealed volumes should not be hot dip galvanized, because any residual water or other solutions contained within the void will evaporate and are likely to generate sufficient pressure to cause an explosion – ejecting molten zinc from the galvanizing bath and compromising operator safety. Distortion can occur in some fabrications because of relief of unbalanced steel production stresses and or fabrication stresses in combination with the thermal stresses brought about during dipping. Articles destined for galvanizing, having been fabricated from elements with very dissimilar geometries (thickness), utilizing high-strength steels, and particularly those adopting designs that incorporate highly restrained joints, can in specific circumstances become more susceptible to steel cracking during galvanizing by one or more mechanisms (strain-age embrittlement, hydrogen embrittlement, or liquid metal assisted cracking), and guidance exists to manage these risks.[10,11]

4.06.6.3 Degreasing and Pickling

Steelwork is commonly degreased in acid or alkaline solutions prior to rinsing in cold water. The work is then pickled in either a sulfuric acid solution or a hydrochloric acid solution. Sulfuric acid is usually operated at a strength of around 14% and at a temperature of 60–80 °C, whereas hydrochloric acid would normally be operated across a range of ~5–14% and at ambient temperatures.[12] Inhibitors are added to the acid to reduce potential for overpickling on clean areas of steelwork. Rather than operate a separate process tank, acidic degreasers can also be added to a pickle tank obviating the need for a separate degreasing stage. Pickling will be followed by another water rinse stage.

Grit blasting is often used to remove tenacious contamination on castings, to remove welding slag from fabricated steelwork, or in specific instances where a rougher steel surface profile is required in order to attract development of a thicker galvanized coating. Where grit blasting is carried out, the work is normally 'flash pickled' to remove any residual loose contamination prior to further processing. Hydrofluoric and mixed acids can also be used to pickle castings, but these are extremely dangerous chemicals and great care is needed when working with these agents.

4.06.6.4 Fluxing

After degreasing and pickling, work is fluxed to prevent further oxidation of the surface and to aid wetting of the surface when it comes into contact with the molten zinc. Fluxing has historically taken place in a variety of ways – 'old dry,' 'dry,' and 'wet' methods Figure 4. The 'dry' method dominates for general galvanizing, while the 'wet' method is still used when processing smaller articles in spin-galvanizing operations for instance.

The 'old dry' method consists of drying the work after pickling and allowing the dried on salts to provide the fluxing action prior to dipping in the molten zinc. The 'dry' method involves dipping the pickled and rinsed work into a flux solution and afterwards drying the work in a pit or oven prior to dipping the work into the molten zinc. The 'wet' method involves passing the pickled and rinsed work through a blanket of flux floating on the top of the zinc melt.

Where the 'dry' process of prefluxing is used, the solutions adopted are usually based upon zinc ammonium chloride (a common form being the double salt $ZnCl_2 \cdot 3NH_4Cl$). Operating strength is usually up to 30% and operating temperatures of up to 80 °C can

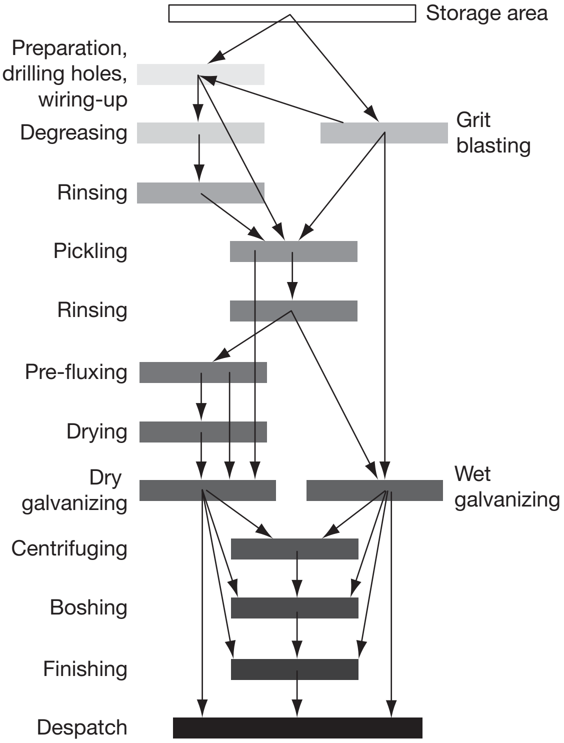

Figure 4 Flow diagram showing handling operations in the galvanizing process. *General Galvanizing Practice*; Galvanizers Association: UK; 1999; p 3.12.

be used. Other fluxes, which include a proportion of sodium chloride or potassium chloride, can also be used. These fluxes, while requiring more care for optimum operation, have been reported to produce fewer fumes during dipping of the work than do the traditional zinc ammonium chloride solutions.[13,14]

When drying the work prior to dipping in the molten zinc, care is needed to ensure that the flux on the work is not degraded by overheating. Normally, article surface temperatures are limited to 150 °C maximum. The time between fluxing and dipping in the molten zinc should be minimized to maintain the effectiveness of the flux.

4.06.6.5 Galvanizing

Upon immersion of the prepared article into the molten zinc a series of iron–zinc intermetallic compounds are formed on the surface of the article (gamma (Γ), delta (δ), zeta (ζ)). Upon withdrawal of the article from the galvanizing bath, a proportion of molten zinc is also withdrawn on the work (forming the eta (η) layer). This solidifies as the work cools (see Figure 5).

'Spin-galvanizing' or 'centrifuge galvanizing' is a variation of the general galvanizing process where articles are contained within a perforated basket during pretreatment and dipping in the zinc melt. After withdrawal, the basket is placed in a container, which spins the work to remove a proportion of the free (semimolten) zinc from the coating. This type of process is often used for small articles such as fasteners and washers. The spinning process produces a thinner coating than that of the general galvanizing process, a factor that is reflected in the standards and specifications associated with products processed in this way.[15]

4.06.6.5.1 Coating development and reactivity of steel

Conventional operating temperatures for galvanizing are between 445 and 465 °C. High temperature galvanizing is carried out between 530 and 560 °C. Galvanizing processes are not operated at temperatures between these two ranges.[16] Operators of the higher temperature process use ceramic galvanizing baths to overcome problem of the increased reaction rate between steel and zinc at these high temperatures. For silicon-free steel, the reaction rate between iron and zinc is parabolic with time in the temperature range 420–490 °C (the lower parabolic range). At temperatures between 490 and 510 °C, the reaction rate is approximately linear with time (known as the linear region). The reaction rate reverts to a parabolic relationship at temperatures above 530 °C (the upper parabolic region).

The thickness of the alloy layers within the coating formed on a steel article will depend principally on (a) the chemistry of the surface of the steel, (b) the surface roughness of the steel, (c) the temperature of the galvanizing bath, (d) the time of immersion, and (e) the rate of cooling.[17]

The role of silicon and phosphorus in development of alloy layers in a galvanized coating has been subject to intense research over many years.[18,19]

Silicon-killed steels, containing Si over 0.3%, produce a thick gray galvanized coating on processing. These thick gray coatings consist predominantly of all zinc–iron alloy (see Figure 6). While offering extended periods of corrosion protection, they are often less resistant to mechanical damage. Steels containing between 0.15% and 0.25% Si often produce

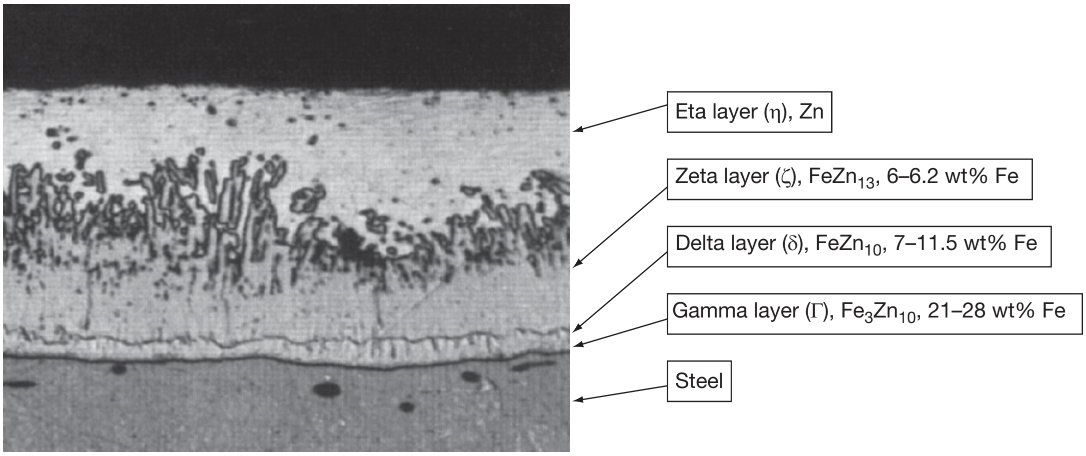

Figure 5 Structure of a galvanized coating on a normal (unkilled) steel. *The Engineers and Architects' Guide: Hot Dip Galvanizing*; UK Galvanizers Association Publication, 1999.

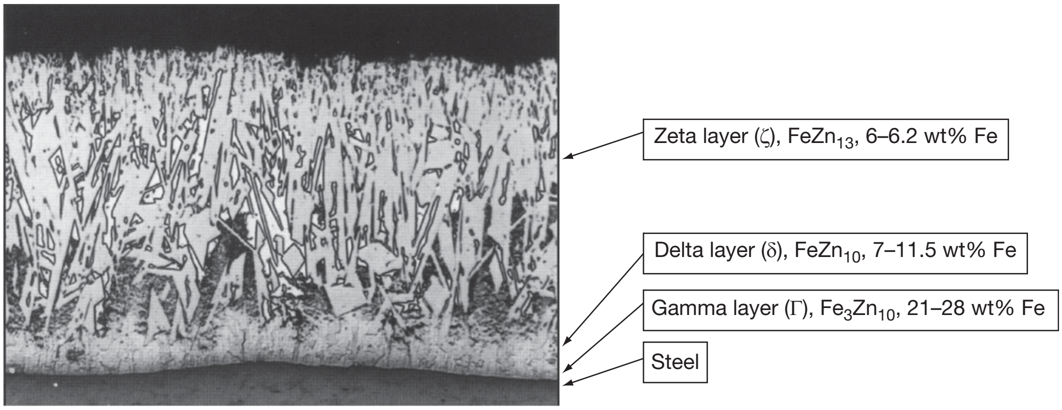

Figure 6 Structure of a galvanized coating on a reactive (silicon-killed) steel. *The Engineers and Architects' Guide: Hot Dip Galvanizing*; UK Galvanizers Association Publication, 1999).

coatings that retain a proportion of zinc on top of the zinc–iron alloy layers.

Where semikilled steels are processed, the results are less predictable. Steels containing between 0.04% and 0.14% Si often produce coatings that are very thick and exhibit poor cohesion. This reactivity range (see Figure 7) is often known as the 'Sandelin peak,' named after the researcher who described the effect some years ago.[20] Phosphorous is more influential in determining coating characteristics at these lower silicon concentrations. The International Lead Zinc Research Organization (ILZRO) has set out a classification system for reactivity of steels, which is broadly in line with the Sandelin data.[21] Hot dip galvanizing of reactive steels is often associated with increased zinc usage.

The effect of silicon can be suppressed by galvanizing at higher temperatures (530–560 °C). High temperature galvanizing is often (but not exclusively) used to process small work also, adopting the 'centrifuge' or 'spinning' process.[15]

Alloy layers tend toward increased thickness on rougher steel surfaces, and because of the increased surface area, they are able to take part in the reaction between the zinc and the iron.[22] In practice, a maximum uplift in coating of ~50% can be achieved for steel that has been grit blasted prior to galvanizing compared with the coating developed on a steel of similar thickness and surface chemistry that has not been subject to blasting.

The alloy layers grow more rapidly as temperature increases – but there are practical limits to the extent to which this factor can be used to control alloy layer growth.[23]

Coating development normally tends to follow a parabolic reaction rate when articles are first immersed in the zinc melt. Very reactive steels

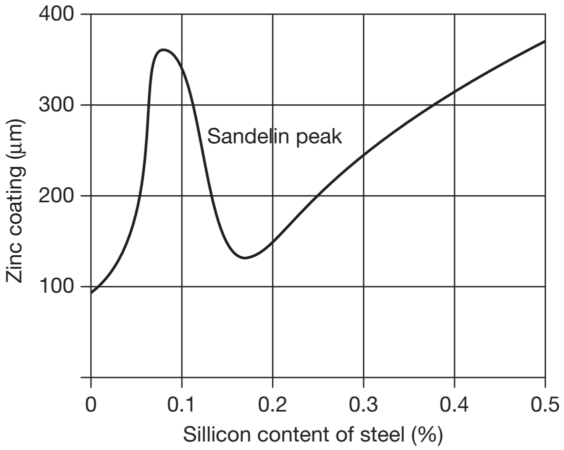

Figure 7 Illustration of the 'Sandelin' curve – Hot dip galvanized coating development with increasing steel surface silicon concentration. *General Galvanizing Practice*; Galvanizers Association: UK; 1999; 1.8.

(particularly those with high (>0.25%) or critical levels (0.04–0.14%) of silicon and phosphorus) exhibit a reaction rate for coating growth that is more linear with time (see Figure 8).

The alloy layer may continue to grow slowly during the cooling of the work after galvanizing. This is rarely an important consideration except when very heavy sections are being processed. In extreme cases, the alloy layer diffuses to the surface to form grey patches. This is often referred to as a 'gray coating' or 'gray bar.'[24]

4.06.6.5.2 Alloying additions the zinc melt

Alloying additions to the galvanizing zinc melt can be made to control the rate of coating development for reactive steels. Depending upon the specific alloying element(s) being introduced to the galvanizing zinc

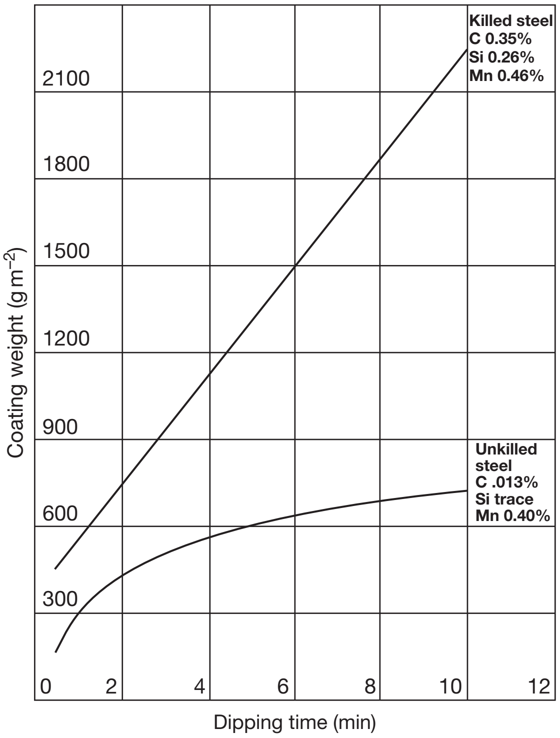

Figure 8 Illustration of galvanized coating development with time for normal (unkilled) and reactive (silicon-killed) steel. *General Galvanizing Practice*; Galvanizers Association: UK, 1999; 1.8.

melt, these additions can be made directly or in the form of a master-alloy.

Most galvanizing melts will contain ~98.5% zinc. Lead will be found in zinc melts produced by melting zinc stock originating from a thermal production route (e.g., imperial smelting process). Although the solubility of lead in zinc is ~1.4% at 450 °C, common concentrations of lead in zinc melts will run up to ~1%. Lead assists wetting of the steel surface and reduces the surface tension of zinc, thereby encouraging greater fluidity and better drainage from the article.[25,26]

Nickel additions to the zinc melt of ~0.05–0.06% have been found to be most effective for controlling coating development on steels that exhibit silicon concentrations up to 0.2%, effectively eliminating the development of reactive coatings in this range.[27,28] The effects of bismuth on the zinc–nickel-based melt have also been studied.[29]

Historically, aluminum additions of up to 0.005% have been used to aid brightening of the work and reduce the rate of oxidation of the zinc.[30,31] Galvanizing melts commonly operate using aluminum levels of ~0.001–0.002%.

Tin additions to the zinc melt at concentrations up to around 2% had been found to be effective in controlling steel reactivity across the range of common silicon concentrations in steels and providing coatings with bright finishes.[32,33] Although the role of tin during galvanizing for concentrations up to 5.0% have also been investigated,[34] tin levels of ~0.3%, particularly when used in combination with bismuth (around 0.1% maximum to improve melt fluidity), have found wider currency in Europe for controlling steel reactivity. Zinc alloy melts using total for tin, bismuth, and aluminum (total Sn/Bi/Al < 1%) have also been developed, which provide a smooth, bright, spangled finish to the galvanized coating.[35] The additions of tin to the melt allow for operation of higher aluminum levels without detriment to coating continuity (development of bare spots).

Use of other alloying additions (alone or in combinations), such as vanadium,[36,37] manganese, and titanium,[38] have also been investigated to either control steel reactivity or develop a more consistent coating thickness, texture, or appearance while maximizing profitability and minimizing production of waste streams.

Almost from 2002, zinc–5% aluminum coatings have also been developed for application through the general galvanizing process, albeit on a more limited scale than coatings developed through conventional zinc melts (zinc concentration 98.5% minimum).[39] Coatings of Zn–23% Al have also been investigated.[40]

4.06.6.6 Post-Galvanizing Treatments

Work which has been galvanized is often either left to air-cool or quenched in water. The quench water may contain a passivation treatment (chromate or phosphate), which retards the early onset of wet storage staining during transport or storage.[41] Quenching the work has the advantage of removing potential flux residues that might stain the work and allowing more rapid cooling of the work, thereby reducing the potential for development of all alloy layered coatings on components fabricated from reactive steels. The work will also be cooler to handle, allowing earlier movement of work away from the processing area.

4.06.7 Continuous Zinc and Zinc Alloy Coating

Large tonnages of wire and sheet are galvanized on automated lines by continuously uncoiling the steel, passing it through the coating line, and recoiling it. In the past 20 years, development of techniques for coating steel sheet with zinc and zinc alloys, and pretreating advanced high-strength steels now demanded by automakers, have been the major advances.[42]

Surface pretreatment is now principally by gaseous treatments in most strip lines and some wire lines; pickling remains for other products. In the gaseous pretreatment processes, steel is fed into the galvanizing bath through a snout, which dips below the surface of the molten zinc and protects the surface against reoxidation. This eliminates the need for fluxing. The strip enters the molten zinc at a temperature of 470–480 °C; most of the heat required for the galvanizing bath is supplied by the sheet itself.

Chemical cleaning and fluxing (wheeling process) without gaseous treatment also has limited use, mainly for building panels and other sheets in which economical development of high tensile strengths is desired. External coating of small diameter tubes in which zinc is pumped over the steel instead of the steel being dipped uses either an inert atmosphere or a flux pretreatment.

Painting of galvanized sheet best involves no-spangle or minimum spangle galvanized surfaces that provide good specular reflectivity without the substrate surface structure being visible. The traditional spangled galvanized surface is now only rarely seen on sheet intended for painting. Spangle reduction is achieved by sweeping the coating with narrow jets of steam or air or by depositing a large number of crystallization nuclei on the surface just before solidification. A skin pass, with a reduction of $<1\%$, after solidification is an alternative method. Paintability (and weldability) is also improved by converting the surface to a zinc–iron alloy (galvannealing) in line.

Steel wire is also galvanized on a continuous basis and the principles of the Sendzimir sheet galvanizing process and later developments have been applied as an alternative to wet cleaning and pickling. Certain grades of wire that require tensile strength may require redrawing of the wire after coating.

For annealed wire, the strands of wire are first taken through a bath of molten lead, where the desired softening and a partial cleaning effect, termed patenting, is achieved. Strands are then pickled, fluxed, and galvanized. Wiping of the wire after galvanizing controls coating thickness. Wires with heavier coatings are drawn through a bed of charcoal, while for thinner coatings, wiper pads are held against the wire by various means. At higher line speeds, gas wiping is practised.

4.06.8 Hot Tinning

Like zinc coatings, hot dip tin coatings posses an intermetallic coating covered with the solidified metallic coating. Cleaning and pickling treatments for prefabricated article are similar to hot dip galvanizing. The aqueous flux solution is also similar to galvanizing solution, consisting typically of 240 g l^{-1} of zinc chloride, 60 g l^{-1} of sodium chloride, 30 g l^{-1} of ammonium chloride, and 6–12 ml l^{-1} of hydrochloric acid (sp. gr. 1.14). Articles, wet with flux solution, are lowered into a bath of molten tin at about 280 °C, having a layer of fused flux floating on it, covering about two-thirds of its surface. The flux cover is composed of a mixture of dry chlorides in the same proportions by weight, as the flux solution being carried over with the work. After the article reaches the temperature of the tinning bath, flux is removed from the immediate surface of the bath and the article is immediately withdrawn through the flux free area of the tin surface. Coating quality may be improved by redipping in a second tinning pot where the tin is covered with a layer of molten grease such as tallow at a temperature of 240–270 °C. Small articles may be tinned in batches using jigs or baskets and then spun in a heated centrifuge to remove excess tin. The brightness of the tin coating may be preserved by quenching the articles in a layer of paraffin or kerosene, 50–100-mm thick, floating on water. Small parts can be separated from one another before the tin coating solidifies by allowing them to fall on a paddle wheel rotating at 500–1000 rpm. For strip, pretreatment uses electrolytic alkaline degreasing followed by electrolytic pickling. Work then passes downward through a layer of molten zinc chloride flux into the molten tin at 300–320 °C on emerging sheet passed through pressure rolls and palm oil at 240 °C to remove tin. A hot dip tin coating on a steel layer has a layer of $FeSn_2$ at the interface between the tin and the steel. This alloy grows very slowly in comparison with the more complex alloy layers formed in galvanizing and then aluminizing. It usually comprises 10–20% of the total coating thickness. Tin–lead coatings containing two or more percent of tin may be applied by hot dip processes to steel, copper, and copper alloys. Steel sheets are commonly coated with alloys containing 7%, 10%, or 25% tin. These are called terne plate with the name tin-terne, sometimes applied to the higher tin coating. Coating quality can be improved by electroplating the steel substrate with nickel before hot dipping in the terne bath.

4.06.9 Hot Dip Aluminizing

Fabricated articles are less commonly hot dip aluminized now, than in the past. Coatings are applied after cleaning the work, including degreasing, pickling in hydrochloric acid, and then preheating. The work is then immersed in a molten salt bath, a flux or reducing atmosphere, prior to immersion in the bath of molten aluminum. Alloying occurs between iron and aluminum at the interface.

Type I aluminized steel strip (used in high temperature conditions) is coated with aluminum–silicon alloy containing typically 5–11% silicon, whereas the Type II grade (for corrosion prevention) is coated with a heavier layer of 'pure' aluminum, although heavier aluminum–silicon coatings are also referred to as 'Type II'. A disadvantage of silicon-containing aluminum coatings is that they darken when subjected to atmospheric corrosion; Type I grade of aluminized steel possesses total coating thicknesses, including the alloy layer, between 14 and 25 μm (80–150 g m^{-2} including both sides) whereas Type II grade has in excess of 40 μm (230 g m^{-2} including both sides). In both cases, about 2–4% of iron is present in the coating alloy. This is iron dissolved from the strip and the coating bath hardware. An alloy layer containing intermetallic compounds can be seen between the coating layer and the steel substrate in both grades. This layer is thicker in the Type II grade. As intermetallic compounds are generally very brittle, it is desirable to keep the alloy layer fairly thin. Silicon additions help control the thickness of the alloy layer. In both grades, it thickens with time and temperature, at a rate that is generally parabolic, but there is a slower rate of thickening of the alloy layer in the Type I grade, likely because of a combination of a higher dissolution rate and a slower solid state growth rate.

Post annealing, an overageing heat treatment carried out for an hour at 400–500 °C, can slightly increase ductility. A coating which has a total thickness of 25 μm in which the alloy layer occupies about 25% of the total has satisfactory bending properties. Excessive deformation causes cracking of the alloy layer or delamination of the coating. The thicker alloy layer in the Type II grade tends to crack more readily than that on Type I.

Aluminized steel has far better heat resistance than do galvanized steel, maintaining a bright metallic surface on exposure to temperatures up to ~500 °C. Higher temperatures will lead to the conversion of any free aluminum at the surface to iron aluminum compounds. Exposure to temperatures up to 700 °C are possible without promoting breakdown of the steel substrate. Aluminized steel does not suffer from the intergranular embrittlement problems arising from intergranular diffusion of zinc reported for galvanized steel at high temperatures. Galvalume, a strip product coated with an alloy containing 55% Al–43.5% Zn–1.5% Si, has also been reported to suffer from intergranular embrittlement at temperatures close to 500 °C, although this can be prevented by increasing the phosphorus content of the substrate steel above 0.04%.

4.06.10 Hot Dip Coatings with Applied Organics: Duplex Systems

Hot dip galvanized coatings by themselves provide a long lasting and cost-effective means of corrosion protection for iron and steel articles in most applications. When organic systems are applied on top of the galvanized article, this becomes known as a duplex coating. Duplex coatings are often used to add color for aesthetic reasons (camouflage or contrast), to increase the economic life of the structure by providing additional corrosion protection, or to provide greater protection in aggressive corrosive environments.

Organic systems used in conjunction with galvanized coatings often provide a life for a structure, which are longer than the sum of the lives of the coatings used independently.[43] EN ISO 12944 provides information on preparation of galvanized coating prior to application of wet paint systems, together with life to first maintenance periods for duplex-coated articles in a variety of exposures (the predicted life to first maintenance relates only to the need for repair of the organic coating and so is likely to be much shorter than the life expected from use of the galvanized coating alone).[44] EN 13438 provides performance requirements for duplex systems involving powder organic coatings applied to galvanized articles.[45]

4.06.11 Applications for Hot Dip Coated Products

All industrial sectors use hot dip coated products of one form or another. Table 5 illustrates a range of application sectors for hot dip coated products. The growing need for cost-effective, long-life, sustainable corrosion protection systems has led to increasing usage of hot dip coated products worldwide. The construction industry and street and outdoor furniture sectors dominate the take up of hot dip galvanized products, followed by agricultural sector and many other, smaller, market segments. Development of coatings with greater formability for application to higher strength steel has increased the usage of these types of coatings in the vehicle manufacturing sector.

4.06.12 Standards

The development of standards for hot dip coatings within the European region, through Comité Européen de Normalisation (CEN), and on a global scale, through the International Standards Organisation (ISO), has burgeoned over the last decade. Table 6 shows a selection of relevant international and European standards for hot dip coatings on articles. Table 7 shows a selection of relevant American standards (developed by the American Society for Testing and Materials (ASTM) International). Where standards are specified, the latest dated document should be used.

Table 5 Applications for use of hot dip coated products

Application	*Examples*
Agricultural	Animal pens, buildings, cattle grids, farm machinery, gates, grain hoppers, glass houses, livestock trucks, and sprinklers
Building components	Balconies, downpipes, fire escapes, gutters, lintels, louvres, reinforcing bar, and window frames
Construction	Bridges, building frames, car parks, telecom masts, ski lifts, tunnels, siding/cladding, corrugated roofing
Industrial	Access bridges, cat ladders, checker plate, conduit, handrail, pipe bridges, stairways and walkways, and platforms
Marine	Boat hulls, buoys, chains, docking pontoons, fish farm equipment, handrailing, offshore platforms
Miscellaneous	Brackets, castings, fasteners, nails
Power generation/ distribution	Cable tray, cooling towers, flues, power station equipment, pylons, transformer boxes, wind turbines
Storage and handling	Conveyor systems, cranes, drums, pallets, racking, and stillages
Street furniture	Benches, bollards, bus stops, crash barrier, lighting columns, manhole covers, palisade fencing, playground equipment, and safety barriers
Transport	Fencing, footbridges, rail gantries, motorway signal gantries, railway station platforms, trailers, and vehicle chassis
Automotive	Components, subframe, body-panels, fuel tanks, baffles, brackets, filler caps
Food	Packaging (cans)
Domestic	Mufflers, furnaces, ovens, ranges, heaters, water heaters, fireplaces, baking pans, air conditioner housings and drying ovens, lighting fixtures

Source: UK Galvanizers Association, 2007.

4.06.13 Recent and Future Developments

Since the previous edition was written, several new directions for development have emerged, and are likely to continue into the future:

Table 6 Selected international and European reference standards relevant for specification and use of hot dip coated sheet/articles

EN/ISO	*Title*
ISO 752	Zinc ingots
ISO 9223	Corrosion of metals and alloys – Corrosivity of atmospheres – Classification
EN 1179	Zinc and zinc alloys – Primary zinc
EN 10240	Internal and/or external protective coatings for steel tubes. Specification for hot dip galvanized coatings applied in automatic plants
EN 13283	Zinc and zinc alloys – Secondary zinc
EN 13438	Paints and varnishes. Powder organic coatings for galvanized or sherardized steel products for construction purposes
EN ISO 1460	Metallic coatings. Hot dip galvanized coatings on ferrous materials. Gravimetric determination of the mass per unit area
EN ISO 1461	Hot dip galvanized coatings on fabricated iron and steel articles – Specifications and test methods
EN ISO 1462	Metallic coatings – Coatings other than those anodic to the base metal – Accelerated corrosion tests – Method for the evaluation of results
EN ISO 10684	Fasteners – Hot dip galvanized coatings
EN ISO 12944 Parts 1-8	Paints and varnishes. Corrosion protection of steel structures by protective paint systems.
EN ISO 14713	Protection against corrosion of iron and steel in structures – Zinc and aluminium coatings – Guidelines

Source: UK Galvanizers Association, 2007.

Table 7 Selected ASTM standards relevant to hot dip coating of steel sheet/articles

ASTM	*Title*
A90/A90M	Standard Test Method for Weight (Mass) of Coating on Iron and Steel Articles with Zinc or Zinc-Alloy Coatings
A123/A123M	Standard Specification for Zinc (Hot-Dip Galvanized) Coatings on Iron and Steel Products
A143/A143M	Standard Practice for Safeguarding Against Embrittlement of Hot-Dip Galvanized Structural Steel Products and Procedure for Detecting Embrittlement
A153/A153M	Standard Specification for Zinc Coating (Hot-Dip) on Iron and Steel Hardware
A308/A308M	Standard Specification for Steel Sheet, Terne (Lead–Tin Alloy) Coated by the Hot-Dip Process
A384/A384M	Standard Practice for Safeguarding Against Warpage and Distortion During Hot-Dip Galvanizing of Steel Assemblies
A463/A463M	Standard Specification for Steel Sheet, Aluminum-Coated, by the Hot-Dip Process
A653/A653M	Standard Specification for Steel Sheet, Zinc-Coated (Galvanized) or Zinc–Iron Alloy-Coated (Galvannealed) by the Hot-Dip Process
A792/A792M	Standard Specification for Steel Sheet, 55% Aluminum–Zinc Alloy-Coated by the Hot-Dip Process
A875/A875M	Standard Specification for Steel Sheet, Zinc–5% Aluminum Alloy-Coated by the Hot-Dip Process
A924/A924 M	Standard Specification for General Requirements for Steel Sheet, Metallic-Coated by the Hot-Dip Process
A1046/A1046M	Standard Specification for Steel Sheet, Zinc–Aluminum–Magnesium Alloy-Coated by the Hot-Dip Process

Source: UK Galvanizers Association, 2007.

- Zinc alloy coatings to control reactivity in galvanizing and fabricated articles.[46]
- Development of zinc–aluminum–magnesium and composite coatings for continuous sheet galvanizing.[47]
- Development of lead-free coatings[46] and duplex coatings.[48]

Very recently, an explanation of the beneficial effects of magnesium alloying in zinc hot dip coatings has emerged. As magnesium is added to zinc coatings, up to around 8 wt% magnesium, a magnesium-based oxide layer gradually replaces the zinc-based oxide layer. It is known that magnesium oxide has a higher band gap than do zinc oxide (5.2 eV compared with 3.5 eV, respectively), and therefore a lower ability to transfer electrons. This results in a reduced efficiency of oxygen reduction. As magnesium in the coating is further increased, the corrosion resistance does not improve and indeed decreases as hydrogen depolarization becomes easier in the higher magnesium content phases that then exist in the coating, for example, ZnMg. At this point, the optimal composition appears to be one that allows for bulk zinc metal to be present in the coating giving an anode, together with magnesium oxide in the surface layer, with its low ability to reduce oxygen.[49] Further improvements are being seen with zinc–aluminum–magnesium hot dip coatings whose mechanisms for improvement appear to be similar to that of zinc–magnesium coatings, but are not yet fully understood.[50]

References

1. Zhang, G. Z. *Corrosion and Electrochemistry of Zinc*; Plenum, New York, 1986; Chapter 7, pp 213–217.
2. Revie, W. R. *Uhlig's Corrosion Handbook*, 2nd ed.; Wiley, 2000; Chapter 40, pp 677–714; Chapter 46, pp 853–862; Chapter 48, pp 887, 903.
3. Lamberigts, M.; Goodwin, F. E. In *Process—tructure Relationships in Commercial Galfan-Coated Sheet Steels, The Physical Metallurgy of Zinc Coated Steel*; Marder, A. R., Ed.; The Minerals, Metals and Materials Society (TMS), 1993; pp 79–87.
4. Mackowiak, J.; Short, N. R. *Int. Metals Rev.* **1979**, *24*(1), 1–19 (reprinted by UK Galvanizers Association).
5. Marder, A. R. *Prog. Mater. Sci* **2000**, *45*(3), 191.
6. Knotkova, D. *International Corrosion Conference*, Houston, TX, USA, 1993; 16.
7. Porter, F. C. *Corrosion Resistance of Zinc and Zinc Alloys*; Marcel Dekker: New York, 1994; Chapter 4, 341.
8. Garcia, C. Assembly 2007 The George Hotel, Edinburgh, UK, June 2007, Proceedings of the European General Galvanizers Association, 2008.
9. EN ISO 14713. Protection against Corrosion of Iron and Steel in Structures – Zinc and Aluminium Coatings – Guidelines British Standards Institution: Chiswick, UK, 1999.
10. *The Engineers and Architects' Guide: Hot Dip Galvanizing*; UK Galvanizers Association Publication, 2007.
11. The British Constructional Steelwork Association Limited. Publication 40/05, Galvanizing Structural Steelwork – An Approach to the Management of Liquid Metal Assisted Cracking, 2005.
12. Viljoen, C. L.; Kirkbride, A. N.; van Wyk, D. In A Comparative Study of the use of HCl and H_2SO_4 in Acid Pickling in the South African Hot Dip Galvanizing Industry, Proceedings of the 16th International Galvanizing Conference, Barcelona, Spain, European General Galvanizers Association, 1991.

13. Allen, C.; Kolisnyk, P. S.; Anderson, N. In Fumeless Flux Developments, Proceedings of the 2nd Asian Pacific General Galvanizing Conference, Kobe, Japan, 1994.
14. Vazquez, A. J.; Garcia, J. In Galvanizing Fluxes without Fumes, Proceedings of the 20th International Galvanizing Conference (Intergalva 2003) Amsterdam 2003, European General Galvanizers Association, UK, 2003.
15. Porter, F. C. *Zinc Handbook: Properties, Processing, and Use in Design*; Marcel Dekker: New York, 1991; Chapter 10, pp 224–225.
16. Porter, F. C. *Zinc Handbook: Properties, Processing, and Use in Design*; Marcel Dekker: New York, 1991; Chapter 10, pp 211–213.
17. *General Galvanizing Practice*; Galvanizers Association: UK, 1999; 1.9.
18. Richards, R. W. In Relationship between Steel Surface Chemistry and the Galvanizing Behaviour of Reactive Steels, Proceedings of the 16th International Galvanizing Conference (Intergalva 1991) Barcelona, Spain, 1991, European General Galvanizers Association, UK, 1991; pp GF4/1–GF4/20.
19. Horstmann, D. Proceedings of the 14th International Galvanizing Conference (Intergalva 1985), Munich, Germany FR, Zinc Development Association, 1985; pp 6/1–6/5.
20. Kirkbride, A. N.; Wells, A. In Studies Relating to the Galvanizing Behaviour of Sandelin Alloys, Proceedings of the Fifteenth International Galvanizing Conference, Rome, Italy, 1988, pp GC1/1–GC1/16.
21. International Lead Zinc Research Organization Inc. Galvanizing Reactive Steels – A Guide for Galvanizers and Specifiers Englewood, 1996.
22. *General Galvanizing Practice*; Galvanizers Association, UK, 1999; 1.11.
23. Porter, F. C. *Zinc Handbook: Properties, Processing, and Use in Design*; Marcel Dekker: New York, 1991; Chapter 10, 222.
24. Horstmann, D. *Faults in Hot Dip Galvanizing*, 2nd ed.; Verlag Stahleisen mbH, Dusseldorf, 1983; pp 64, 65.
25. Reumont, G.; Perrot, P. In Fundamental Study of Lead Additions in Industrial Zinc Baths, Proceedings of the 18th International Galvanizing Conference (Intergalva 1997) Birmingham, UK 1997, European General Galvanizers Association, UK, 1997.
26. Krepski, R. P. In The Influence of Lead in After-fabrication Hot Dip Galvanizing, Proceedings of the 14th International Galvanizing Conference (Intergalva 1985), Munich, Germany FR, Zinc Development Association, 1985; pp 6/6–6/12.
27. Taylor, M.; Murphy, S. In A decade of Technigalva, Proceedings of the 18th International Galvanizing Conference (Intergalva 1997) Birmingham, UK 1997, European General Galvanizers Association, UK, 1997.
28. Lewis, G. P.; Pederson, N. In Optimizing the Nickel–Zinc Process for Hot Dip Galvanizing, Proceedings of the 3rd Asian Pacific General Galvanizing Conference, Queensland, Australia, 1996.
29. Pederson, J. In The Effects of Bismuth on Nickel–Zinc Galvanizing, Proceedings of the 4th Asian Pacific General Galvanizing ConferenceKuala Lumpur, 1999.
30. Krepski, R. P. *The Influence of Bath Alloying Additions in Hot Dip Galvanizing*; St. Joe Minerals Corporation, Monaca, PA, 1980.
31. Davies, J. R. *Surface Engineering for Corrosion and Wear Resistance;* ASM International, 2001; Chapter 6, pp 139–142.
32. Pankert, R. In Five years' experience with the Galveco Alloy, Proceedings of the 10th Hot Dip Galvanizing Conference, 4–6 October 2004, Hotel Plejsy, Krompachy, Slovak Republic; Czech Galvanizers Association & Slovak Galvanizers Association, 2004; pp 18–26.
33. Gilles, M.; Sokolowski, R. In The Zinc–Tin Galvanizing Alloy: A Unique Zinc Alloy for Galvanizing any Reactive Steel, Proceedings of the 18th International Galvanizing Conference (Intergalva 1997) Birmingham, UK 1997, European General Galvanizers Association, UK, 1997.
34. Avettand-Frénöel, M. N.; Reumont, G.; Perrot, P. In The Effect of Tin on the Reactivity of Silicon-Containing Steels, Proceedings of the 21st International Galvanizing Conference (Intergalva 2006) Naples 2006, European General Galvanizers Association, UK, 2006.
35. Zervoudis, J.; Anderson, G. A Review of Bath Alloy Additives and their Impact on the Quality of the Galvanized Coating, 6th Asian Pacific General Galvanizing Conference Cairns: Australia, May 29–June 2, 2005.
36. Zervoudis, J. In Reactive Steel Galvanizing with Zn–Sn–V (Ni) alloys, Proceedings of the 19th International Galvanizing Conference (Intergalva 2000) Berlin 2000, European General Galvanizers Association, UK, 2000.
37. Alonso, C.; Fullea, J.; Recio, F. J.; Sanchez, M.; Soldado, R.; Bernal, M.; Tierra, P. In The Adhesion of Hot Dip Galvanized Coatings and Zn–Ni–V (Ecozinc) Alloy to Steel Reinforcement, Proceedings of the 21st International Galvanizing Conference (Intergalva 2006) Naples 2006, European General Galvanizers Association, UK, 2006.
38. Reumont, G.; Foct, J.; Perrot, P. In New Possibilities for the Galvanizing Process: The Addition of Manganese and Titanium to the Zinc Bath, Proceedings of the 19th International Galvanizing Conference (Intergalva 2000) Berlin 2000, European General Galvanizers Association, UK, 2000.
39. Memmi, M.; Cecchini, M.; Colibri, C.; Goodwin, F. In New Batch Zinc–5% Aluminium Hot Dip Galvanizing Process for Fabricated Steel Parts (Part II: Process Simplification), Proceedings of the 21st International Galvanizing Conference (Intergalva 2006) Naples 2006, European General Galvanizers Association, UK, 2006.
40. van Ooij, W.; Ranjan, M.; Joshi, A.; Verstappen, J.; Zervoudis, J.; Poag, G. In Update on the Status of the Development of a High-Al Alloy for General Galvanizing, Proceedings of the 21st International Galvanizing Conference (Intergalva 2006) Naples 2006, European General Galvanizers Association, UK, 2006.
41. *General Galvanizing Practice*; Part 4; Galvanizers Association: UK, 1999; pp 4.1–4.4.
42. Fujine, M. In Expectation for Steel Sheet in View for Future Automobile Application, Proc. Galvatech 2007, Osaka, 18–22, ISIJ, Tokyo, Nov 2007; pp 374–379.
43. van Eijnsbergen, J. F. H. *Duplex Systems – Hot-dip Galvanizing plus Painting*; Elsevier: New York, 1994; Chapter 2, pp 7–9.
44. EN ISO 12944: Paints and Varnishes – Corrosion Protection of Steel Structures by Protective Paint Systems, British Standards Institution, Chiswick, UK.
45. EN 13438. Paints and Varnishes – Powder Organic Coatings for Galvanized or Sherardised Steel Products for Construction Purposes British Standards Institution: Chiswick, UK, 2005.
46. Proceedings of the 21st International Galvanizing Conference (Intergalva 2006) Naples 2006; European General Galvanizers Association, UK, 2006.
47. Schuhmacher, B.; Klare, B.; Steinhorst, M.; Schulzki, R. In Novel Surface Coated Products for ThyssenKrupp Steel – Innovation Road Map of DOC Dortmunder Oberflachencentrum GmbH, Proc. Galvanizing Steel Sheet Forum, 30–31 May 2006, Dusseldorf, Germany, International Lead Zinc Research Org., Inc, 2006.

48. Bjordal, M.; Knudsen, O. O.; Haarberg, S.; Osen, K. S. In Pinholes in Powder Coatings on Hot Dip Galvanized Steel – Sources and Prevention, Assembly 2005, Radisson SAS Alacron Hotel, Prague, Czech Republic, June 2005, Proceedings of the European General Galvanizers Association, 2005.
49. Prosek, T.; Nazarov, A.; Bexell, U.; Thierry, D.; Serak, J. In Corrosion Properties of Model Zinc-Magnesium Alloys, Proc. Galvatech, Osaka, 18–22 Nov 07, ISIJ, Tokyo, 2007; pp 592–597.
50. Vlot, M.; Bleeker, R.; Maalman, T.; van Perlstein, E. In MagiZinc – a new generation of hot-dip galvanised products, Proc. Galvanizing Steel Sheet Forum, 30–31 May 2006, Dusseldorf, Germany, International Lead Zinc Research Org., Inc, 2006.

Further Reading

Zhang, G. Z. Corrosion and Electrochemistry of Zinc Plenum: New York, 1986.

Porter, F. C. Corrosion Resistance of Zinc and Zinc Alloys Marcel Dekker: New York, 1994.

Porter, F. C. Zinc Handbook: Properties, Processing, and Use in Design Marcel Dekker: New York, 1991.

van Eijnsbergen, J. F. H. Duplex Systems – Hot-dip Galvanizing plus Painting Elsevier: New York, 1994.

European General Galvanizers Association, UK. General Assembly and Intergalva Proceedings 1994–2007.

General Galvanizing Practice; Galvanizers Association: UK, 1999.

High Temperature Galvanizing; International Lead Zinc Research Organization, 1980.

Relevant Websites

www.galvalume.com.
www.galfan.com.
www.galvanizing.co.uk.
www.galvanizeit.org.

4.07 Plated Coatings

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Abbreviations

ABS Acrylonitrile–butadiene–styrene
AC Alternating current
DC Direct current
IMF Institute of Metal Finishing (Birmingham, UK)
PNS Post-nickel strike
TFS Tin-free steel

4.07.1 Approach

There are books and reviews dealing with electroplating which approach it as a commercial technology, a useful art, or an interesting process for scientific enquiry. In this case, the emphasis is on the production of coatings for the control of corrosion and the consequences of action taken at various stages of electroplating for the control of corrosion events. Corrosion control is not the sole function of electroplated coatings; indeed most authors play down corrosion control in favor of ‘more positive’ virtues such as decoration (sales appeal), reflectivity, wear resistance, solderability, or low contact resistance. However, to preserve these properties, it is essential to prevent corrosion; in essence, electroplated metal coatings are required to confer corrosion resistance together with one or more of the other properties, the nature of which provides the criteria on which selection of a coating is made. Corrosion protection is a common factor.[1–7]

4.07.2 Origin

The production of electricity by metallic corrosion in Volta’s pile (1786) was followed by the reduction of metal ions to metal by electrons at a metal–solution interface.[8] Electroplating is an application of electrodeposition to produce thin, coherent, adherent coatings of solid metal, and is one of the important methods for producing coatings. Brugnatelli,[9] a Professor of Chemistry at the University of Pavia, published an account of silver plating in 1800, and is said to have gold plated silver coins using Volta’s pile as early as 1805. Wollaston deposited copper (presumably a very small quantity) on silver wire using current from an electrostatic generator. Electrodeposition was developed energetically in the succeeding three decades, and by 1840, commercial electroplating had advanced to the stage where patent protection was being sought for various processes. The breakthrough was made in 1839–1840 through the discovery of cyanide as a versatile complexant for first silver and gold and later other metals. The main source of electricity for the first six or seven decades was the primary galvanic cell, and progress was aided by the invention of cells such as those of Daniell, Meidinger, Grove, and Bunsen, which were capable of delivering large currents for long periods without polarisation. Faraday discovered electromagnetic induction in 1831, and Pixii used the commutator in 1832 to produce a direct current generator, but it was not until about 1870 that several independent inventors used electromagnetic field coils to generate the heavy currents needed for electrolysis. Large scale electroplating enterprises were established by the latter part of the nineteenth century. In 1883, the Postal Telegraph Company of New York used 200 copper plating cells to deposit 250 kg day^{-1} onto steel wire. Aqueous solutions have always been by far the most important electrolytes. There have been many investigations of nonaqueous solutions or ionic melts, and Davy deposited the alkali metals from the latter in 1807. Aqueous solutions and their associated pre- and postplating treatments are so well established that they are likely to remain preeminent for the immediate future.[8–16]

4.07.3 Substrates

Metallic substrates which are good electron conductors and nonmetallic ones which are not can both be electroplated with adherent coatings, but the preliminary procedures or ‘pretreatment’ differ markedly. The commonly plated metal substrates are mild and low-alloy steels, zinc alloys for diecasting, and copper or high-copper alloys like brasses, bronzes, and beryllium coppers. A large number of other alloys can be electroplated, but their use is restricted to particular industries, and they often require special pretreatments. Aluminum alloys, stainless steels, titanium alloys, and refractory metals are examples. The three major substrates are plated with corrosion control as one of the important objectives, but with less common substrates this may not be the case. There has been a rapid growth in electroplated parts made from plastic material. The main objective is to make the part look metallic for reasons of appearance rather than function. A complicated acrylonitrile–butadiene–styrene copolymer dispersion (ABS) was the first plastic material to be plated on a large scale. It was followed by polypropylene, and the development of plating grades of other plastics (e.g., polysulphone, polycarbonate, epoxide resins, glass-reinforced polyester) is at hand. Metallic corrosion problems arise as soon as plastics have been plated, creating a new field for the corrosion enthusiast to investigate.

By exercising ingenuity, most nonconducting objects may be electroplated, and this is a long-established small-scale operation. The usual aim is artistic or a search for novelty, a good example being the preparation of a heavily gold-plated haggis for the 1973 conference of the Institute of Metal Finishing, which took place in Edinburgh.

4.07.4 Pretreatments

4.07.4.1 Metallic Substrates[17–21]

This is considered in detail in **Chapter 1.08, Stress Effects in High Temperature Oxidation**, but a brief review is relevant here in relation to electroplating.

Metallic articles arrive at the electroplating stage with a surface film of soil derived from earlier production processes. These are divided into three classes:

a. Organic films, oils, greases, and perhaps polymeric films.
b. Fine particles suspended in (a), often of siliceous material, that is, dirt.
c. Films of the substrate oxide or other corrosion products.

With few exceptions, it is more efficient and economical to use at least two different pretreatments, that is, degreasing processes which deal with (a) and (b), and pickling processes which remove oxide and corrosion films. Degreasing comes first, as pickling processes fail on hydrophobic surfaces.[17–21]

4.07.4.1.1 Degreasing

Hydrocarbon or mineral oils are removed by solvents; vapor degreasing with chlorinated solvents or emulsification, is a common alternative. Greases of animal or vegetable origin, which are fatty acids, alcohols, or esters, are removed with hot aqueous solutions of high-pH (alkaline degreasing). They react with alkali to form water-soluble soaps. Electrolytic alkaline degreasing is considerably faster than soak cleaning. The work, immersed in hot alkali, is usually the cathode. A mass of hydrogen bubbles formed at the solution–metal interface undermines and removes the grease very effectively; saponification takes place more slowly later. Ferrous metals may be degreased anodically, the metal surface becoming passive, but nonferrous metal anodes corrode in hot alkaline solutions. Anodic cleaning produces only half the volume of gas (oxygen) and is less effective on that count. However, there is an advantage. During use, small amounts of metal enter the cleaning solution; other metals enter as impurities in the salts and make-up water. A thin metal film may be electrodeposited during cathodic cleaning, which if it remains can decrease the corrosion resistance of the main deposit. Anodic cleaning avoids this danger, even when the cleaning bath is contaminated. For steel and occasionally for copper alloys, a cleaning cycle is employed, with the work being cathodic for degreasing; but the current is reversed for the final few seconds, during which any thin film of metal impurity is removed by anodic dissolution.

Alkaline cleaning solutions are compounded from sodium hydroxide, trisodium phosphate (TSP), sodium silicate, sodium carbonate, soaps and detergents, and other materials. The higher the pH, the more effective is the saponification, but with nonferrous metals, the greater is the danger of corrosion. Zinc diecastings and aluminum need much less aggressive alkalis than those which are safe with steel. For aluminum and its alloys, a high concentration (10%) of sodium silicate acts as a corrosion inhibitor and as a cleaner.

To check the efficacy of grease removal, the alkali solution is rinsed away or neutralized by dipping in dilute acid. If, after removal from the acid, the draining metal surface remains wetted evenly all over for 30–60 s (or until it dries by evaporation), hydrophobic soils have been removed. Traces of grease cause the surface to dewet, and surface tension draws the water into separate droplets. This is the water-break test. Traces of grease which remain when the work is plated do not prevent electrodeposition, but are detrimental to adhesion and corrosion resistance by increasing the incidence of coating porosity.

Particulate dirt is usually removed together with the grease which binds it, although there are a few exceptions. Sheet steel may carry a ‘smut’ of finely divided carbon (or perhaps iron carbide) left from pickling processes in steelmaking. This is not removed with grease, and if evenly distributed, it is not apparent until the work is rubbed locally. Left in place, it leads to porous and poorly adherent coatings. While it can be removed by mechanical means, for example, vigorous brushing, this is impracticable when automatic plating machines are used. Steel which shows this defect may be unsuitable for plating.

4.07.4.1.2 Removal of oxides and corrosion products

Oxide and corrosion-product films are removed by dissolution in aqueous solutions. Hydrochloric and sulfuric acid are the most common. Concentrations and temperatures are varied according to the substrate. For mild steel, for example, cold 15 wt% HCl is suitable, but for zinc diecastings the concentration must be reduced to 0.25 wt%, and the pickling time must be kept very short to avoid excessive attack. Rust is more quickly removed by acid pickling when, in the prior degreasing stage, the work is made the cathode rather than the anode. Cathodic cleaning partially reduces rust to magnetite and iron, which undergo rapid reductive dissolution in the acid. Mixed acids containing wetting agents are supplied as proprietary mixtures; hydrochloric, sulfuric, and phosphoric acids are common. Inhibitors – generally amino compounds – may be added, but strongly adsorbed films of inhibitors or their breakdown products may cause trouble later. Electrolytic pickling is used for special purposes, but hydrochloric acid is unsuitable for this purpose because of its volatility and the possibility of chlorine evolution. Cathodic pickling of steel in 10–20 wt% sulfuric acid enables thick rust or scale to be dissolved without losing metal, which is cathodically protected. Anodic pickling in 42 vol.% (about 55 wt%) sulfuric acid is used to remove a thin surface layer from steel. A high current density is used and dissolution, which is under diffusion control, is uniform. After 10–20 s, the metal becomes passive and dissolution ceases. Disordered and fragmented metal produced by abrasion or machining is removed to leave a surface which favors good adhesion of an electrodeposit. Oxide and corrosion products on copper and its alloys may be removed in hydrochloric or sulfuric acids, less concentrated than that used for steel. Sulfuric acid allows the dissolved copper to be recovered and the acid to be regenerated by electrolysis. However, when copper alloys are cathodically degreased, cuprous oxide is reduced to loose copper particles which do not dissolve in acid. An electroplated coating over loose metal is likely to be defective. A much more aggressive mixture of sulfuric and nitric acids known as a bright dip or sometimes (wrongly) aqua fortis is used. This is a rudimentary chemical-polishing system and produces a bright surface from which the loose particles have been removed.

4.07.5 Nonconductors

Plating plastic articles has become a widespread commercial process fairly recently. The main plastics in use at the time of writing are ABS and polypropylene. Both replace diecast and pressed metal in various fields. Molded parts have smooth surfaces unsuited to producing adherent plate, and the first step is to 'etch' the plastic surface by using strongly oxidizing acids, usually chromic plus sulfuric acid mixtures. The plastic must have dispersed in its surface small areas more susceptible to oxidation than the surrounding matrix, and these are introduced in a variety of ways during manufacture. Etching produces a pattern of small pits. The second step is to produce within the pits and over the surface a fine metallic precipitate. One method is to dip in solutions of stannous and palladium salts in succession, which produces fine palladium particles, but there is a variety of proprietary processes available. The metal particles become nuclei for the deposition of a metal coating from an electroless plating bath. This is an aqueous solution of a metal salt containing a reducing agent that is able to reduce the metal ions to metal. The solution is unstable, but is compounded and used so that homogeneous electron transfer does not occur, and there is neither homogeneous precipitation of metal, nor heterogeneous precipitation on nonconducting surfaces, but only on the metallic nuclei on the plastic surface. Several electroless plating processes have been devised, but only those for copper or nickel are widely used for plastics. Once a continuous coating of metal has been produced, the substrate can be transferred to an electroplating bath for the application of any desired coating. Most plastic articles are finished with nickel and chromium.[22–32]

4.07.5.1 Mechanical Pretreatments

Mechanical processes which cold-work a substrate have important effects on electrodeposits. Examples are grinding and abrasive polishing, grit and shot blasting, cold rolling, and severe cold deformation. They alter the metallurgical structure of the substrate, reducing the surface grain size and in some cases produce small crevices filled with nonmetallic debris. Abrasive processes which act parallel to the surface (e.g., grinding, polishing) may leave splinters and leaves of metal attached at one end but otherwise separated from the surface on which they lie. In addition, nonmetallic abrasive material is embedded in the surface. Surfaces which are neither annealed nor otherwise treated to remove mechanically disturbed surface layers, affect the structure and properties of metal electroplated over them, as mentioned below. In many cases, one result of the modification of the electrodeposit is to reduce the corrosion protection it affords. Where the same topographical alteration of a substrate can be achieved by nonmechanical means, for example, electrochemical polishing, electrochemical machining, chemical milling, the surface left is not cold-worked and does not disturb an electrodeposit to the same extent.[33–40]

4.07.6 Plating Processes

4.07.6.1 Electroplating

The metallic substrate, clean and rinsed, is immersed wet in the plating cell. The base metals which are usually plated present an essentially metallic surface to the electrolyte, and the slight corrosive action of the rinse water in preventing the formation of any substantial oxide film is important. A critical balance of corrosion processes in the initial stages is vital for successful electroplating, and for this reason, there is a severe restriction on the composition of the electroplating bath which may be used for a particular substrate. This will be discussed later. The substrate is made of the cathode of the cell; it may be immersed without applied potential ('dead' entry) or may be already part of a circuit which is completed as soon as the substrate touches the electrolyte ('live' entry). Live entry reduces the tendency for the plating electrolyte to corrode the substrate in the period before the surface is covered by the coating. The main cathodic process is usually the reduction of dissolved ions to metal in the form of an adherent, coherent coating.

The ions reduced may be aquo cations, for example,

$$[\mathrm{Ni(H_2O)}_x]^{2+} + 2\mathrm{e}^- = \mathrm{Ni} + x(\mathrm{H_2O})$$

or oxyanions, for example,

$$\mathrm{Sn(OH)_6^{2-}} + 4\mathrm{e}^- = \mathrm{Sn} + 6\mathrm{OH}^-$$

or complex ions, usually cyanides, for example,

$$\mathrm{Au(CN)_2^-} + \mathrm{e}^- = \mathrm{Au} + 2\mathrm{CN}^-$$

Cations are assisted by the electric field to migrate to the cathode. On the other hand, the field impedes the migration of anions, and diffusion has to overcome this. It is rare for metal reduction to be the sole cathode process, as water and other dissolved substances are reduced simultaneously. Many compounds are added intentionally to take part in the cathode process, with the object of modifying the nature of the coating. Such materials are called addition agents and are subdivided into classes on the basis of their main effect (e.g., brighteners, levelers, grain refiners, stress reducing agents). In all aqueous solutions, water may be reduced: either

$$2\mathrm{H_2O} + 2\mathrm{e}^- = \mathrm{H_2} + 2\mathrm{OH}^-$$

or

$$2\mathrm{H}^+ + 2\mathrm{e}^- = \mathrm{H_2}$$

This reaction becomes thermodynamically possible whenever the cathode potential falls below

$$E = \frac{RT}{2F}\ln\frac{(a^2\mathrm{H}^+)}{p\mathrm{H_2}} \qquad [1]$$

where R is the gas constant, T the temperature (K), F the Faraday constant, and $p\mathrm{H_2}$ is the relative partial pressure (strictly, the fugacity) of hydrogen in solution, which for continued evolution, becomes the total external pressure against which hydrogen bubbles must prevail to escape (usually 1 atm). The activity of water $a\mathrm{H_2O}$ is not usually taken into account in elementary treatments, as it is assumed that $a\mathrm{H_2O} = 1$, and for dilute solutions this causes little error. Note that in some concentrated plating baths $a\mathrm{H_2O} \neq 1.0$ and neither is it in baths which use mixtures of water and miscible organic liquids (e.g., dimethyl formamide). However, by far the most important term is the hydrogen ion activity; this may be separated so that eqn [1] becomes

$$E = -\frac{RT}{2F}\ln p\mathrm{H_2} - \frac{2.303RT}{F}p\mathrm{H} \qquad [2]$$

As $p\mathrm{H_2} \approx 1(\approx a\mathrm{H_2O})$

$$E \approx -0.059p\mathrm{H} \qquad [3]$$

These considerations have been entirely on the basis of thermodynamics and take no account of the overpotential, which is dependent on the rate of the process and the nature of the surface at which the reaction occurs. For this reason, the rate of reduction of H^+ or $\mathrm{H_2O}$ is usually low, and remains so to potentials from 0.5 to 1.0 V, below that given in eqn [1]. Even so, the instability of water is an insuperable obstacle to electrodepositing metals whose ions are so stable in aqueous solutions (e.g., Al^{3+} aq.) that water reduction becomes the sole cathode process.

Much time has been devoted in recent years to study the mechanism of electrodeposition. Most investigators have assumed that electrodeposition should follow a mechanism akin to that for the deposition of a crystalline coating by condensation of a vapor. The solvated metal ion approaches and adsorbs on the cathode, losing some of its solvation sheath as the cathode gains the requisite electrons. The adion, which is mobile, diffuses over the cathode surface until it reaches an atomic step. It adsorbs on the step, losing more water of solvation, and having its freedom reduced to diffusion along the step. Further desolvation and coordination follows when it reaches a kink in the step, at which stage it is immobilized. When other adions following this path eventually join and submerge the first, coordination with water in the electrolyte is exchanged fully for coordination with metal ions in the metallic lattice. This view of the mechanism of electrodeposition is plausible and compatible with both current views on metallic crystals and their defects, and certain properties of electrodeposits. It is, however, a preconceived notion, and considerable experimental difficulties in the way of producing evidence are responsible for both the numerous different investigations in the field, and the fact that the evidence produced is impressive more for its volume than its conclusive force.

Current enters through the metal–electrolyte interface of the anode, which is usually made from the same metal as is plated on the cathode. The anode dissolves replacing the metal lost at the cathode:

$$\mathrm{M} = \mathrm{M}^{n+} + n\mathrm{e}^-$$

The overall process is metal transfer from anode to cathode via the solution. The form of anode corrosion is important, and materials may be added both to the anode metal and to the electrolyte, to influence it. There are important instances where an insoluble anode is used, and the anode reaction becomes the oxidation of water or hydroxyl ions: either

$$2\mathrm{H_2O} = \mathrm{O_2} + 4\mathrm{H}^+ + 4\mathrm{e}^-$$

or

$$4\mathrm{OH}^- = \mathrm{O_2} + 2\mathrm{H_2O} + 4\mathrm{e}^-$$

and also the oxidation of any other susceptible materials. Oxidation of water may occur at an anode, which was intended to be soluble, if the metal becomes passive. The minimum potential, above which the anode must rise before oxidation of water occurs, is:

$$\mathrm{E} = E^0 + \frac{RT}{4F}\ln(p\mathrm{O_2} \times a^4_{\mathrm{H}^+}) \qquad [4]$$

In this equation, E^0 is the standard electrode potential of the water/oxygen reaction, that is, $-\Delta G^0_{\mathrm{H_2O}}/nF$. Simplifying, eqn [4] at 298 K becomes

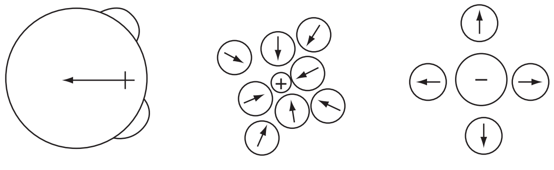
$$E = 1.23 - 0.059\,p\mathrm{H} \qquad [5]$$

There is often an overpotential of about 0.5 V before the rate of oxidation of water becomes rapid.[41–43]

4.07.6.2 Aqueous Electrolytes

Aqueous solutions have a complex structure. Liquid water is anomalous; properties estimated by interpolation from those of neighboring hydrides in the periodic table fall wide of the observed properties. For example, estimated melting and boiling points are −43 and −11 °C, respectively. Molecular interaction (hydrogen bonding) imposes short range order in the liquid, which the anomalous properties reflect. Some of the crystal structure of ice is retained in the liquid, though the structure is less open, and water shares this peculiarity with diamond, silicon, and germanium, as in each case the liquid is denser than the solid at the melting point. A simple view of water is as a fluid with two species, small local regions with an ice structure and others with a strongly associated but irregular structure $(\mathrm{H_2O})_n$. The 'icebergs' and random groups are in dynamic equilibrium, exchanging individual molecules throughout the lifetime of the larger groups, which are not themselves permanent.

Water has a permanent dipole moment (strictly it is a quadrupole moment) caused by the asymmetry of the molecule and the greater electron affinity of oxygen. When soluble strong electrolytes, for example, nickel sulphate, dissolve, they dissociate completely, and the interactions between the charged ions and the dipole water molecules considerably modify the water structure. The small nickel ions with their high charge density will cause more disruption than the larger sulphate ion, but both become strongly associated with a sheath of water molecules (Figure 1). The bonding between the ion and solvation sheath confers a high degree of stability on the



(a) (b) (c)

Figure 1 (a) Water molecule, dipole structure, (b) solvation of a small cation, for example, Ni^{2+} and (c) solvation of a larger anion, for example, $\mathrm{SO_4^{2-}}$.

ions in aqueous solutions. The dipolar nature of the solvent, able to stabilize ions of either charge sign equally well, makes water an excellent ionic solvent. Ionic solvation destroys the ice-like component of the liquid with a result similar to that observed on melting, that is, a decrease in volume as the 'space-wasting' ice structure is removed, and many strong electrolytes have a negative volume of mixing.

Aqueous solutions of nonelectrolytes, especially of nonpolar solutes, may show the reverse effect and increase the proportions of ice-like components. The nonpolar part of organic electrolytes such as soaps and wetting agents may predominate in increasing the ice component. Thus solutes can be divided into two classes: structure making and structure breaking, and in some metal-finishing process solutions of both types of solute may be added. In certain cases, it is impossible to satisfy both, and there is a decrease in solubility of the least successful component. For example, a soap such as sodium palmitate, which in water is mainly

$$CH_3(CH_2)_{14}COO^-Na^+$$

is very soluble, and the proportion of ice-like water increases to minimize interaction with the hydrophobic hydrocarbon chain. If sodium chloride is added to a concentrated soap solution, the ice-like structure is broken, and the increased concentration of 'free water' causes the palmitate to separate. Polar nonelectrolytes such as the lower alcohols have an even greater effect on the water structure than soaps. Being themselves capable of forming hydrogen bonds, they enter the 'iceberg' structure, increasing its stability. Methyl or ethyl alcohol added to solutions saturated with structure-breaking electrolytes, for example, $NiSO_4$, in a plating bath, can withdraw water from the ionic solvation sheaths to form ice-like water, and now it is the electrolyte whose solubility falls. Soap, on the other hand, is more soluble in alcohol–water mixtures.

The ability of water to be oxidized or reduced at the plating-bath electrodes is in practice an important advantage, though it has a few drawbacks. The drawbacks are overemphasized in textbooks and the advantages ignored. An ion which is much more stable towards reduction than water is unaffected in the region of the cathode during electrolysis. With the margin of polarization of 0.5–1.0 V, the manganous aquocation is the most stable that can be reduced in aqueous solutions, but because of the shortcomings of the metallic coating, manganese is not used, and the zinc aquocation is the most stable ion that can be reduced in large scale electroplating. A drawback is that the aquocations of aluminum, titanium, zirconium, niobium, and tantalum are too stable. Their known corrosion resistance would make them important coatings, but they cannot be electrodeposited. On the other hand, there are numerous electrolytes whose presence is desirable in a plating bath but whose cations must not be reduced during electrolysis. The complete stability of cations like Na^+, K^+, NH_4^+, Li^+, Mg^{2+}, Ca^{2+}, and Al^{3+} is then an advantage. Should the cathode be depressed (accidentally) below the normal working value, they are safe from reduction as hydrogen evolution acts as a 'safety valve' for excessive currents. The products of water reduction, hydrogen gas and OH^- ions, are less likely to contaminate a large volume of valuable solution than are the reduction products of other materials.

Similar considerations apply to oxidation. An anion, which is considerably more stable than water, will be unaffected in the neighborhood of the anode. With a soluble anode, in principle, an anion only needs be more stable than the dissolution potential of the anode metal, but with an insoluble anode, it must be stable at the potential for water oxidation (eqn [4] or [5]), plus any margin for polarization. The metal salts, other than those of the metal being deposited, used for electroplating are chosen to combine solubility, cheapness, and stability to anode oxidation and cathode reduction. The anions most widely used are SO_2^{2-}, Cl^-, F^- and complex fluorides BF_4^-, SiF_6^{2-}, Br^-, CN^- and complex cyanides. The nitrite ion is usually avoided because it is too easily reduced at the cathode. Sulfite, which is used for gold plating, is nevertheless too readily oxidized at the anode, and provides an example of an ion used in one instance despite its drawbacks. The oxidation of water at the anode is also a reaction which does not contaminate the solution.

Much laboratory work has been performed to develop nonaqueous plating baths, using either organic solvents or ionic melts. Insofar as the reduction of water is concerned, there are two rather different aims in view. Firstly, there is a search for solvents or melts sufficiently stable to allow electrodeposition of coatings of aluminum, titanium, etc., which is impossible with water as the solvent. Secondly, there is a need for a nonaqueous solvent for metals such as cadmium, whose electrodeposition from water, while practicable and satisfactory, is always accompanied by hydrogen which can embrittle cathodes of certain high strength steels and other alloys. Here, the aim is to avoid hydrogen discharge.

A practical drawback to the use of nonaqueous solvents is the accumulation of the by-products of solvent–electrode reactions leading eventually to the bath being poisoned.[44]

4.07.6.3 Simple and Complex Ions

Amongst the common metals of the electroplating industry, only nickel is invariably reduced from its aquocation. Copper, silver, gold, cadmium, and zinc are normally deposited from solutions of complex cyanides; tin and chromium from oxyanions, and tin, in other cases, from a complex fluoride. Platinum-metal plating baths contain ions, all of which are complex; it is doubtful if any platinum-metal aquocation can exist in aqueous solution, as such is the high tendency of these metals to form complexes. If a ligand, such as cyanide, can displace water from an aquocation to form a complex ion, the complex must be more stable, and the deposition potential is always more negative for a complex ion than for the equivalent simple ion. Let the equilibrium between aquocation M^{n+}, ligand X^{x-} and complex ion $\{M(X)_p\}^{(px-n)-}$ be:

$$M(X)_p^{(px-n)-} \rightleftarrows M^{n+} = pX^{n-}$$

and

$$K = \frac{aM^{n+} \times a^pX_{x-}}{aM(X)_p^{(px-n)-}}$$

where K is the instability constant for the complex ion, p is the coordination number. The potential below which deposition becomes possible is

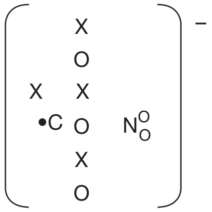
$$E = E^0 + \frac{RT}{nF} \ln \frac{K \times aM(X)_p^{(px-n)-}}{a^pX^{x-}}$$

or

$$E = E^0 + \frac{RT}{nF} \ln K + \frac{RT}{nF} \ln \left(\frac{aM(X)_p^{(px-n)-}}{a^pX^{x-}} \right) \qquad [6]$$

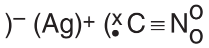
where E^0 is the standard electrode potential for the simple ion–metal equilibrium. The two bracketed terms on the right of eqn [6] constitute a sort of 'E^0' for the complex ion, and as K is usually very small, the second term is negative.

Complex ions used for electroplating are anions. The cathode tends to repel them, and their transport is entirely by diffusion. Conversely, the field near the cathode assists cation transport. Complex cyanides deserve some elaboration in view of their commercial importance. It is improbable that those used are covalent coordination compounds, and the covalent bond breaks too slowly to accommodate the speed of electrode reactions. The electronic structure of the cyanide ion is shown below.



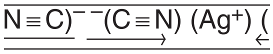
Here, electrons are contributed by the carbon atom (x), the nitrogen atom (o), and the cation (•), for example, Na^+ in the case of a sodium cyanide solution.

A soluble cyanide added to silver nitrate solution precipitates silver cyanide as an ionic compound:



$$)^- (Ag)^+ (\overset{x}{\bullet} C \equiv N_o^o$$

The precipitate redissolves in excess soluble cyanide, and the complex ion is probably an ion-dipole coordination compound, that is,



$$\overline{\underline{N \equiv C)^-}\ \underrightarrow{{}^-(C \equiv N)}\ (Ag^+)\ \underleftarrow{(}}$$

The solubility of $Ag(CN)_2^-$ in water stems from the overall negative charge encouraging solvation with water dipoles, which uncharged AgCN does not. It is likely that the other cyanide complex ions of low coordination number have a similar structure.

When ions with this structure diffuse to the vicinity of a negative cathode, the ion is distorted by the field to become polarized, with the positive silver core nearest the cathode (see **Figure 2**). Once within a critical distance the field can assist transport of the distorted complex, discharge the silver core and eventually repel the released cyanide anions. There are several practical advantages in plating from complex cyanides. The reduction in deposition potential is most important in the application of relatively noble metals to base substrates, when avoiding severe cathode corrosion. The important case of the copper cyanide bath is discussed later. The impeded diffusion of the complex anion, the energy needed to polarize and reduce the anion, and the diffusion 'barrier' produced by the high concentration of cyanide near the cathode, all contribute to a high overpotential for electrodeposition, which aids the production of even coatings on cathodes of uneven shape. The cyanide ions released after discharge of the metal from the

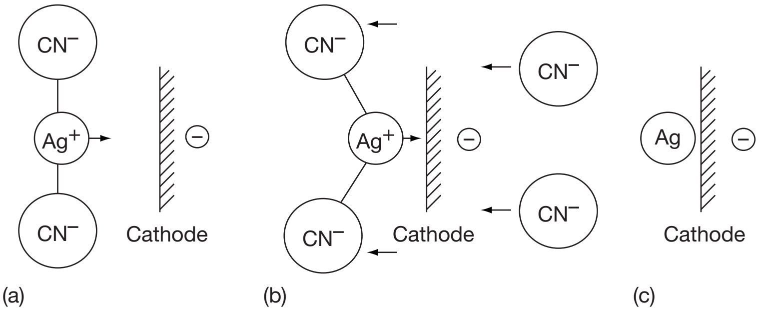


Figure 2 Ion distortion by the field in the vicinity of a negative cathode. (a) Diffusion of anion to cathode, (b) diffusion and migration of distorted complex and (c) release of CN-ions and incorporation of Ag into the lattice.

complex modify the structure of the coating in a manner similar to that of addition agents, and it is probable that some cyanide is adsorbed. The result is that cyanide bath coatings are fine grained, hard, and may contain small amounts of carbon.

Some disadvantages stem from the same phenomena: impeded diffusion reduces the maximum practical rate of plating to well below that possible with aquocation baths. The cyanide ion is not entirely stable; both oxidation and reduction products accumulate, including carbonate. Carbonate is also formed in the alkaline cyanide baths (all cyanide baths are alkaline except some based on aurocyanides) by absorption of CO_2 from the air, and it is necessary either to replace or purify baths periodically. Much has been made of the toxicity of cyanides, but the other process solutions used in plating are generally extremely toxic and corrosive or caustic, and it is necessary to treat them all with respect.

Oxyanions are important in chromium and tin plating. Although chromium plating baths have a simple formulation (chromium trioxide, sulfuric acid, and water), hydrolysis and side reactions form a variety of polychromate ions. The cathode reactions are numerous and imperfectly elucidated; only about 5% of the charge passed produces chromium. As in cyanide baths, the by-products behave as addition agents. The grain size of chromium electroplated under the normal conditions is the smallest encountered amongst metals. Tin coatings plated from stannate solutions are reduced from the $Sn(OH)_6^{2-}$ ions, and are fine-grained.

The platinum-group metals are necessarily plated from complex solutions, as all platinum-metal salts form complex ions in water. The development of aqueous baths has hinged upon finding complex ions sufficiently unstable to be reduced; all the platinum group cyanides are far too stable. Because all the platinum metals are good catalysts for hydrogen evolution (high exchange current density) there is no useful margin of hydrogen overpotential over that predicted by eqn [2]. Nevertheless, aqueous plating baths have been devised for the entire platinum group, although only palladium, rhodium, and platinum find commercial use at present.

The complex cyanides of transition metals, especially the iron group, are very stable in aqueous solution. Their high coordination numbers mean the metal core of the complex is effectively shielded, and the metal–cyanide bonds, which share electrons with unfilled inner orbitals of the metal, may have a much more covalent character. Single electron transfer to the ferricyanide ion as a whole is easy (reducing it to ferrocyanide, with no alteration of coordination), but further reduction does not occur.[45]

4.07.6.4 Conducting Salts, Addition Agents, and Other Ingredients of Plating Baths

Plating baths contain a number of salts and compounds in addition to those of the ion to be reduced to metal. Much commercial electroplating is from 'proprietary' solutions whose use is covered by patents, and which are supplied completely or partly compounded. The precise composition is generally a trade secret, and the patents may sometimes be very widely drawn to include a larger range of compositions and ingredients than is successful. A broad classification of additional ingredients includes the following:

(a) Those which maintain certain conditions but do not take part in electrode reactions; examples are electrolytes added to improve conductivity, pH buffer systems, and ions which maintain complex ion equilibria.
(b) Those which take part in the anode reaction, added to promote efficient dissolution of a soluble anode.

(c) Those which take part in the cathode reaction by adsorption, codeposition, or both, or by modifying the reaction; these ingredients alter the structure and properties of the coating and have an important bearing on its corrosion properties. The term addition agents is generally used for this class.

A particular ingredient often acts in more than one category.

Conducting salts are usually sodium, potassium, or ammonium salts, or the acid of a stable ion already present from other ingredients. Apart from energy conservation, the higher the conductivity of a bath the better the distribution of thickness on complex shapes.

Addition agents are subdivided according to the main effect they have on the coating, that is, grain refiners, brighteners (primary), brighteners (secondary), levelers, stress reducers, and antipitting agents. Apart from the last, all these addition agents modify the growth process profoundly. They may be the ions of foreign metals which can codeposit, or polar or ionic organic materials. They introduce irregular atoms or molecular fragments into the metal lattice or grain structure of the main metal of the coating, and alter the crystal structure. The macroscopic results are suggested by the terms: smaller grain size, mirror-like surface, or a relatively smooth (level) surface on an initially rough substrate. These characteristics are not achieved without corresponding disadvantages. Foreign material from the addition agent is incorporated, up to 5% by weight for metallic codeposition, less for organic agents. First- and second-order tensile stresses usually increase, hardness rises, and ductility falls. First-order tensile stress can exceed the tensile strength of the coating, but for some metals, particularly nickel, addition agents (stress reducers) are known which decrease first-order stress, though second-order stress is not reduced. The mechanical results are detrimental to corrosion protection, but the topographical results, fine grain, and level and bright coatings, are favorable. The chemical results, on the evidence available, vary. The most extensively investigated case is nickel. Here, it is almost universal practice to employ several addition agents together in a bright plating bath, one of which causes the incorporation of a small amount (about 0.02%) of sulfur, and reduces the corrosion resistance of bright nickel. There are other systems (benzotriazole brighteners in copper, aldehyde–amine brighteners in tin) which enhance corrosion resistance.[46–49]

4.07.6.5 Electroplating Anodes

The anode is usually soluble, and is made from a high purity form of the metal being deposited, or occasionally from an alloy. A soluble anode is often the cheapest and most convenient means of replacing the metal reduced at the cathode. Effective anode corrosion is important, and different examples present a variety of types of dissolution.

Copper anodes in the acid sulphate bath are an example of active anodic dissolution. They etch uniformly with low polarization at 100% efficiency, forming little anode debris or sludge. Idle anode corrosion is very slow with dissolved oxygen reduction as the cathodic reaction. Copper anodes in the cyanide bath corrode easily provided that there is sufficient excess or 'free' cyanide present. Polarization is higher than in the acid bath, with a much lower maximum current density. At high current densities, the rate of dissolution of copper exceeds the rate of supply of cyanide ions needed to form the cuprocyanide complex, and blue cupric aquocations form. Eventually, the anode becomes passive and evolves oxygen. For special purposes where anode area is limited (e.g., in a Hull cell), an insoluble mild-steel anode avoids these troubles. A proportion of insoluble anodes or alternate use of soluble and insoluble ones is necessary, because anode efficiency exceeds cathode efficiency, and the metal content of the solution would rise continually if soluble anodes alone were used.

Nickel is normally plated from mixed solutions of nickel sulphate and chloride using soluble anodes. The standing potential of pure nickel anodes indicates they are passive in the idle bath, while in operation dissolution is by pitting corrosion brought about by chloride (**Figure 3**). In all sulphate solutions, nickel anodes are passive and insoluble. Dissolution is aided by adding small amounts of sulfur or carbon to the nickel anode, which aid the breakdown of passivity ('depolarized anodes'). Nickel anodes produce a fine particulate 'anode sludge'; anode bags of finely woven cloth are used to retain much of this, and continuous filtration is needed to remove the rest, otherwise the corrosion resistance of the coating is severely degraded. Nickel can be used in the form of small 'chips' in baskets of titanium mesh. The titanium is passive and the surface is effectively insulated from electrolytic current exchange, but electrons released by the dissolving chips of nickel are able to pass via the metal–semiconductor contact with the basket to the outside circuit. Anode efficiency slightly exceeds cathode efficiency, but not sufficiently to increase the metal

Figure 3 Part of an anode from a nickel plating bath, showing dissolution by pitting corrosion.

concentration, unless rigorous precautions are taken to return all the solution lost on surfaces removed from the bath.

Tin anodes dissolve by etching corrosion in acid baths based on stannous salts, but in the alkaline stannate bath, they undergo transpassive dissolution via an oxide film. In the latter, the OH^- ion is responsible for both film dissolution and for complexing the tin. Anodes must not be left idle because the film dissolves and thereafter corrosion produces the detrimental divalent stannite oxyanion. Anodes are introduced 'live' at the start of deposition, and transpassive corrosion is established by observing the color of the film (pale yellow for correct operation) and the anode polarization, and by adjusting the immersed area. The anodes retain a smooth, quasipolished surface, and no anode bags are needed. An alternative, where anode filming is inconvenient, is to use insoluble (passive) mild-steel anodes, and replaces tin by adding a colloidal dispersion of stannic oxide.

Chromium plating from hexavalent baths is carried out with insoluble lead–lead peroxide anodes, as chromium anodes would be insoluble (passive). There are three main anode reactions: oxidation of water, reoxidation of Cr^{3+} ions (or more probably complex polychromate compounds) produced at the cathode, and gradual thickening of the PbO_2 film. The anode current density must balance the reduction and reoxidation of trivalent chromium so that the concentration reaches a steady state. From time to time, the PbO_2 film is removed as it increases electrical resistance.

Gold plating is another process where insoluble anodes are the rule. Soluble gold anodes would be technically satisfactory in some baths, but too tempting to thieves. A factor in their decline is the disappearance of gold coins, whose temporary sojourn in the anode circuit is alleged to have provided a form of corrosion beneficial to gold platters of earlier times. Insoluble stainless-steel anodes are now widely used, with graphite, platinized titanium, and platinum mesh as alternatives. All suffer gradual deterioration. Stainless-steel anodes are pitted, especially in areas of high current density, and the corrosion products may eventually give trouble. Platinized titanium sheds its platinum coating, becoming steadily more polarized. Platinum anodes used with cyanide solutions slowly corrode.

The potentials and corrosion data for some anodes in typical plating baths are listed in **Table 1**.[50,51]

With the exception of Pb/PbO_2 for chromium plating, the main or even sole anode reaction is oxygen evolution from water. Selection of insoluble anode materials traditionally only took account of mechanical stability and corrosion resistance, and not of the evolution overvoltage which usually lies in the range 1–3 V. This represents a significant (and unproductive) proportion of the total cell or tank voltage drop of 5–9 V. Consequently, searches for anodes with lower overvoltages have led to adoption of the so-called catalytic anodes, which in the context of chlorine and seawater cathodic production technologies have been termed dimensionally stable anodes (DSAs). These were originally based on titanium substrates coated with platinum; product development has led to niobium or tantalum substrates with palladium, iridium, ruthenium, and mixed oxide coatings depending upon the application. In particular, the use of mixed oxides on titanium has established a reputation as the most catalytic anode available. Such anodes are specialist products and offer good service lives when carefully chosen.

However, the criteria for that reputation have been very misleading. They have been based on chlorine electrochemistry initially and later the oxygen reaction itself without regard to side reactions which might occur. One class of side reaction has proved to be problematical, that is, the possible oxidation of organic additives in solution for the purposes of brightening, leveling, wetting, etc. This has always been recognized as a loss, because of the slow oxidation by air used for agitation in industrial operations, but the loss has increased substantially and unacceptably since the introduction of catalytic anodes. The remedy may therefore be threefold:

Table 1 Behavior of anodes in plating baths

Plating bath	*Anodes*	*Corrosion process*		*Current density*	*Potential (V)*
		Idle	*Working*	*(Am^{-2})*	*(vs.SHE)*
1. Watts' nickel					
$NiSO_4 \cdot 7H_2O$, 330 gl^{-1}	Nickel slab	Passive	Pitting	0	+0.08
$NiCl_2 \cdot 6H_2O$, 45 gl^{-1}				65	+0.23
H_3BO_3, 30 gl^{-1}				130	+0.27
pH 2.5				195	+0.30
55 °C					
2. Bright nickel					
as (1) plus saccharin	Nickel slab	Passive	Pitting	0	+0.03
and 2–3 butyne 1–4 diol				390	+0.36
pH 2.2					
50 °C					
3. Acid copper					
$CuSO_4 \cdot 5H_2O$, 150 gl^{-1}	Pure copper	Slow etching	Uniform etching	0	+0.28
H_2SO_4, 50 gl^{-1}				130	+0.32
pH < 0				260	+0.35
18 °C				390	+0.38
4. Rochelle copper					
CuCN, 27 gl^{-1}	Pure copper	Slow etching	Uniform etching	0	−0.38
NaCN, 38 gl^{-1}					
Na_2CO_3, 35 gl^{-1}					
$KNaC_4H_4O_6 \cdot 4H_2O$, 45 gl^{-1}					
pH 12.0	Mild steel	Passive	Passive, evolving O_2	0	+0.21
55 °C				130	+1.09
5. Silver					
AgCN, 50 gl^{-1}	Fine silver	Slow etching	Uniform etching	0	−0.24
KCN, 30 gl^{-1}				32	−0.01
K_2CO_3, 50 gl^{-1}			↓	↓	
pH 11.5			passive. evolving O_2	65	+6.0
25 °C					
6. Acid zinc					
$ZnSO_4 \cdot 7H_2O$, 250 gl^{-1}	Zinc	Etching, rather rapid, H_2 evolved	Uniform etching	0	−0.63
NH_4Cl, 15 gl^{-1}				163	+0.30
$Al_2(SO_4)_3 \cdot 18H_2O$, 30 gl^{-1}				325	+1.86
Dextrose, 75 gl^{-1}					
pH 4.0					
18 °C					
7. Chromium					
$CrO_3 \cdot 400$ gl^{-1}	Pb/PbO_2	Passive	Passive, evolving O_2, reoxidising Cr^{3+}, etc.	0	+1.5
H_2SO_4, 4 gl^{-1}				1075	+2.65
pH < 0					
37 °C					

a. be more careful in the selection of anode by distinguishing between reductions of the oxygen overvoltage;
b. introduce an organic reductant to be 'sacrificially' oxidised by the anode, for example, ascorbic acid;
c. introduce an inorganic redox metal ion, for example, iron, to divert the oxidizing tendency.

The first choice is clearly the best, because it avoids further additions, which may cause build-up of products and be more expensive. Furthermore, the other choices are patented. The incentive is obvious – the saving of 1–2 V or 10–15% of power supplied to the process. Other uses can also be identified; for example, the oxidation of Cr^{3+} to CrO_4^{2-} in a solution drag-out recovery operation for which diamond-like coatings may be the best. Similarly, the use of a selected anode can achieve oxidation of CN^- in a cyanide destruction stage of effluent treatment.[52–55]

4.07.6.6 Corrosion of the Cathode

At the start, the cathode is invariably a metal different from that to be deposited. Frequently, the aim is to coat a base metal with a more noble one, but it may not be possible to do this in one step. When a metal is immersed in a plating bath, it will corrode unless its potential is sufficiently low to suppress its ionization. Fortunately, a low rate of corrosion is tolerable for a brief initial period. There are cases, where even when a cathode is being plated at a high cathodic (net) current density, the substrate continues to corrode rapidly, because the potential (determined by the metal deposited) is too high. No satisfactory coating forms, if the substrate dissolves at a high rate concurrently with electrodeposition. This problem can be overcome by one or more of the following procedures:

(a) The use of a complex anion bath.
(b) The use of a 'strike' bath.
(c) The use of intermediate electrodeposits (undercoats or underplates).

The principles are illustrated by the following important commercial examples.[52–57]

4.07.6.6.1 Zinc diecastings: complex baths and undercoats

Diecastings are made from zinc with up to 8% aluminum, but from the viewpoint of corrosion they behave like zinc. Diecast parts are often plated with nickel and chromium for protection and decoration, but when zinc is immersed in a typical nickel plating solution, it corrodes rapidly. There are two cathodic reactions: hydrogen is evolved and spongy nickel precipitates. If a diecasting is immersed 'live,' corrosion and electrodeposition occur together as the potential for nickel deposition still leaves the cathode too positive to suppress zinc corrosion (**Figure 4**). Standard practice is first to plate the zinc with an undercoat of copper, which is too noble to evolve hydrogen or reduce nickel ions. In the bath to which the data of **Figure 4** are applied, the potential of copper was +0.042 V. Prolonged immersion led only to slow copper corrosion, with the reduction of dissolved oxygen as the cathodic reaction. This does not interfere with satisfactory nickel plating, and is entirely suppressed by live entry. The problem of applying a copper undercoat is solved by using the cuprocyanide complex bath. The acid cupric bath would present a worse problem than the nickel bath, with its lower pH and the greater oxidizing power of the cupric ion. The stabilities of zinc and copper are reversed in alkaline cyanide, and zinc will not displace copper from cuprocyanide. Zinc immersed in the cuprocyanide bath can corrode to form either zincate or a complex zinc cyanide ion $Zn(CN)_4^{2-}$, with two possible cathodic corrosion reactions, that is, dissolved oxygen reduction or hydrogen evolution. However, high polarization prevents either supporting rapid corrosion, and the situation is like that for copper in the nickel bath; a sound coating is possible and live entry suppresses corrosion. Once a coherent copper coating envelopes the zinc, the part is rinsed and transferred to the nickel bath.

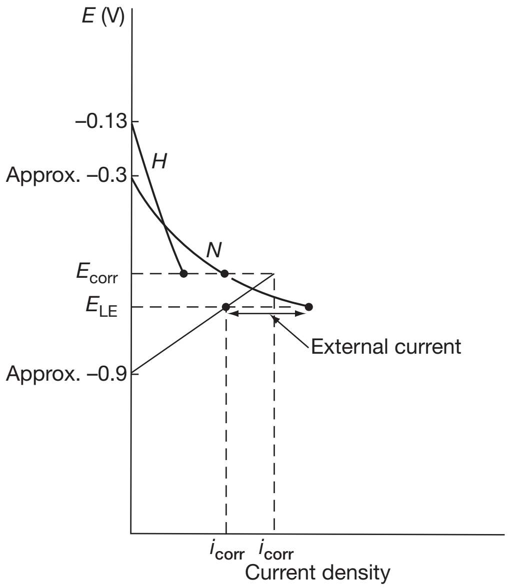


Figure 4 Corrosion diagram for a zinc diecasting in a nickel plating bath, pH 2.2. There are two possible cathodic reactions, hydrogen evolution (H) and nickel ion reduction (N). The corrosion current icorr is the sum of the partial cathode currents. Even with 'live entry' the potential ELE is still too high to suppress corrosion, though the rate is reduced to i¢corr.

The cuprocyanide plating bath is invaluable in numerous similar cases, where a base substrate cannot be plated directly with the chosen coating. Steels, brass, bronze, beryllium copper, and other substrates are copper underplated. Aluminum articles are ennobled, usually in two stages, that is, first coated with zinc, which is in turn copper plated as described. Such is the utility of the cuprocyanide bath in circumventing cathode corrosion that although copper finds no significant use as a coating in its own right, cuprocyanide baths are found in almost every electroplating establishment.

4.07.6.6.2 Silver plating: 'strike' baths

A 'strike' is usually a solution of special composition in which electroplating is initiated. After a short period of 10–150 s, the cathode is transferred to a normal bath. The term strike is also used when plating is initiated in the normal bath, but for 10–150 s under very different conditions (often much higher current density), continuing normally afterwards. Silver is electroplated from argentocyanide anions, that is, $Ag(CN)_2^-$. The bath is alkaline and contains 'free' CN^-. The argentocyanide ion is the least stable of the soluble complex cyanides, and therefore, $Ag(CN)_2^-$ is a strong oxidizing agent towards other metals which form soluble cyanide complexes. Generally, the reaction

$$nAg(CN)_2^- + (p-2n)CN^- + M = nAg + M(CN)_p^{(p-2n)-} \qquad [7]$$

proceeds as written where M is a more base metal of valency n. Copper, gold, zinc, iron, etc. are all base metals by comparison, so a copper undercoat does not solve the problem. An immersion deposit of silver leads to blistering and loss of adhesion, if electrodeposition is continued over it. The 'nobility gap' between copper and silver can be bridged by combining a shift in the equilibrium of eqn [7] with live entry. As a first step, the cathode may be given a copper undercoat. The deposition potential for silver (special case of eqn [7]) is

$$E = E^0 + \frac{RT}{F}\ln K_{\text{instab.}} + \frac{RT}{F}\ln\frac{aAg(CN)_2^-}{a^2CN^-} \qquad [8]$$

where

$$K_{\text{instab.}} = \frac{aAg + a^2CN^-}{aAg(CN)_2^-} = 1.8 \times 10^{-19}$$

At 298 K, eqn [8] is

$$E = -0.310 + 0.059\log\frac{aAg(CN)_2^-}{a^2CN^-} \qquad [9]$$

and may be depressed by reducing the ratio in the last term. Therefore, a silver strike bath has a small concentration of metal and a large concentration of free cyanide. Equation [7] shows that a high concentration of free cyanide further decreases the nobility of the substrate, so some of the advantage is lost. One way of redressing the balance would be to have the substrate complex $M(CN)_p^{(p-n)-}$ present in solution. Silver strike baths are formulated with cuprocyanide in solution, but curiously these are usually recommended for striking steel, while those recommended for copper alloys omit the cuprocyanide. The author uses the cuprocyanide silver strike for ferrous and copper alloys alike. The combination of low silver and high cyanide concentrations means the cathode potential at a relatively high current density is very low, and both charge transfer and diffusion polarization are high. With live entry, the low potential suppresses substrate ionization, and a detrimental immersion deposit of silver is avoided. A thin underplate – called a flash – is deposited from the strike, after which the normal bath is used. Dilute strike baths working at high current density cannot deposit thick coatings; continued electrolysis produces incoherent, powdery material. They have a low cathode efficiency and evolve considerable hydrogen.

4.07.6.6.3 Electroplating passive alloys

Another application of strike baths reverses the case illustrated in the previous example. The strike is used to promote a small amount of cathode corrosion. When the passivation potential of a substrate lies below the cathode potential of a plating bath, deposition occurs onto the passive oxide film and the coating is nonadherent. Stainless steel plated with nickel in normal baths retains its passive film and the coating is easily peeled off. A special strike bath is used with a low concentration of nickel and a high current density, so that diffusion polarization (transport overpotential) depresses the potential in the active region. The bath has a much lower pH than normal. The low pH raises the substrate passivation potential Epass, which theoretically follows a relation

$$E_{\text{pass.}} = E^0_{\text{pass.}} - 2.303\frac{RT}{F}\text{pH} \qquad [10]$$

When stainless steel is 'struck,' the passive film is reduced and an adherent flash of nickel forms on the active metal surface. Deposition is continued in a normal bath.

Electroplating aluminum and its alloys require a similar technique. In aqueous solutions, it is impossible to lower the potential sufficiently to reduce an alumina film, so the substrate is immersed in a strongly alkaline solution capable of dissolving it:

$$Al_2O_3 + 2OH^- = 2AlO_2^- + H_2O$$

The solution also contains a high concentration of zinc (as zincate), which is noble relative to aluminum. As metallic aluminum is exposed, it corrodes, reducing zincate ions and forming a coating of zinc:

$$Al + 4OH^- = AlO_2^- + 2H_2O + 3e^-$$
$$ZnO_2^{2-} + 2H_2O + 2e^- = Zn + 4OH^-$$

The immersion deposit is necessarily somewhat defective, for the reasons already mentioned, though immersion deposits from complex ions are finer grained and more satisfactory than those reduced from aquocations. The zinc coating is, under the best conditions, an acceptable basis for a copper undercoat from the cuprocyanide bath, on which other coatings can be plated, but there is usually a fair proportion of rejects in commercial operation. Other processes similar in principle use tin or bronze immersion coatings.[56–61]

4.07.6.6.4 Service corrosion effects

Undercoats, 'flash' deposits produced by strike baths, and immersion deposits are potential sources of weakness. If their structure is faulty, it affects the subsequent layers built on the faulty foundation. The greater the number of stages, the higher is the probability of faults. Additional metal layers can create bimetallic corrosion cells, if discontinuities appear in service. The layer of copper beneath cadmium plate on aluminum (using a zincate plus cuprocyanide deposition technique) can cause corrosion problems. When aluminum is plated with nickel and chromium, rapid service corrosion in the zinc layer causes exfoliation.

4.07.6.6.5 Corrosion potentials in plating baths

The standing potentials of steel and copper (before application of current) are shown in Table 2, together with the standing potential of the plated metal and the potential below which hydrogen should, in theory, be evolved. The potential of the cathode during deposition at a typical current density is also given.

4.07.6.6.6 Agitation and high-speed electrodeposition

There are a number of applications for electrodeposition where high speed is the essence. These include coated strip (e.g., tinplate and galvanized steel), electroforming, and jet plated connectors/contacts. Such high speeds can be achieved either by exploiting solution characteristics or by applying agitation techniques. In simple terms, this can be understood by consideration of the Nernst diffusion equation, where the limiting current density is defined as,

$$i_L = nFCD/\delta(1-t)$$

Thus i_L is maximized by increasing C, the metal concentration in solution, through using near-saturated solutions, selection of highly soluble salts or complexes, or increasing D, the diffusion coefficient, by using high temperatures. Alternatively it can be maximized by minimizing δ, the cathode diffusion layer thickness, by agitation or reducing t, the transport number, or by using highly conducting solutions through use of support salts (e.g., acids) in solution. In practice, all these can be exploited within the

Table 2 Corrosion potentials of substrates of copper and steel, plated and unplated in same plating solutions

Plating bath	*Copper*	*Steel*	*During plating*	*Plated copper*	*Plated steel*	*Hydrogen evolved below*
Watts nickel, pH 2.5, 55 °C (not agitated)	+0.112	−0.238	−0.65 (130)	+0.132	−0.173	−0.148
Bright nickel, pH 2.2, 50 °C (air agitated)	+0.042	−0.293	−1.22 (388)	−0.003	−0.138	−0.130
Cupric sulphate, pH < 0, 20 °C	+0.275	approx. −0.35	−0.15 (388)	+0.265	–	>0
Cuprocyanide, pH 12, 55 °C	−0.378	−0.353	−1.21 (130)	−0.378	−0.388	−0.71
Argentocyanide, pH 11.5, 20 °C	–	–	−0.58	−0.24	–	−0.68
	immersion deposit impedes measurement)		(65)			
Zinc sulphate, pH 4.0, 20 °C	+0.122	−0.578	−1.213 (162)	−0.64	−0.65	−0.24
18% (w/v) HCl pickle for ferrous metal, pH < 0	–	−0.17				>0
3% (w/v) HCl pickle for copper alloys, pH 0	+0.17					0

Deposition potential is accompanied by current density (A m^{-2}) in parentheses; the plated substrate's coating thickness was 2.5 mm. The final column gives the potential below which hydrogen evolution is possible; only in the cuprocyanide is it observed.

constraints of practicality, such as solution boiling and evaporation, heat loss costs, effluent treatment, etc. Thus, high speed solutions have been formulated for tin, zinc, nickel, gold, and silver using these principles.

Agitation has been more problematical. In the past, poor distinction has been made between solution mixing and diffusion layer thickness reduction. Traditional methods of cathode reciprocating movement and air bubbling or sparging are simple and cheap, but not very effective in the context of high-speed electrodeposition. Consequently, other techniques have been developed. Moving the cathode at high velocity is very effective provided it has symmetry of shape and can be done equally for all points on the deposition surface, for example, coating of continuous strip or wire substrates, or rotation of the cathode is possible as for cylinders, flywheels, tubes, bearings, etc. Alternatively, pumping the solution along or at the electrode interface is feasible by using focused jets or capillary-type gaps at the interface. The use of submerged eductor jets has become ecologically important, because there is little or no atmospheric spray produced and the venturi-induced flow can be substantially greater than the direct pumped flow.

Specialist forms of agitation have been developed for certain types of process. For example, deposition of composite coatings requires the particles to be suspended in solution and captured by the growing deposit. This is difficult with pumped flow agitation, where the particles are in fast continuous movement. In these situations vibratory agitation may be best or the solution could be made more viscous and agitation disregarded.

Comparison of the efficacy of agitation techniques has always been problematical because speed *per se* is inadequate – deposit quality must be assured. Theoreticians may prefer to define diffusion layer thicknesses or mass-transport numbers, but in practical terms the current density to attain a given deposit quality is easier to measure. From this, an agitation enhancement factor (EF) can be used for comparison, the EF value for a static solution being taken to be unity. Typical values are then as follows:

Cathode reciprocation	EF = 2
Air bubbling	2–5
Cathode movement	5–20
Cathode rotation	5–50
Jetting/eductor flow	10–25

Distinction should be made between agitative fluid flow and ultrasonic agitation. Ultrasonics are effective at displacing solids from interfaces in a cleaning mode and for modifying physical properties of the growing deposit but are not specifically effective at moving or thinning the liquid-phase diffusion layers.[62–64]

4.07.6.6.7 Pulse plating

The use of pulsed current as a means of improving deposition rates and yielding improved deposits is a development of periodic reverse techniques, long used in the metal extraction and refining industries to produce smoother/leveled deposits. The reasoning was that high currents may give high deposition rates but generally yield rougher surfaces. However, reversing the current for a short time can ideally cause preferential anodic dissolution of the protuberances, thereby, leading to smoother surfaces. Thus a degree of inefficiency of overall production can be withstood in the attainment of better deposit surfaces. The times for forward and reverse currents are usually of the order of minutes.

While it may be easy to use sine wave alternating current waveforms, this is limited to 50 or 60 Hz and square waves are usually generated by an electronic waveform generator. The waves themselves may be on/off, but more usually, pulse/reverse, superimposed pulses, duplex pulse, etc. The choice depends upon intention with regard to electrode kinetics or mass transfer, electrocrystallization modification, deposit properties, etc. Furthermore, the technique has been explored for virtually every metal and alloy, which can or has been researched. Some metals, alloys, and solutions are more susceptible than others although in some cases the systematic research may not have been adequate. Successes have commonly been to modify deposit grain size and stress, to improve surface smoothness, distribution and brightness, to increase net deposit rates, and to enable layered deposits to be produced. The literature is now so large that it must be referred to by search engines and not general reviews.

When the time intervals are of seconds or less, the term pulse plating has become usual, for which a number of terms must be defined:

- The waveform is the shape of the current/time graph; it is usually square but could be sine wave. The pulses may be forward only or pulse/reverse (forward and negative). Other patterns are possible.

- The pulse frequency is the number of pulse cycles per second.
- The duty cycle (%) is the on time related to the total time.
- The mean current is the duty cycle × the peak current

Many plating processes have been studied but relatively few have been used industrially or commercially. A number of reasons can be noted, especially the cost of pulsing large currents because of the dissipation of energy; but a particular reason is that each metal and solution has its own characteristics, which normally have to be individually studied or optimized, with transposition from another system only rarely successful. Consequently, apparent failure is often because of lack of perseverance! Puippe and Leaman in 1986[65] have demonstrated the huge stock of research data; what is lacking is this perseverance.

4.07.6.7 Factors Influencing Structure

4.07.6.7.1 Substrate effects: epitaxy and pseudomorphism

Both the words epitaxy and pseudomorphism are derived from classical Greek, the former meaning literally, close to or close upon an arrangement, row or series (technically an arrangement imposed upon a skin or layer, for example, an electrodeposit, which is close upon a substrate) and the latter, false form (technically a mineral or crystal displaying a form more characteristic of another material than its usual one). For many years, the two terms were held to be synonyms for one phenomenon in electrodeposits. Since 1936, it has become clear that there are two related phenomena, on each of which one of the names is bestowed. Not all authors recognize this, nor is the usage employed here adopted uniformly. Both phenomena are of great practical importance.

Pseudomorphism received methodical study from about 1905. A microsection taken across the interface between a substrate and an electrodeposit shows the grain boundaries of the former continue across the interface into the deposit (Figure 5). As grain boundaries are internal faces of metal crystals, when they continue into the deposit, the latter displays in the form of the substrate. Hothersall's 1935 paper contains numerous excellent illustrations with substrates and deposits chosen from six different metals, crystallizing in different lattice systems and with different equilibrium spacing. Grain boundary continuation and hence pseudomorphism is evident despite the differences.

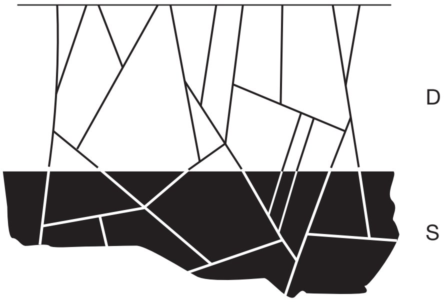


Figure 5 Pseudomorphism; grain boundaries in the substrate (S) are continued in the electrodeposit (D).

Epitaxy is a relation on the atomic scale between substrate and electrodeposit. Imagine that the interface of the microsection is magnified about 107 times so that the rows of atoms in the metal lattice become visible. If the deposit shows epitaxy, there will be an ordered and regular relation between substrate and deposit atom positions (Figure 6(a)). A nonepitaxial deposit shows no such relation (Figure 6(b)). Direct experimental demonstration of epitaxy was first made in 1936 by Finch and Sun. Earlier, metallographers argued that pseudomorphism (which they could see) meant there must be epitaxy (which they could not), as grain boundaries are surfaces where the direction of lattice rows of atoms changes; if epitaxy were assumed to exist, pseudomorphism should result. Reversing the argument, pseudomorphism was taken as evidence for epitaxy (Figure 6(c)).

Electron diffraction investigations showed that epitaxy did indeed exist when one metal was electrodeposited on another, but that it persisted for only tens or hundreds of atomic layers beyond the interface. Thereafter, the atomic structure (or lattice) of the deposit gets altered to one characteristic of the plating conditions. Epitaxy ceases before an electrodeposit is thick enough to be seen with an optical microscope, and at thicknesses well below those at which pseudomorphism is observed.

Epitaxy reflects the formation of metallic bonds between the dissimilar atoms at the interface. When the two metals crystallize in different systems, their relative orientation is that which promotes the maximum coordination and the maximum metallic bonding. The stability achieved by epitaxy overrides any lost because of the lattice strains imposed. These strains may be considerable; 'stresses' calculated from the bulk elastic moduli are correspondingly high, and sometimes puzzle the uninitiated if they

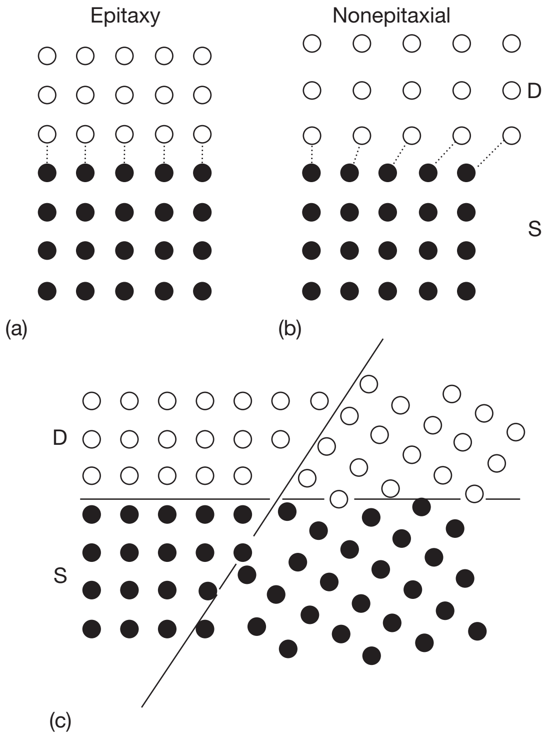


Figure 6 (a) Coordination across a substrate S-electrodeposit D interface on the atomic scale produces epitaxy, (b) a nonepitaxial deposit has no coordination and (c) epitaxy would be expected to produce grain boundary continuation at the interface, though in fact grain boundaries often continue to thicknesses far greater than those at which epitaxy disappears.

exceed the bulk tensile strength. It is an oversimplification to regard the interface as being highly stressed; were the 'stress' which seems to be parallel to the interface reduced by some means to zero, the energy that would have to be put into the bonds normal to the interface would be much greater than that released. The simple concept of stress in a homogeneous alloy is not applicable to the peculiar case of a substrate–electrodeposit interface. The latter is unique in having metallic bonds carried across a very sharp boundary.

The practical result of epitaxy is a very high degree of adhesion between coating and substrate. The force needed to separate the interface is similar to that needed to break the metals on either side. Where a true metallic bond forms at an epitaxial interface, it is only possible to measure adhesion if the bond is the weakest of the three near the interface. An adhesion test based on breaking the joint indicates only which of the three is weakest. For practical purposes, any epitaxial joint will have strength more than adequate for service conditions.

Nonepitaxial electrodeposition occurs when the substrate is a semiconductor. The metallic deposit cannot form strong bonds with the substrate lattice, and the stability conferred by coordination across the interface would be much less than that lost by straining the lattices. The case is the converse of the metal–metal interface; the stable arrangement is that in which each lattice maintains its equilibrium spacing, and there is consequently no epitaxy. The bonding between the metallic lattice of the electrodeposit and the ionic or covalent lattice of the substrate arises only from secondary or van der Waals' forces. The force of adhesion is not more than a tenth of that to a metal substrate, and may be much less.

Epitaxial growth is prevented if semiconducting films of grease, oxide, sulfide, etc. cover the cathode surface. These occur when pretreatment is inadequate, when plating baths are contaminated, or when, as with stainless steel, aluminum, titanium, etc. an oxide film reforms immediately after rinsing. Low adhesion resulting from nonepitaxial electrodeposition is used in electroforming to promote easy separation of deposit and substrate. When semiconductors or nonconductors are to be electroplated, a form of dovetail mechanical joint (achieved as outlined above) is essential. Means similar to those for stainless steel and aluminum have been devised to deal with other alloys, which are passivated readily. Sometimes, even with special methods, some oxide remains so that the electroplated coating is anchored only by small epitaxial areas. There is risk of failure. Thermal stress or relatively mild abrasion may part the interface and cause the unanchored areas to blister. Adhesion is improved by postplating annealing. The oxide at the interface is dissolved in one or other metal, or diffuses to grain boundaries and alloying at the interface produces the desired metallic bond.

Pseudomorphism has less desirable consequences, and usually means are sought to suppress it. If the substrate has been scratched, ground, or abrasively polished, or if it has been cold rolled or cold formed, the surface is left in a peculiar state. Cold working reduces the surface grain size, and produces deformed, shattered, and partly reoriented metal. It may produce microcrevices between the deformed grains, and, with some processes, nonmetallic impurities and oxides are embedded in the surface. The disturbed state of the substrate is copied by a pseudomorphic electrodeposit with several consequences (Figure 7). One is aesthetic, as it has often been noted that almost invisible abrasion of the substrate develops, as more prominent markings in the deposit. A chalk mark on steel produces local abrasion, hardly noticeable when the chalk is wiped away. If a strongly pseudomorphic electrodeposit is applied, the chalk mark reappears indelibly on its surface. A bright deposit may have its luster greatly reduced by pseudomorphic growth on a deformed surface (Figure 8). The corrosion protection is reduced if pseudomorphism with a deformed substrate leads to discontinuities at ill-fitting deposit grains (Figure 9). A pseudomorphic coating usually presents a dull or rough crystalline appearance. When the crystal form of the substrate is copied in the deposit, growth generates faces of simple index. An artificial face of high index soon grows out when plated. Tradition demands a featureless mirror surface on metal coatings, and a way of producing this, which has attracted much commercial effort, is by using brightening addition agents. Microsections of electrodeposits from the more effective bright plating baths do not exhibit pseudomorphism. The deposit usually shows no grain structure, but instead a series of light and dark bands parallel to the substrate (Figure 10). Pseudomorphism is suppressed by the addition agent adsorbing on, and blocking areas taking part in, pseudomorphic growth. In the initial stages of bright plating, the addition agents adsorb at similar points on the substrate. Growth commences from fewer substrate nuclei when annealed nickel is plated in a bright nickel bath than in a dull (Watts') bath without additions. In the earliest stages of deposition, replicas of the surface show evidence of pseudomorphism even in bright baths (the substrate grain boundaries are carried into the deposit) but this is suppressed rapidly as the thickness increases. The aim with bright plating baths is to inhibit growth sufficiently to suppress pseudomorphism, but not so much as to suppress epitaxy and adhesion. An excessive concentration of addition agent will also suppress epitaxy, so that deposition occurs on to an adsorbed layer of brightener. Brightener adsorption is often potential dependent and trouble may occur first at high current density (low potential) areas.[58–64]

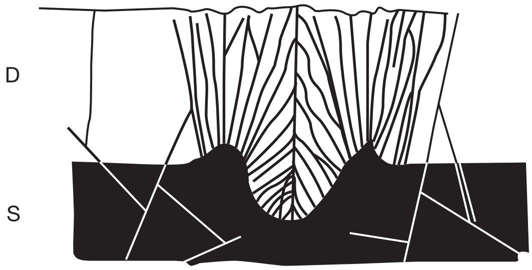


Figure 7 The disturbed structure of a scratch, with fragmented and distorted grains, is perpetuated by a strongly pseudomorphic electrodeposit.

4.07.6.7.2 Electrolyte effects

As a deposit becomes thicker, the influence of the substrate diminishes, and eventually the structure is characteristic only of the electrolyte composition, the temperature, current density, and mode of agitation. A great variety of structures are observed; some are analogous to those seen in cast metals, but others are obtained only by electrodeposition. Crystalline deposits

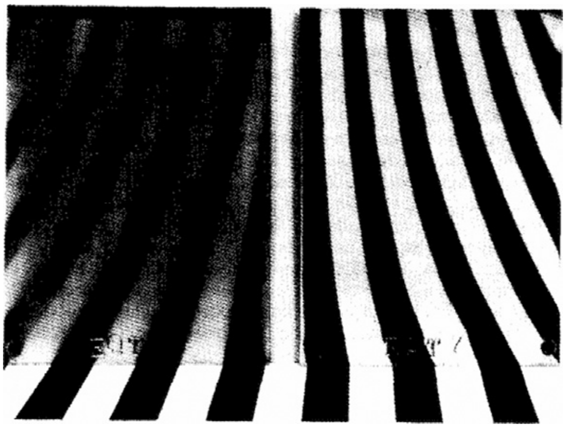


Figure 8 A fairly strongly pseudomorphic bright tin deposit (left) has its brightness impaired by the shattered surface layer produced on steel by cold rolling. When this layer is removed, the deposit is mirror bright (right). Coating 5 mm thick.

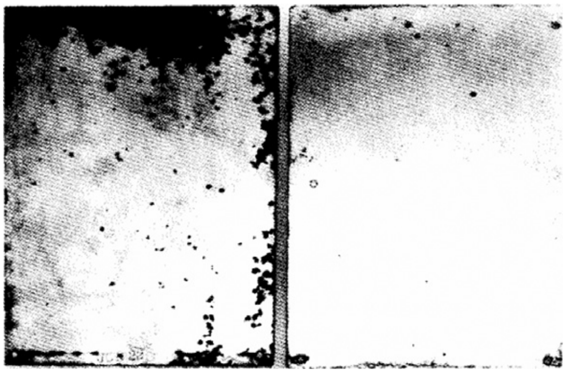


Figure 9 Corrosion resistance of tin–nickel electrodeposit impaired by pseudomorphic porosity originating on cold-rolled steel surface (left). Panel on right has had the shattered grain surface removed by chemical polishing (0.125 mm removed). Coating thickness 15 mm; panels exposed 6 months to marine atmospheric corrosion (Hayling Island).

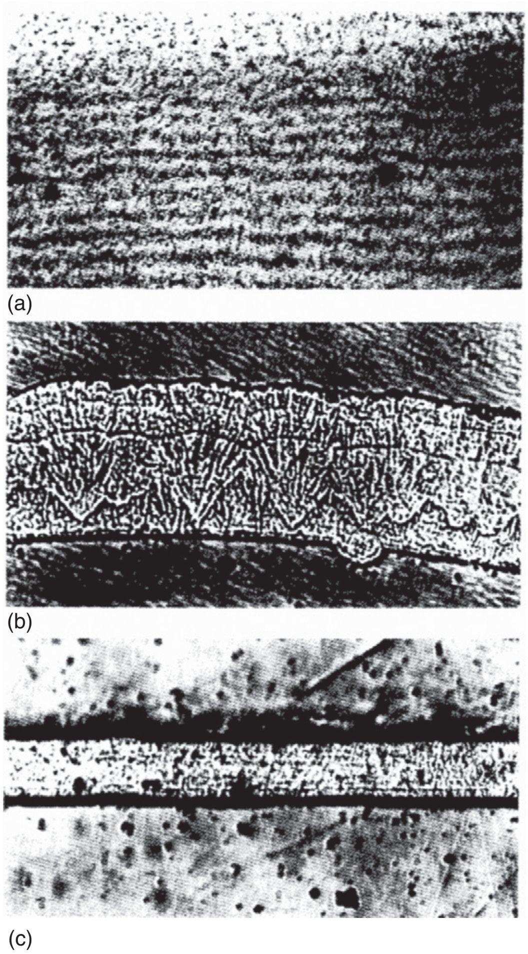


Figure 10 Banding often observed in microsections of bright electrodeposits. (a) Bright tin (courtesy of the Tin Research Institute), and (b) and (c) bright gold.

from baths containing little or no addition agent often develop a preferred orientation texture. Some bright deposits show a texture, but in general as growth processes are progressively inhibited by increasing addition agent concentration or by using more active materials, the deposit becomes progressively finer grained and loses preferred orientation textures.

The compositions of baths, chosen for practical use, result in initial rates of lateral growth much greater than the rate of outward growth. This is a desirable feature; it causes the coating to become continuous at low thicknesses. The opposite condition of a faster rate of outward growth is undesirable, and results in a noncoherent deposit. Predominantly, outward growth occurs when the transport of metal ions becomes slow compared to their rate of discharge, that is, it is favored by high current density, low temperature, and lack of agitation. Lateral growth processes are then starved of material to support them, but outward growth moves the deposit towards the supply, and the prominences formed benefit from greater diffusive flux. There are strong pressures in industrial production to increase electroplating rates, which carries a danger of using high current density and causing a shift to outward growth. In baths where the coating is electroplated from aquocations at high cathode efficiency, the onset of lateral growth is fairly sharp. Cathodes have a range of local current density, and the coating on the high current density areas becomes friable, dark colored, and rough as the transition is reached. Such coatings are termed 'burnt' and the corrosion protection is degraded. With baths working in the acid pH range, there is the complication that once an appreciable part of the current is used to reduce water, the pH at the cathode rises and insoluble hydroxides are precipitated and incorporated in the coating. With complex cyanide baths, the onset of 'burning' is less sharp. There is normally considerable simultaneous hydrogen discharge, and as the current density rises, there is no sharp limiting current density for metal discharge. Addition agents raise the lateral–outward transition to higher current densities by inhibiting outward growth. Nevertheless, all electroplated coatings show signs of deteriorating properties if the baths in which they are produced are worked at sufficiently high current density.[66–70]

4.07.6.7.3 Form of current passed through cell

Commercial electroplating began with pure DC from galvanic cells. Later, for many years, DC generators were used. Their current output is unidirectional but with a superimposed ripple. Part of the ripple stems from the angular motion of the armature coils during the period they supply current to a commutator segment and part from variations of contact resistance at the commutator. Generators have been superseded by transformers and rectifiers. Copper-oxide, mercury-arc, selenium, germanium, and silicon rectifiers have been used and examples of each are to be found in service. These devices supply varying unidirectional current whose form depends on the number of phases in the input and the circuit used. A half-wave single-phase rectifier provides a pulsating current; a full-wave three-phase set has a much smoother output.

Alternating currents with asymmetric forms have been used, mainly for electroforming and thick engineering deposits. Where the cycles are slow, for example, several seconds, the term periodic reverse current (p-r-c) is used. The benefit claimed for p-r-c plating is that smoother, thick deposits result from selective dissolution of peaks in the reverse part of the cycle. This assumes the electrode process reverses during the anodic period, which is not always the case. In chromium plating, the coating becomes passive in anodic periods, while in acid gold baths based on aurocyanide, the process is also irreversible. More recently, asymmetric AC with a much higher frequency of 500 Hz was found to alter beneficially the properties of nickel from chloride baths.

Pulses of unidirectional current have been used to modify coating properties. When plating starts, it is possible, for a time, to use a current much higher than the steady-state limit, drawing on the stock of ions near the cathode. Provided sufficient time is allowed between pulses, a coating can be built of layers plated at much higher current density than normal. Improved gold coatings were produced by relatively rapid pulses. The technique of barrel plating results in pulse plating of an irregular sort, with pulse durations of the order of seconds and inactive periods rather longer.

Chromium plating from chromic acid baths is more sensitive to the source of current than most other processes, sufficiently so for commercial operators to use at least three-phase rectifiers as a rule, and to take precautions against any temporary break of current during voltage regulation. A recent investigation showed that the ripple introduced by thyristor control of rectifiers was detrimental to chromium electrodeposits.[71–80]

4.07.6.8 Industrial Electroplating Techniques

Electroplating is usually a finishing technique applied after an article has been completely fabricated. Fairly large articles, from cutlery to motorcar bumpers, are dealt with by vat plating. They are suspended by a conducting connection in a rectangular tank or vat of electrolyte. The anodes are arranged about the periphery of the tank. For small runs the cathodes may be suspended by copper wire wrapped round a suitable part, but for longer runs a plating jig is used. This is a copper frame with phosphor bronze spring contacts to hold the work and insulated, usually with a PVC coating, on all but the contact points. The point of contact between wire or jig and the article becomes a weak part in the coating, and some thought should be given to providing or selecting contact points in insignificant areas.

Vat plating is used sometimes with articles too large for complete immersion. Printing, calendering, drying, and similar rolls are part-immersed and revolved continuously during plating. However, it is much more difficult to plate half an object, reverse it, and complete the other half later; the ‘join’ between the two deposits is rarely satisfactory.

Small objects, nuts, bolts, screws, and small electrical parts are plated in a revolving barrel. Electrical connection is made by a conductor immersed in the tumbling mass, and electrodeposition, which is confined to the outer layer of the mass at any instant, takes place in intermittent stages for any individual object. The coating is abraded during the process. The peculiarities of chromium deposition set it apart, and the normal barrel-plating processes are not used. In the so-called chromium barrels, the small parts travel and tumble along a helix inside a rotating cylinder during deposition, and are electroplated for a much greater proportion of the time than are parts in normal barrels.

Brush plating is a special technique which dispenses with a container and uses a swab soaked in electrolyte applied to the work. In jet plating, a stream of electrolyte is applied to the cathode. Both are methods of selective plating, applying an electrodeposit to only a part of an article. Little has been published about the techniques or the properties of coatings they produce.

Continuous plating of wire and strip is, unlike the preceding techniques, a prefabrication process. The production of tinplate is the largest scale continuous operation, but any electrodeposit may be applied this way. Subsequent fabrication processes are likely to damage the coating, so that precoating is best reserved for ductile coatings which are anodic to the substrate in service, as is the case for tin.[81–83]

4.07.6.9 Rinsing

Between all stages of immersion (cleaning, pickling, plating, postplating treatment) work has to be rinsed. Once the hydrophobic solid has been removed, metal surfaces withdrawn from solutions carry a film of liquid. The solution lost this way is known as drag-out. A film 10 mm thick is the minimum retained by smooth, well drained, vertical surfaces. On rough or horizontal surfaces, and in recesses it is much thicker, as it is also with viscous solutions. During rinsing, the film is diluted, and the ratio of the final concentration to that present initially is the dilution ratio. The dilute material is carried forward to the next process, and clearly the highest concentration of impurity permissible before the subsequent process is affected adversely determines the maximum dilution ratio that can be allowed. Sometimes there is a minimum dilution ratio; between nickel plating and chromium plating it is essential that the rinsed metal surface does not become passive, and prolonged rinsing carries a danger of eliminating the slight but important amount of rinse water corrosion which keeps the surface active between stages.

Usually rinsing troubles are caused by a dilution ratio that is too high. If incoming work passes through a process stage, and the drag-out from that stage is in turn discarded in a subsequent rinse, the maximum concentration of material carried into the bath is equal to that in the film carried over. However, there is an increasing tendency to conserve materials and steps are taken to return drag-out losses. In so doing, the impurities are also returned, so conservation measures require a reduction in the dilution ratio of the preceding rinse. Inadequate intermediate rinses are detrimental to the corrosion resistance of the coating because carried-over impurities impair the functioning of plating baths. Inadequate final rinsing leads to increased corrosion of the coating, and to staining. Staining, which is a serious aesthetic problem with decorative coatings, may itself arise from corrosion. Some stains are caused by the precipitation of dissolved solids when rinse water evaporates, but in other cases, they are caused by corrosion supported by the presence of an electrolyte in the rinse water.[84–93]

4.07.6.10 Postplating Treatments

Where the corrosion resistance of a coating depends upon its passivity, it is common to follow plating with a conversion coating process to strengthen the passive film. Zinc, cadmium, and tin in particular are treated with chromate solutions which thicken their protective oxides and also incorporate in it complex chromates. There are many proprietary processes, especially for zinc and cadmium. Simple immersion processes are used for all three coatings, while electrolytic passivation is used on tinplate lines. Chromate immersion processes are known to benefit copper, brass, and silver electrodeposits, and electrolytic chromate treatments improve the performance of nickel and chromium coatings, but they are not used to the extent common for the three first named.

The tin coatings as deposited in tinplate manufacture are not bright. Until comparatively recently, bright tin electrodeposition was not practiced commercially, there being no reliable addition agents. To produce bright tin on tinplate and other products, the process of flow melting or flow brightening is used; tinplate is heated by induction or resistance, and plated articles are heated by immersion in hot oil to melt the tin, which flows under surface tension to develop a bright surface. While the tin is molten it reacts to form an alloy layer with the substrate. The alloy layer alters the corrosion behavior.

Other electroplated articles are heated after plating to expel hydrogen which has entered the substrate during cleaning, pickling, and plating, and which embrittles some metals, mainly high-strength steels. Generally speaking, alteration of the deposit structure and properties is not desired. Another use of postplating heat treatment is to improve adhesion, as already mentioned (**Section 4.07.6.7.1**).

Mechanical polishing, formerly the principal means of producing bright coatings, has become less important with the extension of the use of brightening addition agents. Mechanical polishing reduces the thickness of a coating, and may cut through to the substrate. As corrosion resistance is related to thickness, mechanical polishing can be detrimental. It may also increase porosity.[94–97]

4.07.7 Properties of Electrodeposits

4.07.7.1 Thickness

Coating thickness is one of the most important quantities connected with corrosion resistance, and its measurement and control are features common to all electroplating operations and in all quality specifications. In some cases, coating thickness has functional importance, for example, where there are fitting tolerances, as with screw threads. However, in most cases, it is the connection with corrosion resistance that makes thickness important. Where the coating is anodic to an area of substrate exposed at a discontinuity, the coating is slowly consumed by corrosion, but the criterion of failure is the appearance of substrate corrosion product. This does not form until almost all the coating is consumed. Coatings which are cathodic to the substrate must have no discontinuities if substrate corrosion is to be suppressed.

The criterion of failure is usually the same. Freedom from discontinuity is also related to thickness. Discontinuities have three origins: spontaneous cracking to relieve internal stress, pores formed during the growth of the coating, and abrasion and wear.

The last two causes, that is, porosity and wear, both exhibit diminishing incidences as thickness rises. Apart from the peculiar case of electrodeposited chromium, internal stress cracking is a sign of incorrect plating conditions. Broadly speaking, thickness and corrosion resistance increase together. The thickness of an electroplated coating is never uniform. On the significant area (i.e., that on which corrosion resistance and other special properties are important) of a plated surface, there are two important thicknesses, that is, (a) average thickness, which determines the production rate and plating costs; and (b) minimum local thickness, which, as the weakest link in the chain, determines the corrosion resistance. The ideal is to make these equal; the larger the difference the greater the waste of metal. The difference can be reduced by special procedures, but at a cost.

When the cathode is being plated, the electrical field is not uniform. Both electrodes are equipotential surfaces, so that prominent parts of the cathode, for example, corners, edges, protuberances, etc. which are relatively nearer to the anode are plated at a higher average current density, resulting in a thicker coating. Recesses and more distant parts are more thinly plated. Distribution of thickness tends to be the reverse of that found with paints, hot-dipped articles, and other coatings that are applied as liquids. Liquid-applied coatings are thin on sharp edges, and thick in recesses because of the effects of surface tension and radii of curvature.

The numerous factors which contribute to the thickness distribution can be divided into two groups, that is, (a) those connected with the nature of the plating bath (see below), and (b) those to do with the geometry of current paths in the bath, including the shapes of the electrodes. (Reference should be made to publications on electrodeposit specifications of the British Standards Institution, American Standards Institution and other standardizing bodies.)

4.07.7.2 Throwing Power

In a given plating cell, thickness distribution is found to vary with bath composition, current density, temperature, and agitation. It is common to speak of the throwing power of a plating bath. The throwing power of chromic acid baths is poor, that is, there is a relatively large difference between maximum and minimum local thickness; conversely, the throwing power of alkaline stannate baths is good, that is, there is much less difference in the local thicknesses. Strictly speaking, the bath composition should be qualified by the conditions of use, as they affect throwing power. Otherwise, the usual conditions are implied. A numerical throwing index can be calculated from the performance of a plating bath in a cell of standard geometry. Two widely used cells are, (a) the Haring–Blum cell, and (b) the Hull cell (Figure 11). The Haring–Blum cell was devised for throwing index measurement; the Hull cell is used mainly to study the effects of varying bath composition.

The Haring–Blum cathode is divided into two equal plane areas, distant l1 and l2 from a common anode, and a quantity called the primary current density ratio P is defined as

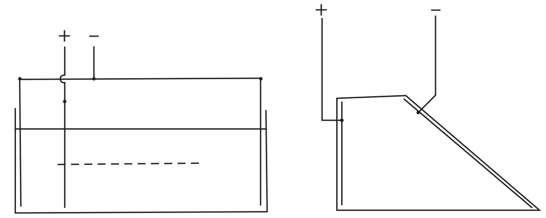
$$P = l_2/l_1$$

This is the ratio in which the current would divide, if electrolytic resistance were to control its flow entirely. The metal distribution ratio M is the ratio of the thicknesses of the coating actually deposited during a measurement. There are several numerical scales of throwing index T, but Field's is widely adopted:

$$T = 100\frac{P - M}{P + M - 2}\% \qquad [11]$$

On this scale, zero represents the case when $M = P$, and electrolyte resistance is the main factor. Throwing power can be worse, down to a limit $T = -100\%$ when $M =$ ¥, that is, no deposit at all on the far cathode. Conversely, when $M < P$, T is positive, where M to reach 1.0 despite the difference in position, $T = +100\%$. At one time, $+100\%$ was regarded as an unrealizable limit, but conditions have been found for which $T = +150\%$ in a Haring–Blum cell equation.

The Hull cell cathode has a continuous variation of current density along its length, and there are



(a) (b)

Figure 11 (a) Haring–Blum cell for throwing index measurement, in elevation and (b) Hull cell (plan view) which can also be used for measuring throwing indices.

equations which give the primary current density at any point not too near the end. If the local thickness is measured at two points for which P is known, T can be calculated. The real current distribution is a function of cathode and anode polarization as well as of the resistance of the electrolyte. The metal distribution ratio will be

$$M = \frac{(V - \Delta E_1)}{(V - \Delta E_2)} \times \frac{l_2}{l_1} \times \frac{\varepsilon_1}{\varepsilon_2} \qquad [12]$$

where V is the cell potential difference between anode and cathode, ΔE is the total potential difference caused by polarization (anode and cathode) on the cathode area indicated by the subscript, and ε is the cathode efficiency as indicated by the subscript.

As ΔE will be a function of current density, T will be a function of electrode area, and comparisons should, therefore, be made with cells of standard size. Equation [12] shows that high throwing indices will result when polarization rises steeply with current ($\Delta E_1/\Delta E_2$) and cathode efficiency falls steeply ($\varepsilon_2/\varepsilon_1$). The primary current ratio, $P = l_2/l_1$, affects the result because by altering the currents the polarization terms are altered. For example, with an acid copper bath in a Haring–Blum cell, 194 A m^{-2} average CD:

P	2	5	11	23
T (%)	+7	+11	+22	+41

An increase in conductivity usually increases T because it increases the proportion of polarization in the total cell potential difference and lowers the ratio $(V - \mathrm{DE1})/(V - \mathrm{DE2})$. Changing the conductivity, an acid copper bath with sulfuric acid produced the following result (291 A m^{-2} average CD, $P = 5$):

Conductivity (S cm^{-1})	0.08	0.15	0.26	0.30
T (%)	+5	+11	+13	+27

where S is the SI unit of conductance (Siemens).

Many baths in which metal is reduced from complex anions (e.g., cyanide baths, stannate baths) give high throwing indices because both polarization and cathode efficiency variation favor a low value of M. The cathode efficiency for a typical copper cyanide bath (40 °C) was

Cathode current density (A m^{-2})	199	253	384	763	1 785	5 130	30 800
Cathode efficiency (%)	0	5.9	11.9	13.9	18.8	22.7	24.4

The throwing index for the cyanide bath is usually about +40% and rises as the cell current is increased to as high as +85%. Aquocation baths give values near $T = 0$, though conditions may be selected which give much higher figures if there is a steeply rising section of the polarization curve. Chromium plating baths invariably have large negative throwing indices, despite deposition from a complex ion. The cause is the anomalous rising trend of cathode efficiency with current density and the existence of a minimum current density below which the efficiency is zero. A typical bath (400 g l^{-1} CrO_3, 4 g l^{-1} H_2SO_4, 38 °C) gave the following data:

Current density (A m^{-2})	32	65	129	258	388
Cathode efficiency	76	68	56	34	21

If the current density on the far cathode in a Haring–Blum cell was 199 A m^{-2} or less, $T = -100\%$.

Throwing indices measured in a Hull cell differ from those in a Haring–Blum cell because of the differences in geometry. In a Hull cell, several pairs of points can be found, which have the same primary current ratio, but for which M and hence T are found to vary because of polarization changes.[98–105]

4.07.7.3 Current Path Geometry

The polarization and cathode efficiency terms in eqn [12] cannot be altered in practice to improve thickness distribution, as they tend to be decided by overriding considerations. It is usual to accept the distribution obtained without special precautions as being the best commercial solution, although the average thickness needed to achieve the necessary minimum local thickness may be high. Where this approach does not serve, there are a number of methods of altering the term l_2/l_1 in eqn [12]:

(a) By using shaped (conforming) anodes, additional (auxiliary) anodes or 'bipolar' anodes to bring anode areas nearer to cathode recesses. Insoluble anodes are better where they are applicable, as they do not alter the original shape during use.

(b) By using nonconducting shields of plastic or glass to equalize the current path lengths.
(c) By placing auxiliary cathodes ('robbers' or 'thieves') near high-current-density points to divert deposition. This does not save metal, but has the merit that auxiliary cathodes can be incorporated into jigs for long runs in automatic plating machines. Auxiliary cathodes are used in heavy chromium deposition, where metal waste is secondary to the cost of removing excess chromium when grinding to precise dimensions. Where a number of small parts are plated together on a jig, it is usually possible to dispose them so that they serve as 'robbers' for each other.
(d) By paying attention to certain 'rules' when designing articles which will be finished by electroplating. Many external contours are chosen for reasons of style. It helps to avoid features like sharp recesses, which are bound to cause trouble. A simple rule is the '1 in ball test' or perhaps the '25 mm ball test': if there is any part of a surface which a ball of this diameter cannot touch when rolled over it, there will be difficulties. There are other design aspects, covered in specialist publications, attention to which improves the corrosion resistance, which can be imparted by plating.[106–110]

4.07.7.4 Structure-Dependent Properties

4.07.7.4.1 Composition of the electrodeposit

Attention has been drawn to the dependence of structure on both substrate and plating conditions, and to the transition in properties which occurs across the section of a deposit. Most commercial electrodeposits have a high purity, yet in a sense impurities are vital to their successful application. Alloy electrodeposition possesses the literature whose bulk attests the subject's fascination for research (which the authors share), but is out of proportion to the extremely limited commercial applications. Alloys in general metallurgical practice provide a variety of mechanical properties; in electroplating the range of properties desired is narrower, and it can generally be achieved by altering the structure of a single metal deposit through changes in the plating bath composition or plating conditions. The microstructure of an electrodeposit can be altered much more than that of a cast and worked metal. This is because the deposit forms well below its melting point, where crystallization processes are hindered by the virtual absence of solid-state diffusion. Consequently, very small amounts of 'impurity' absorbed at important growth sites on the surface cause large changes in the structure of what is, chemically, almost pure metal. The structure is metastable, but permanent as long as the electrodeposit is not heated. A variety of mechanical and physical properties are a reflection of the structure: hardness, ductility, tensile strength, internal stress, electrical and thermal conductivity, etc. As the structure of an electrodeposited metal is altered by changing the plating conditions, the mechanical and physical properties also alter. A plot of structure-dependent properties against the plating variable usually shows the various properties moving in parallel or inverse motion, and over ranges not accessible in cast and worked metal of the same composition. However, if electrodeposits are heated to temperatures where moderate mobility of the atoms is possible, their properties rapidly revert to 'normal.' The corrosion resistance of electrodeposits depends much more on chemical composition than on structure, so that the corrosion resistance of a particular metal is retained for a wide range of mechanical and physical properties.

The 'impurities' responsible for modifying the structure may originate from water (dispersed oxides); adsorbing ions, especially cyanides; organic addition agents parts of which are incorporated; or ions of a second metal which are codeposited. Some regard deposits in which the impurity is a small amount of a second metal as an alloy, but generally, they have the same sort of metastable structures as are obtained with nonmetallic impurities, rather than the structures of stable alloys of the same composition. The 'alloying' metal serves to cause and perpetuate a nonequilibrium structure whose real basis is the low temperature of the electrocrystallization process. Generally, the corrosion properties of the various different structures of a given metal are much the same, with the notable exception of nickel containing sulfur from addition agents, which has already been mentioned.[111–116]

4.07.7.5 Internal Stress

Electrodeposits are usually in a state of internal stress. Two types of stress are recognized. First order, or macrostress, is manifest when the deposit as a whole would, when released from the substrate, either contract (tensile stress) or expand (compressive stress) (Figure 12). Second order, or microstress, occurs when individual grains or localities in the metal are stressed, but the signs and directions of the microstresses cancel on the larger scale. The effects of first-order stress are easily observed by a variety of techniques.

Second-order stress is difficult to observe and much less extensively studied. The causes of internal stress are still a matter for investigation. There are broad generalizations, for example, 'frozen-in excess surface energy,' 'a combination of edge dislocations of similar orientation,' and more detailed mechanisms advanced to explain specific examples.

Tensile first-order stress is a corrosion hazard in coatings cathodic to the substrate. Compressive stress is not usually troublesome, nor is the stress of either sign in anodic coatings. Less can be said about high second-order stress, though it may well cause brittleness. If tensile stress is large enough, the coating cracks and a cathodic coating will fail to protect, as illustrated in Figure 13. Tensile stress below the level needed for spontaneous cracking lowers the fatigue limit of a substrate. Tensile stress can in several cases be reduced to safe values by fairly minor changes in microstructure and plating conditions, insufficient to upset other desirable properties. Saccharin is an addition agent for reducing stress in nickel; additions of ammonium chloride reduce stress in tin–nickel alloy; and small changes in bath temperature and CrO_3:H_2SO_4 ratio reduce stress in chromium.

Figure 12 An electrodeposit showing unusually high compressive stress. A 150 × 150 mm copper sheet was insulated with lacquer on one side and electroplated with Sn-35 Ni alloy. The high compressive stress has caused the sheet, originally flat, to coil in the manner shown, with the electrodeposit outside.

The effects of tensile stress in the various layers of nickel plus chromium coatings are complex, and internal stress in both chromium and nickel (post-nickel strike or PNS) layers can be harnessed to produce beneficial cracking ('microcracking') [117–120].

4.07.7.6 Ductility, Hardness, Wear, Strength

The mechanical properties reflect very closely the structures of electrodeposits. The softest, most ductile, weakest form of a particular metal is that with a large crystal size, deposited with minimum polarization from baths, which have no addition agents. This is the type of deposit in which pseudomorphism is strongest. In terms of the accepted deposition mechanism, there is the least inhibition of adion mobility as the deposit grows, and least inhibition of those sites at which equilibrium growth would occur. This electrodeposit has properties the nearest to those for the annealed metal, but even so tends to be somewhat harder. Because of pseudomorphism the properties near the substrate interface may be greatly modified if the latter has a metastable structure, especially one

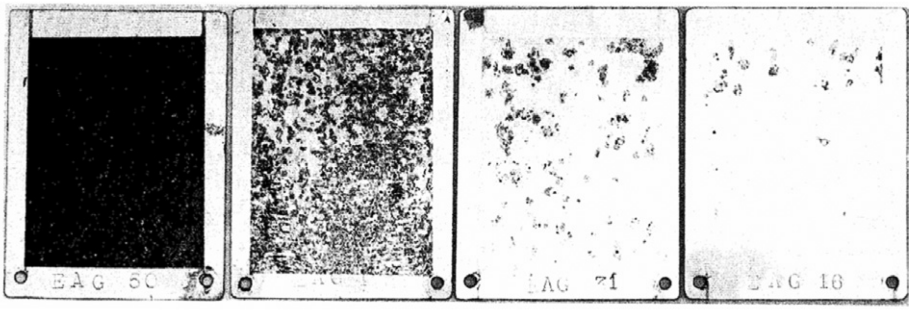


Figure 13 Cracking in a cathodic coating due to a tensile stress that exceeds the cracking strength, leading to loss of protection. All 5 μm coatings of Sn–Ni alloy on steel. From left to right, values of stress in N mm^{-2}; 134 tensile, 86 tensile, 57 tensile, and 127 compressive.

with very small grains produced by mechanical working. The deposit in turn becomes 'work hardened' by pseudomorphic growth.

When electrodeposition is inhibited, the metal becomes harder and less ductile, and tensile strength is increased. Metals deposited from acidic solutions of aquocations become harder when the pH is raised to near the value at which the hydroxide precipitates. Codeposited oxide acts as an addition agent, giving small-grained, hard deposits. Hard nickel is produced for engineering surfacing from high-pH baths. Many metals can be electrodeposited in extremely hard forms from inhibited baths, but they tend to become brittle, with high internal stress, so that the true tensile strength is hard to establish. Ductility necessarily falls as hardness rises, and coatings become more susceptible to damage by impact, reducing their protective value if they are cathodic to the substrate. Some applications of electroplating depend on the production of unusually hard and wear-resistant forms of corrosion-resistant metals. Thick coatings of chromium and nickel are applied to numerous steel parts to combine wear resistance with corrosion resistance. Thick or engineering chromium electrodeposits crack repeatedly during deposition, but the cracks are subsequently sealed and none should traverse the entire coating. Thick chromium coatings have practically no ductility, and because of their defective structure they have a low effective strength. They serve best on stiff substrates.

Gold coatings on separable electric contacts and slip rings make use of the high hardness possible with electrodeposition to resist wear. Rhodium is another metal which can be exceptionally hard. Thick coatings have a cracked-sealed structure similar to that of chromium.[121–124]

4.07.7.7 Interdiffusion with the Substrate

A thin metal coating on a metal substrate is not a stable entity; greater stability would be attained if the coating were to diffuse evenly throughout the substrate. Fortunately, at ambient temperatures most of the usual combinations interdiffuse sufficiently slowly to present no practical problem. At high temperatures, however, many coatings diffuse quickly. Diffusion in a few systems at moderate temperatures causes corrosion problems. Difficulties can occur with tin, which, with its low melting point of 231 °C, is relatively 'hot' at room temperature. On copper and copper-alloy substrates, diffusion transforms the tin into the intermetallic phases Cu_6Sn_5 and Cu_3Sn. At 100 °C, the transformation is accelerated, and 5 mm of tin may become wholly alloyed within a year. The alloy coating may pass as tin having a silvery color, but it is much harder and has a very stable passivity. One use of tin on copper is to facilitate easy joining by soldering, but the alloy has a high melting point and is not easily wet by solder. Thin 'tin' coatings on copper which have become wholly alloyed in storage are difficult to solder. Sometimes extremely thin coatings (0.25 mm) used purely for solderability become wholly alloyed in a few weeks. Parts should not be stored too long and very thin coatings are a false economy.

Tin will protect copper from corrosion by neutral water. Pure tin is anodic to copper, and protects discontinuities by sacrificial corrosion. Both intermetallic phases are strongly cathodic to copper and corrosion is stimulated at gaps in wholly alloyed coatings. An adequate thickness of tin is needed for long service, for example, 25–50 mm. Another diffusion problem occurs with tin-plated brass. Zinc passes very quickly to the tin surface, where under conditions of damp storage zinc corrosion products produce a film which greatly impairs solderability. An underplate of copper, or better still nickel, usually cures this trouble.

A similar problem, that is, diffusion of the substrate through the coating to corrode at the surface, arises with gold-plated copper. Many gold coatings are used to ensure a low electric contact in electrical connectors. Gold is preeminent because of the absence of stable-corrosion-product films under most service conditions, but it is expensive, so coatings are kept as thin as possible. Electronic devices may operate at fairly high temperatures (100–150 °C), and significant amounts of copper may diffuse through the coating to produce a film of oxide on the surface, nullifying the contact value of the gold. Nickel underplate mitigates this trouble (though increasing plating difficulties). To reduce costs, attempts have been made to dilute gold with cheaper metals, while retaining gold-like corrosion properties. Cadmium has been used as a diluent, but while quite high cadmium-golds are gold-like at 25 °C, at higher temperatures, cadmium gets oxidized at the surface. Pure gold is preferred for high temperature contacts.[125,126]

4.07.7.8 Porosity

In the very earliest stages of electroplating, the substrate carries discontinuous areas of deposit growing around nuclei. Lateral growth causes the great majority of growing edges to coalesce with sufficient perfection to be impervious to corrosive gases and liquids. On normal metallic substrates, a few edges do not grow together, and a gap remains in the coating. As the coating thickens, the gap is propagated as a channel through the coating, to form a pore. Under the conditions chosen for practical electroplating, pores diminish in cross section as deposition continues, and pore density (pores per unit area) falls as thickness increases. The corrosion which occurs when pores allow liquid and gaseous corrosive agents to reach the substrate varies in importance according to the relation between the corrosion potentials of deposit and substrate, the corrosive environment, and the function of the coating.

If the environment favors wet corrosion processes, relative polarity is the main consideration. If the coating is anodic, porosity is seldom of any serious consequence. The cathode is the very small area of substrate exposed at the base of the pore, and the restricted channel limits the diffusion of reactants and products. The large anode area provided by the coating reduces the bimetallic corrosion current density thereon. Two important examples of this type are zinc coatings on steel in cold waters or the atmosphere and tin coatings on steel on the inside (but not the outside) of a sealed, air-free can of wet food. In the first case, oxygen is the cathodic reactant; in the second it is hydrogen ions (or water). Where the coating is cathodic, porosity enables the exposed substrate to corrode. In most cases, this is detrimental; the exception is found in some multi-layer nickel plus chromium coatings where certain forms of porosity in the chromium layer are harnessed to divert the direction of corrosion to the overall benefit of coating life. In other cases, corrosion at pores causes trouble. In wet atmospheric corrosion, substrate corrosion product, if colored and insoluble, spoils decorative appearance. In immersed conditions or humid atmospheres, if the corrosion product is soluble, intense pore corrosion will perforate sheet metals. Here, a porous coating may accelerate corrosion when compared to the uncoated substrate.

Porosity causes little trouble when corrosion is restricted to dry processes (oxidation). Corrosion products block the pores and stifle the reaction.

There was much research into the causes of porosity in nickel deposits when it was thought to be the main cause of failure in nickel and chromium plates. Much was discounted as it became clear that nickel pitting at discontinuities in the chromium was the factor determining service life. Porosity remains relevant to the corrosion resistance of simpler cathodic coatings, and especially for gold. The use of gold for contact surfacing since around 1950 has revived the importance of studies of porosity. Pores in gold coatings allow films of substrate corrosion product to contaminate the surface and to destroy the low contact resistance of the gold. Sulfides, which are one of the products of corrosion by service atmospheres, have a particularly high rate of spreading over gold in the solid state (Figure 14).

Pores originate on substrate areas known as precursors, which are of at least three types. Firstly, an obvious cause is an inclusion of foreign material which is a semiconductor or insulator – particles of oxide, sulfide, slag, polishing abrasive, etc. When electrodeposition starts, inclusions will not be nucleation sites, and they will impede the lateral growth and coalescence of crystals from neighboring nuclei. Secondly, substrates whose surface grain structure has been severely disturbed by cold working (abrasion, cold rolling, drawing, etc.) have precursors whose physical state (rather than chemical difference as in the first type) precludes coalescence of the electrodeposit. This is probably an effect of pseudomorphic growth. Relatively low-temperature annealing (as low as 210 °C for steel) greatly reduces the effect, and further cold work increases it again (Figure 15). The third type of precursor is a crevice in the substrate. If the depth is great relative to the width, the electric field is excluded and deposition does not occur within the crevice. Lateral growth is impeded once the edges from neighboring nuclei reach it in much the same way as with a nonconducting inclusion. A pore caused by any type of precursor in one

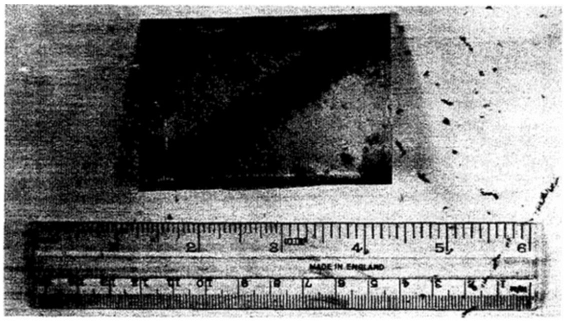


Figure 14 Spread of silver sulphide from discontinuities in gold electrodeposits on silver substrates. The gold was deliberately scratched and the specimen exposed for 24 h to an atmosphere containing 10% SO_2. Immediately after this the sulphide stain extended 0.2 mm. Five years later, the stain extends to about 13 mm, after storage in a normal indoor atmosphere.

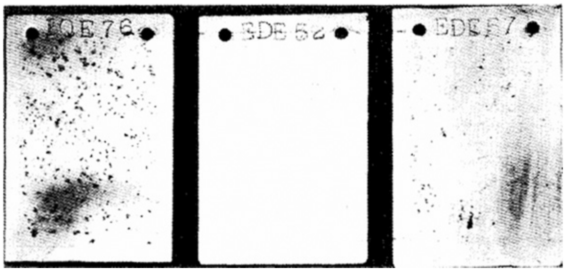


Figure 15 Porosity caused by a cold-worked substrate. Left (EQE 76) cold-rolled steel as received; centre (EDE 52) steel bright-annealed in vacuum before plating, 2.5 h at 700 °C; right, annealed steel, further cold-rolled (0.914 mm to 0.864 mm) produces porosity again. No steel was removed from the surface; 5 mm tin–nickel electrodeposit.

electrodeposit becomes in turn a precursor for a second deposit plated over it. There may be other forms of precursor.

In a particular area of substrate, there will be a number of precursors, distributed over a range of sizes, and reflecting the nature, composition, and history of the metal. In principle, anything affecting the substrate surface will affect porosity in an electroplated coating.

As deposition continues, growth gradually diminishes the surface opening of a pore and, if continued to a sufficient thickness, closes it, leaving a sealed cavity filled with solution. Small precursors will generate pores which seal relatively early, large ones will require greater thicknesses. The total pore density, revealed by a test which renders pore sites visible, falls as thickness increases. The minimum thickness required to seal a precursor of fixed size will depend on the rate of narrowing of the surface opening, and as a growth process, this will reflect the plating conditions. Because of this, the density of pores still open at a fixed thickness is a function of all the plating conditions, that is, the composition of the plating bath, temperature, current density, agitation, and anything affecting deposit growth.

Postplating treatments affect pore density, either by closing pores which are still open or opening sealed ones. It has been asserted that mechanical polishing in general and flow-melting for tin are both processes which could seal pores and reduce porosity. It is also conceivable that polishing might cut-open sealed pores, and likewise under flow-melting conditions, the vaporization of solution trapped in sealed pores could disrupt the coating and recreate discontinuities. The author has come across no convincing demonstration of porosity reduction by either treatment, but has found experimental evidence for porosity increases (Figure 16).[127–139]

Figure 16 Increase in porosity of an electrodeposit caused by mechanical polishing. Left, 7.5 mm unpolished coating; right, polished with lime finishing compound. The average thickness removed by abrasian was 0.1 mm.

4.07.8 Plating from Ionic Liquids

At first, this concept seems to be obvious and indeed the name is not well chosen. It relates to essentially nonaqueous solutions which are conducting and ionic, a field that was formerly referred to as organic or nonaqueous plating. None of these titles are entirely satisfactory.

The need arises from several difficulties with conventional processes:

a. The reactive base metals (e.g., Al, Mg, Ti) cannot be deposited from aqueous solutions.
b. If the base metals can be deposited, inevitably the current efficiency is poor (e.g., Cr).
c. If the substrate is steel, the inefficient production of hydrogen may be disastrous for its mechanical properties.

In the 1960s, the driving force lays with aluminum on the basis that aluminum-coated steel was an ideal combination for many corrosion needs; hot-dipped coatings were limited to thicknesses over ~20 μm. A number of solvents based on alcohols, ethers, and ketones were used which gave poor results with major fire hazards; processes by Philips and Siemens had much publicity but no commercial success. Since 1990, alternative organic solvents based on low melting point (<100 °C) eutectic mixtures have been explored; the eutectic is formed from a metal complex salt such as borofluoride, phosphofluoride, or thicyanate and a methyl or ethyl imidazolinium, pyridinium, or quaternary ammonium (choline) salt. The requirement is that the mixture should be highly conductive, have low viscosity, high metal solubility, and no propensity to absorb water.[140,141]

Research progress has been fairly rapid and all the common metals have been studied with especial concentration on Al, Cr, and Zn and its alloys. The possibility of electroless deposition has also been considered. No commercial operation has been reported yet, probably because while the cathode efficiencies are high, the practical current densities are still rather low: a report on an EU project *IONMET* has stated the challenges succinctly. However, the field must be considered promising for future development.[140–143]

4.07.9 Recent Developments

Although the basic principles of electroplating remain unchanged, the extent of development and variety of application have widened substantially.[144] In this section, some notable developments will be cited.

The development of new solutions and processes continues unabated, driven, as ever, by commercial and proprietorial needs as well as pressure from pollution and effluent control demands and simply for the need to supersede some less-than-satisfactory solutions. Noncyanide solutions are continually being sought for metals such as gold, copper, cadmium, and zinc, but cyanide remains preeminent as the most effective and best understood complexant available and few competitors have been discovered. The other ecological bête-noire is hexavalent chromium, and several commercial bodies offer nontoxic trivalent chromium plating solutions, both aqueous- and organic-based, although only the former is believed to be industrially viable. The solutions are on the basis of chromic sulphate or chloride salts, a complexant such as hypophosphite, glycollate, thiocyanate, etc. and a depolarizing anode reactant which could include ammonium ions or a separated anode compartment. The cathode efficiency is still below 50% and only thin coatings can be reproducibly produced (10 μm max.), but pollution difficulties are largely eliminated. This has proved to be a difficult area, but the number of successes is expected to increase.[145–148]

A separate problem is the establishment of a good process for electroplating aluminum which must necessarily be on the basis of a nonaqueous electrolyte. This field is a history of many discoveries, but few developed processes have been claimed, although recent work suggests that at least two good possibilities exist which may make inroads in the electronics field rather than in the other important area of wide steel strip aluminizing.[149,150]

In his classic treatise, Brenner[2] reported that over 500 alloy electrodeposition systems had then been studied in depth – that number has now been substantially increased – yet barely 10–20 have any real degree of industrial exploitation. The list continues to grow and the present type of work on alloys can be divided into three classes:

1. The development of new alloys in new fields; for example the development of alloys of molybdenum and tungsten with iron, cobalt, or nickel for coating of dies and nozzles, or the development of palladium–nickel alloy as an alternative to gold for connectors.
2. The development of new alloys as a means of modifying existing electrodeposits; for example the production of hard gold alloy by codeposition of copper, cadmium, etc., to yield 23 or 18 carat alloys, or the use of zinc alloys for improved electrogalvanized coatings.
3. The development of new solutions for established alloys; for example, the replacement of fluoborate for lead–zinc brasses.

With industry proving to be so conservative about binary alloys, it is hardly surprising that ternary alloys receive little attention. Nevertheless, two ternary alloys at least have become commercially available: iron–chromium–nickel (so-called stainless steel) for both functional and domestic markets and an electronic connector and solderable alloy based on copper–zinc–tin.

The field of composite materials has been the major growth area of materials engineering in the last twenty years, based mainly on ceramic and polymer materials. While electroplated (and electroless) composites show more modest growth, this is attributable to the necessary limitation of metal matrices. Thus, the principle is to take a well established metal deposition process (gold, cobalt, copper, nickel, tin) and to induce codeposition of second-phase particles, thereby, enhancing coating properties such as hardness, wear, and oxidation resistance. The key to successful codeposition is having particles of appropriate size and density, typically 0.1–10 mm size, suitably suspended in solution by a nonswirling agitation technique, that is, codeposition occurring by physical entrapment or electrophoretic attraction. Such particles include oxides (e.g., Al_2O_3, TiO_2, ZrO_2, etc.) or refractory hard compounds (e.g., Cr_7C_3, WC, Mo_2C, etc.), abrasives such as diamond, lubricants such as MoS_2 or graphite, and low-friction material such as PTFE. A substantial literature exists, relating to both process and product characteristics and reference should be made to two notable reviews.[151,152] Several obvious applications have, to a large extent, been achieved; for example, second-phase hardening by Al_2O_3 of gold without serious loss of electrical conductivity, high temperature erosion or wear resistance of nickel, nickel–cobalt gas turbine, or jet engine alloys improved by using carbide incorporation, and improved surface lubrication of nickel by incorporation of PTFE particles.

The use of current or voltage pulsing during electroplating has long been known to have a beneficial effect on the deposition process rate and on the deposit itself in terms of grain-size variation, internal stress, leveling, etc. Periodic reverse techniques (cycle time of 10–102 s) are widely employed in electrowinning and electrorefining operations while pulse plating (cycle time of 10^{-3} to 1 s), which requires more sophisticated electronics, is now of considerable interest for metal finishing. The basic theory has been discussed by Ibl[153] who has defined the parameters involved. Claims for improved brightening, leveling and throwing power are of especial interest in electronics but are not yet fully substantiated in many instances.[154] The cooperation of industrial and engineering designers with the metal finishers, who are frequently required to perform the near-impossible as a consequence of poor communication, is notoriously bad, largely as a consequence of the nature of subcontract industrial relationships. To meet this need, an important new standard – BS 4479 – has been issued; although it is ostensibly a revision of the old standard, it is in reality a new standard written essentially as a code of practice. Invaluable advice is given to finishers and designers alike: the challenge now is to have it widely read and appreciated!

Increasing awareness of the cost-effectiveness of electroplating processes has led to critical appraisals being made of cell design, not only to improve the product through improved efficiency and economics of the process itself, but also typically through the costs of electricity. Thus the use of more conductive solutions, combined with minimization of the anode–cathode spacing can yield a 40% saving in electrical power. However, not all of this saving is necessarily desirable if chemical costs, thereby, increase and the peripheral cost of solution heating has also to be increased. Similarly, improved agitation and filtration may also be considered for optimization studies. This 'chemical engineering' approach has found increasing value,[155–159] not least in the development of new types of plating cell specifically for metal recovery from trade effluent, dragouts, and rinses.[160–162] In fact, the number of new designs far outnumbers the number of optimizing and independent assessment studies so that it is not possible to name a 'best-buy,' and time is needed for commercial realities to eventually declare a winner, albeit not on entirely objective terms.

The largest-scale electroplating activities have always been carried out by the steel industry in an atmosphere largely divorced from traditional metal finishing. Upwards of 20% of all steel produced may be coated, the products of relevance to this chapter being tinplate, its alternative for packaging 'tin-free steel,' and zinc electrogalvanized steel in the form of sheet, strip, and wire. During the last twenty years, little advance has been made in the electroplating stage of tinplate production, the electrolytes and additives have changed little, and the plant design remains essentially the same – marked changes have occurred in other aspects of tinplate production, however. The alternative 'tin-free steel' or TFS, has settled into a well established sector of the market, largely for lacquered beer and beverage cans and noncritical container applications such as oil, polish, some paints, etc. Its invention is attributed to Japan in the period 1958–1965, and it has been widely exploited. The technology is on the basis of that of tinplate, as a fast cathodic process (1–20 s) in a chromic acid-based solution yielding a coating (<0.1 mm) consisting of chromium metal and chromium oxide, Cr_2O_3.[163,164] Its virtue is cost-effectiveness for every specific application, and as such, it has replaced tinplate for 10–40% of the market, depending upon the country concerned.

By contrast, the zinc coating product area is seeing rapid developments after a relatively static period when hot-dipped and electrogalvanized products occupied well defined niches for thick (20–150 µm) and thin (5–20 µm) coatings, respectively. The driving force can be found in the automotive industry which is looking towards car bodies having 5–10-year warranties for which paint and phosphating treatments on steel sheet are inadequate. Two separate types of coated product are emerging. First, electrogalvanizing combined with a modified TFS process giving a highly passivated zinc coating: this is probably the cheapest and easiest option.[165] Second, alloyed zinc electrogalvanizing to give improved sacrificial corrosion performance whilst remaining relatively thin (<15 µm), a requirement imposed by the body-forming processes. To this end, the zinc alloys favored are those with nickel, iron, manganese, or tin at 0.5–10% levels.[166] It is too early to predict which alloy will dominate the field.

References

1. Blum, W.; Hogaboom, G. B. *Principles of Electroplating and Electroforming*; McGraw-Hill: New York, 1949.
2. Brenner, A. *The Electrodeposition of Alloys*; Academic Press: New York, 1963.
3. Dennis, J. K.; Such, T. E. *Nickel and Chromium Plating*; Newnes-Butterworths: London, 1972.
4. Graham, A. K.; Pinkerton, H. L. Eds. *Electroplating Engineering Handbook*; Reinhold: New York, 1956.
5. Lowenheim, F. A. Ed. *Modern Electroplating*; Wiley: New York, 1974.
6. Raub, E.; Müller, K. *Fundamentals of Metal Deposition*; Elsevier: Amsterdam, 1967.
7. Vagramyan, A. T.; Soloveva, Z. A. *Technology of Electrodeposition*; Robert Draper: Teddington, 1961.
8. Barclay, W. R. *J. Electrodepositors’ Tech. Soc.* **1937**, *12*, 169.
9. Brugnatelli, L. *Ann. Chim. (Pavia).* **1800**, *18*, 152. (Silver).
10. Dubpernell, G. *Plating* **1960**, *47*, 35. (History of chromium plating).
11. Dubpernell, G. *Plating* **1959**, *46*, 599. (History of nickel plating).
12. Durose, A. H. *Plating* **1970**, *57*, 793. (USA developments).
13. Elkington, G. R.; Elkington, H. U.K. Patent 8 447, March 1840.
14. Passal, F. *Plating* **1959**, *46*, 629. (Copper).
15. Smee, A. *Elements of Electrometallurgy*, 2nd ed.; Longmans Green: London, 1843.
16. Wormwell, R. *Electricity in the Service of Man*; Cassell: London, 1897.
17. Edwards, J.; Swanson, C. J. *J. Electrodepositors’ Tech. Soc.* **1953**, *29*, 290.
18. Graham, A. K. *Trans. Inst. Met. Fin.* **1954**, *31*, 259.
19. Meyer, W. R. *Trans. Inst. Met. Fin.* **1954**, *31*, 290.
20. Moreley, E. *Trans. Inst. Met. Fin.* **1956**, *33*, 102.
21. Westman, A. E. R.; Mohrnheim, F. A. *Plating* **1955**, *42*, 154, 281, 417.
22. Beacom, S. E. *Plating* **1969**, *56*, 129.
23. Hepfer, I. C.; Hampel, K. R.; Vollmer, T. L.; Boehm, D. R. *Plating* **1971**, *58*, 333.
24. Jostan, J. L.; Bogenschutz, A. F. *Plating* **1969**, *56*, 399.
25. Logi, G. R.; Rantell, A. *Trans. Inst. Met. Fin.* **1968**, *46*, 91.
26. Murphy, N. F.; Swansey, E. F. *Plating* **1971**, *58*, 583.
27. Perrins, L. E. *Trans. Inst. Met. Fin.* **1972**, *50*, 38.
28. Prince, D. E. *Plating* **1971**, *58*, 588.
29. Rantell, A. *Trans. Inst. Met. Fin.* **1969**, *47*, 197.
30. Saubestre, E. B. *Trans. Inst., Met. Fin.* **1969**, *47*, 228.
31. Saubestre, E. B.; Khera, R. P. *Plating* **1971**, *58*, 464.
32. Woldt, G. *Trans. Inst. Met. Fin.* **1969**, *47*, 236.
33. Moore, A. J. W. *J. Electrodepositors’ Tech. Soc.* **1952**, *28*, 117.
34. Pinner, W. L. *Proc. Amer. Electroplater’s Soc.* **1953**, *40*, 83.
35. Raub, E.; Mietka, M.; Beeskow, H. *Metalloberfläche* **1959**, *13*, B153.
36. Samuels, L. E. *Electroplat. Met. Fin.* **1959**, *11*, 130.
37. Samuels, L. E. *J. Inst. Met.* **1956**, *85*, 177.
38. Samuels, L. E. *Plating* **1961**, *48*, 46.
39. Research Report No. 38, American Electroplaters’ Society, 1958.
40. Research Report No. 39, American Electroplaters’ Society, 1959.
41. Fleischmann, M.; Thirsk, H. R. In *Advances in Electrochemistry and Electrochemical Engineering;* Delahay, P., Tobias, C. W., Eds.; Interscience: New York, 1963; Vol. 3, ch. 3.
42. Vetter, K. J. *Electrochemical Kinetics*, English edn.; Academic Press: New York, 1967.
43. Bockris, J. O. M.; Razumney, G. A. *Fundamental Aspects of Electrocrystallisation*; Plenum Press, 1967.
44. Eisenberg, D.; Kauzmann, W. *The Structure and Properties of Water*; Oxford University Press, 1969.
45. Lyons, E. H. In *The Chemistry of Co-ordination Compounds*; Bailar, J. C., Ed.; Reinhold: New York, 1956.
46. Edwards, J. *Trans. Inst. Met. Fin.* **1964**, *41*, 169.
47. Kendrick, R. J. *Plating* **1961**, *48*, 1099.
48. Saubestre, E. B. *Plating* **1958**, *45*, 927.
49. Saubestre, E. B. *Plating* **1958**, *45*, 1219.
50. Hardisty, D. W. *Plating* **1969**, *56*, 705.
51. Knapp, B. B. *Plating* **1971**, *58*, 1187.
52. Gabe, D. R. *Met. Fin. J.* **1971**, *7*(11), 276–282.
53. Gabe, D. R. In *Oxides and Oxide Films*; Vijh, A. K., Ed.; Dekker: New York, 1981; Vol. 6, pp 147–250.
54. Gabe, D. R.; Cobley, A. *Trans IMF.* **2002**, *80*, B13–B16.
55. Gabe, D. R.; Cobley, A. J. *Circuit World* **2006**, *32*(3), 3–10.
56. Bailey, G. L. J. *J. Electrodepositors’ Tech. Soc.* **1951**, *27*, 233.
57. Beyer, S. J. *Plating* **1969**, *56*, 257.
58. Longkind, J. C. *Trans. Inst. Met. Fin.* **1967**, *45*, 155.
59. Vandenberg, R. V. *Trans. Inst. Met. Fin.* **1967**, *45*, 161.
60. West, E. G. *J. Electrodepositors’ Tech. Soc.* **1946**, *21*, 211.
61. Wyszynski, A. E. *Trans. Inst. Met. Fin.* **1967**, *45*, 147.
62. Cobley, A. J.; Gabe, D. R. *Circuit World* **2001**, *27*(3), 19–25.
63. Gabe, D. R. *Trans IMF* **2003**, *81*, 7–12.
64. Gabe, D. R. *Trans IMF* **2006**, *84*, 67–78.
65. Puippe, J. Cl.; Leaman, F. *Theory and Practice of Pulse Plating*; Amer. Electropl. Surf. Fin.: Orlando, FL, 1986.
66. Brenner, A.; Zentner, V.; Jennings, C. W. *Plating* **1952**, *39*, 865.
67. Clarke, M.; Chakrabarty, A. M. *Trans. Inst. Met. Fin.* **1970**, *48*, 124.
68. Fischer, H. *Elektrolytische Abscheidung und Elektrokristallisation von Metallen*; Springer-Verlag: Berlin, 1954.
69. Weil, R. *Met. Fin.* **1955**, *53*(11), 60. *53*(12), 60.
70. Wilman, H. *Trans. Inst. Met. Fin.* **1955**, *32*, 281.
71. Avila, A. J.; Brown, M. J. *Plating* **1970**, *57*, 1105.
72. Baeyens, P. A. *Trans. Inst. Met. Fin.* **1954**, *31*, 429.
73. Beckmann, M. E.; Maass-Craefe, F. *Metalloberfläche.* **1951**, *5*, A161.
74. Crossley, J. A.; Kendrick, R. J.; Mitchell, W. I. *Trans. Inst. Met. Fin.* **1967**, *45*, 59.
75. Davies, G. R. *Trans. Inst. Met. Fin.* **1973**, *51*, 47.
76. Hicklin, A.; Rothbaum, H. P. *Trans. Inst. Met. Fin.* **1957**, *34*, 53. 199.
77. Jernstedt, G. W. U.S. Patents 2,451,340 and 2,451,341 1948.
78. Kendrick, R. J. *Trans. Inst. Met. Fin.* **1966**, *44*, 78.
79. Vagramyan, A. T.; Soloveva, Z. A. *Technology of Electrodeposition*; Robert Draper: Teddington, 1961. ch. 3.
80. Wernlund, C. J. U.S. Patent 2,701,234 1955.
81. Geissmann, W.; Carlson, R. *Proc. Am. Electroplaters’ Soc.* **1952**, *39*, 153.
82. Nanis, L. *Plating* **1971**, *58*, 805.
83. Rasmerova, N. J. *J. Electrodepositors’ Tech. Soc.*; **1937**, 13. paper 11.
84. Clarke, M. *Chem. Indust.* **1970**, 329.
85. Clarke, M. *Trans. Inst. Met. Fin.* **1968**, *46*, 201.
86. Clarke, M.; Ashburn, R. J. *Trans. Inst. Met. Fin.* **1969**, *47*, 18.

87. Clarke, M.; Kieszkowski, M. *Trans. Inst. Met. Fin.* **1974**, *52*, 79.
88. Clarke, M.; Zaya, P. *Trans. Inst. Met. Fin.* **1972**, *50*, 54.
89. Soderberg, K. G. *Proc. Amer. Electroplaters' Soc.* **1936**, *24*, 233.
90. Tallmadge, J. A.; Buffam, B. A. *J. Water Pollution Control Fed.* **1961**, *33*, 817.
91. Tallmadge, J. A.; Mattson, R. A. *J. Water Pollution Control Fed.* **1962**, *34*, 723.
92. Tallmadge, J. A.; Barbolini, R. R. *J. Water Pollution Control Fed.* **1966**, *38*, 1461.
93. Walker, C. A.; Tallmadge, J. A. *Chem. Eng. Prog.* **1959**, *55*(3), 73.
94. Hoare, W. E. *Tinplate Handbook*; Tin Research Institute: Greenford, various editions, 1950, 1956, 1965.
95. Jenkins, H. A. H.; Freeman, D. B. *Trans. Inst. Met. Fin.* **1964**, *42*, 163.
96. Raub, E.; Müller, K. *Fundamentals of Metal Deposition*; Elsevier: Amsterdam, 1967. Section 5.6.
97. Thwaites, C. J. *The Flow Melting of Electrodeposited Tin Coatings*; Tin Research Institute: Greenford, 1956.
98. Agar, J. N.; Hoar, T. P. *Disc. Faraday Soc.* **1947**, *1*, 162.
99. Clarke, M.; Bernie, J. A. *Electrochem. Acta.* **1967**, *12*, 205.
100. Field, S. *Metal. Ind. (London)* **1934**, *33*, 564.
101. Garmon, L. B.; Leidheiser, H. *Plating* **1961**, *48*, 1003.
102. Leffler, E. B.; Leidheiser, H. *Plating* **1957**, *44*, 388.
103. Wagner, C. *J. Electrochem. Soc.* **1951**, *98*, 116.
104. Wagner, C. *Plating* **1961**, *48*, 997.
105. Watson, S. A. *Trans. Inst. Met. Fin.* **1960**, *37*, 28.
106. de Bruijn, W. *J. Electrodepositors' Tech. Soc.* **1951**, *27*, 1.
107. Layton, D. N. *Design for Electroplating*; International Nickel Co.: London, BS4479, 1991.
108. Leadbeater, C. J. *J. Electrodepositors' Tech. Soc.* **1944**, *19*, 35.
109. Tope, N. A. *J. Electrodepositors' Tech. Soc.* **1947**, *22*, 29.
110. *Design for Metal Finishing*; Institute of Metal Finishing: London, 1960.
111. MacNaughtan, D. J.; Hothersall, A. W. *Trans. Faraday Soc.* **1935**, *31*, 1168.
112. MacNaughtan, D. J.; Gardam, G. E.; Hammond, R. A. F. *Trans. Faraday Soc.* **1935**, *31*, 729.
113. Mohrnheim, A. F. *J. Electrochem. Soc.* **1970**, *117*, 833.
114. O'Sullivan, J. B. *Trans. Faraday Soc.* **1930**, *26*, 89.
115. Schlotter, M. *Trans. Faraday Soc.* **1935**, *31*, 1177.
116. Dennis, J. K.; Such, T. E. *Nickel and Chromium Plating*; Butterworths: London, 1972.
117. Kendrick, R. J. *Trans. Inst. Met. Fin.* **1963**, *40*, 19.
118. Walker, R. *Internal Stress in Electrodeposited Metal Coatings*; Industrial Newspapers: London, 1968.
119. Watson, S. A. *Trans. Inst. Met. Fin.* **1963**, *40*, 41.
120. Weil, R. *Plating* **1970**, *57*, 1231; **1971**, *58*, 50; **1971**, *58*, 137. Review and Bibliography.
121. Angus, H. C. *Trans. Inst. Met. Fin.* **1962**, *39*, 20; **1965**, *43*, 135; **1966**, *44*, 41.
122. Antler, M. In *Proceedings of the 6th International Conference on Electr. Contact Phenomenon*, Chicago 1972.
123. Fairweather, A. *Proc. Inst. Elec. Eng.* **1953**, *100A*, 174.
124. *Nickel Plating*; International Nickel Co.: London, 1963.
125. Britton, S. C.; Clarke, M. *Trans. Inst. Met. Fin.* **1959**, *36*, 230.
126. Clarke, M.; Britton, S. C. *Trans. Inst. Met. Fin.* **1963**, *40*, 205.
127. Berdick, M.; Lux, G. A. *Proc. Am. Electroplaters' Soc.* **1942**, *30*, 19.
128. Britton, S. C.; Clarke, M. In *Proceedings of the 3rd European Corrosion Congress*, 1963.
129. Clarke, M. *Trans. Inst. Met. Fin.* **1973**, *51*, 150.
130. Clarke, M.; Britton, S. C. *Trans. Inst. Met. Fin.* **1959**, *36*, 58; **1960**, *37*, 110, 230.
131. Clarke, M.; Chakrabarty, A. M. *Trans. Inst. Met. Fin.* **1970**, *48*, 99; **1972**, *50*, 11.
132. Clarke, M.; Leeds, J. *Trans. Inst. Met. Fin.* **1965**, *43*, 50; **1968**, *46*, 1, 81; **1969**, *47*, 163.
133. Clarke, M.; Sansum, A. J. *Trans. Inst. Met. Fin.* **1972**, *50*, 211.
134. Evans, U. R.; Shome, S. C. *J. Electrodepositors' Tech. Soc.* **1950**, *26*, 137.
135. Frant, M. S. *J. Electrochem. Soc.* **1960**, *107*, 1009.
136. Hothersall, A. W.; Hammond, R. A. F. *Trans. Electrochem. Soc.* **1938**, *73*, 449.
137. Jones, M. H.; *et al. Proc. Am. Electroplaters' Soc.* **1957**, *44*, 53; **1958**, *45*, 45; **1959**, *46*, 113.
138. Shome, S. C.; Evans, U. R. *J. Electrodepositors' Tech. Soc.* **1951**, *27*, 129.
139. Clarke, M.; Subramanian, R. *Trans. Inst. Met. Fin.* **1974**, *52*, 48.
140. Wasserscheid, P.; Walton, T. *Ionic Liquids in Synthesis*, 2nd ed.; Wiley-VCH: Weinheim, 2008.
141. Ohno, H. Ed. *Electrochemical Aspects of Ionic Liquids*; Wiley: New York, 2005.
142. Abbott, A. P.; Ryder, K. S.; König, U. *Trans. Inst. Met. Fin.* **2008**, *86*, 106.
143. König, U.; Sessler, B. *Trans. Inst. Met. Fin.* **2008**, *86*, 183.
144. Romankiw, L. T.; Turner, D. R. Eds. Proceedings of the Electrochemical Society, USA, **1987**; pp 87–17.
145. Crowther, J. C.; Renton, S. *Electropl. Met. Fin.* **1975**, *28*(5), 6.
146. Lyde, D. M. *Prod. Fin. (London)* **1978**, *31*(9), 14.
147. Hoare, J. P. *J. Electrochem. Soc.* **1979**, *126*, 190.
148. Smart, D.; Such, T. E.; Wake, S. J. *Trans. Inst. Met. Fin.* **1983**, *63*, 104.
149. Daene, T.; van der Berg, J.; Dijk, G. V. *Trans. Inst. Met. Fin.* **1985**, *63*, 104.
150. Birkle, S.; Gehring, I.; Stoger, K.; Vries, H. *Metallurgy* **1982**, *36*, 673.
151. Celis, J. P.; Roos, J. R. *Rev. Coat. Corros.* **1982**, *5*, 1.
152. Simon, H.; Thoma, M. *Angewandt Oberflachentechnik fur metallische Werkstoffe*; Carl Hanser: Munich, 1985.
153. Ibl, N. *Surf. Technol.* **1980**, *10*, 81.
154. Puippe, J. C.; Leamon, F. *Theory and Practice of Pulse Plating*; Amer. Electropl. Soc.: Orlando, FL, 1986.
155. Newman, J. S. *Electrochemical Reactor Design*; Prentice-Hall: New Jersey, 1973.
156. Pickett, D. J. *Electrochemical Reactor Design*, 2nd ed.; Elsevier: Amsterdam, 1979.
157. Coeuret, F.; Storck, A. *Elements de genie electrochimique*; Lavoisier: Paris, 1984.
158. Snyder, D. D.; Landau, U.; Sard, R. In *Proceedings of the Electrochemical Society*, Pennington, USA, **1983**; pp 83–112.
159. White, R. E. Ed. *Electrochemical Cell Design*; Plenum Press: New York, 1984.
160. Gabe, D. R. *I. Chem. E. Symp. Ser.* **1983**, *77*, 291.
161. Gabe, D. R.; Makanjuola, P. A. *I. Chem. E. Symp. Ser.* **1986**, *96*, 221.
162. Marshall, R. J.; Walsh, F. C. *Surf. Technol.* **1985**, *24*, 45.
163. Fukuda, N., *et al. J. Electrochem. Soc.* **1986**, *116*, 398.
164. Yonezaki, S. *Sheet Metal Ind.* **1971**, *48*(1), 25.
165. Memmi, M.; Bruno, R.; Palladino, M. *Mat. Perform.* **1983**, *22*(2), 9.
166. Sard, R. *Plating Surf. Fin.* **1987**, *74*(2), 30.

4.08 Sprayed Coatings

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Abbreviations

APS	Atmospheric plasma spraying
CAPS	Controlled atmosphere plasma spraying
CGDS	Cold gas dynamic spraying
D-Gun	Detonation gun
ESD	Electrostatic spray deposition
HPPS	High-pressure plasma spraying
HVAF	High-velocity air fuel
HVLP	High-volume low pressure
HVOF	High-velocity oxy-fuel
HVOLF	High-velocity oxy-liquid-fuel
HVSFS	High-velocity suspension flame spraying
IPS	Inert plasma spraying
LPPS	Low-pressure plasma spraying
PTA	Plasma-transferred arc
RF	Radio frequency
RFS	Reactive flame spraying
SPS	Shrouded plasma spraying
TBC	Thermal barrier coating
VPS	Vacuum plasma spraying
YSZ	Yttria stablized zirconia

4.08.1 Coating Deposition Techniques

4.08.1.1 Nonthermal Spray Deposition Techniques

4.08.1.1.1 Air spraying

Paints, including inorganic paints, may be deposited by a variety of spray guns. Air spraying has also been used to deposit conversion coatings.[1] Air spray guns are simple devices that operate in atmospheric conditions, though they may be housed in a spray booth to contain fumes and paint spray. Air spray guns are based on venturis. A stream of high-velocity gas is passed through a tube connected to the paint reservoir. The high velocity of the gas lowers the pressure in the venturi and this draws paint from the reservoir and atomizes it. The paint droplets are then propelled toward the substrate by the gas flow. Paint spray guns can be gravity fed or pumped. The high-velocity gas stream is usually compressed air.

High-volume low-pressure (HVLP) spraying is an air spraying variant, which uses a lower-pressure gas supply. The advantage of HVLP is that the deposition efficiency is increased to ~65% compared with something in the region of 30% for standard air spraying. The deposition efficiency can be further improved by using low-volume low-pressure air spraying; however, the coverage rate is decreased.

4.08.1.1.1.1 Variants of air spraying

Airless spraying is achieved by using a high-pressure pump to force paint through a spray gun. The advantages of this technique are that uniform thick coats of paint are produced, reducing the number of times an area must be coated. The high pressure also increases the penetration of the paint into surface features such as crevices. Spin spraying is a hybrid process combining spray coating with spin coating.[2] Spray pyrolysis is another hybrid process; a liquid precursor is deposited by air spraying and the coated substrate is then heated to induce pyrolysis.[3]

4.08.1.1.2 Electrostatic spray deposition

In electrostatic spray deposition (ESD), the deposition efficiency is improved by the use of an applied potential difference between the spray nozzle and the substrate. A liquid feedstock is atomized and charged by being pumped through the nozzle. The electrostatic field between the nozzle and the substrate accelerates the charged droplets toward the substrate.[4] Functional ceramic thin films are one type of coating that has been produced using ESD.[5]

4.08.2 Thermal Spraying: An Overview

The overall technology of thermal spraying is now a century old. A whole list of thermal spraying variants is now currently used in industry, with further developments constantly being made. Dedicated professional and academic societies such as the International Thermal Spray Association, the ASM Thermal Spray Society, and Japan Thermal Spray Society actively disseminate research results and good practice. There is a high degree of research activity in the area: a brief search of the scientific literature shows that 967 thermal spray papers and patents were published in 2007, as against 624 in 2000, 442 in 1990, and 78 in 1980.

Despite the proliferation of thermal spray variants, the coatings produced in each case share many common features and would all be recognized as thermal spray coatings by Max Ulrich Schoop, the Swiss inventor of thermal spraying, who first established the technology around the beginning of the twentieth century.

In all thermal spray technologies, particles of the coating material are propelled toward the substrate. On impact, the particles deform and adhere to the substrate primarily by mechanical interlocking.

The differences between the various thermal spraying techniques are primarily in the details of how the particles are propelled toward the substrate. Different methods of propulsion result in the particles experiencing different temperatures and velocities while in flight between the spray gun and the substrate. Depending on the process used, particles arrive at the substrate in solid, molten, or partially molten form. Additional variations on the thermal spray theme are created by the form of the feedstock coating material: powder, wire, or molten metal; the use of additional processes to produce hybrid processes such as laser-assisted thermal spraying; the atmosphere in which the spraying is carried out: vacuum or atmospheric.

Thermal spray coatings have a distinctive lamellar microstructure due to the formation of the coating from individual deformed particles, frequently referred to as splats. Porosity is an important issue in thermal spray coatings. Insufficient particle deformation on impact can create intersplat pores. For particles which arrive partially or completely molten, solidification shrinkage can add to porosity. Oxides may also be present in thermally sprayed coatings, which is a particular issue for metallic corrosion-resistant coatings, as in-flight oxidation of particles can result in discontinuous and hence nonprotective oxides in the coating. Another characteristic of as-sprayed thermally sprayed coatings is the distinct substrate–coating interface. In metallic coatings on metallic substrates, this interface is frequently strengthened and simultaneously made more diffusive by a diffusion heat treatment.

Thermal spraying techniques which induce extensive melting, including plasma spraying, flame spraying, and arc spraying suffer from high residual stresses. These limit the thickness of the coating that will remain adhered to the substrate.

4.08.3 Thermal Spraying: Variants

The following table gives an overview of the typical key features of the main thermal spraying variants. Further details of each process are given in the following text (**Table 1**).

4.08.3.1 Flame Spraying

Flame spraying is the original thermal spraying process used by the first thermal sprayer, Max Ulrich Schoop. Approximately 100 years later, the technique is still in widespread use. Metals, alloys, ceramic,[8] and polymer coatings may all be formed by flame spraying.[7]

A flame spraying torch is relatively simple, consisting of a flame combined with a system that introduces the feedstock coaxially with the flame. A fuel gas–oxygen mixture is combusted to produce the flame: oxyacetylene is typically used. The feedstock material, which may be in the form of powder, wire, or rod, is continuously fed into the flame and melted. For wire and rod feedstock, the melted material is broken into discrete particles by jets of compressed air. This is not required when a powder feedstock is used. The molten particles are accelerated toward the substrate by the expanding gas flow from the flame, additional acceleration coming from the compressed air jets if present.[7] Spray distances are typically 120–250 mm.[6]

The type of feedstock used can affect the properties of the final coating. The atomization of molten rod or wire tends to generate finer particles than are found in powder feedstock. The resultant coatings are generally found to be smoother and denser than those formed using powder. The increased smoothness simply results from the finer droplet, and hence splat, size. The effect on density is largely due to the greater degree of melting, which is achieved for rods and wires, as their positioning in the flame can be controlled more precisely than for powder feedstocks.[7]

In addition to atomizing the molten feedstock and providing some acceleration of the sprayed particles, compressed air jets can be used to modify the shape, and hence temperature and flow characteristics of the flame.[7]

The flame may also be controlled by modifying the fuel–oxygen ratio. The highest flame temperatures are achieved when a stoichiometric fuel–oxygen mixture is used. Excess fuel or oxygen will cool the flame simply due to the introduction of a noncombusting material. Fuel-rich mixture is used when spraying metallic coatings, which results in a reducing environment in the flame and hence minimizes in-flight oxidation.

Flame spraying is a low-cost thermal spraying technique. Interfacial bond strengths achievable by flame spraying are generally lower than those of

Table 1 Characteristics of the different thermal spray techniques

Spraying process	*Materials that can be sprayed*	*Powder size (μm)*	*Particle velocities (m s^{-1})*	*Deposition rates (m^2 h^{-1})*	*Interfacial bond strength (MPa)*	*Coating porosity (%)*
Flame	Metals, alloys, ceramics, polymers (with specialist torches)[6]	5–100[6]	50–100[7]	1–23[6]	30 (metals and alloys)[6]	10–20[6]
Wire arc	Metals, alloys, cermets[6]	Wire size 1.6–5 mm[6]	50–150[6,7]	50–1000 g min^{-1}[6]	10–70[6,7]	10–20[6]
Plasma	Metal, alloys, ceramics[6]	20–90[6]	200–800[7]		70 (metals and alloys)[6]	1–10[6,7]
Vacuum/low pressure plasma	Metals, alloys	5–20[6]	200–600[7]		>80[6]	1–10[6,7]
Detonation gun	Carbide reinforced composites[6]	5–60[6]	800[7]		70–83[6]	0.5–2[6]
HVOF	Metals, alloys, cermets, ceramics	5–45[6]	200–1000[7]		68–90[6,7]	1–5[6,7]
Cold spray	Metals, alloys, cermets[6]	5–20[6]	600[6]		26–62[6]	3–5[6]

other thermal spraying variants.[9] Reproducibility issues are a concern for all thermal spraying methods, but have been reported as being a particular issue for flame-sprayed coatings.[10]

4.08.3.1.1 Variants of flame spraying

High-velocity suspension flame spraying (HVSFS) is a recent development of flame spraying. The key advantage is that very fine powders can be sprayed. Fine powders are normally very difficult to thermally spray, since they do not flow easily. Forming a liquid suspension enables fine powders to be handled in a controlled manner. Once the suspension feedstock is injected into the flame, the liquid is evaporated or burnt off leaving the fine powder in the flame to be heated and accelerated as in any other thermal spray process. The technique is still at a very early stage and the process needs to be optimized; however, demonstration such as the deposition of ~50-μm thick $CaO–ZrO_2–SiO_2$ indicates that this technique has great potential for corrosion applications.[11]

Reactive flame spraying (RFS) is another process that has been developed from flame spraying. RFS combines flame spraying with self-propagating high temperature synthesis to give a single process in which the feedstock material is both produced and deposited.[12] Clearly, this technique is suitable only for materials that can be formed by self-propagating high temperature synthesis: TiC–Fe cermet coatings[12] have been successfully formed by this method. The advantage is that the reaction products are fine scaled; the overall process is low in cost and the energy released by the exothermic reaction acts as an additional heat source.[12]

Flame spraying can be combined with an induction heating postprocessing step to improve corrosion performance by fusing the coating, thereby decreasing porosity and increasing the effectiveness of the coating as a barrier.[13] This has been demonstrated on nickel-based self-fluxing alloys used to protect furnace wall tubes in Taiwanese waste incineration plants.[13]

There are numerous corrosion protection applications for flame-sprayed zinc and aluminum.[9] Flame-sprayed zinc is generally used to protect structural steelwork, and aluminum is used in more demanding applications.[9] Flame-sprayed Zn/15Al can provide cathodic protection to steel substrates.[14] $SiO_2–Al_2O_3–Y_2O_3$ glasses have been deposited by flame spraying as candidate corrosion-resistant coatings for engine applications.[15]

4.08.3.2 Wire Arc Spraying

Wire arc spraying is also known as electric arc spraying or arc spraying. In this spraying process, the coating feedstock is a pair of metallic wires, between which an electric arc is struck. The arc melts the ends of the wires; the molten material is then atomized and accelerated toward the substrate by a jet of compressed air.[9] Materials that can be arc sprayed must be electrically conductive, and hence the technique is generally used for metals. Arc spraying is often used to deposit aluminum coatings for anticorrosion applications in the marine and petrochemical industries.[9]

The thermal efficiency of wire arc spraying is greater than that of other thermal spray processes, since the feedstock material is directly heated by the arc.[7] Heating occurs only at the ends of the wires where the arc forms. As soon as the atomized droplets of molten material start to be propelled toward the substrate, they start to cool.[7] Unlike other thermal spray processes, there is no in-flight heating in wire arc spraying, since the droplets are propelled by an air jet as opposed to any kind of flame. Relatively short spray distances of 50–170 mm are used to minimize the in-flight oxidation.[6,7]

Another consequence of the highly localized heating is that the heat input to the substrate is low, primarily because there is no hot gas or plasma jet directed at the substrate.[7] Hence, wire arc spraying can be used to form coatings on materials such as polymers that would not withstand the heat input from other thermal spray processes.[7]

The electric arc must be stable for the spraying process itself to be stable and proceed in a uniform manner.[7] This means that the positioning of the ends of the wires is very important; both the absolute position and feed rate must be accurately controlled in order to maintain a stable arc.[7] The straightness of the wires is therefore significantly more important in wire arc spraying than it is in other wire feedstock thermal spray methods. Wire arc spraying is well suited to high-rate deposition, and hence is used for coating large steel structures including bridges and storage tanks.[7]

4.08.3.2.1 Variants of wire arc spraying

Shrouded arc spraying is a variant of wire arc spraying where an inert gas is used to isolate the sprayed droplets from the surrounding environment, thereby minimizing in-flight oxidation.

4.08.3.3 Plasma Spraying

Plasma spraying produces denser and more adherent coatings than does flame spraying.[15] The increased complexity of the spray gun, the power consumption, the requirements of water cooling, and regular electrode replacement as well as the cost of process gases all combine to make plasma spraying costlier than flame spraying.

In plasma spraying, a plasma torch is used to heat and accelerate the feedstock material. The plasma temperature is very high, in the region of 10 000 K. The flame is capable of melting any material, and consequently, plasma spraying is frequently used to deposit coatings of otherwise difficult-to-melt materials such as zirconia, which are hard to deposit using other thermal spray methods.

The plasma spray gun consists of a central cathode, around which the process gases flow to exit through the anode, which forms the nozzle at the end of the gun. The central cathode is made from thoriated tungsten, as it not only has a high melting point but is also a good thermionic emitter, meaning that it easily releases the electrons required to maintain the arc.[7] The addition of thoria enhances the arc initiation process. The anode is copper, chosen for its high thermal and electrical conductivity, and must be water cooled.

The plasma is generated by a high-voltage discharge between the cathode and the anode. This discharge ionizes the gas between the cathode and the anode, forming a conductive path, which allows an arc to form. The arc heats the gas to temperatures that may exceed 10 000 K. Due to the very high temperatures created, the gas ionizes to form a plasma. The plasma then expands through the nozzle of the gun, creating a plasma jet, which heats and accelerates any feedstock material injected into it.

A variety of gases may be used to form the plasma. Argon and helium have low enthalpies of ionization; hence it is relatively easy to form a plasma from these gases.[7] An additional benefit of argon is its high atomic mass, which helps to stabilize the arc.[7,16] Nitrogen and hydrogen may also be used, despite their larger enthalpies of ionization, since they improve heat transfer from the plasma to the coating particles.[6] Gas viscosity also needs to be considered: higher gas viscosity reduces the mixing of the plasma with the surrounding air.[10,16] This is advantageous as the hot core of the plasma jet is maintained over a longer distance, improving heat and momentum transfer. In the temperature range of interest, that is, 10 000 K and above, argon and helium have high viscosities.[16] Taking these factors into consideration, the gases and gas mixtures used are typically argon, argon–helium, argon–hydrogen, argon–nitrogen, and nitrogen–hydrogen.[6,7] Three gas mixtures of argon–helium–hydrogen and argon–helium–nitrogen have also been used,[7,10,17] an argon–helium–hydrogen mixture being commercially available.[6]

Electrode erosion is an important issue in plasma spraying. A combination of high temperatures and the intense arc means that the electrodes are operating in extreme conditions and consequently need to be periodically replaced. The erosion of the anode is more severe than the erosion of the cathode, resulting in anodes being replaced two to five times more often than cathodes.[7] Electrode lifetimes depend on the operating conditions, but are typically in the range of tens to hundreds of hours.[7] The heat flux in the regions where the arc terminates at each electrode can be in the region of $10^8\,\mathrm{W\,m^{-1}}$.[7] The resulting electrode deterioration can result in the failure of the spray gun and can lead to coating contamination by fragments of the electrodes.[7]

Electrode erosion is most severe when a single arc is struck consistently in the same place. Two approaches have been used to minimize electrode erosion: vortex stabilization and multielectrode guns. Vortex stabilization ensures that the anodic arc root is constantly moving over the anode surface. This is achieved by simply ensuring that the plasma-forming gases have a vortex flow.[7] An alternative is the use of multielectrode guns. Instead of having a single arc, these guns have multiple arcs, each carrying a fraction of the current, and thus decreasing the damaging heat flux at the arc root.[10,18]

4.08.3.3.1 Variants of plasma spraying

The mixing of the plasma jet with surrounding air during air plasma spraying can result in in-flight oxidation of metallic particles.[7] This is generally undesirable, and therefore, several plasma spraying variants have been developed to ensure lower levels of oxidation.

Shrouded plasma spraying (SPS) uses an inert gas to surround the plasma jet in an effort to separate it from the surrounding atmosphere.[7] This can be achieved by simply flooding the area between the nozzle and the substrate with a blanket of inert gas, usually argon or nitrogen.[7,19] The disadvantage of this approach to shrouding is that large volumes of inert gas are used.[7] An alternative that results in a lower usage rate of inert gas is to surround the plasma jet by a layer of inert gas.[7] These approaches are each achieved by attaching a gas flow device to the front of a plasma spray gun.[7] Both the processes have been shown to produce metallic coatings with significantly lower oxide levels than would be possible with non-SPS. CoNiCrAlY SPS coatings have been reported with 0.3% oxide content,[20] approximately a third to a half of the extent of oxidation expected from atmospheric plasma spraying (APS).[7]

SPS is the cheapest way of plasma spraying in an inert environment, but not the most effective. In order to provide greater separation of the plasma jet from atmospheric air, it is necessary to spray in an enclosed chamber. Such a chamber may be filled with an inert gas as is the case in inert plasma spraying (IPS), or evacuated as it is done in vacuum plasma spraying (VPS) or low-pressure plasma spraying (LPPS).[6] Using such processes essentially eliminates oxidation, oxygen levels of 1500 ppm and 700 ppm being reported for LPPS[21] and VPS[22] respectively.

Another controlled atmosphere variant is high-pressure plasma spraying (HPPS), which is carried out in a pressurized gas-filled chamber, with typical pressures of 100–350 kPa.[23] The higher gas pressures used in HPPS increase heat transfer to the sprayed particles.[23,24] Hence, HPPS is well suited to the spraying of higher melting point materials and is generally used for ceramics. Compared with APS, HPPS coatings have lower porosity levels, improved properties, and uniformity.[23,25] Lower levels of oxidation and contamination are additional advantages.[25]

For IPS, VPS, LPPS, and HPPS, there is a significant increase in equipment cost compared with air plasma spraying due to the requirement of an air-tight or pressure chamber.[10] However, once a plasma spray gun has been installed in an air-tight chamber, it is of course possible to use it in different ways. Controlled atmosphere plasma spraying (CAPS) is an umbrella term covering IPS, VPS, LPPS, and HPPS. CAPS systems are commercially available, which can operate in IPS, VPS, LPPS, and HPPS modes as well as APS.[23,25]

Another plasma spraying variant is radio frequency (RF) induction plasma spraying.[26] An induction coil surrounds the gun, through which the plasma gas and powder feedstock are injected axially.[27] RF torches have a large internal nozzle diameter, which results in relatively low plasma jet velocities, and hence, low particle velocities.[7,27] These are typically 20–50 m s^{-1}, that is, an order of magnitude lower than is generally seen for other plasma spray processes.[7,27] This results in particles being in the hot plasma jet for a longer time, typically ~20 ms compared with ~1 ms for other plasma spray processes,[28] resulting in an increased overall heat transfer.[27] The extensive melting produced by RF plasma spraying results in good spreading of the particles on impact and the production of nearly fully dense coatings.[28] The improved heat transfer also means that larger powder sizes can be used while retaining a high level of particle melting.[27] The key advantage of this is that larger, and hence generally cheaper, feedstock powder can be used.[10,27] Another important advantage of RF induction plasma spraying, particularly for metallic coatings, is the lower levels of oxidation resulting directly from the lower surface-to-volume ratio of larger feedstock powder.[10]

A further development is supersonic RF plasma spraying. In order to generate the higher particle velocities desirable for improved coating properties, supersonic nozzles have been fitted to RF plasma spray guns.[27] In these systems, melting occurs while the particles are at low velocity; they are then accelerated by gas expansion resulting in particle velocities of up to 600 m s^{-1} comparable to other plasma spray techniques.[7,27] Another advantage of RF spraying is the absence of electrodes.[28] There is no danger of coating contamination by electrode erosion.[7] It is also possible to use reactive gases in RF, which is ruled out in other plasma spray methods, since contact with the hot electrodes would severely reduce electrode life.[7,28,29]

In plasma-transferred arc (PTA) spraying, an arc is initially generated between a central tungsten cathode and a water-cooled copper anode. The interaction of this arc with the gases flowing through the gun generates a plasma. So far, this is exactly the same as in normal plasma spraying. The difference in PTA is that the ionized gas that forms the plasma provides a conductive path and the arc transfers from the anode and instead strikes the substrate surface.[30] The resulting high heat flux at the substrate surface induces substrate melting. Therefore, on solidification, a metallurgical bond is formed between the coating and the substrate,[30] which is much stronger than the mechanical interlocking that is found in other sprayed coatings. Some dilution of the coating with the substrate is unavoidable, the dilution generally being 5–10%.[31] Since the workpiece becomes part of the electrical circuit, this technique is restricted to electrically conductive coatings and substrates.

4.08.3.4 High Velocity Oxy-Fuel Spraying

The high-velocity oxy-fuel (HVOF) process and the closely related high-velocity air fuel (HVAF) process both produce relatively dense and oxide-free coatings by accelerating feedstock powder to relatively high velocities in a relatively cool flame. This cool, fast approach ensures sufficient plastic deformation to produce an adherent coating. Due to the lower temperatures used, melting, and hence oxidation, is minimized. HVOF coatings typically have less than 1% porosity. WC–Co coatings are frequently deposited by HVOF; an additional advantage of the lower temperatures is that carbide decomposition is minimized.[10]

In HVOF spraying, powder feedstock is heated and accelerated by expanding combustion gases. Fuel gases are usually hydrogen or hydrocarbon gases like ethylene, propylene, propane, or acetylene,[6,7] though liquid fuels such as kerosene may also be used.[7] As for detonation gun (D-Gun) spraying, the HVOF gun is relatively simple, consisting of a combustion chamber linked to a barrel by a nozzle. Powder injection may be axial or radial.[7] HVOF spray guns require water cooling.[6] Spray distances used in HVOF tend to be a bit higher than those used in plasma spraying due to the enthalpy release in the flame, which may lead to excessive convective heating of the substrate.[6]

A key feature of HVOF spraying is the limited extent of melting. This makes it one of the few thermal spraying processes suitable for spraying nanostructured feedstock, since the feedstock microstructure is retained. The specific corrosion-related interest in forming nanostructured coatings is that the refined grain size may increase the density of fast diffusion paths, hence increasing the speed and effectiveness of passivation.[32] Ji *et al.*[32] have successfully created nanostructured HVOF FeAl-based coatings; however, the corrosion resistance was less than that of the bulk material. Current densities of 10^{-2} A cm^{-2} and $10^{-4.4}$ A cm^{-2} were measured in the passive region of potentiodynamic tests in 0.5 M H_2SO_4 for the sprayed coating and bulk material respectively.[32]

The relatively low temperatures encountered in HVAF and HVOF spraying limit the materials that can be deposited by these methods, since some materials do not exhibit sufficient plasticity at the combustion temperatures, ~3300 and 2300 K, encountered in HVOF and HVAF flames respectively. This means that HVOF and HVAF spraying of high melting point brittle materials such as ceramics becomes difficult.[33] This has led to interest in more highly thermal-efficient guns, such as those with two chambers, which enable easier HVOF spraying of these otherwise problematic materials.[33]

HVOLF is a variant of HVOF, which uses a liquid fuel, that is, kerosene. Using a liquid fuel produces higher gas velocities, and hence higher particle velocities and a lower temperature.[34] This can result in lower oxide content for HVOLF coatings compared with those made using HVOF.[34] A disadvantage of using a liquid fuel is the lower deposition efficiency, typically only two-thirds that of a gas-fuelled HVOF gun.[7]

Hasan *et al.*[35] have designed and demonstrated a multipowder feed variant of HVOF, which can create functionally graded materials by simply adjusting the flow rate of powder from each of two separate powder feeders to continuously control the composition of the coating deposited. The idea is that the resultant coating has a gradual change in composition with thickness, which decreases the overall residual stresses.[35]

4.08.3.5 Detonation Gun Spraying

D-Gun spraying is a Union Carbide/Praxair technology that was initially available only as a service with research work appearing only from the mid 1990s onwards,[10] D-Gun WC–Co coatings being a popular research area.

D-Gun spraying can be considered a variant of HVOF spraying, sharing HVOF's advantages of high particle velocity and low temperatures. In D-Gun, spraying powder is injected into the gun along with a mixture of oxygen and fuel. A spark ignites the oxygen–fuel mixture, which explosively combusts. The powder in the combustion chamber is heated and accelerated by the expanding combustion gases, and is directed toward the substrate by the geometry of the gun barrel. This process is repeated at a frequency of 1–55 Hz with a nitrogen purge between each shot.[6]

4.08.3.6 Cold Gas Dynamic Spraying

In thermal spraying, the feedstock is generally heated, commonly to a molten state, to ensure sufficient deformation, and hence bonding on impact. Cold-gas dynamic spraying (CGDS) takes a different approach; here, the emphasis is on increasing particle velocity while maintaining a low particle temperature. Deformation on impact is then solely due to the large momentum of the particles. There is a material-dependent critical velocity, dependent on both particle size and material yield strength, which must be exceeded for deposition to occur. The lack of any significant heating means that CGDS can be used to spray substrates, such as polymers, that would be thermally damaged by other higher heat input thermal spray processes.

Despite the name, there is some heating in CGDS. A carrier gas, typically nitrogen, or helium, or a mixture of one or both of these with air, is compressed and then heated.[6] Helium is more effective than nitrogen at transferring momentum to the injected powder; however, it is also more expensive. Powder is injected into the gas, which then passes through a converging–diverging de Laval nozzle that accelerates the gas to supersonic velocities.[6] The gas is heated, and hence there is some heating of the feedstock powder; however, this is insignificant compared with other thermal spray processes. The temperature of the powder remains well below the melting point[6] and particle temperatures of 500 K have been calculated for CGDS Cu.[6,36]

Although details of particle adhesion in the CGDS process are still under investigation, it can be said that particle melting is avoided and adhesion of particles requires plastic deformation on impact. Therefore, CGDS is suited only to materials that can undergo plastic deformation in the solid state. This rules out ceramics and makes CGDS best suited to ductile metals. CGDS has been successfully used to deposit aluminum,[37] copper,[38] titanium,[39] nickel,[40] nickel alloys[40] as well as some composite coatings such as aluminum with SiC and Al_2O_3 inclusions,[41] and NiCr with Cr_3C_2.[42]

The key advantage of CGDS is the low thermal input, which results in low oxide levels and enables the spraying of substrates that would be thermally damaged by other thermal spray processes.

4.08.3.7 Other Thermal Spray Techniques and Variants

Metallic glasses have good corrosion resistance; however, they are expensive to produce. There is, therefore, interest in producing metallic glass coatings. Iron-based metallic glass has been successfully deposited by gas tunnel plasma spraying.[43] This is a variant of plasma spraying where a vortex flow is used to produce a higher-temperature and higher-energy density plasma than is typical of other plasma spray processes.[44]

4.08.3.8 Liquid Feedstock

Thermal spraying using a liquid feedstock is the current area of interest.[11] Liquid feedstock variants of plasma spraying and HVOF[11,45] have been reported. These including high velocity suspension flame spraying, see Section 4.08.3.1.1. An important advantage of using a liquid feedstock is that finer particles can be sprayed by spraying a liquid suspension,[11] for example, plasma spraying of submicron WC–Co powder.[46] This results in finer splats, and consequently, a denser microstructure[11]; fully dense Inconel 625 coatings have been reportedly formed by HVOF spraying of a suspension of fine particles of Inconel 625.[47] For metallic coatings a simple suspension of fine particles is used. There is a second form of liquid feedstock that may be used for ceramic coatings: a liquid containing precursors, referred to as solution precursor plasma spraying.[45]

4.08.3.8.1 Nanostructured coatings

Reports of increased fracture toughness of nanostructured ceramic coatings have led to interest in this area.[48] For processes such as HVOF, where the feedstock powder is not fully melted, it is possible to obtain a nanostructured coating by using a nanostructured feedstock powder.[48] Other thermal spray variants suited for the generation of nanostructured coatings are suspension plasma spraying and solution precursor plasma spraying.[49]

4.08.3.8.2 Laser-hybrid techniques

The various laser-thermal spray hybrid techniques use the additional heat input from a laser beam to enhance the extent of melting to produce a denser coating, thereby improving corrosion resistance, as ingress of corrosive species is inhibited.[50–52] Antou *et al.* showed that an *in situ* laser remelting technique could reduce the interconnectivity of the porosity present in APS YSZ coatings, thus improving the effectiveness of the coating as a barrier to ingress of foreign species.[51] Techniques that melt the entire coating also enhance coating adhesion, as the usual mechanically bonded interface is replaced by metallic bonding.[52,53] An additional advantage is the reduction of residual stresses. The laser treatment and thermal spraying may happen simultaneously[52]; they may alternate or the thermally sprayed coating may simply be laser melted some time after spraying.[53] Provided that suitable laser processing parameters are used to ensure crack-free coatings, laser remelting can significantly improve corrosion resistance.[52] One of the many examples is the use of a hybrid laser-flame spraying method to generate Metco 12C coatings with a superior corrosion resistance to similar HVOF coatings.[52]

An extreme of the hybrid spray techniques is surface alloying of a preplaced thermally sprayed coating, a method, which can be used to enhance corrosion resistance.[54] Electron beam melting of a flame-sprayed Al coating has been used to enhance the corrosion resistance of the underlying Mg alloy substrate.[54]

4.08.3.9 Thermal Spraying: Periphery Processes

4.08.3.9.1 Preprocessing processes

Abrasive blasting is widely used to achieve suitable surface roughness and to activate the surface by removing any preexisting oxides.[55] Substrate preheating is less widely used and its effectiveness varies with the deposition method. It has been shown to enhance substrate wettability for flame spraying. A similar, though lesser, effect was seen for plasma spraying of Al on mild steel. In HVOF spraying, minimal melting occurs, and hence there is no wettability-linked effect of preheating; however, some increase in adhesion was noted, highlighting the different bonding mechanism in HVOF coating.[55]

4.08.3.9.2 Postprocessing techniques

Various posttreatments are frequently used with thermally sprayed coatings. These enable higher quality coatings to be produced than can be formed from simply optimizing spraying parameters.[50] The prime reason for this is a desire to eliminate the detrimental effect of porosity, particularly interconnected porosity. Organic sealants can be applied to seal the sprayed coating[56,57]; however, such sealants may have a relatively low maximum operating temperature.[58] Alternatively, corrosion resistance can be ensured by adding a corrosion-resistant layer between the substrate and coating. This technique is used when the outer coating has an additional function. Aluminum bond coats have been successfully used in this role in HVOF wear-resistant WC–Co coatings on Mg alloy substrates that otherwise corrode rapidly in salt spray tests.[56] MCrAlY bond coats are widely used in the same role in thermal barrier coatings. A further variant has been demonstrated by Ishikawa *et al.*, [58] who used a duplex wire flame-sprayed system consisting of an 80Ni–20Cr underlayer covered with a layer of aluminum. The outer aluminum layer then improved corrosion resistance by acting both as a sacrificial anode and essentially as a sealant.[58]

Laser remelting has successfully improved the salt spray resistance of plasma-sprayed Ni-coated WC coatings by densification on resolidification, reducing the porosity from an initial 6.67% to 0.76%.[59] The alternative process of vacuum annealing was also used on the same coatings, which also decreased the porosity but was less effective, resulting in 2.24% porosity.[59] Induction heating is another remelting process that has successfully been used to seal porosity, and hence improve the effectiveness of thermally sprayed coatings as barriers to corrosive species.[13]

4.08.4 Corrosion Applications of Metallic Sprayed Coatings

Large scale steel structures such as bridges, girders, and ski lifts are commonly provided with corrosion protection by thermally sprayed coatings.[6,7] For such applications, zinc and aluminum, as well as their alloys, are widely used.[7] Coating thicknesses of 50–500 μm are typical.[7] Thermally sprayed aluminum coatings are also used to protect a large number of steel marine structures, including components on off-shore oil rigs.[7] These coatings are generally deposited by arc spraying[6] or flame spraying.[7] Zinc is also used for some immersion applications such as components on dams.[7] Other uses of thermally sprayed aluminum include preventing corrosive chemicals from attacking storage containers.[7] For most of these applications, any porosity present, as is typical of thermal spray coatings, will not be a great problem, because both zinc and aluminum provide cathodic protection. Hence, the corrosion protection provided by these coatings is not lost by simple breaches in the coating.[7] However, if the coatings are to be used in immersed conditions or if there is any danger of aluminum–thermite sparking, a sealant is used.[7]

In the automotive industry, wire arc- or flame-sprayed aluminum coatings are used to protect various exhaust components from hot corrosion.[7] Wire arc-sprayed zinc has been used to provide corrosion protection for steel steering stop brackets.[7] There is a clear driving force for the increased use of light alloys, specifically aluminum and magnesium alloys in the automotive industry. In many potential automotive applications, coatings are required to improve both the wear and corrosion resistance of the underlying alloy. Magnesium alloys particularly need to be protected against corrosive environments. There is great scope for the use of thermally sprayed coatings, particularly APS and HVOF, in such applications.[60]

The relatively low melting point of aluminum, 660 °C, restricts the use of these coatings to maximum service temperatures of ~550 °C.[7] MCrAlY coatings tend to be used for high temperature corrosion protection; such coatings would generally be deposited by plasma spraying or HVOF.[61]

The harsh operating environments encountered in gas turbines are withstood only with the aid of various coatings. MCrAlY alloys are widely used to provide high temperature corrosion resistance. These alloys are used both as overlay coatings on components such as stators and as the bond coat in thermal barrier coatings.[7] VPS and LPPS are the techniques most commonly used to deposit these coatings.[6] This minimizes the formation of noncontinuous, nonprotective oxides during coating deposition, which would decrease the corrosion protection offered by the coating.

Boilers require high temperature corrosion resistance in aggressive environments; these are frequently thermal sprayed to protect against temperature, abrasion, and corrosive elements from fuel.[6,7] Plasma spraying, wire arc spraying, and HVOF coatings of stainless steel,[6] nickel alloys, high-chromium alloys, and chromium–nickel alloys[7] have been used to extend the life of boiler components such as superheater tubes and waterwalls.

Very demanding corrosive conditions are encountered in the glass-making industry.[7] The only materials that can withstand extended contact with molten glass are the precious metals and their alloys.[7] Precious metal glass-making components are often coated with thermally sprayed ceramics in order to extend corrosion life.[7] Plasma-sprayed molybdenum or molybdenum alloys are used to protect a variety of glass-making components, including moulds and stirrers.[7]

Unsurprisingly, corrosion-resistant coatings are required in the chemical processing industry where aggressive chemicals are stored and piped.[7] APS nickel-based alloys, including Hastelloy C, Hastelloy B, and Inconel 600, have been successfully used to extend the service life of pressure vessels.[7] Plasma-sprayed niobium doped with palladium has been used to protect welds in aluminum alloy tanks used to contain nitric acid.[7] Various glass-lined chemical reactors have been repaired using APS tantalum.[7] HVOF spraying of a molybdenum coating on stainless steel components used in a high temperature sulfur and ammonia environment has proved to be a cost-effective alternative to component replacement.[6,62]

Applications of thermally sprayed corrosion resistance coating in the petrochemical industry include HVOF-sprayed tungsten carbide coatings used to increase wear as well as corrosion resistance of valves.[7] Such coatings are also used to protect the blades of cutting machines in the paper industry.[7] HVOF stainless steel coatings with high molybdenum contents are used to provide corrosion resistance to dryer rolls used in tissue making.[7] APS NiCrSiB/CuSn/MoS_2 coatings have successfully increased the lifetime of steel hydraulic mine props by providing protection against corrosive attack by mine water.[6,63]

The formation of sacrificial anodes for cathodic protection systems is another corrosion-related application of thermal spraying.[7] Plasma spraying and arc spraying have been used to deposit zinc and titanium sacrificial anodes; flame spraying has also been used for zinc.[7] Whether or not a given coating will act as a sacrificial anode depends on the substrate material and the surrounding electrolyte as well as any impressed current.[7] Semiconducting ceramics can be used as sacrificial anodes in impressed current systems. These can also be made by thermal spraying.[7] Plasma-sprayed ferrite coatings have cathodically protected metals such as titanium, niobium, and tantalum when they have been used in oil or specific chemical environments.[7]

The general increasing acidity of printing inks as well as the tight tolerances required result in several applications of thermally sprayed coatings in the printing industry.[7] Engraver rolls are coated with APS ceramic, either TiO_2–Al_2O_3 or Cr_2O_3, which, as for TBCs, is deposited on top of a metallic bond.[7] The bond coats used for engraver rolls are made using APS.[7] In this application, it is interesting to note that the large size of the components is instrumental in the choice of thermal spray method, the rolls being far too large for any CAPS chamber.[7]

APS may also be used for the large rolls used in continuous annealing lines.[6] These rolls require coatings that provide both wear and corrosion resistance[6]: cermets such as Cr_2C_3/NiCr and MCrAlY/oxide deposited by APS, D-Gun, or HVOF spraying.[6,64]

The provision of alternative coatings to hard chrome is an important area in which thermal spraying can be applied.[7,65] HVOF WC–Co is widely used as a hard chrome replacement. Both the US air force and navy use HVOF WC–Co, which resulted from the work of the Hard Chrome Alternatives Team (HCAT) set up by the United States military, on landing gear components.[7] However, the dimensions of HVOF guns rule out HVOF spraying of some components, particularly inner diameters of landing gear and hydraulic components.[66] For such applications, plasma spraying may be used. The Sulzer Metco F300 gun has been demonstrated to be able to coat components with inner diameters of 1.6 in.[66] A standard spray gun is fitted with an extension to permit insertion into internal diameters. These tend to be 12 or 24 in. long, and it is the length of the extension that limits the depth to which spraying can occur.[66] Both Praxair and Sulzer Metco produce guns specifically for inner-diameter spraying applications.[66] The rotation of the component around the gun ensures uniform coating deposition.[66]

In other applications, such as the coating of engine cylinders, a rotating gun is used. These are commercially available and include the SulzerMetco RotaPlasma®. From approximately 2000 onwards, Volkswagen has routinely used a 200-μm thick air plasma-sprayed Fe–Mo coating on the cylinder walls of diesel and petrol engines. These coatings enhance both the tribological performance of the underlying aluminum alloy and corrosion resistance.[67]

4.08.5 Corrosion Applications of Inorganic Sprayed Coatings

Thermal barrier coatings (TBCs) are perhaps the most widely known example of thermally sprayed inorganic corrosion-resistant coatings. TBCs consist of two layers. The inner layer is a metallic bond coat, which is frequently a VPS- or LPPS-deposited MCrAlY (M=Co, Ni, or NiCo) coating.[61] A relatively recent innovation is the use of HVOF to deposit denser bond coats.[61] An important role of the bond coat is to enhance adhesion of the outer layer. For nonrotating components, APS zirconia is frequently used for the outer layer, with electron beam physical vapor deposition used to deposit the ceramic outer layer on rotating components. The main role of this outer ceramic layer, the top coat, is to form a thermal barrier, protecting the underlying component from the high temperatures of the hot gas path, and thus improving corrosion resistance. A ~250 μm top coat can reduce the surface temperature of the underlying component by 200 K.[68] The thermally grown oxide that forms on the underlying MCrAlY bond coat in service is the main corrosion protection mechanism in TBCs.[68] TBCs are used on various components along the hot gas path, including combustors and nozzle guide vanes.

Among other corrosion uses of thermally sprayed ceramic coatings, APS Al_2O_3–TiO_2 coatings have been used to protect blast furnace stave cooling pipes from carburization.[6,69]

Conversion coatings are widely used to enhance corrosion resistance. The chemical treatment of the material to be protected produces a surface layer of insoluble compounds, usually oxides, chromates, or phosphates.[70] This layer acts as a barrier between the substrate and the corrosive environment.[70] Air spray is one method that has been used for the deposition of cerium oxide conversion coatings, which are chromate-free alternatives to chromate conversion coatings.[1,71]

There is a wide variety of commercially available zinc-pigmented paints and zinc-rich coatings. These typically consist of zinc in an organic binder; however, inorganic versions are available. The inorganic zinc-based coatings use a silicate binder in place of the epoxy binders used in the more established organic zinc-based coatings. Zinc silicate coatings can outperform zinc epoxy coatings.[72] As with the organic versions of such coatings, the inorganic zinc coatings can also be used in multilayer coating systems.[72]

References

1. Jones, P. S.; Yu, P.; Pinc, W. R.; O'Keefe, M. J.; Fahrenholtz, W. G.; O'Keefe, T. J. *Int. J. Appl. Ceram. Technol.* **2008**, *5*, 63–73.
2. Hai, T. H.; Van, H. T. B.; Phong, T. C.; Abe, M. *Physica B: Condens. Mater.* **2003**, *327*, 194–197.
3. Ibáñez, R. L.; Barrado, J. R. R.; Martín, F.; Brucker, F.; Leinen, D. *Surf. Coat. Technol.* **2004**, *188–189*, 675–683.
4. Huang, H.; Yao, X.; Wu, X.; Wang, M.; Zhang, L. *Microelctron. Eng.* **2003**, *66*, 688–694.
5. Chen, C. H.; Emond, M. H. J.; Kelder, E. M.; Meester, B.; Schoonman, J. *J. Aerosol. Sci.* **1998**, *30*, 959–967.
6. Pawlowski, L. *The Science and Engineering of Thermal Spray Coatings;* Wiley, 2008.
7. Davis, J. R. *Handbook of Thermal Spray Technology*; ASM International, 2004.
8. Lima, R. S.; Krugera, S. E.; Marplea, B. R. *Surf. Coat. Technol.* **2008**, *202*, 3643–3652.
9. Thermal Spray Coatings Protect Petro-Chemical Components from Corrosion. *International Thermal Spray & Surface Engineering,* 2008. 16–18.
10. Fauchais, P.; Vardelle, A.; Dussoubs, B. *The International Thermal Spray Conference*; ASM International: Singapore, 2001.
11. Bolelli, G.; Rauch, J.; Cannillo, V.; Killinger, A.; Lusvarghi, L.; Gadow, R. *Mater. Lett.* **2008**, *62*, 2772–2775.
12. Liu, H. Y.; Huang, J. H.; Yin, C. F.; Zhang, J. G.; Lin, G. B. *Ceram. Int.* **2007**, *33*, 827–835.
13. Matsubara, Y.; Sochi, Y.; Tanabe, M.; Takeya, A. *J. Therm. Spray Technol.* **2007**, *16*, 195–201.
14. Panossian, Z.; Mariaca, L.; Morcillo, M.; Flores, S.; Rocha, J.; Peña, J. J.; Herrera, F.; Corvo, F.; Sanchez, M.; Rincon, O. T., *et al. Surf. Coat. Technol.* **2005**, *190*, 244–248.
15. Sainz, M. A.; Osendi, M. I.; Miranzo, P. *Surf. Coat. Technol.* **2008**, *202*, 1712–1717.
16. Aubreton, J.; Elchinger, M. F.; Fauchais, P.; Rat, V.; André, P. *J. Phys. D: Appl. Phys.* **2004**, *37*, 2232–2246.
17. Janisson, S.; Vardelle, A.; Coudert, J. F.; Meillot, E.; Pateyron, B.; Fauchais, P. *J. Therm. Spray Technol.* **1999**, *8*, 545–552.
18. Schein, J.; Zierhut, J.; Dzulko, M.; Forster, G.; Landes, K. D. *Contrib. Plasma Phys.* **2007**, *47*, 498–504.

19. Planche, M. P.; Liao, H.; Coddet, C. *Surf. Coat. Technol.* **2007**, *202*, 69–76.
20. Sakakibara, N.; Manabe, Y.; Hiromoto, Y.; Kobayashi, Y. *Sci. Technol. Weld. Joining* **2008**, *13*, 344–348.
21. Steffens, H. D.; Hohle, H. M.; Erturk, E. *Thin Solid Films* **1980**, *73*, 19–29.
22. Vasen, R.; Doring, J. E.; Dietrich, M.; Lehmann, H.; Stover, D. *International Gas Turbine Conference*, Tokyo, 2003.
23. Beauvais, S.; Guipont, V.; Borit, F.; Jeandin, M.; Español, M.; Khor, K. A.; Robisson, A.; Saenger, R. *International Thermal Spray Conference*; ASM International: Singapore, 2001.
24. Guipont, V.; Español, M.; Borit, F.; Llorca-Isern, N.; Jeandin, M.; Khor, K. A.; Cheang, P. *Mater. Sci. Eng. A* **2002**, *325*, 9–18.
25. Sarafoglou, C. I.; Pantelis, D. I.; Beavais, S.; Jeandin, M. *Surf. Coat. Technol.* **2007**, *202*, 155–161.
26. Boulos, M. I. *J. Therm. Spray Technol.* **1991**, *1*, 33–48.
27. Fauchais, P. *J. Phys. D: Appl. Phys.* **2004**, *37*, R86–R108.
28. Boulos, M. I. *J. Therm. Spray Technol.* **1992**, *1*, 33–48.
29. Fauchais, P.; Vardelle, A.; Denoirjean, A. *Surf. Coat. Technol.* **1997**, *97*, 66–78.
30. Deuis, R. L.; Yellup, J. M.; Subramanian, C. *Compos. Sci. Technol.* **1998**, *58*, 299–309.
31. d'Oliveira, A. S. C. M.; Vilar, R.; Feder, C. G. *Appl. Surf. Sci.* **2002**, *201*, 154–160.
32. Ji, G.; Elkedim, O.; Grosdidier, T. *Surf. Coat. Technol.* **2005**, *190*, 406–416.
33. Evdokimenko, Y. I.; Kisel, V. M.; Kadyrov, V. K.; Korol, A. A.; Podchernyaeva, I. A.; Panasyuk, A. D. *Powder Metall. Met. Ceram.* **2003**, *42*, 578–586.
34. Zhang, D.; Harris, S. J.; McCartney, D. G. *Mater. Sci. Eng. A* **2003**, *344*, 45–56.
35. Hasan, M.; Stokes, J.; Looney, L.; Hashmi, M. S. J. *Surf. Coat. Technol.* **2008**, *202*, 3215–3220.
36. Stoltenhoff, T.; Voyer, J.; Kreye, H. *International Thermal Spraying Conference*; Essen, 2002.
37. Lee, H.; Shin, H.; Lee, S.; Ko, K. *Mater. Lett.* **2008**, *62*, 1579–1581.
38. Calla, E.; McCartney, D. G.; Shipway, P. H. In *International Thermal Spray Conference*, Osa: Japan, 2004.
39. Price, T. S.; Shipway, P. H.; McCartney, D. G. *J. Therm. Spray Technol.* **2006**, *15*, 507–512.
40. Raletz, F.; Vardelle, M.; Ducos, M. *International Thermal Spray Conference*, Osa: Japan, 2004.
41. Lee, H. Y.; Yu, Y. H.; Lee, Y. C.; Hong, Y. P.; Ko, K. H. *J. Therm. Spray Technol.* **2004**, 184–189.
42. Limaa, R. S.; Karthikeyanb, J.; Kayb, C. M.; Lindemannb, J.; Berndt, C. C. *Thin Solid Films* **2002**, *416*, 129–135.
43. Kobayashi, A.; Yano, S.; Kimura, H.; Inoue, A. *Surf. Coat. Technol.* **2007**, *202*, 2513–2518.
44. Arata, Y.; Kobayashi, A. *J. Appl. Phys.* **1986**, *59*, 3038–3044.
45. Berghaus, J. O.; Legoux, J. G.; Moreau, C.; Tarasi, F.; Chraska, T. *J. Therm. Spray Technol.* **2008**, *17*, 91–104.
46. Berghaus, J. O.; Marple, B.; Moreau, C. *J. Therm. Spray Technol.* **2006**, *15*, 676–681.
47. Ma, X. Q.; Roth, J.; Gandy, D. W.; Frederick, G. J. *J. Therm. Spray Technol.* **2006**, *15*, 670–675.
48. Varis, T.; Knuuttlia, J.; Turunen, E.; Lelvo, J.; Silvonen, J.; Oska, M. *J. Therm. Spray Technol.* **2007**, *16*, 524–532.
49. Fauchais, P.; Rat, V.; Coudert, J. F.; Etchart-Salas, R.; Montavon, G. *Surf. Coat. Technol.* **2008**, *202*, 4309–4317.
50. Coddet, C. *Surf. Coat. Technol.* **2006**, *201*, 1969–1974.
51. Antou, G.; Montavon, G.; Hlawka, F.; Cornet, A.; Coddet, C.; Machi, F. *Surf. Coat. Technol.* **2004**, 180–181.
52. Suutala, J.; Tuominen, J.; Vuoristo, P. *Surf. Coat. Technol.* **2006**, *201*, 1981–1987.
53. Voisey, K. T.; Liu, Z.; Stott, F. H. *Surf. Coat. Technol.* **2006**, *201*, 637–648.
54. Ye, H.; Yan, Z. L. *5th International Conference on Surface Engineering*; Dalian Univ Technol: alian, China, 2007.
55. Paredes, R. S. C.; Amico, S. C.; d'Oliveira, A. S. C. M. *Surf. Coat. Technol.* **2006**, *200*, 3049–3055.
56. Parco, M.; Zhao, L.; Zwick, J.; Bobzin, K.; Lugscheider, E. *Surf. Coat. Technol.* **2006**, *201*, 3269–3274.
57. Mazraeh, M.; Hocking, M.G.; Sidky, P.S. *International Conference on Corrosion in Refinery Petrochemical and Power Generation Plants*; Venice, Italy.
58. Ishikawa, K.; Suzuki, T.; Tobe, S.; Kitamura, Y. *J. Therm. Spray Technol.* **2001**, *10*, 520–525.
59. Xie, G.; Lin, X.; Wang, K.; Mo, X.; Zhang, D.; Lin, P. *Corros. Sci.* **2007**, *49*, 662–671.
60. Friedrich, C.; Gadow, R.; Scherer, D. *Functional Ceramic and Metallurgical Coatings on Magnesium Components* The International Thermal Spray Conference; ASM International: Singapore, 2001.
61. Lima, C. R. C.; Guilemany, J. M. *Surf. Coat. Technol.* **2007**, *201*, 4694–4701.
62. Moskowitz, L. N. *The 1st Gorham's International Thermal Spray Coatings Conference*, Cambridge, MA, USA, 1992.
63. Matejka, D.; Berezovsky, M.; Palka, V.; Kolanciak, V.; Ivan, L. *1st Plasma Technik Symposium*, 1988.
64. Fukubayashi, H. H. *International Thermal Spray Conference*; Osaka, Japan, 2004.
65. Wasserman, C.; Boecking, R.; Gustafsson, S. *Replacement for Hard Chrome Plating in Printing Machinery;* International Thermal Spray Conference; ASM International: Singapore, 2001.
66. Legg, K. *Replacement of Internal Diameter Hard Chrome with Plasma Spray Coatings at NADEP Jacksonville – Implementation Assessment*; Rowan Technology Group: Libertyville, IL, 2004.
67. Lampe, T.; Eisenberg, S.; Cabeo, E. R. *Surf. Coat. Technol.* **2003**, 174–5; 1–7.
68. Padture, N. P.; Gell, M.; Jordan, E. H. *Science* **2002**, *296*, 280–284.
69. Hoffman, J. W. *International Thermal Spray Conference*; The Hague, The Netherlands, 1980.
70. Gray, J. E.; Luan, B. *J. Alloys Compd.* **2002**, *336*, 88–113.
71. Johnson, B. Y.; Edington, J.; Williams, A.; O'Keefe, M. J. *Mater. Charact.* **2005**, *54*, 41–48.
72. Keijman, J. M. *PCE '99 Conference*, Brighton, UK, 1999.

4.09 Laser Applied Coatings

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Glossary

Laser-assisted thermal spray Laser-assisted thermal spraying is a one-step coating method, in which a high-power laser is combined with thermal spraying to create denser and more adherent coatings, with a metallurgical bond between the coating and the base material, than achieved by normal thermal spraying processes.

Laser chemical vapor deposition (LCVD) Laser chemical vapor deposition is a technique to deposit thin to moderate films by a chemical reaction activated by a laser beam inside a gas chamber via either a pyrolytic or a photolytic effect.

Laser cladding (LC) Laser cladding is a process for fusing a powdered/wire/sheet material by using a laser on a substrate with minimum dilution.

Laser melt/particle injection (LMI) Laser melt/particle injection is a process for generating a metal matrix composite on a substrate by the injection of ceramic/higher melting point particles into a laser-induced melt pool.

Laser surface alloying (LSA) Laser surface alloying is a process that utilizes a laser to melt a metal coating and a portion of the underlying substrate to form a surface layer that is different from the coating and the substrate.

Laser surface melting (LSM) Laser surface melting is a process in which a thin layer of substrate surface is melted by a high-power laser beam and followed by rapid solidification to alter surface microstructures.

Pulsed laser deposition (PLD) Pulsed laser deposition is a thin-film deposition technique in which the target material is ablated by a high-power pulsed laser beam inside a vacuum or an inert-gas chamber and then deposited as a thin film on a substrate.

Abbreviations

CVD	Chemical vapor deposition
HPDL	High-power diode laser
HVOF	High-velocity oxy-fuel
LC	Laser cladding
LCVD	Laser chemical vapor deposition
LGN	Laser gas nitriding
LMI	Laser melt/particle injection
LSA	Laser surface melting
MMC	Metal matrix composite
Nd:YAG	Neodymium-doped yttrium aluminium garnet
PLD	Pulsed laser deposition
PVD	Physical vapor deposition
TBC	Thermal barrier coating
YSZ	Yttria stabilised zirconia

Symbols

G Thermal gradient (Km^{-1})

R Solidification rate (ms^{-1})

4.09.1 Lasers and Laser Beam Interactions with Materials

LASER is an acronym for light amplification by stimulated emission of radiation. Material processing with lasers takes advantage of virtually all the characteristics of the laser beam, including monochromaticity, coherency, high radiance, low beam divergence, and the ability to focus on a small spot.

When a laser beam strikes an opaque surface, a part of the radiation is reflected and the remaining part is absorbed in the substrate of the material. The absorption process depends on beam wavelength, temperature, and nature of the surface. Shorter wavelengths, elevated temperatures, and rougher surfaces usually lead to a higher absorptivity for metallic materials. The absorption of laser energy results in the excitation of free electrons (in metals), vibrations (in insulators), or both (in semiconductors). This excitation energy is rapidly converted into heat, and followed by various heat transfer processes such as conduction into the material and radiation from the surface. The generation of heat at the surface and its conduction into the material establish the temperature distribution in the material. Depending on the thermophysical properties of the material and laser parameters, a thin layer of the material surface could be heated, melted, or even vaporized, and then followed by rapid solidification to generate refinement/homogenization of microstructures.

Many types of lasers have been operated in material processing, but only four types of lasers are of sufficient energy and robustness to be used effectively for surface treatments: the CO_2 laser (with wavelength of 10.6 μm), the Nd:YAG laser (1.06 μm), the high-power diode laser (HPDL: 800–950 nm), and the excimer laser (248 nm for KrF). Due to their long wavelengths, surface modification by continuous-wave (CW) multikilowatt CO_2, Nd:YAG, and HPDLs occurs through heating effects, with a typical melt depth in the range of 50 μm–2 mm. In contrast, the excimer laser is pulsed and ranges in energy up to 1 J per pulse. Due to the short wavelength, surface modification by an excimer laser occurs through a combination of photochemical and heating effects. The typical melt depth caused by an excimer laser is a few micrometers, with a much faster cooling rate compared with the other three lasers. Recently, many special features of HPDL interaction with materials have been identified.[1] These features include better surface finish, better beam absorption, better morphological characteristics, more consistent and repeatable results, fewer cracks, and less porosity generation. These benefits are due to the multiple beam integration and shorter wavelength of the HPDLs, compared with Nd:YAG and CO_2 lasers. In addition, HPDLs have the advantages of being potentially low in cost, high in energy efficiency, and more reliable, as well as having longer service life, and portability. Therefore, HPDLs are ideal for industrial applications of surface treatments.

4.09.2 Solidification Microstructures

Solidification induced by a laser beam leads to high solidification rates due to the rapidly moving temperature fields and the associated high cooling rates and large supercooling. At very high solidification rates (greater than the local diffusion rate), equilibrium at the interface cannot be established and the solute atoms are frozen into solid at the same composition as they arrive at the interface (solute trapping).[2] This provides a unique opportunity for the development of a wide variety of novel alloys with extended solid solution. These alloys with nonequilibrium phases offer the possibility of new materials with properties that cannot be achieved by conventional processing techniques. In addition, the rapid cooling rate results in the homogenization/refinement of microstructure and dissolution/redistribution of precipitates or inclusions. In the case of CW lasers with a multikilowatt power level, a cooling rate of 10^3–$10^6\,\mathrm{K\,s^{-1}}$ is quite common. The cooling rate can rise up to $10^{11}\,\mathrm{K\,s^{-1}}$ for the low energy input surface skin processes.[3] The solidification microstructure is determined by the constitutional supercooling theory. For a specific alloy, the solidification microstructure depends on the local solidification conditions, that is, solidification rate, R, and temperature gradient, G, at the solid–liquid interface. In general, the morphology of solidification microstructures can be described as planar, cellular, cellular/dendritic, or dendritic, depending on GR. The values of G, R, and G/R vary within the melt pool. Therefore, different solidification morphologies can be found, for example, with a planar front zone at the melt pool–substrate interface and then cellular and dendritic structure toward the surface of the melt pool. On the other hand, the size of microstructure, which is often characterized by the secondary dendritic arm spacing, is determined by G/R, which is the cooling rate. The higher the cooling rate, the finer the resulting microstructure.

4.09.3 Laser Applied Coatings

A wide range of laser applied coating techniques is available today. Laser cladding (LC) and laser melt/particle injection are usually used to provide thick coatings with minimum dilution of substrate material. Laser surface remelting is applied to coatings produced by conventional techniques, such as thermal spraying, in order to modify microstructures and eliminate defects for the improvement in properties. Laser-assisted thermal spraying, also called laser hybrid spraying, is a one-step coating method, in which a high-power laser is combined with thermal spraying, to create denser and adherent coatings with much increased processing efficiency than normal thermal spray process. Pulsed laser deposition (PLD) and laser-assisted chemical vapor deposition (LCVD) produce thin films. Laser surface alloying (LSA), on the other hand, is applied to alter surface chemistry and composition by melting and mixing the substrate, with a coating material or a component of a gas, and can be used for either thick coatings or thin films.

4.09.3.1 Laser Cladding

LC is used to produce a relatively thick, typically from 50 μm to 2 mm, and homogeneous overlay of coating material on the substrate with a fusion bond. LC can be achieved by a high-power laser beam to slightly melt the surface of the substrate with simultaneous delivery of powdered materials into the molten pool, as described in Figure 1. LC can be also performed by completely melting materials predeposited on the substrate or through wire feeding with minimum dilution.

LC has many advantages over conventional cladding techniques such as thermal spray and arc welding. These advantages include a fusion bond and a reduction (or elimination) of porosity and cracks in comparison with thermal spray; a reduction in dilution (typically <5%), extremely narrow heat-affected zones with a low thermal distortion, and a reduction in postcladding machining costs in comparison with arc welding. For most LC applications in the field of surface protection, CW CO_2 and Nd:YAG lasers are typically used. However, in recent years, HPDLs have been increasingly used, especially in industrial environments, with the advantages of a reduction of operating and investment cost, high plug efficiency, and compact size. LC enables the generation of very fine, homogenous microstructures and nonequilibrium alloys due to the inherent rapid cooling rate associated with the process, which promotes the formation of either an amorphous phase or nonequilibrium crystalline phases with extended solid solution.

LC has found relatively widespread use for the protection of materials against corrosion and oxidation in a variety of applications, including Al alloys, Mg alloys, carbon steels, stainless steels, and various metal matrix composites. LC on Mg alloys with Al, Al alloys, and other alloying elements significantly enhances the corrosion resistance, along with wear resistance. For example, the corrosion rate of laser-clad $Mg_{27}Al_{73}$ is one order of magnitude lower than that of commercially produced AZ91B and two orders of magnitude lower than that of Mg in 3.5% NaCl solution,[2] This is due to the passive film on the clad material, which is much more stable than that of the AZ91B and Mg substrates, due to the refinement of microstructure and extended solid solution of Al. Additionally, LC of amorphous alloy $Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5}$, with a thickness of 1.5 mm, on a commercially pure Mg substrate resulted in corrosion resistance and wear resistance superior to those of the uncoated substrate, with the corrosion current density being lowered by three orders of magnitude in 3.5% NaCl solution.[5] In addition, the corrosion current density of laser-clad Al_2O_3 is three orders of magnitude lower than that of AZ91HP Mg alloy in 3.5% NaCl solution.[6]

LC can also be applied for extending the solid solubility limits of rare-earth additions (e.g., yttrium, rhenium hafnium, and cerium) in nickel-based superalloys to improve their resistance to oxidation at elevated temperatures. Under equilibrium conditions, the maximum solid solubility of rare-earth metals is ~0.2 wt% at room temperature. However, alloys produced by LC of Ni–(Fe,Cr)–Al–Hf–Re resulted in a uniform distribution of alloying elements in the clad matrix with an extended solid solubility of alloying additions, a greatly refined microstructure, and the formation of metastable rhenium- and hafnium-rich phases.[7,8] Under thermal cycling oxidation conditions, the clad material exhibits negligible change in weight, while the substrate

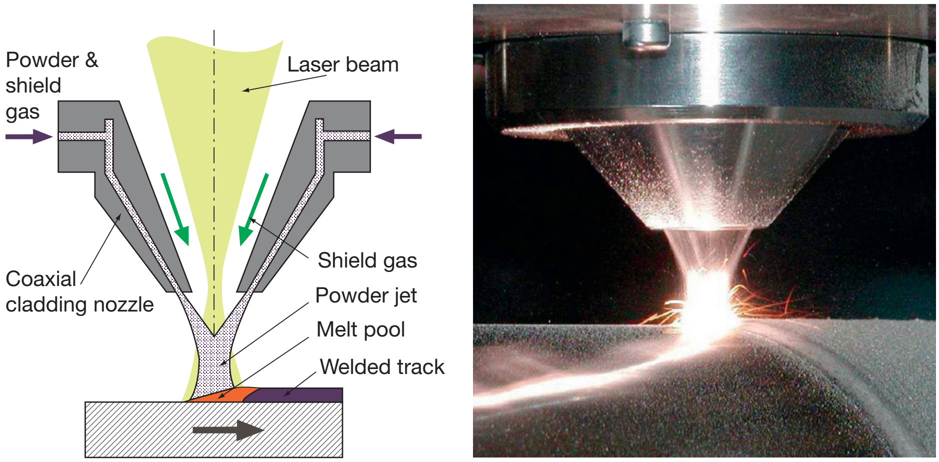

Figure 1 Laser cladding with coaxial powder feeding.[4]

(Rene80) suffers from extensive spalling of the scale.[9] In addition, LC of NiCrAlY alloy on a Hastelloy X substrate produces a columnar dendritic structure, free of porosity and microcracks, consisting of γ-Ni solid solution and a small amount of $Al_5Y_3O_{12}$ close to the surface, which exhibits excellent isothermal oxidation behavior.[10]

A new type of thermal barrier coating (TBC) has been developed for gas turbine blades by LC of yttria-stabilized zirconia (YSZ) on superalloy substrates.[11] The LC produces an oriented epitaxial growth, closely packed columnar structure during rapid solidification processing. This promotes the formation of an alumina layer between the NiCoCrAlY layer and the columnar ceramic layer that provides the adherence of the columnar layer to the NiCoCrAlY layer. A good metallurgical bond between the ZrO_2 layer and the NiCoCrAlY alloying layer, and between the alloying layer and the substrate. The chemical modification of ZrO_2 can be adopted to eliminate microcrackings of the coatings. The oxidation resistance of such laser-clad thermal barrier coatings in air at 1200 °C is significantly higher than that of plasma-sprayed coatings. In addition, LC with 60% Ni, 19% Cr, 11% Al, and 6.4% Fe showed an excellent corrosion resistance than the Incoloy 800H,[12] so that these coatings can be used as an oxidation barrier in high temperature applications at temperature levels over the maximum limit where the Incoloy 800H can be used.

Titanium-based alloys are high-strength, light materials used extensively in the aerospace industries for airframe structures and component parts of aircraft engines (e.g., airfoils). However, titanium alloys have poor oxidation resistance at temperatures above 600 °C. The most critical section of the airfoil is its tip, which is generally exposed to high temperatures >500 °C during engine operating conditions. LC of 50Nb–50Ti alloy on the tip of airfoils (Ti–6A1–4V alloy) has resulted in an excellent oxidation resistance at 1000 °C in air. In contrast, the unclad Ti–6Al–4V alloy formed a 500-μm thick, porous oxide layer, which tends to spall from the substrate, forming a 100-μm oxide in 48 h with a good adherence.[13] Important features of such LC processes for industrial applications include that the laser beam is capable of following the contour of the airfoils; good bonding between the laser-clad niobium and airfoils, and readily controlled thickness and composition of the clad.

In municipal waste incinerators (MWI), critical components such as superheater or boiler tubes are often degraded by corrosion. Especially in modern waste-to-energy (WTE) plants, the need for increased efficiency requires operation at higher temperatures, which in turn enhances the corrosion rates. LC has been successfully used for the production of anticorrosion and antierosion coatings on superheater and boilers tubes. Compared with protective coatings produced by flame spraying, LC is virtually porosity free and ensures metallurgical bonding to the substrate, so that the clad tubes can be bent without any damage from cracking or spalling. This is an important development for the construction of the bends of the superheater coils and the production of integral laser clad superheater assemblies. One automatic diode laser workstation available for industrial production of MWI superheater and boiler clad tubes has been demonstrated and installed in European MWI plants.[14]

4.09.3.2 Laser Surface Melting

In the laser surface melting (LSM) process, a thin surface layer is rapidly melted by a high-power laser beam, followed by a rapid solidification to produce a microstructure different from that of the bulk material. High cooling rates of the molten surface layer can promote the formation of an amorphous material, metastable phases, or a fine-grained microstructure resulting in improved surface properties, such as wear, corrosion, and fatigue resistance. The principal advantage of LSM is that it alters the microstructure without changing the composition, compared with other laser surface modification techniques introduced later. More importantly, LSM has been utilized as a posttreatment for other surface coating techniques. The most commonly encountered example is laser melting of thermally sprayed coatings. In this case, it is also referred to as laser remelting.

Thermal spraying processes are widely used to apply a variety of coatings, including metallic coatings, metal matrix composite coatings (MMC), and ceramic coatings, on different substrates. However, despite the efforts made to improve spraying techniques, such as high-velocity oxy-fuel (HVOF) and plasma spraying, the coatings may still exhibit certain defects such as unmelted particles, oxide layers at splat boundaries, porosity, and microcracks, which are detrimental to corrosion performance. Furthermore, the bonding to the substrate is usually not metallurgical or fusion based. Interconnected porosity and lamellar grain, splat-structures, with oxide inclusions at interlayer boundaries, result in potential failure of the coatings due to penetration of corrosive agents into the interlayer and eventual debonding of the coatings. The use of LSM to modify the structures of thermal sprayed coatings is referred to as laser sealing or laser glazing. In this technique, melting is induced in the near-surface coating by a relatively high intensity and short duration of laser irradiation.

For thermally-sprayed metallic coatings, laser melting is an effective technique for a significant improvement in the corrosion resistance by elimination of defects in the original thermal-sprayed layers. Normally, high-power CW lasers, such as CO_2 laser, Nd:YAG laser, and HPDLs, are chosen with appropriate selection of laser operating conditions enabling fully controllable melt pool dimensions. Therefore, thermal-sprayed coatings can be either partially melted (i.e., top-layer only), or fully melted (i.e., whole layer together with a small portion of substrate material). In both the cases, the defects in the original thermal-sprayed coatings can be completely eliminated, while fully melting offers an advantage of the formation of a metallurgical bond compared with the mechanical interlocking in the original coatings. For example, plasma-sprayed Ni31Cr11Al0.6Y coating on Alloy 800H, as a physical barrier to carbon ingress, improves the metal dusting resistance, with limitation due to the presence of interconnected porosity. Laser remelting of such coatings further improves the metal dusting resistance of the thermal-sprayed coated alloys due to improving the effectiveness of the coating by elimination of interconnected porosity.[15] In addition, laser remelting of HVOF-sprayed Inconel 625 coatings resulted in the homogenization of the sprayed structure, and the removal of oxide inclusions between splats and interconnected porosity, leading to a significant improvement in resistance to wet corrosion and high temperature corrosion. The corrosion resistance of the sprayed coatings after laser treatment is equivalent to that of the wrought alloy.[16]

For MMC, which are normally applied using HVOF, apart from the role of common defects of thermal-sprayed coatings described earlier, the corrosion processes are dominated by complex microgalvanic and interfacial mechanisms. First, the interface between the hard phase and the matrix represents a physical microcrevice, providing an inherent driving force for localized attack due to classic mechanisms of differential aeration; second, the difference in electrochemical potentials between the coating constituents provides additional driving force for localized corrosion due to microgalvanic corrosion. Third, the existence of interconnected porosity and lamellar grains, splat-structures with oxide inclusions at interlayer boundaries results in another major concern to the failure of the coatings due to corrosion penetration into the interface and eventually debonding of the coatings. Laser remelting of such HVOF MMC coatings is an obvious option owing to its unique features over conventional heat-treatments, for example, precise control of treatment depth with or without melting. The resultant microstructural homogenization, such as the removal of the splat-structure and porosity, the reduction of sharp compositional gradient between the hard phase and the matrix, and the improvement in adhesion bonding between coating and substrate, can be readily achieved. Compared with metallic coatings, special attention should be paid to an appropriate selection of laser operating conditions to avoid formation of cracks and porosity within laser-melted layers. Laser remelting of Inconel 625-based tungsten carbide (WC) HVOF-sprayed MMC coatings significantly improves the corrosion resistance as a result of the elimination of a discrete splat-structure, microcrevices, and porosity, and also reduces the microgalvanic driving force between the WC and the metal matrix. In addition, an improved wear resistance of the laser-treated coatings results due to the formation of a faceted dendritic structure of the WC phase.[17] Therefore, laser remelting shows potential benefits for the improvement in HVOF coatings in tribocorrosive environments.

A typical example of ceramic coatings is thermal barrier coatings consisting of $ZrO_2 + 8\,wt\%\ Y_2O_3$ as the outer coating and NiCrA1Y layer as a bond-coat on Ni-base substrate. Such TBC coatings, normally applied by plasma spray on hot-section components of gas turbines, offer significant advantages of increased operating temperatures and protecting the coatings from hot corrosion. The coatings retain a substantial amount of interconnected pores and microcracks, with high porosity providing a better thermal protection. However, the life of the coatings is limited by the oxidation of the metallic bond coat due to the penetration of corrosive fuel through the porosity, which causes the failure of the coatings by the spalling of ceramic coating layer. Laser surface remelting shows great potential for the improvement in plasma-sprayed thermal barrier coating properties by reducing surface roughness, eliminating open porosity on the surface, and modifying microstructures from lamellar to columnar. In laser-melted ceramic materials, cracks frequently occur in the densified layer perpendicular to the surface, generated by shrinkage and thermally induced stresses. However, it is possible to generate a controlled segmented crack network by properly selecting laser operating conditions, so that improvement in thermal shock resistance can be achieved. For example, laser glazing increases thermal cyclic lifetimes of plasma-sprayed thermal barrier coatings about fourfold by improving the strain accommodation through segmented cracks.[18] Laser glazing has also resulted in enhancement, approximately fourfold, in the lifetimes of plasma-sprayed thermal barrier coatings by in high temperature corrosion tests involving V_2O_5 salts.[19] However, the existence of macroscopic vertical cracks may provide a path for oxygen and molten salts to attack the TBC system. Therefore, special care must be taken in the consideration of a compromise between the desirable and undesirable properties.

4.09.3.3 Laser-Assisted Thermal Spray

As described earlier, the improvement in integrity and performance of thermal-sprayed coatings can be achieved by laser remelting. However, such a process requires additional steps. Although LC has a potential to be developed as an effective technique for coatings in practice, it is inefficient for large-area coverage in industrial applications; more than 10 times slower than thermal spraying in terms of materials deposition rate. In addition, LC of ceramic materials also produces numerous macrocracks.

An effective combination of laser processing and conventional thermal spray systems, namely laser-assisted thermal spray, has been developed and provided the opportunity for depositing dense coatings on large surface areas with improved structural integrity and performance, and acceptable process efficiencies for industrial applications. The laser in such a combined system can be used to reduce microstructural defects, improve cohesion within the coatings, and achieve fusion bonding between the coating and the substrate. The thermal spray jet can provide an effective heat source for increasing the processing rate (relative to LC) and controlling the temperature gradients and thermal stresses during processing. This could be of considerable benefit to process and manufacturing engineers.

Lasers can be combined with various types of thermal spray techniques. For example, laser-assisted flame hybrid spraying process has been developed to deposit alumina coatings on alumina-based refractory ceramics.[20] Flame spraying is a cost-effective and highly flexible surface coating technique; however, the resulting coatings are porous and have a low mechanical bonding to the substrates. LSM can produce very dense surfaces and fused bonded layers; however, cracks in the treated layers readily occur and the process velocity is often too slow for industrial applications. The combination of flame spraying and laser beam decreases, and may even overcome the drawbacks of the individual processes, thus forming an efficient method for depositing coatings with improved structural integrity. Coatings with dense microstructures and fusion-bonded to the substrate are especially desirable for refractory materials used for lining furnaces and incinerators. In addition, laser-assisted plasma spray systems have been used to produce dense NiCrBSi coatings on small mild steel components,[21] and to deposit a Ni/Ti coating onto a Ti–6Al–4V substrate.[22] The shear strength of the Ni/Ti coating was increased sixfold compared with a conventional plasma coating, as a result of the improved bond between the coating and the substrate.[22] A similar laser-plasma hybrid spraying system has been applied to deposit Y_2O_3 stabilized ZrO_2 thermal barrier coatings, with modified crack system and pore connectivity leading to a significantly decreased permeability in the produced coatings compared with laser posttreated coatings. Therefore, combined laser and thermal spray processes are promising for depositing denser coatings, with much increased processing efficiency, to achieve improved structure integrity and performance.[23]

4.09.3.4 Laser Melt/Particle Injection

Laser melt/particle injection (LMI) can be considered as a special form of LC, which is aimed at producing a metal–matrix composite layer on top of a substrate. The laser beam melts the substrate locally while particles of additional material with a high melting temperature, usually ceramics, are simultaneously injected. Another version of LMI uses a laser beam to melt coaxially fed metallic powder and simultaneously inject ceramic particles into the melt pool. These particles are trapped when the melt pool rapidly solidifies after the laser beam has passed. Unlike LC, in LMI, the interaction between ceramic particles and laser beam is limited so that the ceramic particles remain mainly in the solid state, but with partial dissolution of the ceramic particulate into the melt pool, forming new phases at/around the interface between the particles and metal matrix.

MMC coatings are normally used for the improvement in wear performance. However, MMC coatings often have poor resistance to corrosion, and applications of such coatings in corrosive environment can be limited. Therefore, there is a need to achieve excellent wear performance with acceptable corrosion resistance. As described earlier, the corrosion properties of MMC coatings produced by thermal spraying are dominated by complex microgalvanic and interfacial mechanisms, as well as by oxide inclusions and porosity. However, it is possible to control the corrosion performance of LMI-produced MMC coatings by suitably adjusting the laser operating parameters to partially dissolve ceramic particles, to promote the formation of interfacial phases, and to eliminate other coating defects. For example, LMI-produced TiC–Ti–6Al–4V exhibits an excellent corrosion resistance in seawater after 1 month exposure.[24] In addition, MMC coatings of Al_2O_3 particle injected Ni–Cr–Al–Hf produced by LMI are possible candidates to meet the technical challenges of particular turbine components, such as the tips of turbine airfoils, requiring thermal stability, high temperature oxidation resistance, and wear resistance.[25] Compared with MMC coatings produced by thermal spray techniques, such as HVOF, LMI results in an improved corrosion resistance by (1) reducing the sharp composition gradient between the matrix and the hard phase through promoting some interdiffusion; (2) forming a uniform distribution of the phase and composition with a much lower number of defects such as porosity and microcracks in MMC coatings.

4.09.3.5 Pulsed Laser Deposition

PLD is a thin-film deposition technique using high-energy laser pulses to vaporize the surface of a solid target inside a vacuum chamber and condensing the vapor on a substrate to form a thin film up to a few micrometers in thickness. Figure 2 shows a schematic diagram of a typical PLD process.

The main advantage of PLD derives from the laser material removal mechanism. PLD relies on a photon interaction to create an ejected plume of material from any target based on rapid explosion of the target surface region due to superheating. Unlike thermal evaporation, which produces a vapor composition dependent on the vapor pressures of the elements in the target material, the laser-induced expulsion produces a plume of material with stoichiometry similar to that of the target. Therefore, it is generally easier to obtain the desired film stoichiometry for multielement materials using PLD than with other deposition technologies.[27] On the other hand, the kinetic

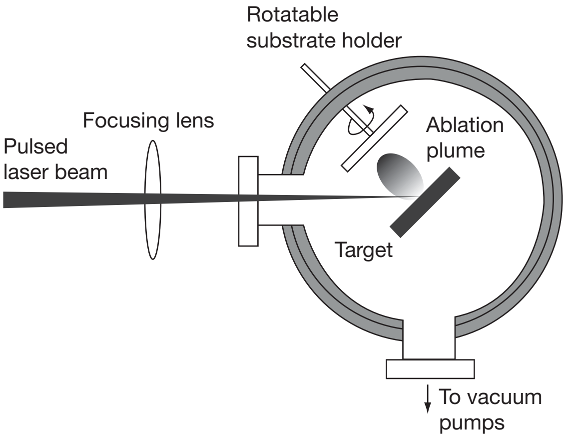

Figure 2 Schematic diagram of PLD process.[26]

energies of ablated particles are typically high enough to promote surface diffusion, but not so high as to induce bulk damage. Thus, PLD can create thin films of a wide range of materials, including metals, semiconductors, and insulators with excellent adhesion. Since PLD results in a high cooling rate during film formation, it is likely to form nanocrystalline or even amorphous alloy films. Some of the films have been applied as protective barriers in corrosive environments.[28–30] For example, amorphous Ta–Ni films produced by PLD offer extremely high corrosion resistance in both acid and alkaline solutions.[28] A 160-nm thick film of Y_2O_3 deposited on Zn–22Al–2Cu alloy produces an improvement of up to 75% in corrosion resistance in aerated water of pH 4.5, compared with the alloy without the Y_2O_3 film.[29] In addition, the PLD technique can be used to form alumina-stabilized zirconia films on fused silica substrate making for both corrosion resistance and thermal barrier purposes.[30]

Since it is possible to control microstructures in a wide range, from amorphous dense to microcrystalline porous, by properly selecting laser operating conditions, PLD offers significant advantages and manufacturing flexibilities for the formation of graded coatings for thermal and corrosion barriers, compared with other methods such as electron beam-physical vapor deposition (EB-PVD) and atmospheric plasma spraying (APS). A German National Science Foundation program has reported a successful deposition of functionally graded thermal barrier coatings on Cu substrates by PLD to sustain extremely high thermal loadings in a hot gas environment.[31] A columnar–lamellar microstructure, with designed column size, graded profile of lamellae thickness and interface modification can be produced, to a large extent, by means of PLD using a combination of nano- and microsecond laser beam pulses.

4.09.3.6 Laser Chemical Vapor Deposition

Laser chemical vapor deposition (LCVD) is employed to generate solid deposits on a substrate by laser beam-induced chemical reactions in a chemical vapor reactant. LCVD processes can be divided into two main categories: photolytic and pyrolytic, depending on the mechanism that activates the chemical reactions.

Photolytic LCVD, as shown in Figure 3(a), utilizes photons of a laser beam to break chemical bonds within the reactive gases. The molecules either recombine or decompose to form a solid deposit on the surface of the substrate. Pulsed lasers in the ultraviolet wavelength, typically excimer lasers with photon energies of several electron volts, are used for photolytic reactions. The main advantage of photolytic reactions is the absence of high temperatures that may adversely affect the substrate or build up thermal stresses within the deposited layers. In pyrolytic LCVD, the energy of a laser beam is used to heat

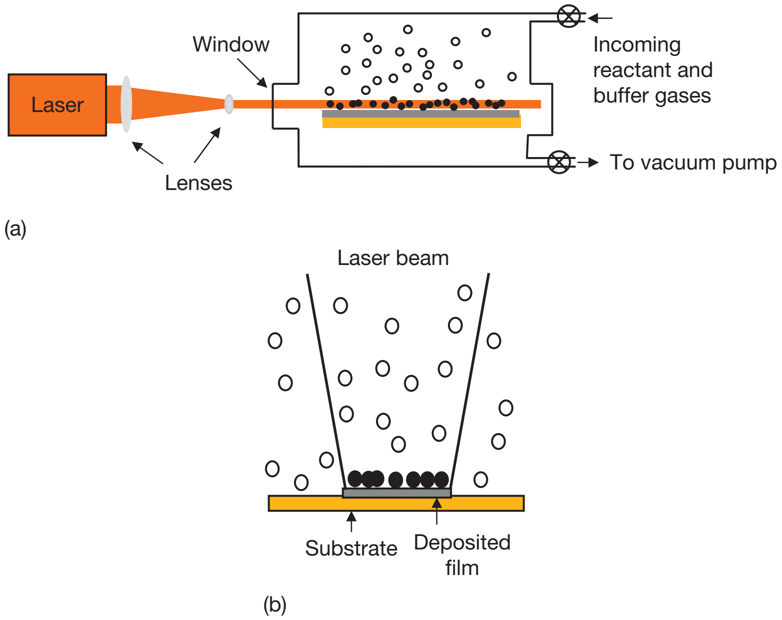

Figure 3 Schematic diagrams of LCVD (a) photolytic and (b) pyrolytic process.

the surface of a substrate to the temperature required for thermally driven chemical deposition, as shown in Figure 3(b). Typically lasers with infrared wavelengths such as CO_2, Nd:YAG, and HPDLs, are used for such processes. Compared with the traditional thermal CVD, LCVD offers the significant advantage of avoiding the heating of the entire substrate to the reaction temperature.

Silica coatings on metallic substrates have been produced using an ArF excimer laser to photolytically induce the reaction between SiH_4 and N_2O.[32] This technique is capable of producing complex silica coatings with graded density, thus efficiently solving the potential problem caused by thermal expansion coefficient mismatch between the metallic substrate and the coating. Protective coatings withstood thermal cycling and long-term corrosion tests at a temperature of 450 °C without spallation. This excellent performance is associated with the reduced elastic modulus of the less dense coating in contact with the metallic substrate and the improved diffusion barrier provided by the fully dense silica deposited on top.[32] In addition, Ta_2O_5 films with columnar, dense structures, prepared by KrF excimer laser CVD from tantalum-penta metoxide ($Ta(OCH_3)_5$, have been shown to reduce the corrosion current density of iron by six orders of magnitude, indicating that the dense LCVD–Ta_2O_5 coating was effective in increasing the corrosion resistance of an iron substrate.[33]

Although CVD has often been considered to be a slow process for the production of thick coatings, a laser CVD process has achieved high deposition rates for YSZ coatings with either a columnar structure (Figure 4(a), $230\,\mu m\,h^{-1}$) or a cone structure (Figure 4(b), $660\,\mu m\,h^{-1}$). At high deposition rates, a large number of nanopores are formed within grains (Figure 4(c)), resulting in a thermal conductivity of $0.7\,W\,mK^{-1}$, which is almost the same as that of EB–PVD YSZ coatings. However, the nanopores in the laser CVD YSZ are relatively stable such that the thermal conductivity does not increase significantly after heat-treatment for more than 20 h at high temperatures of ~1000–1100 °C.[34] Laser CVD is also capable of forming other oxides, such as Al_2O_3 and TiO_2 coatings, at deposition rates ~1–2 $mm\,h^{-1}$. The thick coatings, of more than several 100 μm, provides at high speeds by laser CVD may find many industrial applications in industries requiring corrosion and abrasion resistance.[34]

4.09.3.7 Laser Surface Alloying

LSA is a process that is used to incorporate additional alloying elements into the surface of a component, by utilizing a laser beam with high power density to melt metal coatings and a portion of the underlying substrate. The typical thickness of the alloyed surface layer ranges from 1 μm to 2 mm. The thickness and the composition of the treated surface can be adjusted by controlling the laser power intensity and the interaction time. Due to the high cooling rate associated with LSA, nonequilibrium phases and supersaturated solid solutions can be readily achieved. LSA processes may be divided into two classes, namely, thin-film alloying and thick-layer alloying.[35]

The thin-film alloying process involves the use of short energy pulses (width range from some nanoseconds up to a few microseconds). The typical alloyed thickness is a few micrometers. The mixing process is based on a diffusion mechanism of mass transfer, with cooling rates of up to $10^{11}\,K\,s^{-1}$, leading to a strong decrease of the alloying elements' concentration with

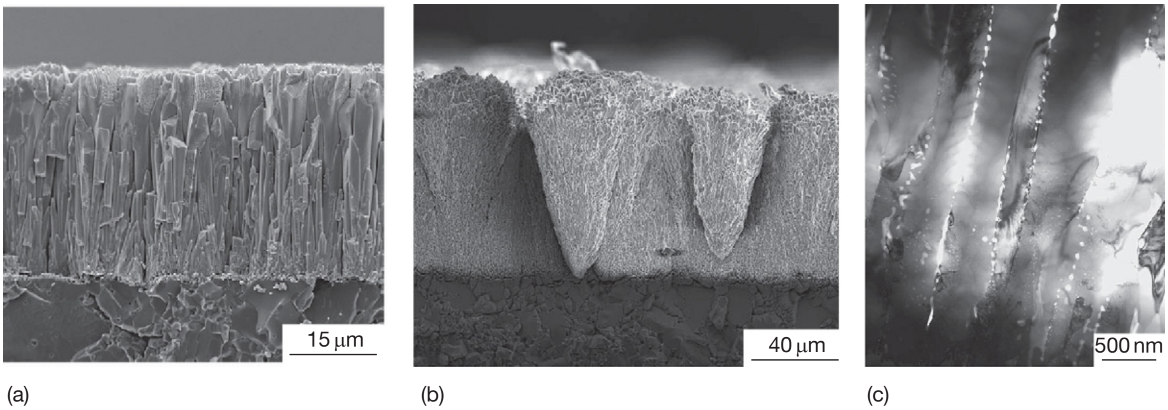

Figure 4 Cross-section of YSZ coatings prepared by laser CVD at a deposition rate of $230\,\mu m\,h^{-1}$ (a), $660\,\mu m\,h^{-1}$ (b), and nanostructure of the YSZ coatings (c).[34]

the increase of the depth in the modified layer. The thick-layer alloying process involves the use of either energy pulses of duration from 1 up to 20 ms or CW radiation, resulting in cooling rates of 10^4 to 10^6 K s^{-1}. The typical alloyed thickness is in the range of 0.1 mm to a few millimeters. The mixing process within the melt pool is mainly controlled by a convective mechanism of mass transfer. Therefore, the chemical compositional homogeneity of the melted layer can vary from relatively uniform to highly nonuniform, depending on the turbulent stirring effect within the melt pool driven by surface tension gradients that result from thermal gradients, that is, Marangoni effect. For metals, the convection speed is several orders of magnitude higher than the laser scanning speed, leading to a rapid homogenization. When the melting temperature of the alloying elements is considerably higher than the melting temperature of the substrate material, or when the alloying elements react with the melt pool material to form insoluble high melting temperature phases, alloying may be difficult.

A main characteristic of LSA is the possibility of producing an almost unlimited range of alloy composition for the surface layer, with fine and homogenized microstructures, tailor-made for the requirement. However, it is difficult sometimes for certain elements to be alloyed into certain material substrates. In selecting elemental combinations for LSA, attention needs to be paid to the relative melting temperature, vaporization temperature, and vapor pressure of alloying elements and substrate materials. Processing will be difficult if the added element vaporizes at a temperature that is lower than the melting temperature of the substrate material; for example, in LSA of Zn into a Cu substrate, since at 1 atm Zn boils at ~900 °C, while Cu does not melt until ~1100 °C.

The rapid cooling rate associated with LSA provides a unique opportunity for the generation of nonequilibrium alloys. The thickness and composition of the treated surface can be adjusted by properly choosing the type of laser and appropriately controlling the laser power intensity and interaction time. In LSA, the extent of solid solubility can be increased as a result of solute trapping arising from rapid rates of cooling. Therefore, more alloying elements can be retained in solid solution, with beneficial effects on corrosion properties or wear properties. There are other methods of producing nonequilibrium metallic alloys, using rapid solidification technology (RST), such as atomization, twin roll quenching, and melt spinning. However, in order to make an engineering component, the materials must be consolidated, involving temperature and pressure cycles that can induce phase transition in a metastable material.[2] Therefore, laser processing has potential benefits for the generation of nonequilibrium materials for industrial applications.

Surface alloying of transition-metal elements, such as Cr, Ni, and Mo, has been applied on low-carbon steel substrates for corrosion protection. For example, LSA of Cr into mild steel produces a uniform Cr distribution in the alloy layer, and consequently, a decrease in the critical current density required for passivation and a decrease in the passive current density in the passive range.[36] In addition, LSA of Mo into 304 stainless steel increases in the critical pitting potential on potentiodynamic polarization in 0.1 M NaCl solution. The critical pitting potential for surface alloys containing 3% Mo is comparable with that of bulk 316 alloy, while surface alloys containing 9% Mo indicate no breakdown up to the oxygen evolution potential.[36] In addition, surface alloys rich in Ni–Mo produced by LSA of 304 stainless steel substrate result in a pitting resistance above that of AISI 316 stainless steel.[37] Fe–Cr–Ni–Mo–C surface alloys with different compositions can be produced on carbon steel.[38] The pitting potential of the Fe–18.7Cr–6.3Ni–3.8Mo–0.14C laser surface alloy is ~200 mV higher than that of AISI 316 stainless steel and Fe–23.2Cr–7.3Ni–4.7Mo–0.13C laser surface alloy does not suffer pitting corrosion in anodic polarization tests in 3% NaCl.

LSA of nonferrous substrates has been applied for the improvement in corrosion properties. LSA of Al + Mn into a Mg alloy (MEZ) produces an alloyed surface consisting of dendrites of Al + Mn and Al + Mg, which significantly reduces the corrosion rate in 3.56 wt.% NaCl solution to 250 mpy, compared with 1520 mpy of the MEZ substrate. This improved corrosion resistance was due to the presence of Al_2O_3 and Mn_3O_4 layer on the alloyed surface, while the microhardness of the alloyed zone was enhanced up to 1250–350 VHN, compared with 35 VHN for the substrate.[39] LSA of Zircaloy-4 with niobium (Nb) significantly improves the resistance to localized corrosion in a chloride solution at 80 °C due to the combined effects of a rapidly cooled, fine microstructure and the Nb alloying. However, it should be noted that the corrosion resistance of such an alloyed surface is reduced in steam at 400 °C.[40]

LSA is a potential option for the improvement in the high temperature oxidation resistance of high temperature alloys. The high temperature oxidation resistance of laser-surface-alloyed Incoloy-800H with

Al is significantly improved at 1000 °C in air, due to the formation of an Al-rich layer close to the surface, which acts as a barrier against oxygen diffusion into the bulk.[41] In a similar way, LSA of Incoloy-800H with Al and Si improves the resistance to metal dusting.[42]

When LSA is used for thin-film alloying by use of excimer lasers, it provides a unique opportunity to produce concentrated alloying elements extending to depths of submicrometers to a few micrometers, without bulk heating or the requirement of a vacuum. A typical example is LSA of 50-µm thick Ti foil with Pd layer of 310-nm thick, using a KrF excimer laser.[43] Using this technique, it was possible to form homogeneous surface-alloy regions by rapid diffusion and intermixing, and demonstrate a major improvement in the corrosion resistance in 0.1 M H_2SO_4 solution at 80 °C, as shown in Figure 5, due to the shifting of the potential to the region of passivity of titanium. Such Pd-alloyed Ti foils have been of interest for increasing the life of titanium foils that are used as electron-transparent windows in the removal of SO_2, NO_x, and volatile organic compounds from flue gas by EBs.

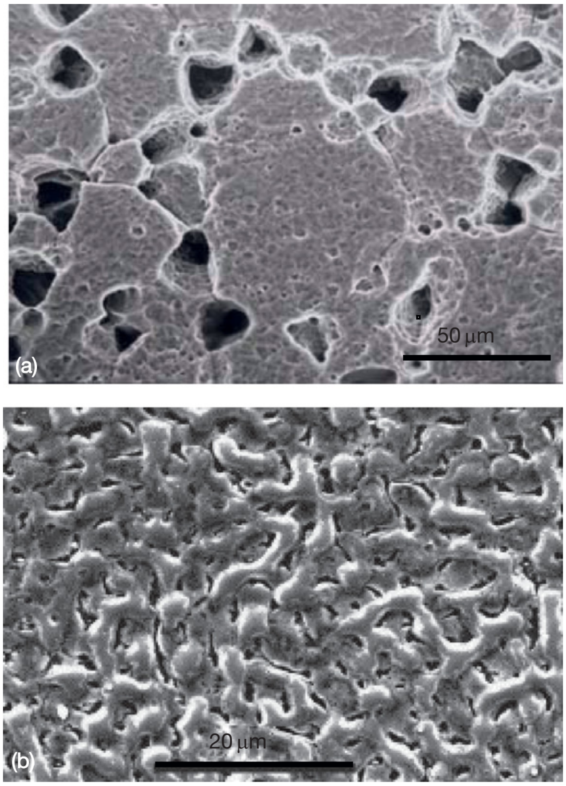

Figure 5 Corrosion morphology of untreated titanium foil (a) and laser-alloyed with Pd after immersion in H_2SO_4 solution (b) at 80 °C.[43]

Laser gas nitriding (LGN) is a special form of LSA by laser melting of a metal surface in a nitrogen gas environment to form a nitride layer on the irradiated surfaces by chemical reactions. Many metals, including iron, carbon steels, stainless steels, and aluminum alloys, can be nitrided by lasers. These layers are metallurgically bonded with the substrate and have better interfacial properties than those produced by other nitriding techniques such as PVD, CVD, and ion implantation. Depending on the type of laser, the typical depth of nitrided surface layers can be in the range of a few microns or up to a few hundred microns. In the LGN process, a major problem to be addressed is cracking. There are two types of cracks on laser nitrided Ti–6Al–4V surfaces: (1) macrocracks induced by the accumulation of tensile stresses during the laser melting process; and (2) microcracks related to the inherent brittleness of TiN.[44] However, such cracks can be eliminated by proper selection of laser operating conditions, such as energy level, pulse width, traverse velocity, and gas environment (e.g., diluted nitrogen gas). Figure 6 shows a typical example of LGN of Ti–6Al–4V alloy, using a Nd:YAG laser with a pulse width of 200 µs.[45] In cross sections, the microstructures mainly consist of an outer thin continuous layer of TiN, followed by a region of nearly perpendicular TiN dendrites, and an intermixture region of small dendrites and large needles of nitrogen-enriched α-Ti phase. The density of TiN dendrites decreases gradually toward the interface between the nitrided layer and the substrate. An improvement in pitting corrosion behavior in 3.5% NaCl solution, associated with the presence of the TiN coating, can be achieved.

When an excimer laser is used for nitriding, the mechanism of formation of the nitrided thin-films

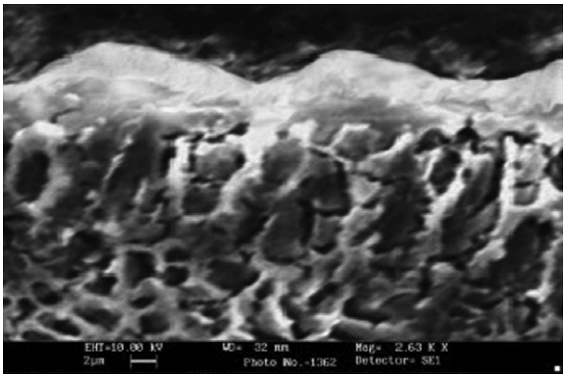

Figure 6 Typical cross-sectional microstructure of laser nitrided Ti–6Al–4V surface.[45]

differs from that with other types of lasers. In the excimer laser nitriding process, the laser beam is focused on an alloy surface in a chamber containing nitrogen gas. At each pulse, the laser–surface interaction leads to metal heating and vaporization. Vapor plasma expands from the surface and a shock wave dissociates and ionizes nitrogen. It is assumed that nitrogen from the plasma in contact with the surface penetrates to some depth, to form a nitride layer several micrometers thick.[46] For example, excimer laser nitriding of $AlSi_7Mg_{0.3}$ alloy produces an AlN (columnar microstructure) top layer (200–500 nm thick) standing on an AlN (grains) in the alloy diffusion layer.[46] Excimer LSM of aluminum alloy 6013 under nitrogen atmospheres forms $AlN–Al_2O_3$ films, which are barriers against corrosion in 3.5% NaCl solution as demonstrated by a reduction in corrosion current density of three orders of magnitude compared with the untreated alloy.[47] Excimer LSM of an $Al\text{-}2009/SiC_w$ composite in nitrogen gas presents an improved corrosion resistance in 3.5% NaCl solution, due to the formation of AlN in the laser-modified layer. In addition, the reduction of both the number of SiC whiskers, caused by excimer laser ablation, and the amount of Cu-bearing compounds in the laser- modified layer were also attributed to the improvement in corrosion performance.[48]

4.09.4 Advantages and Limitations of Laser Applied Coatings

Table 1 summaries the laser applied coating techniques introduced in this chapter.

Since a laser generates extremely concentrated beam energy, laser-applied coatings offer significant advantages over more conventional surface engineering techniques. The laser techniques can be used to selectively modify surface composition and microstructure without affecting surrounding material properties and causing thermal distortion. Hence, these processes are applicable to processing of critical regions of a component. In addition, a unique advantage of laser coating techniques is the rapid cooling rate, which enables the formation of amorphous or microcrystalline surfaces, modification of

Table 1 Summary of various laser applied coating techniques introduced in this chapter

Coating techniques		*Coating thickness*	*Coating materials*	*Type of lasers*
Laser cladding		Thick-layer (50 μm to 2 mm)	Metallic alloys; ceramics	CW CO_2, CW Nd:YAG, HPDL
Laser melt/particle injection		Thick-layer (a few hundred micrometers to 2 mm)	Metal matrix composites	CW CO_2, CW Nd:YAG, HPDL
Laser surface remelting (laser sealing; laser glazing) of thermal sprayed coatings		Fully or partially melting (melt depth greater than/equal to or less than thermal sprayed coating thickness)	Metallic alloys; metal matrix composites; ceramics	CW CO_2, CW Nd:YAG, HPDL
Laser-assisted thermal spray		Thick-layer (50 μm to 2 mm)	Metallic alloys; metal matrix composites; ceramics	CW CO_2, CW Nd:YAG, HPDL
Pulsed laser deposition		Thin-film (up to a few μm)	Metallic alloys; ceramics.	High energy pulsed lasers with ns pulse width, e.g., Excimer laser.
Laser chemical vapor deposition	Pyrolytic	Thin to moderate films (a few micrometers to a few hundred micrometers)	Metallic alloys, ceramics.	CW CO_2; CW Nd:YAG, HPDL
	Photolytic	Thin-film (up to a few micrometers)		Excimer laser
Laser surface alloying		Thick-layer (up to 2 mm)	Metallic alloys	CW CO_2; CW Nd:YAG; HPDL
		Thin-film (up to a few micrometers)		Pulsed Nd:YAG laser with ns pulse width; Excimer laser
Laser nitriding		Thick-layer	Metal nitrides	CW CO_2, CW Nd:YAG; HPDL
		Thin-film		Pulsed Nd:YAG laser with ns pulse width; Excimer laser.

grain size and orientation, and control of inclusion morphology and distribution for improved surface microstructure at both the micro and macro levels. For thick coatings, laser techniques produce relatively pore-free surfaces compared with thermal spray coatings, which are integral to the substrate, and thereby eliminate the problem of debonding. For thin-film deposition, laser processing penetrates to greater substrate depths compared with ion beam treatments, which may result in a longer lifetime of the coatings.

On the other hand, a laser beam with sufficient energy density for coating processes has a limited size. Therefore, a laser-applied coating technique is less efficient than other conventional methods like thermal spraying, in terms of coverage rate; in addition, coverage of large area components by laser-applied coatings requires overlapping of individual tracks. This overlapping process could result in an inherently nonuniform microstructure in the treated surface due to the reheating of a small portion of the previous track. Such microstructural changes may or may not have significant influence on corrosion properties, depending on coating materials.

Generally, laser coating techniques, except PLD, require no vacuum conditions, thereby providing substantial manufacturing flexibility. They provide chemically clean, noncontact, possibly remotely operated procedures that can be automated and integrated into other conventional production processes. Therefore, laser-applied coatings have become the preferred choice in many applications. Applications of laser-applied coating techniques can be limited to small areas, complex shapes, and high value/high cost items. However, the interest in laser-applied coatings, especially LC, of large components is increasing. With reductions in the cost of laser power, increased reliability and output power, and capacity of fiber delivery systems, coatings over large areas have become cost effective. These improvements have enabled lower-value items to benefit from laser-based coating techniques. For example, the power generation industry has begun to use LC of boiler tubes and water walls in steam generators, which can be justified in terms of the environmental improvement resulting from the reduced use of chromium. In addition, the development of an effective combination of laser processing and conventional thermal spray systems has provided a new opportunity for depositing dense coatings with improved structural integrity and performance on large surface areas at acceptable process efficiencies for industrial applications.

As with all laser-based processes, a lack of familiarity with the process may be an obstacle to industrial application. However, as more sophisticated operating systems become available, in which computer-generated models are integrated with automated beam and alloy delivery, the scope of applications of laser-applied coating is increasing considerably.

References

1. Li, L. *Opt. Lasers Eng.* **2000**, *34*, 231–253.
2. Mazumder, J. In *Non-equilibrium Synthesis by Laser for Tailored Surface*, Proceeding of the NATO Advanced Study Institute on Laser Processing: Surface Treatment and Film Deposition, Sesimbra, Portugal, July 3–16 1994.
3. Wu, J. D.; Wu, C. Z.; Song, Z. M.; Li, F. M. *Thin Solid Films* **1997**, *311*, 62–66.
4. http://www.ccl.fraunhofer.org/download/innovations_in_diode_laser_cladding.pdf.
5. Yue, T. M.; Su, Y. P.; Yang, H. O. *Mater. Lett.* **2007**, *61*, 209–212.
6. Gao, Y. L.; Wang, C. S.; Yao, M.; Liu, H. B. *Appl. Surf. Sci.* **2007**, *253*, 5306–5311.
7. Singh, J.; Mazumder, J. *Acta Mater.* **1987**, *35*, 1987.
8. Singh, J.; Naganathan, K.; Mazumder, J. *High Temp. Technol.* **1987**, *5*, 131–137.
9. Ribaudo, C.; Mazumder, J. *Mater. Sci. Eng. A* **1989**, *121*, 531.
10. Paetes, K.; Giolli, C.; Borgioli, F.; Bardi, U.; Seefeld, T.; Vollertson, F. *Surf. Coat. Technol.* **2008**, *202*, 2208–2213.
11. http://www.shvoong.com/exact-sciences/1607816-structure-oxidation-properties-thermal-barrier/.
12. Dedamborenea, J.; Lopez, V.; Vazquez, A. J. *Surf. Coat. Technol.* **1994**, *70*, 107–113.
13. Singh, J. *J. Mater. Sci.* **1994**, *29*, 5232–5258.
14. Fantini, V. In *Laser Cladding: A New Technology for Corrosion and Erosion Protection of Boiler Tubes*, Proceedings of the International Thermal Spray Conference and Exposition, May 14–17, 2007. Beijing, China.
15. Voisey, K. T.; Liu, Z.; Stott, F. H. *Surf. Coat. Technol.* **2006**, *201*, 637–648.
16. Tuominen, J.; Vuoristo, P.; Mantyla, T.; Kylmalahti, M.; Vihinen, J.; Andersson, P. H. *J. Therm. Spray Technol.* **2000**, *9*, 513.
17. Liu, Z.; Cabrero, J.; Niang, S.; Al-Taha, Z. Y. *Surf. Coat. Technol.* **2007**, *201*, 7149–7158.
18. Tsai, P. C.; Hsu, C. S. *Surf. Coat. Technol.* **2004**, *183*, 29.
19. Tsai, P. C.; Lee, J. H.; Hsu, C. S. *Surf. Coat. Technol.* **2007**, *201*, 5143–5147.
20. Li, J. F.; Li, L.; Stott, F. H. *Thin Solid Films* **2004**, *453–454*, 67–71.
21. Nowotny, S.; Scharek, S.; Zieris, R.; Naumann, T.; Beyer, E. In *Innovations in Laser Cladding*, Proceedings of the 19th International Congress on Applications of Lasers & Electro-Optics (ICALEO), 89, A11–15 Michigan, October, 02–05, 2000.
22. Hiraga, H.; Inoue, T.; Kamado, S.; Kojima, Y.; Matsunawa, A.; Shimura, H. *Surf. Coat. Technol.* **2001**, *139*, 93–100.
23. Antou, G.; Montavon, G.; Hlawka, F.; Cornet, A.; Coddet, C.; Machi, F. *J. Eur. Ceram. Soc.* **2006**, *26*, 3583–3597.
24. Cooper, K. P.; Slebodnick, P. L.; Lucas, K. E.; Hogan, E. A. *J. Mater. Sci.* **1998**, *33*, 3805–3816.

25. Wolfe, D.; Singh, J. *J. Mater. Sci.* **1998**, *33*, 3677–3692.
26. Michael, N. R.; Ashfold, F. C.; Gareth, M. F.; Henley, S. J. *Chem. Soc. Rev.* **2004**, *33*, 23–31.
27. http://pulsedlaser.net/index.html.
28. Yano, T.; Ooie, T.; Yoneda, M.; Katsumura, M. In *Proceedings of the Laser Materials Processing Conference,* 1996; Vol. 81, pp A67–A74.
29. Guerrero, R.; Farias, M. H.; Cota-Araiza, L. *Surf. Coat. Technol.* **2002**, *154*, 218–222.
30. Qadri, S. B.; Horwitz, J. S.; Chrisey, D. B.; Donovan, E. P.; Skelton, E. F. *Surf. Coat. Technol.* **1996**, *86–87*, 149–152.
31. Schulz, U.; Peters, M.; Bach, F.-W.; Tegeder, G. *Mater. Sci. Eng. A,* **2003**, *362*, 61–80.
32. Pou, J.; González, P.; García, E.; Fernández, D.; Serra, J.; León, B.; Saunders, S. R. J.; Pérez-Amor, M. *Appl. Surf. Sci.* **1994**, *79/80*, 338–343.
33. Mukaida, M.; Osato, K.; Watanabe, A.; Imai, Y.; Kameyama, T.; Fukuda, K. *Thin Solid Films* **1993**, *232*, 180–184.
34. Goto, T. *Surf. Coat. Technol.* **2005**, *198*, 367–371.
35. Smurov, I.; Ignatiev, M. In *Innovative Intermetallic Compounds by Laser Alloying*, Proceedings of Laser Processing: Surface Treatment and Film Deposition, Sesimbra, Portugal, July 3–16, 1994.
36. McCafferty, E.; Moore, P. G. *J. Electrochem. Soc.* **1986**, *133*, 1090–1096.
37. Grover, A. K.; Kumar, D.; Goswami, G. L.; Pappachan, A. L.; Totlani, M. K. *Lasers Eng.* **1998**, *7*, 119–131.
38. Anjos, M. A.; Vilar, R.; Li, R. *Surf. Coat. Technol.* **1995**, *70*, 235–242.
39. Majumdar, J. D.; Maiwald, T.; Galun, R.; Mordike, B. L.; Manna, I. *Lasers Eng.* **2002**, *12*, 147–169.
40. Lee, S.; Park, C.; Lim, Y.; Kwon, H. *J. Nucl. Mater.* **2003**, *321*, 177–183.
41. Gutierrez, A.; de Damborenea, J. *Oxid. Met.* **1997**, *47*, 259–275.
42. Ejaz, M.; Prescott, R.; Liu, Z. In *Resistance to Metal Dusting by Aluminium Laser-Alloyed Alloy 800H*, EURCORR 2007.
43. Blanco-Pinzon, C.; Liu, Z.; Voisey, K.; Bonilla, F. A.; Skeldon, P.; Thompson, G. E.; Piekoszewski, J.; Chmielewski, A. G. *Corros. Sci.* **2005**, *47*, 1251–1269.
44. Xue, L.; Islam, M.; Koul, A. K.; Bibby, M.; Wallace, W. *Adv. Perform. Mater.* **1997**, *4*, 25–47.
45. Razavi, R. S.; Salehi, M.; Monirvagheft, M.; Mozafarinia, R. *ISIJ Int.* **2007**, *47*, 709–714.
46. Sicard, E.; Boulmer-Leborgne, C.; Andreazza-Vignolle, C.; Frainais, M. *Appl. Phys. A* **2001**, *73*, 55–60.
47. Yue, T. M.; Mei, S. M.; Chan, K. C.; Man, H. C. *Mater. Lett.* **1999**, *39*, 274–279.
48. Xu, W. L.; Yue, T. M.; Man, H. C. *Surf. Eng.* **2007**, *23*, 284–290.

4.10 Paint Application

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Glossary

Thinners A low-viscosity liquid, commonly a solvent, which is added to paint prior to coating application in order to reduce its viscosity and permit easier and more rapid paint application, especially by spraying.

Transfer efficiency The ratio, as a percentage, of liquid paint to the quantity of organic coating that is applied to the surface. This can approach 100% for manual brush and roller application but is usually in the 40–70% range for spray application.

Abbreviations

HVLP High velocity low pressure
ICATS Industrial coatings applicator training scheme
ICorr UK Institute of Corrosion
VOC Volatile organic compounds

4.10.1 Introduction

Paints and organic coatings may be applied by many methods,[1,2] and it is not possible to consider all of them in detail in a chapter of this size. The main emphasis has been placed, therefore, on the methods of paint application used most commonly to protect constructional steelwork from corrosion[3,4] at either the fabrication stage or when the maintenance painting is required.

4.10.2 Methods of Applying Paints and Coatings

There are four main methods of applying paints and coatings for corrosion protection:

- by spreading, for example, by brush or roller;
- by spraying, for example, by air-assisted spray, airless spray and electrostatic spray;
- by dip coating and flow coating;
- by electrodeposition (this method is considered elsewhere in this volume).

For most steel fabrications and structures, protective coating systems are applied by spray. Application by brush is used to a much lesser extent, mainly for minor coating repairs during maintenance painting programs. At factory work, pipes and small fabrications may be dip coated and, during maintenance, some small, relatively inaccessible tanks, for example, may be flow coated.

4.10.2.1 Brush Application

The application of paints by brush is labor-intensive and time-consuming. Success depends to a very large extent on the quality and suitability of the brush, the rheological properties of the coating, and the diligence of the painter. Industrially, therefore, more rapid and efficient methods of paint application are now preferred.

Brushing is still seen, however, as a very suitable method of application for maintenance painting of small areas, for stripe coating of sharp edges and for coating awkward or restricted areas where spray application would be either difficult, or may not be permitted for reasons of health and safety.

When paints are applied by brush, there is minimal wastage and, usually, very little contamination of adjacent areas. A transfer efficiency approaching 100% is possible. Brushes can also be cleaned easily after use and, thereby, maintained in good condition.

The shape, length, and mechanical properties of the bristles of a paint brush determine its potential performance. The bristles must be capable of holding sufficient paint to allow coverage of a reasonable area from each loading. Bristles made from Chinese hog are excellent in this respect and continue to be favored by many painters, over brushes made with synthetic bristles of nylon or polyester fiber.

The size and shape of a paint brush determine its suitability for a particular coating task. Wide, flat brushes, for example, are most appropriate for coating large flat surfaces. Small round or oval brushes are most appropriate for specialist tasks, such as the coating of more complex surfaces with bolt heads and possible crevices. The action of brushing paint into relatively inaccessible spaces forces the coating into contact with the surface and promotes the wetting needed for full coverage and subsequent good adhesion.

Brushing is not a suitable method of application for paints, which dry rapidly by solvent evaporation, such as vinyl coatings, for example, as the viscosity of the applied film can increase rapidly and may quickly become difficult to apply satisfactorily to give an even film, free from brush marks.

4.10.2.2 Roller Application

The application of paints manually by roller to large, flat areas can be up to four times faster than coating the same area with a brush. Brushes may still be needed, however, to coat corners and edges satisfactorily. As cleaning of the roller after use can be time-consuming, industrial painters will often discard some types of roller cover (the cheaper ones), without cleaning: these thus become effectively ‘single-use’ items. The roller cover types used most commonly are mohair, lambswool, nylon and polyester. The cover material selected and the length of the nap will be determined usually by the type of coating to be applied and the surface finish required. The roller itself must be resistant chemically to solvents in the coating and also to any thinners used.

While most hand rollers are loaded simply by dipping them into a tray of paint, it is possible also to mechanize the procedure and feed paint to the roller with an electric pump. The inlet to the pump, typically a flexible tube with a filter on the end, is immersed in the can of paint. Flow to the roller is then controlled by a finger valve on the applicator handle. It is possible to achieve very high transfer efficiency, often better than 95%, when paints are applied by roller.

4.10.2.3 Air Atomized Spray Application

Air atomized spray guns were the first type of spray guns to be used commercially. They allow paint to be applied up to eight times more quickly than by brush, with better control and uniformity of film thickness. Losses of paint are, however, considerably higher than those incurred by either brush or roller application and considerable skill is needed to produce quality finishes at an economic cost.

In air atomized spray application, also known as conventional spray application, compressed air is used not only to atomize the paint, but also to propel it towards the surface to be coated. As the paint passes through the orifice of the fluid nozzle, it is mixed with compressed air and atomized at pressures, typically between 0.2 and 0.4 MPa.

Paint may be fed to the spray gun by gravity, by suction or by compressed air from a pressurized container. In the gravity feed system, the paint is placed in a cup on top of the spray gun and is fed to the nozzle by gravity. Gravity fed guns are ideal for small spray painting tasks, as they can be cleaned relatively easily after use. In the suction feed system, the paint is contained in a cup fixed to the underside of the gun and is drawn upwards into the gun as a result of the partial vacuum created at the nozzle by the flow of compressed air. The most common conventional spray gun, when used to paint large areas, relies on the paint being fed to the nozzle by compressed air, via a hose from a pressurized container.

Over-spray and bounce back are the two main disadvantages of conventional air atomized systems. Transfer efficiency is relatively poor and is, typically, between 30 and 45%. Overspray occurs when the paint misses the object being coated. The extent of overspray will depend on the size and shape of the object. It is influenced also by the spraying pressure, spraying distance, skill of the sprayer, and characteristics of the paint itself. Overspray may often contaminate other nearby surfaces on which it settles.

Bounce-back is a consequence of the high pressure of compressed air needed to atomize the paint. The air 'bounces' off the component, or the surface being sprayed, and, in doing so, creates an air barrier to the paint sprayed subsequently. The result is a fog or mist of the atomized paint, a characteristic feature of this method of application.

4.10.2.4 High Volume Low Pressure (HVLP) Spray Application

HVLP spray application is not a new process, but a novel spraying technique that has been developed further commercially to improve transfer efficiency and reduce the emission of volatile organic compounds (VOCs) to the environment, when solvent-borne coatings are applied by an air atomizing spray method. HVLP spray guns have now replaced conventional air atomized spray guns for many paint finishing operations. The HVLP spray gun still relies on air atomization but uses higher volumes of air at low pressures. Paint is delivered to the nozzle of the gun under pressure and is then atomized by this low-pressure air. In order to accommodate the larger volumes of air required, the air passages in the spray cap of the HVLP gun are much larger than those in a conventional spray gun.

HVLP spray application systems were developed originally in France in the 1950s. The earliest systems used a turbine to generate the high volumes of low-pressure air required. They were self-contained, requiring only an electrical supply to power them. Today, most HVLP spray guns use standard compressed-air systems for motive power. In the compressed-air HVLP spray application system, the air entering the gun is at a pressure of around 0.5 MPa. It is converted to low pressure, typically 0.05 MPa, inside the gun through either a series of valves and chambers designed to promote rapid expansion of the compressed air, or by means of a specially designed baffle located near the tip of the gun. At the low pressures which result, the forward velocity of the spray pattern is reduced considerably, in comparison with the forward velocity of atomized paint from a conventional compressed-air spray gun. As a consequence, there is significantly less overspray and substantially less bounce-back because of the lower velocity of the paint. The combined benefit is a much improved transfer efficiency of at least 65%. Speed of application is comparable with that of conventional air atomized spraying.

4.10.2.5 Airless Spray Application

This method of spray application is very different from the conventional techniques described previously. In airless spray equipment, the paint is not atomized by air. A fluid pump is used to force paint at high pressure through a fluid hose to the gun. Atomization is achieved by the release of highly pressurized liquid paint through a small orifice in the spray tip. Fluid nozzle sizes range, typically, in diameter from 0.03 to 0.15 mm. On exit from the small orifice in the spray tip, the paint atomizes into a cloud of ultrafine particles which then move forward slowly towards the surface to be coated. The slowing down is caused by the resistance of the atmospheric air and the cloud of ultrafine particles impacts on to the surface at a relatively slow speed, in comparison with conventional spray application. As there is no overspray and no bounce back, a transfer efficiency of well over 50% can usually be achieved. Penetration of the paint into crevices and recesses is good and, in the absence of entrained atomizing air, little or no solvent evaporation occurs during the spraying process. As a result, the subsequent flow out of liquid paint on the surface of the work piece is good.

Typically, the fluid pumps used with airless spray equipment have multiplication ratios of 48:1 or 60:1. This is the ratio of fluid output pressure to air input pressure. As the fluid output pressure at the spray tip can be of the order of 27 MPa, airless spray guns can deliver paint very rapidly and enable large areas of steel structures, for example, to be coated quickly. A surface area of 300 m^2, for example, can be coated in 1 h. The skill and experience of the sprayer will always determine the evenness of coverage and the final quality of the finish. Careful choice of tip size and spray width (the ‘fan’) is critical to success and the guidance given by the paint manufacturer on the technical data sheet for the coating product to be sprayed needs always to be observed.

It is important to note that airless spray guns can be dangerous in unsafe hands because, close to the nozzle, the paint being delivered is at a very high pressure. To prevent operators from carelessly, in effect, ‘injecting’ them with paint, all airless spray guns are fitted with tip safety guards.

4.10.2.6 Air-Assisted Airless Spray Application

As its name implies, air-assisted airless spray is a hybrid of airless spray application and conventional air atomized spray application. The purpose of introducing a compressed air supply is to aid atomization and improve fan pattern shaping, without creating excessive bounce back. Air-assisted spray application requires a lower fluid pressure than airless spray application; typically between 3 and 10 MPa. Spray tips with larger nozzle orifices can, therefore, be used. Transfer efficiency is typically between 65 and 70%.

The major difference in construction between an air-assisted airless spray gun and an air atomized spray gun is the atomizing tip. The air-atomizing tip has a fluid nozzle and an air cap which delivers a ring of atomizing air around the fluid nozzle. In addition, two fine jets or air are emitted from ports in small ‘shoulders’ on each side of the tip. The purpose of these two air jets is to break up any large droplets of paint, formed as a consequence of lowering the fluid pressure, and complete the atomization.

4.10.2.7 Heated Spray Application

Both conventional air atomized spray and airless spray equipment can be used to apply paint coatings which have first been heated to 60–80 °C. Raising the temperature of the paint to this level lowers its viscosity (by as much as two-thirds of its viscosity at ambient temperature), aids flow and reduces drying time. If the heated paint is applied by the conventional air atomized spray, for example, the air pressure needed can often be halved and transfer efficiency improved. If the heated paint is applied by airless spray, a lower fluid pressure is needed and the efficiency of the equipment as a whole is improved.

More sophisticated heated spray application equipment has been developed in previous years to apply some solvent-free two-pack coatings, notably epoxies. In this type of spray equipment, base and curing agent are heated separately, pumped to the gun and then mixed either with a small agitator in the gun itself or, with arguably less efficiency, in the turbulence of the emerging spray. Accurate metering of the two components is essential whichever mixing method is used and this is achieved with the aid of carefully calibrated pumps. Twin-feed heated airless spray equipment is expensive and needs always to be maintained well. Specially trained operators are usually required.

4.10.2.8 Electrostatic Spray Application

This application method takes advantage of electrostatic attraction to improve transfer efficiency. When paint droplets are passed through a powerful electrostatic field, they become charged. If the work piece is earthed, the charged droplets are attracted and will coat not only the front face of the work piece but also some of the back face. The extent of coating ‘wrap round’ achieved, will depend on the size of the work piece and its depth.

In most manual electrostatic spray guns, the power pack delivers, typically, a voltage of 60–85 kV at a current of 150 μA to a point electrode close, but external to the spray head. The air in the immediate vicinity of the spray head becomes highly charged and the charge is transferred partially to the atomized paint droplets, as they pass through. It is also possible for paint to be charged directly by an electrode fitted inside the gun itself. For electrostatic spray guns with internal charging, an operating voltage of 30 kV is typical.

All of the spray application methods, which have been described above, can benefit from the addition of electrostatic charging. Transfer efficiency is improved throughout, often by as much as 20%. For steelwork, the main advantage of applying paints by electrostatic spray is gained when long runs of perimeter-fencing or similar ‘open’ structures need to be coated.

Electrostatics add significantly to the cost of the spray equipment and, as a consequence of the charge imparted to the spray droplets, only relatively thin coatings can be applied easily. Electrostatic spraying methods are used most commonly for industrial finishing operations, in particular the automated application of coating powders.[5]

4.10.2.9 Dip Coating

Small fabrications, which may be both difficult and time-consuming to paint satisfactorily by brush and difficult to paint by spray, can often be painted more effectively by dipping. Steel pipes are also often coated in this way. Specially formulated liquid paints are needed for dipping tanks and, in use regular checks on the viscosity of the paint are required. Additions of solvent have to be made from time to adjust the viscosity of the paint to its specified level. Dip coating is a rapid process in which all accessible areas are coated at one time. However, controlled withdrawal of the work piece from the bath is critical to success to minimize the presence of 'runs' and sags in the finish. Sharp edges, if present in the work piece, will not be coated to the same thickness as the main surfaces.

4.10.2.10 Fluidized Bed Coating

Thermoplastic coating powders can be applied, at works, to heavy metal pipes by a somewhat different dipping method called *fluidized bed coating*.[5] The coating powder to be applied is loaded on a porous membrane near the bottom of the dip tank and air, at low pressure and in high volume, is passed upwards though the membrane to 'fluidize' the powder. Low-pressure air blowers are used for this purpose. The work piece is first heated to a little above the melting point of the coating powder. It is then lowered into the fluidized bed and subsequently withdrawn. The dwell time, which may range from a few seconds to several minutes, as required, will determine the thickness of coating achieved. If the coating powder being applied is a thermosetting type, the coated work piece will need then to be postcured in an oven. Very thick powder coatings can be built up on heavy gauge steel pipes very satisfactorily by this relatively simple application method.

4.10.2.11 Flow Coating

In a variation on the dipping process of paint application, small fixed items of intricate shape are often best recoated on site by flow coating. Electrical transformer radiator tanks, for example, can be recoated most effectively in this way.[3] Paint is poured into a temporary tank built around the item and allowed to flow into any corners and crevices. The excess paint is then drained; if still clean, can be used again. Specially formulated paints are again required. For the process to be successful, very thorough precleaning, usually with solvent, is essential.

4.10.3 Application Conditions

The main environmental conditions which can have a bearing on the success of any paint application method are temperature, relative humidity and ventilation. The paint itself needs also to be in good condition and within shelf-life. Temperature will influence the viscosity of the paint, rate of evaporation of solvent (which may be water), drying time, and curing time of the coating. Application of paints at low ambient temperatures to cold surfaces will extend drying time, curing time and increase the overcoating interval. Conversely, application of paints at high ambient temperatures will increase solvent evaporation, drying time, curing time and may shorten the overcoating interval.

The level of moisture present in the air when paint is being applied is equally important. If the relative humidity is too high, unwanted condensation may occur on the surface of the workpiece. Any moisture on the surface may interfere with paint adhesion and may also interfere with the curing of some two-pack chemically cured coatings. Conversely, if the coating being applied relies on the presence of moisture in the air to cure it, then low relative humidity can also become a problem. Good ventilation is always desirable, as it will aid initial drying of the coating and help to maintain air safety in the working environment.

4.10.4 The Applicator

The final outcome of any paint application process will be determined, to a great extent, by the skill and diligence of the applicator. In 2005, the UK Institute of Corrosion (ICorr) launched an Industrial Coating Applicator Training Scheme[6] (ICATS). The scheme, which is operated through the ICorr trading subsidiary Correx Ltd., is a comprehensive structured program for the training, certification and registration of industrial surface preparation and coating operatives.

References

1. Roobol, N. R. *Industrial Painting: Principles and Practices*; Hanser, 1997.
2. Tank, G. F. *Industrial Paint Finishing Techniques and Processes*; Ellis Horwood, 1991.

3. Chandler, K. A.; Bayliss, D. A. *Corrosion Protection of Steel Structures*; Elsevier, 1985.
4. Bayliss, D. A.; Deacon, D. H. *Steelwork Corrosion Control*; Taylor & Francis, 2002.
5. Cowley, M.; Griffiths, M. *Coating Powders and their Application: A Practical Guide*; Paint Research Association, 2004.
6. Goldie, B. P. F. *Corros. Mgmt* **2005**, *64*, 10–11.

4.11 Paint Formulation

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Abbreviations

AA 2024T3 An aluminum alloy commonly used in aircraft; see common alloy numbering system
ASTM American Society for Testing and Materials
B117 Salt spray accelerated aging testing protocol, as per ASTM B117
CPVC Critical pigment volume concentration
EDX Energy dispersive X-ray (spectroscopy)
EIS Electrochemical impedance spectroscopy
ENM Electrochemical noise methods
FBE Fusion bonded epoxy
NACE National Association of Corrosion Engineers
NDSU North Dakota State University
OCP Open circuit potential or free corrosion potential
OEM Original equipment manufacturer
PUR Polyurethane system
PVC Pigment volume concentration
RM Raw material
SEM Scanning electron microscopy
SSPC Society for Protective Coatings
UV Ultraviolet light, light in the frequency range of 10–400 nm
XPS X-ray photoelectron spectroscopy
XRD X-ray diffraction

Symbols

E_{corr} Open-circuit potential (OCP) or free corrosion potential
F Formula
h Thickness of a coating
$R_{\mathrm{ft}}(t)$ Electrochemical noise resistance as a function of time
R_{n} Electrochemical noise resistance
T_{g} Glass transition temperature
$|Z(t)_0|$ Low-frequency electrochemical impedance modulus as a function of time
$|Z_0|$ Low-frequency impedance modulus
$Z(\omega)$ Electrochemical impedance as a function of frequency ω
Λ Reduced PVC, pigment volume concentration/critical pigment volume concentration. A quick and useful number for indicating whether a given PVC is above or below the system's CPVC
ϕ Volume concentration or fraction of a species

4.11.1 Introduction

How does one formulate/design a corrosion protective coating? This is the key question that this chapter seeks to answer. Before 1900, the process of formulating/designing organic coatings was an art form, similar to that of developing food recipes. Around the dawn of the twentieth century, awareness of natural oil film formation and crosslinking began to be developed, as well as the optical and physical effects of pigmentation. (It is noteworthy, in the context of the timing of coating science development, that research and development on paints and coatings began formally at North Dakota State University in 1905, and the authors' academic department is a direct descendant of this coatings research program.) The first science impacting directly on coatings was chemistry, and later chemistry's great twentieth century offshoot, polymer chemistry and science. Since then, optical physics, composite science, and materials science[1] have all contributed to the science and design/formulating of organic coatings. One of the most important functions of organic coatings is to protect substrates of all types. When the substrate is a metal, the primary function of the coating is to protect the metal substrate from corrosion. Most OEM coatings, whether for automobiles, aircraft, or metal furniture, have the primary function to protect against corrosion. The entire class of coatings known as 'industrial maintenance' coatings have corrosion protection as their primary purpose. The least expensive method, in reality, of protecting an object against corrosion is to coat the object with a film of the proper organic coating system. Consider making a car entirely from stainless steel versus producing it as a painted steel frame, galvanized steel sheet outer system, and plastic composite bumper system that is the modern car. From this, one easily sees the efficiencies in cost and appearance in using organic coatings for protecting against materials degradation.

The objectives of this chapter are as follows:

(a) describe briefly the material components of coatings;
(b) describe how the performance requirements of a corrosion protective coating are specified;
(c) describe how one designs a corrosion protective coating;
(d) describe briefly how a corrosion protective coating is tested to determine whether it meets its performance requirements.

While pursuing these objectives, we have to include general discussions concerning the component materials of a coating, specifying coating performance requirements, the process of the coating design, and the testing of coatings. As much as possible, the focus of these discussions will be on corrosion protective coatings, and the emphasis will be on considerations of the rapid and efficient design of such coatings.

All the components of a corrosion-protective coating system must function properly for it to provide all the elements of physical protection and optical performance that it was designed to provide. To ensure proper coating system functions over its desired lifetime, one must have the capacity to define, measure, and evaluate the properties that determine these functions in use. For corrosion-protective organic coatings, the desired properties can be summarized as mechanical/chemical protection of the metal substrate, with acceptable appearance parameters. This is easily enough said, but difficult to achieve in practice. There are many properties one can measure in a corrosion-protective coating system. Indeed, the present cohort of designers and users of these systems are uncertain about which set of measurements to choose. They seek the set that will give the maximum amount of pertinent information with least effort and expense. The *sine qua non* of such properties is yet to be determined, but the current 'best practice' thinking among the coating-science community focuses on adhesion, solvent resistance, corrosion protection, and appropriate optical performance over its lifetime. It also takes into account the effects of UV exposure, hot and cold organic fluids, seawater, humidity and temperature cycles, mechanical stress, and abrasion. All these must be considered while choosing the tests/results protocol that the coatings/pretreatment must undergo to be 'fit for use.' We discuss the current thinking on the measurements/exposures for corrosion protective coatings as well as the accuracy/validity they provide in practice. We also discuss spectral, optical, and electrochemical testing of coatings system properties and their changes in simulated and field exposure. The differences between test performance and real use performance are considered, especially with respect to film application uniformity and film damage[2] (taken with some changes from the introduction/abstract of Bierwagen and Tallman).[2]

One of the overriding themes of this chapter is that organic coatings, especially those for corrosion protection, are random two-phase composite materials and must be specified, designed and tested as such.[3] As clearly stated in Chapter 1 of *Random Heterogeneous Materials*,[4] the proper way to interpret the behavior of pigmented organic coatings is as a random heterogeneous composite where the volume fraction of the pigment phase is a crucial measure of concentration of materials. This measure, known now in the coatings industry as the pigment volume concentration (PVC),[3,5,6] is the crucial measure of pigment concentration for the characterization and design of pigmented coatings. Another crucial measure of pigmentation for coatings formulation is the critical pigment volume concentration (CPVC). We discuss this in Section 4.11.6.1.

4.11.1.1 Materials Used in Coatings

In general, when considering liquid coatings, one chooses the materials comprising a corrosion-protective coating from the three classes of materials shown in Figure 1. Many of the negative environmental impacts of coatings come from the solvents emitted during coating application and curing/drying. If one uses powder coatings, for example, the use of solvents is abandoned. One should note here, that in many dispersions, because of environmental considerations, water is a carrier liquid for a fine particle dispersion of polymer and pigment rather than a true molecular solvent for the coating. The resins are the organic polymer matrices of coatings; pigments are the solid, insoluble particles that assist the coating in supplying color and other functions, including protection of a substrate.

4.11.1.2 Protection of Surfaces by Paints and Organic Coatings

Figure 2 gives a general description of the methods by which one stops corrosion. A proper choice of substrates may accomplish some of these, but often, a coating is also used as a supplemental protection.

Corrosion-protective coatings work in three modes[7]: (i) barrier protection; (ii) cathodic/sacrificial protection (i.e., zinc rich coatings)[8–10]; and (iii) inhibitive/passivation protection (i.e., coatings formulated with partially soluble inhibitive pigments and/or additives). The latter two modes are what may be designated as 'active' protection, that is, a protection that is provided to the metal substrate in damaged areas of a coating by such processes as dissolution,

Figure 1 Primary components of organic coatings.

mass transport, chemical reaction, and adsorption. Barrier protection is the passive mode, by which intact coatings provide protection to metal substrates, and is the protection provided by the reduction of the transport of materials, ions, or charge.[11–13] Barrier properties that are important for coatings are the resistance to the transport (small diffusion coefficients) of the chemical species of the corrosion reactions, which are in most cases H_2O, O_2, and electrolyte ions.

4.11.1.3 Unique Properties of Paints and Coatings for Corrosion Control

Coatings decorate and protect the substrate to which they are applied. One can summarize the unique features required in corrosion-protective organic coatings for the protection of metal substrates. Such a coating must have a combination of barrier, sacrificial and inhibition/passivation protection of the coating–metal substrate interface. For this protection to occur, the prime features of the painted metal system are as follows:

Dry film properties:

A. Wet/dry adhesion-keeping coating in contact with the substrate under exposure conditions;
B. Low ion, water, and oxygen permeability of the coating film – barrier effects;
C. Low coating/film conductivity – minimize flow of current in local corrosion cells and stop ion and electron motion in film;
D. Coating/film stability to its environment, stability to hydrolysis and UV radiation, thermal stability, etc.;
E. Strong adsorption of coating to substrate interface – good wetting of the substrate by the coating system;
F. Coating pigmentation for passivation/inhibition (chromates), sacrificial (Zn-rich coatings, $\Lambda = 1$), or barrier ($\Lambda = \text{PVC}/\text{CPVC} \cong 0.85$) coatings.

System properties:

A. Good quality metal substrate and pretreatment;
B. Coating film be applied uniformly in a defect-free manner to metal substrates of all shapes and sizes.

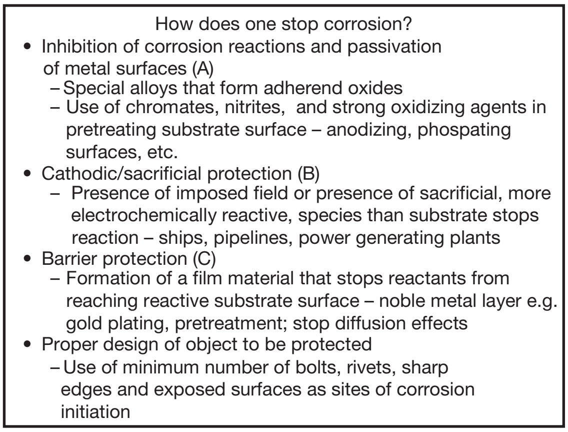

How does one stop corrosion?
- Inhibition of corrosion reactions and passivation of metal surfaces (A)
  - Special alloys that form adherend oxides
  - Use of chromates, nitrites, and strong oxidizing agents in pretreating substrate surface – anodizing, phospating surfaces, etc.
- Cathodic/sacrificial protection (B)
  - Presence of imposed field or presence of sacrificial, more electrochemically reactive, species than substrate stops reaction – ships, pipelines, power generating plants
- Barrier protection (C)
  - Formation of a film material that stops reactants from reaching reactive substrate surface – noble metal layer e.g. gold plating, pretreatment; stop diffusion effects
- Proper design of object to be protected
  - Use of minimum number of bolts, rivets, sharp edges and exposed surfaces as sites of corrosion initiation

Figure 2 Summary of modes of corrosion protection of metal substrates.

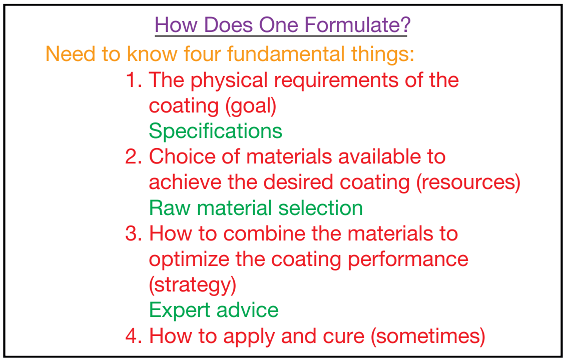
In this list, adhesion to metal substrates, strong absorption to metal substrates, and wetting of metal substrates are all unique features of organic systems, as they interact with metal–metal oxide surfaces. The ability to be applied uniformly with no defects is crucial to the performance of corrosion-protective coatings. This means that for corrosion protective coatings, the method of application is almost as important as the properties of the coating being applied. Each of these topics will be discussed in more detail below.

4.11.1.4 Formulation as a Scientific Design Activity

The basics of coating formulation have been discussed often,[14] but the primary issues of designing a coating still remain the same. The complexity of the design process is quite extensive. This has been noted as a general issue of the design process, as well as specifically for coating designs (**Figure 3**).[15,16]

4.11.1.5 Testing of Corrosion Protection by Paints and Organic Coatings and Feedback to Coatings Design

The final stage of coating design is the testing of the coating to determine whether it meets the design


How Does One Formulate?

Need to know four fundamental things:

1. The physical requirements of the coating (goal)
   Specifications
2. Choice of materials available to achieve the desired coating (resources)
   Raw material selection
3. How to combine the materials to optimize the coating performance (strategy)
   Expert advice
4. How to apply and cure (sometimes)

Figure 3 Schematic of multilayer coating system.

specifications. This is often done using standardized test methods (often from ASTM or SSPC) for measuring the obvious parameters such as color, density, and hardness.[17] The testing of corrosion performance is often much less of a standardized issue, and many of the ASTM Test Methods for Corrosion Protection by Coatings, including B117, have met with serious disagreement from many researchers in their application. Much of the work on the testing of coatings for corrosion protection has involved the use of electrochemical methods to supplement or even replace the more traditional subjective test methods still in use for this purpose.[18] This is discussed in more detail in subsequent sections.

As the coating is tested, many small incremental modifications of the original design are made to achieve the best combination of the properties that still satisfy the original specifications. The final design is thus a nonideal choice of materials, which optimizes the total performance, but is often less than optimal among the many physical and chemical properties of the coating.

4.11.2 Overview of Corrosion Control by Paints and Organic Coatings

As stated earlier, there are several general routes by which paints and coatings protect metal substrates from oxidation/corrosion. More specifically, they provide barrier protection for the substrate, cathodic/sacrificial protection by metal pigments more reactive than the metal substrate, and inhibition/passivation of the metal substrate by dissolution/ion exchange/controlled release from pigments or additives in the coating. Coatings are applied to substrates largely to protect them from the corrosive environments in which they function. Therefore, one can say that the passive barrier function of coatings is the primary mode by which they protect substrates. The active corrosion protective functions of coatings, the release or dissolution of inhibitors, or passivating chemicals, and sacrificial protection, occur in most cases when the coating is damaged and then breached, or by defects in the coating application process, which give incomplete coverage to the substrate.

Most often in the use of organic coatings for corrosion protection, the total coating system is multilayered.[2] The first organic coating layer applied to the metal substrate, or as is often the case, over a thin inorganic pretreatment layer on the metal substrate, is often called the primer layer. This layer is that portion of a coating system that most frequently contains the active components, metal pigments, or soluble pigments that give active functionality to the total coating system. The subsequent coatings on top of the primer often provide most of the barrier properties of the total system. For example, the multilayered coating system usually contains (at a minimum) a primer/pretreatment layer, primer, base coat, and top coat. The optical functions of the total coating system, such as hiding, color, and camouflage, are provided most often by the coatings applied over the primer.

4.11.2.1 Barrier Protection by Coatings

It is known that the primary function of a corrosion-protective coating system is to be a barrier between the coating system and the environment. However, no coating system now in use stops completely the transport of oxygen, water, and ions to the coatings–metal interface. Barrier protection is the reduction of the transport of materials, ions, or charge to the surface of the metal substrate.[11–13] Barrier properties that are important for coatings are resistance to the transport (small diffusion coefficients) of the chemical species of the corrosion reactions, in most cases, H_2O, O_2, and electrolyte ions usually Cl^-, SO_4^{2-}, and a mixture of cations such as Na^+, K^+, NH_4^+, and Ca^{2+}. Along with these barrier properties, high resistance to the flow of charge, electronic and ionic, is also important, as has been observed by Mayne[12] and Funke.[11] The barrier properties of polymer and paint films are known to be increased by their exposure to various gases and liquids.[13] The exposure of polymer and paint films to solvents that plasticize them greatly increases the transport properties of these films if they reduce the effective T_g of the films below the temperature of film use. Also, the exposure of these films to aqueous electrolyte solutions causes many coating films to swell and develop conductive pathways not present in the film before exposure.[19] Thses also severely reduce the barrier properties of the coating.

Let us examine an idealized multilayered coating system of three layers as shown in **Figure 4**.

In most coating systems, the outermost layer, in this case Coating III, is the layer whose primary function is barrier protection. This means that the polymer of this layer has to reduce the transport of water, and of oxygen to a lesser extent, into the coating film, as well as prevent the movement of dissolved ionic species through the film. The coating

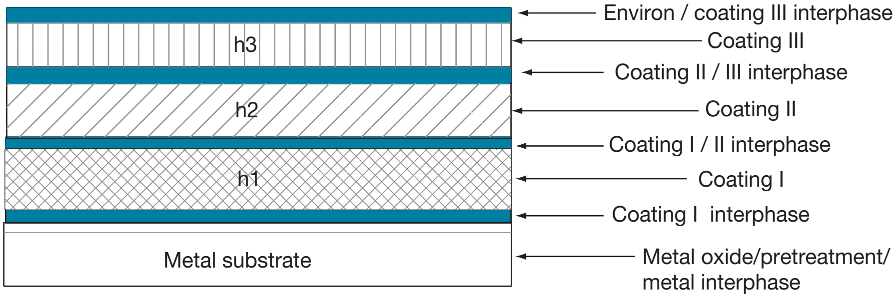


Figure 4 Schematic of multilayer coating system.

polymers that achieve this best are those that are hydrophobic and resist photooxidation in exposure. Examples of these are exterior quality urethanes, fluorourethanes, and fluorocarbon-based polymers such as kynar. One should note that the interphase region between each layer in the coating is separately identified, because this region often performs in a manner superior to the bulk of the coating *vis à vis* resistance to transport. In a recent paper from this laboratory, the interfacial region was identified separately in an equivalent circuit description of a coating, and this enabled one to identify this region and its contribution to the barrier properties of the system.[20] The issue of the interfacial layer and its importance in coating design performance are described in detail in several references.[3,21]

The barrier properties of coatings can be estimated by the use of electrochemical impedance spectroscopy (EIS) and electrochemical noise methods (ENM).[22–24] The monitoring of the low-frequency impedance modulus and/or the electrochemical noise resistance with exposure time (either natural exposure or accelerated exposure), $|Z(t)_{\mathrm{low}f}|$ or $R_{\mathrm{n}}(t)$, have shown themselves to be very useful techniques for following the changes in coating performance in the field or accelerated testing. Measuring the diffusion of water into a coating by single frequency EIS measurements is also a powerful tool for monitoring aqueous diffusion in coatings.[25] This group of electrochemical techniques provides a strong set of measurement tools for examining the barrier properties of organic coatings over metal substrate. Permeability measurements for water and oxygen performed by the use of a film and a sensing device of a gravimetric measurement for the permeant have also been performed, for example, for water, weight change in a desiccant on the other side of a film. There is a considerable literature in this area.[26] Gravimetric measurement of water pickup by coatings can supplement the methods just described.

4.11.2.2 Active Metal Pigmentation and Cathodic Protection

The other modes in which coatings provide corrosion protection are active modes. In the case of metal-rich coatings, the protection comes from the chemical activity, or oxidation of an active metal pigment to provide sacrificial, cathodic protection to a less active metal substrate. Metal-rich coatings provide protection for metal substrates in a unique manner. They provide cathodic protection to the underlying substrate through high volume concentration of a more reactive metal than the substrate.[27,28] At the later stages of their performance, the basic metal oxides created from the particulate metal in the coating help to generate a barrier and passivation protection. A general description of these coatings is that they are designed with high volume fraction of metal pigment particles (near CPVC) dispersed in a nonconductive polymer or inorganic matrix. They were originally designed in the late 1930s with particulate Zn in matrix over steel. As particle volume fraction is high enough to give almost complete particle-to-particle contact, when a coating is applied to a metal substrate, it provides sacrificial/cathodic protection to the substrate. In effect, Zn-rich coatings act as a galvanizing layer that can be applied *in situ* to metal objects that cannot receive a galvanizing Zn or Zn/Al alloy layer. Metal-rich coatings are most often used as a primer, with a decorative or functional top-coat, which mainly provides barrier protection. Metal-rich coatings need basic material research to enhance their design and function. North Dakota State University has been active in this area recently applying metal-rich methods to the protection of Al alloys and other metals more reactive than steel.[29–31] This work indicates that Mg-rich coatings can provide similar protection to aerospace Al alloys such as AA 2024 T-3. This is the first completely Cr-free (no Cr-based pigments or pretreatments) protection system that gives long-term protection to such alloys.

The protection of automobile steel sheet outer bodies by galvanizing was first introduced by Porsche in circa 1970, and has been extended to all types of automobiles throughout the world. In conjunction with cationic electrodeposition coatings at about the same time, galvanized sheet steel increased the corrosion protected lifetime of the automotive coating systems considerably. Pure Zn as well as Zn–Al alloys are the common metallic layers used to protect sheet steel.[32] The warrantees in cars for perforation corrosion protection are now commonly about 10 years[33] and the automotive companies have current goals of 15 years of perforation protection with 10 years of cosmetic appearance protection. The use of Zn-rich coatings has always aimed at providing protection similar to the galvanizing metal layers used on sheet steel. A review of the production and properties of galvanized steels has been published fairly recently.[34] Further, the problems in edge protection by galvanized layers have been studied recently and remain some of the major problems in the use of galvanized sheet.[35]

In the original paper on Mg-rich coatings,[29] a summary of the performance of a Zn-rich coating was given and was utilized to design and predict the performance of metal-rich coatings in general. This summary is paraphrased as follows:

1. This class of coatings uses either organic or inorganic matrices, and is used mainly as a primer.
2. They are pigmented with particulate Zn, in either spherical, random shape, or flake form.
3. The PVC of the Zn pigment in the coating should equal or exceed the CPVC for the coating to properly provide sacrificial/cathodic protection to the underlying steel substrate. At or above the CPVC, the Zn particles are all in mutual contact as well as in electrical contact with the steel substrate. The CPVC values in Zn-rich coatings range from 40 to 60%. There is some evidence that the electrical connectivity of the Zn particles carries over from the PVC = CPVC (~60–70% by volume) to PVC = volume percolation threshold[36] for Zn (~30% by volume for spherical particles). Therefore, some sacrificial protection occurs over this range even while the Zn is being consumed by sacrificial oxidation. The percolation threshold for flake pigments may be different depending on particle alignment.[37]
4. The mode of protection is sacrificial as long as the Zn is electrically connected to the steel, as the Zn is more anodic (reactive) than Fe (major constituent of steel) in the electrochemical series. Then the mixed Zn oxides formed in the sacrificial oxidation fill the damaged areas and also sometimes passivate the steel surface by their basic nature.
5. The organic or inorganic matrix of the coating must be stable under the basic conditions created by the zinc oxide, hydroxide, etc., formed from the oxidation of Zn in the presence of the electrolyte. It must also adhere well to the steel alloys and be stable in a corroding environment.
6. These primer coatings are usually top-coated to function optimally and have a long field lifetime. When used properly, these primers provide almost as much protection to steel as galvanizing. The coating system of a Zn-rich primer and an exterior durable topcoat provide both barrier and damage (sacrificial/cathodic) protection to steel substrates.

Much of what has been said concerning Zn-rich coatings holds true for Mg-rich coatings as well.[29–31] Other metals and alloys have also been used as active metals in metal-rich coatings. Mn in particulate form has been used in coatings as an active metal pigment in the protection of steel[38]; various blends of Al pigments and Zn pigments have been proved to give corrosion protection to various steel alloys.[39] In summary, if one can get a stable metal M_1 pigment – organic (or inorganic) matrix dispersion formed, and cast a film that will adhere to a less active metal M_2 substrate such that there is electrical connectivity between the M_1 particles and the M_2 substrate, this substrate is now cathodically protected. For practical protection, the mixed potential developed at the M_2 substrate surface, E_{M_1/M_2}, should be 100 mV below the M_1 open circuit potential (OCP).

4.11.2.3 Inhibitor Release Coatings

Like the cathodic protective coatings described, inhibitor release coatings that provide corrosion protection are active coatings, not just a passive barrier. In this class of coatings, the physical activity of dissolution and the physicochemical activity of substrate inhibition give protection to the substrate. Inhibitors are always discussed in books[40,41] and articles on corrosion control, but they are very far from being understood. Inhibitor release coatings are almost always designed and pigmented in an empirical manner with inhibitor release rates and time of release sustenance most often chosen by trial-and-error experimentation rather than by rational design. A paper by del Amo *et al.* is an example of this type of formulation methodology.[42] Sinko[43] gives an interesting description of how important the solubility properties and other nonelectrochemical properties of inhibitive chromate pigments are to their successful use in coatings, and the challenges faced by those seeking to replace them for environmental reasons. Kendig and Buchheit also review chromates as inhibitors for Al alloy protection in coatings and give some very useful observations on the requirements for inhibitor pigments and the problems in controlling the 'controlled release' of inhibitors from coatings.[44] There are a considerable number of recent publications discussing new corrosion inhibitors and inhibitive pigments, but very little is said about their release rates in a lifetime of effective corrosion inhibition.

Water or aqueous electrolyte solutions, are the primary solvents that cause release of inhibitors from coatings. Therefore, the barrier properties of the coating toward water are important in inhibitor release. Very few studies have been published on the modeling of inhibitor release and the effects of solubility, water, geometry of coating, damage to coating, etc.[45,46] In general, organic inhibitors are more soluble and tend to leach out of the coatings much more rapidly than inorganic inhibitors. Many of the inorganic inhibitors used are so slightly soluble that they are classified as pigments. As is the case in most issues of coating design, the coating matrix polymer also helps to determine the release rate of inhibitors. The inhibitor release from a primer is minimized by the barrier properties of the topcoat in areas of no physical damage or defects. It appears that in undamaged coating systems, the small amounts of inhibitor dissolved near the primer coating–substrate interface may play a role in keeping any corrosion that occurs under the coating general and uniform at a low rate. Most inhibitors are controlled release materials in that they are only dissolved and become mobile in the presence of water, but many materials dissolve and disappear at a rate much faster than is necessary for corrosion inhibition, and hence have short lifetimes in coatings. An example of this is molybdate pigments, compared to chromate pigments. Even though the former may give inhibition, their solubility is great enough to leach out so rapidly that they cannot be considered true substitutes for chromates.

4.11.2.4 Comments on 'Smart Coatings' and their Relative 'Intelligence'

Much has been written lately about 'smart coatings,' and 'smart corrosion inhibitors'.[47,48] It is clear that most of the authors seek to describe any coating or pigment from which the process of release is not 'dumb.' (Dumb apparently means that it dissolves in an uncontrolled manner whenever water is present.) They are trying to describe a coating system in which the release or chemical reaction within the coating that provides protection to the metal substrate occurs only in response to some external stimuli. Dramatic claims for release in the presence of threat from 'physical damage' or chloride ion concentration provide arguments for new designs of pigments or encapsulated inhibitors. This author insists on great care in accepting many of these arguments in differentiating one material from another. None of the writings in this field shows any numerical modeling or analysis of inhibitor release and substrate passivation and lifetime prediction, but only describes release testing into bulk solutions or trial-and-error formulated coating testing. This area of research has only been active for about 5 years (see, for example, Provder and Baghdachi,[49] and the coatings market place is very slow to accept new ideas or materials, so it is unlikely that many of these 'smart' coatings will appear in common use soon.

4.11.3 Components of Organic Coatings for Corrosion Control

As described in **Section 4.11.1.1**, the four basic component classes of a coating are polymeric binders, pigments, solvents, and additives. The polymeric binder matrix of a coating is the continuous phase of a well formed coating, which often provides a major part of the barrier protection provided by the coating. A brief survey of the most commonly used polymer classes for corrosion protective coatings follows. For further details on the properties of such polymers and their use, one needs to examine the general textbooks on coatings.[16,50,51] The focus in the following discussion is on the properties and uses of coating polymers unique to corrosion protection. The *Journal of Protective Coatings and Linings, Materials Performance* and the *Journal of Coatings Technology* often present articles on polymer suppliers and users and details of specific polymer use in corrosion protective coatings. In a general net or preapplication coating system, the solvent composition by volume ranges from 10 to 50% (zero in powder coatings), the polymer volume fraction ranges from 20 to 50%, the pigment volume concentrations range from 0 to 35%, and additives usually are at 15% or less.

4.11.3.1 Polymer(s) for Corrosion Control Coatings

In Section 4.11.1.3, the desired attributes of a corrosion protective coating are given, and from these, the specific properties required of polymers for use in a corrosion-protective coating can be listed as follows:

1. Wet/dry adhesion – keeping the coating in contact with the substrate.
2. Low ion, water, and oxygen permeability – physical barrier effects.
3. Low conductivity – inhibit flow of current in local corrosion cells and stop ion and electron motion in film – electrical barrier effects.
4. Stability to its environment, stability to OH-driven basic hydrolysis and UV radiation, thermal stability, etc.
5. Strong adsorption of coating polymer to substrate interface – provides good wetting of substrate by coating system and reinforces the wet adhesion of the polymer mentioned in property 1.

These attributes are somewhat vague in qualitative definition and hard to define in numerical terms. All the properties described in the list can be altered by a detailed polymer composition as well as additives such as wetting agents. This must be taken into account when considering the information given on specific polymer classes as given in the following sections (Table 1).

4.11.3.1.1 Epoxies

Perhaps the class of polymer type most commonly used in corrosion protective organic coatings is the epoxy class of polymers because of their good wetting of metal–metal oxide surfaces, excellent adhesion to most substrates, good to excellent chemical resistance, good dry electrical properties, relatively easily controlled crosslinking, wide range of commonly available molecular weights, relative ease of forming pigment dispersions, wide range of crosslinking reactions available, and relatively good water resistance; epoxy type polymers can be modified to become a polymer engineer's dream. Epoxy polymers are very stable in the locally high pH ranges encountered due to oxygen reduction at metal substrates when corrosion occurs. Because of the good wetting and adhesion properties, epoxy-based coatings are more tolerant of poor substrate preparation than are many other polymer types. These polymers wet pigments and fibers well, and form stable composite films and structures with many pigments and fillers. A wide range of curing temperatures can be achieved, and by a suitable choice of the crosslinker, a wide range of polymer physical properties is available. Epoxies have a relatively strong tendency to pick up water due to humidity effects as well as in immersion, and they are plasticized by water.[23,25] Further, as a general class of polymers, epoxies tend to have poor UV resistance, because many epoxy precursors have phenyl groups in their structure. For this reason, many two-layer corrosion-protective coating systems use epoxy-based primers, while using a more UV-resistant polymer in the topcoat.

Epoxy materials can be designed to require heat curing as well as ambient curing. They have been applied in all types of commonly used equipment and can be used as solvent-borne systems, powder coatings, and waterborne, high-solid, and 100% solid variations. One specific class of epoxies that deserves special notice is the so-called fusion bonded epoxy (FBE) pipeline coatings class. Epoxy–polyamide polymers are often used in Zn-rich coatings because of their chemical resistance and adhesion to steel substrates. These coatings are high temperature cured epoxy powder coatings used for pipeline corrosion protection.[52] Further, qualitative comments specific to epoxy polymer use in corrosion protective coatings are given in several introductory texts discussing this class of polymeric materials.[40,41]

Table 1

Polymer	*Property 1 wet adhesion*	*Property 2 chemical barrier*	*Property 3 electrical resistance*	*Property 4 exterior durability*	*Property 5 substrate wetting*	*Relative cost*
Epoxies	+	+	+	+	+	Medium
Polyurethanes/polyureas	+	+	+	+	−	Medium to high
Acrylics	−	−	−	−	−	Medium
Alkyds	−	−	−	−	−	Low
Silicones	−	$-O_2/+H_2O$	−	+	−	Medium
Inorganic/sol-gels, etc.	−/+	−	−	+	+	Medium to high
Vinyls	−	+	+	−	−	Low

4.11.3.1.2 Isocyanate-based polymers: polyurethanes and polyureas

The second most commonly used class of polymers used for corrosion protection is isocyanate-based polymers, which includes polyurethanes of all types and the so-called polyurea coatings. Polyurethanes provide an excellent matrix for corrosion-protective coatings, but they are less tolerant as a class, being ill prepared substrates compared to epoxy coatings, with less wetting and adhesion properties. Aliphatic polyurethane (PUR) coatings are often used as topcoats in corrosion-protective systems because of their excellent UV resistance and barrier properties. Chemical resistance, abrasion resistance, and design flexibility are among the other strengths of coatings in this class of polymers. Aircraft coating systems,[2] chemical agent resistant coatings for military vehicles, and many other coating systems, including bridge coatings, have aliphatic PUR topcoats. Polyurethanes are based on reactions of monomeric or oligomeric isocyanates with polyhydroxyl oligomers[53] and vary in use from room temperature reactive curing to high temperature blocked isocyanate chemistry.[54] Most types of pigments, including active metal pigments such as Zn, have been used in PUR coatings. PUR-type coatings are sometimes difficult to use in primers as they are difficult to wet and adhere to as a substrate.

4.11.3.1.3 Acrylics

Acrylic polymers have been used in the coating industry for some time[55] and have great usefulness because of their UV stability and wide range of use. There are very many acrylic monomers so that copolymers of many types can be prepared using basic acrylic free radical polymerization. Similarly, very many side-groups of acrylic monomers are available, which allow crosslinking chemistries with many other polymer types.

4.11.3.1.4 Alkyds

Alkyds are among the longest used polymer classes in the modern coating era. They still have extensive use because of their relatively low costs and wide range of use. This class of polymers is, however, sensitive to basic hydrolysis, so use of unmodified alkyd polymers in purely corrosion-protective systems is definitely on the decline.

4.11.3.1.5 Vinyl polymers

Vinyl polymers is a name often used to identify polymers based on the vinyl group, $\mathrm{NCH{=}CH_2}$, but really has been used to identify polymers and copolymers of vinyl chloride.[3,16,40,41] These polymers have been used extensively in the past for corrosion protective systems, but they often need large amounts of strong solvents to be apply properly, and thus their use has been heavily curtailed by VOC regulations for coatings. They also as a class have poor outdoor durability in UV exposure. They do, however, have excellent barrier properties, especially water resistance, and they are still used in some situations. They are often used as thick films applied in multiple layers. Chlorinated rubbers are often considered in this class of polymers.

4.11.3.1.6 Mixtures including silicones

Many of the polymer matrix systems for corrosion-protective coating systems are mixtures of more than one type of polymer. A full discussion of all the types of polymer chemistries available, is beyond the scope of this chapter, but is available in reviews and textbooks.[41,50]

4.11.3.1.7 Sol–gel and hybrids

Some coating matrix systems use ceramic-like chemistries for film formation, and have found use in corrosion-protective coatings, especially in Zn-rich primers (see Chapter 10 of Smith[41]). There is a current review on how these systems can handle a broad range of coating problems.[56]

4.11.3.2 Pigments

Pigments are the second group of materials from which coatings are designed/formulated. As the heterogeneous phase in what might best be called a random two-phase particulate composite, pigments perform appearance functions and help provide protective functions. As discussed earlier, pigments help coatings provide corrosion protection by cathodic protection, barrier protection, and inhibitor release protection. In addition, colored pigments are used in corrosion-protective coatings for appearance purposes or to provide visual feedback to applicators about proper film thickness/opacity coverage.

4.11.3.2.1 Inhibitive pigments

Inhibitive pigments are perhaps the largest class of pigments used in corrosion-protective organic coatings. They include partially soluble inorganic compounds such as chromates, which are used in aircraft primers[43,57] and phosphates[58] as well as other related materials such as molybdates.[59] Other materials of this type are organic inhibitive pigments, controlled release pigments[60] (the inhibitor is given off by the pigment in a controlled release manner), and ion exchange pigments.[61] These materials dissolve or release materials at a slow rate in the presence of water, and are thus present in high concentrations near a damaged site in a coating in exterior exposure. The release of materials from such pigments has been studied by several authors and found to be related to the efficiency of the pigment/coating polymer system.[43,62] The commercial literature of this area of materials is full of a lot of claims, and the formulator of coatings using such pigments is cautioned to carefully study coatings based on inhibitive pigments in tests that reflect the proper use conditions. In the case of chromate-replacement pigments, especially, matching release rates and inhibitive performance with no-chromate materials is very difficult indeed, and claims of replacement pigment manufacturers should be examined very carefully.

4.11.3.2.2 *Reactive metal pigments: spherical, lamellar, and platelet/flake*

The next class of pigments important in the formulation of corrosion-protective coatings are the reactive metal pigments used in formulating metal-rich, cathodic protective coatings. As discussed in **Section 4.11.2.2**, metal-rich coatings are formulated with active metal pigments that are more reactive than the metal substrate the coating protects. Zn-rich coatings used for steel were the first such coatings of this type, and much of the literature on pigments for metal-rich coatings perforce concerns Zn pigments. However, this class of materials is expanding, and now includes Al,[39] Mg,[29,30] and Mn[38] pigments. A recent publication has even described the use of nano-Ti particles in corrosion-protective coatings, but gives no claims of cathodic protection.[63]

The important properties of metal pigments for use in coatings are as follows:

1. Particle size;
2. Particle size distribution;
3. Particle shape;
4. Surface oxide layer thickness or pretreatment.

The reactivity of metal particles is determined by their size (surface-to-volume ratio, specifically), increasing (3/radius) for spherical particles. The shape of the particles, flakelike, needlelike, or spherical, affects their connectivity and thus their connectivity and percolation threshold.[36,37] Because of the importance of connectivity, metal-rich primer coatings are formulated near the CPVC, and thus particle size, size distribution, and particle packing efficiency in such coatings are very important formulating issues that must be considered in the design of such coatings.[1,3,27] Their shape is also important for connectivity and percolation threshold determination, and the advantages of flakelike Zn pigments compared to an equivalent volume of spherical Zn pigments have been claimed.[37]

4.11.3.2.3 *Inert/extenders pigments*

The other class of coatings important for their use in corrosion-protective coatings is the inert/extender pigments. These pigments are used to control the PVC-related properties of coatings such as the dielectric, transport, and mechanical properties. They also tend to be lower in cost than other pigments, which helps explain their extensive use. Their function in coatings has been extensively discussed elsewhere,[1,3,5,51] and will not be discussed here. However, a subclass of extender pigments that is extensively used in corrosion-protective coatings is inertflake pigments such as Al, mica, exfoliated clays, and related materials. Because such pigments often align parallel to the substrate during coating film formation, they decrease transport in such films more effectively on a volume basis than spherically shaped pigments. Thus, if one wishes to increase the barrier properties by a given volume of extender pigments, those in a flakelike form are the most efficient if they align parallel to the substrate.[62]

4.11.3.2.4 *Colored pigments*

Colored pigments are used in corrosion-protective films to help provide a more pleasing appearance to such coatings and the substrates they protect. The use of colored pigments also helps provide a visual guide to hand-applied coatings. The major issues requiring consideration in colored pigments in corrosion-protective coatings is whether the coatings will be used on the exterior or the interior. For the former, pigments should be UV stable and not cause photo-oxidation, as do untreated TiO_2 pigments. Most often, inexpensive colorants such as iron oxide red, carbon black, or yellow iron oxide are used in corrosion protection systems because of their stability.

4.11.3.3 Additives: Surfactants, Rheological Control Agents, Flow Agents, Defoamers, Wetting Agents, Dispersants, etc.

The term additives is a general term used for describing those materials that are added in small amounts, usually less than 1% by weight, to coatings to control the properties of the liquid coating before and during application. Included in this class of materials for coating formulation and design are surface active materials, such as wetting agents, pigment dispersants and defoamers, biocides, and materials for rheological control of the liquid coatings. Coalescents and plasticizers, which affect the short-term behavior of polymers during film formation, are also included in this class of materials. Some additives are used to control and improve the properties of the solid film, and these include UV absorbers, light stabilizers, mildew retardants, and fire retardants.[36,37]

4.11.3.4 Solvents/Carrier Fluids

Solvents and dispersion carrier fluids (i.e., water in latex-based paints) play a key role in coatings, as they are liquids that enable the coating to be in liquid form for proper coating application. For cost, environmental, and legal reasons, the minimum amount of solvent is used in formulating a coating, and the type of solvents one can use in coatings is subject to severe restrictions. The legislation in this area is continually changing, and the formulator is advised to check on the specific regulations on solvent use that apply to the location of his coatings.

For corrosion-protective coatings, a primary consideration is, whether the solvent remains in the coating long enough for the coating to complete film formation, and then leaves the coating and does not interfere with the full development of coating properties. For example, if the formulator uses a solvent that does not completely leave the film during film formation, the residual solvent can act as a plasticizer and lower the effective T_g of the coatings, which will reduce the coating barrier properties. If the solvent leaves the film before polymer crosslinking is complete, the film formation process will remain incomplete, and the full development of coating properties will not occur. Again, the formulator is referred to monographs on coatings for further guidance on solvent choice and usage.[51]

4.11.3.5 Catalysts for Reactive Polymer (Usually Two Component) Curing

Catalysts to accelerate the curing of coating polymers are also an important type of additive.[50,58] Many of the polymers used in corrosion protective coatings are two-component systems that use reactive cure as the mode of film formation. These curing systems often require catalysts to crosslink and undergo film formation properly.[16,17,52–54] Epoxy-based coatings require catalysis in their use, and detailed information on individual coating polymers is most often available from the polymer manufacturer. Similarly, catalysts are commonly used in polyurethane/polyurea coatings, but recommendations from the manufacturer of the polymer under consideration are probably the best starting point for formulation practice in PUR systems.

4.11.4 Coatings Application Methods and Corrosion Protection

Since corrosion in coated metal substrates is a problem that begins locally and then may grow into a global concern, the elimination of all coating defects during the coating application process is of great concern. For this reason, the method by which a corrosion-protective coating is applied to the metal substrate is extremely important for the successful use of such a coating. Also very important to the proper performance of a corrosion-protective coating is the proper preparation of the metal surface to receive the coating. For example, an improperly applied spray coating will make a coating–metal substrate system liable to corrosion. For this reason, corrosion-protective coatings that are field applied are inspected after application to ensure that no defects are present before a coating system is allowed to go into field use. The Society for Protective Coatings (SSPC, see www.sspc.org) has several manuals for coating inspection and the National Association of Corrosion Engineers, Intl (NACE, see www.nace.org) has an extensive set of training programs for training personnel as coating inspectors.

A corrosion-protective coating correctly applied to a well prepared metal substrate is crucial for achieving the proper performance from the coating substrate system. This is especially crucial for systems in situations where field repair of coating imperfections is not achievable, such as buried pipelines or off-shore oil platforms. Because of this, proper coating application is paramount for corrosion-protective coatings. Much of the high-quality corrosion protection inherent in recent automobiles is due to the use of cathodic electrodeposition primers used over Zn/Zn-alloy galvanized steel.

A more detailed discussion of the application methods and procedures of corrosion-protective organic coatings is given in this volume, and this subject receives no further discussion here. For further reading in this area, see the references listed under Further Reading.

4.11.5 Coating Wetting and Adhesion in Coatings

General wisdom has it that adhesion, especially 'wet adhesion,' is a key attribute for corrosion-protective coatings.[7] To function properly, a coating must wet and adhere to the metal substrate it is being used to protect.[1,11] Many adhesion problems in actual use are solved by properly preparing the surface of the substrate for the coating application process. Additives for improved wetting are often used in corrosion-protective coatings. Because of their high surface energies, the ideal surfaces for wetting have been considered to be clean metals or metal oxides. Such surfaces, along with coatings that strongly wet them, such as epoxy–polyamide-based coatings over pretreated steel, have given excellent adhesion of the coatings and thus good corrosion protection. However, recent developments in science have been giving the hope of achieving improved adhesion by true covalent bonding across the coating–substrate interface. There are many claims for such pretreatments/coatings, which achieve covalent bonding directly across the coating–substrate interface. Many of these claims are based on the use of functional silanes and their metallic analogs. The surface density of such covalent bonds is still highly variable, and no good tests are available to measure the extent of covalent bonding across an interface in the coating–metal substrate situation. Most of the difficulties in this area lies with issues of measurement of 'adhesion' several recent articles[65,66] indicate that there measurements in 'adhesion' have improved and that further improvements in this area may be expected soon.[67,68]

4.11.6 Coatings Formulation/Design

4.11.6.1 Principle Objectives of Formulation – Coatings Design

For many systems, the coating design process can be summarized as shown in Figure 5. One first determines the desired properties (specifications) of the coating, translates these to the physical properties required of the coatings, and then attempts to convert these requirements to material choices for the composite, that is, the coating. Converting materials specifications to materials choice is one of the most difficult steps in the design process.[15] Additionally, it should also be noted that the 'best' coating for any situation is likely going to be a balance between minimizing cost while achieving – within tolerances – the performance requirements.

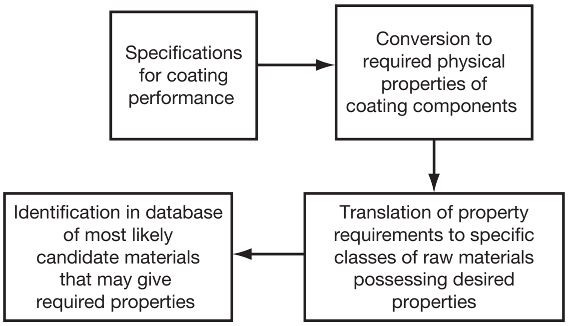


Figure 5 Idealized case of raw material selection.

While working on coating design, work at North Dakota State University (NDSU) has been performed to accomplish the following:

- Put coating design on the same strong technical basis as any other type of engineering design;
- Identify the logic of paint formulation;
- Emulate as much as possible the practice of paint formulation development;
- Determine steps in setting coating specifications – performance property requirements – and converting them into a set of raw material identities, concentrations, and rules for coating manufacture (order of addition, etc.) and application to a substrate;
- Develop basis for coating design system to assist coating formulators;
- Software development for formulator support.

One can think of each of the processes shown in Figure 5 as an operation on a set of databases of material information, specification information, and coating application information. From this alternative viewpoint, the process of formulation would schematically appear as shown in Figure 6. (At the bottom of Figure 6, the F is used to represent formula.) One might think of each step in choosing materials and processes and applying specifications, as applying a mathematical filter to a database of choices yielding reduced databases, from which the formulator/designer makes his final choices. This type of analysis of the formulation process seeks to reduce the often intuitive reasoning that is common in many paint laboratories to a more scientific process analagous to the design process used in many scientific disciplines.[69,70]

Another description of the coating ‘formulation’ or design process is given in Figure 7, in which the consideration of legal/environmental restrictions, curing restrictions due to the site or substrate, and the requirements of individual coating classes are also considered. Other constraints faced by the formulator/designer are production equipment capacity for producing paints of various classes, application equipment available to the user, and substrate size, solvent and temperature sensitivity, corrosion sensitivity, and surface preparation.

There are various ways to organize a database for formulation, and in the following section, several schemes that fit in with the logic of Figures 6 and 7 are presented.[14] Figure 8 shows a raw material (RM) database structure compatible with these operational methods of formulation. Figure 9 gives an alternative RM data base focusing on polymer/binder classes for coatings as well as coatings classes.

If the RM databases are cast in the proper format, one can use the formulation/design logic discussed earlier, shown in a more detailed form in Figure 10.

If one wishes to consider previous formulations/designs to reduce the amount of decision making that needs to be performed in these processes, one can use the flow process shown in Figure 11. Once an original candidate coating design/formulation is available, the development and testing protocol found in Figure 12 can be used.

These processes can be quite slow when run in the sequential, serial form as shown in Figure 12. There are also several problems in trying to reduce the formulation process to a computer-driven procedure. Among these are difficulties in the correlation of coating specifications with design rules developed for translating RM properties to RM choice, the need to narrow the range of raw material availability, or conversely, database limitations due to RM availability. Raw material variability from single or multiple sources is another problem that must be

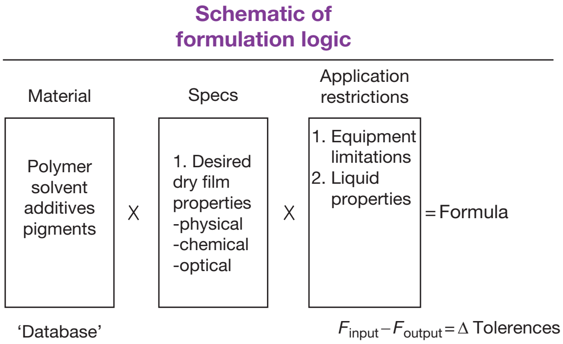


Figure 6 Schematic of formulation logic – alternative view.

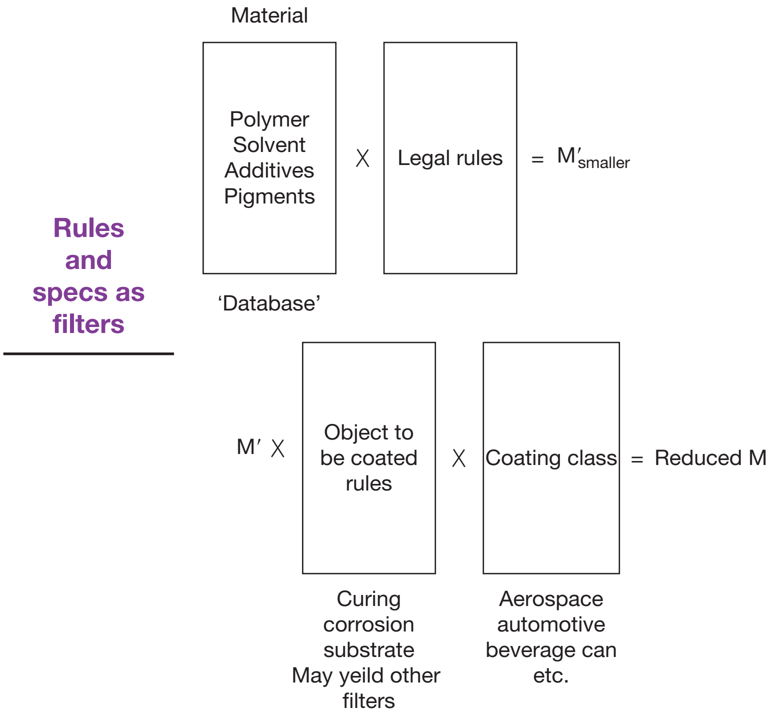


Figure 7 Alternate schematic of materials choice in coating design/formulation.

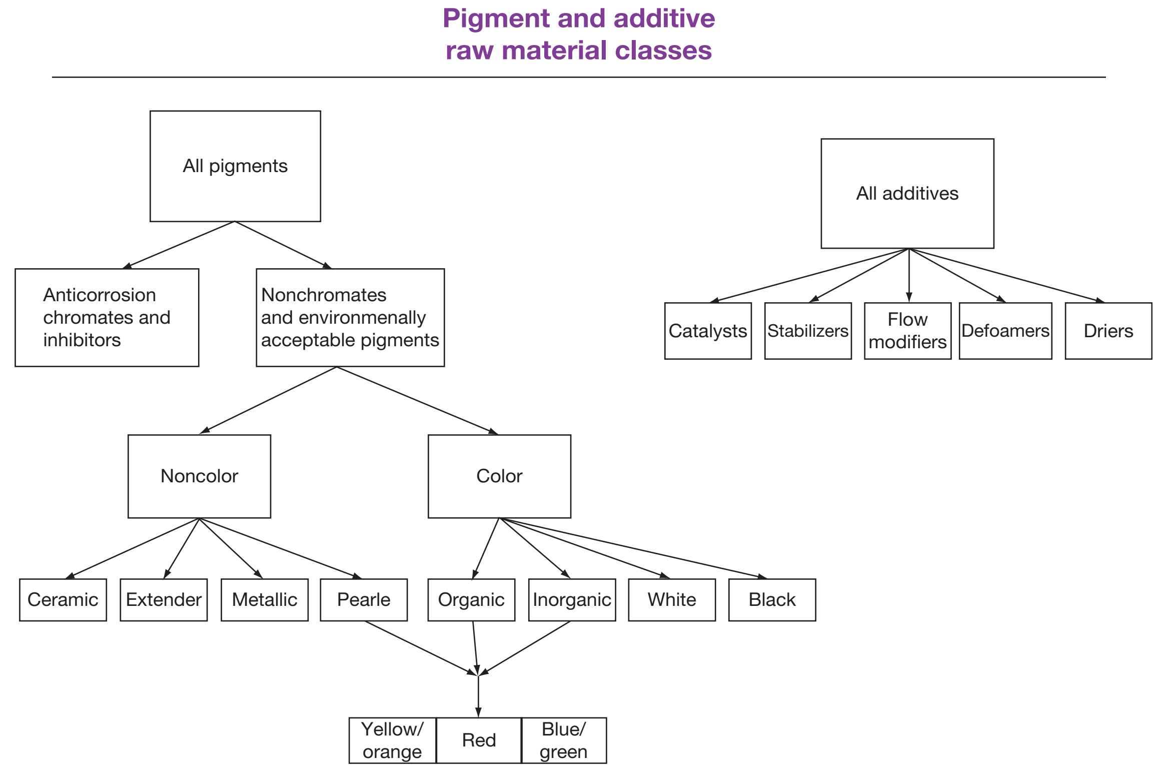


Figure 8 Schematic of possible coatings raw material database organization.

considered, and procedures included in the formulation process to examine the final properties and quality of the coating for sensitivity to RM variability.

4.11.6.2 Volume Effects in Coatings

As mentioned earlier, and reiterated in a recent publication,[1] volume effects are extremely important in pigmented organic coatings, as the volume concentration of materials is the relevant concentration parameter for many of the physical properties of coatings. This is especially true for pigments and the term PVC is commonly used in coating studies. Because of system requirements, it is often considered fruitful to formulate at fairly high PVC levels. Although the specifics differ for every coating system, in general the most expensive component of the system is the pigment or colorant. This is followed by the binder system. The least expensive materials are the solvent (which is not present in the dry film) and the filler or extender pigment. This has made knowledge of the CPVC an important formulating variable, and crucial to coating design and the understanding of corrosion-protective coatings.[71] The CPVC measures the highest volume fraction of solid pigment that can be packed into a coating without introducing air voids. The parameter Λ ($\equiv$ PVC/CPVC, the reduced pigment volume concentration) is often used in interpreting and predicting coating behavior. Coating properties that are directly affected by Λ are given in Table 2. The use of Λ in coatings design is discussed extensively in Bierwagen,[1,6,7] Bierwagen *et al.*,[3] Hare,[27] and Nanna and Bierwagen.[29] Theoretical studies of nonuniformities in particle packing and their impact on CPVCs in 'real' coating systems have given further insight into PVC issues in coatings.[72,73] The knowledge of coating performance as a function of Λ is often utilized in coating design once the pigments to be used in the coating are identified. As discussed in Section 4.11.3.2.2, this is especially critical in metal-rich coatings.

Numerical guidelines for Λ levels for formulation of corrosion-protective coatings have focused on the effects of the CPVC on coating performance characteristics. Some figures describing the qualitative variation of coating properties with PVC or Λ, pertinent to corrosion protection are given in the following section. Figure 13 (taken and modified from Bierwagen *et al.*)[3] shows the relation between pigment and polymer components, including the adsorbed layer on the pigment and void fraction above the CPVC, that occur

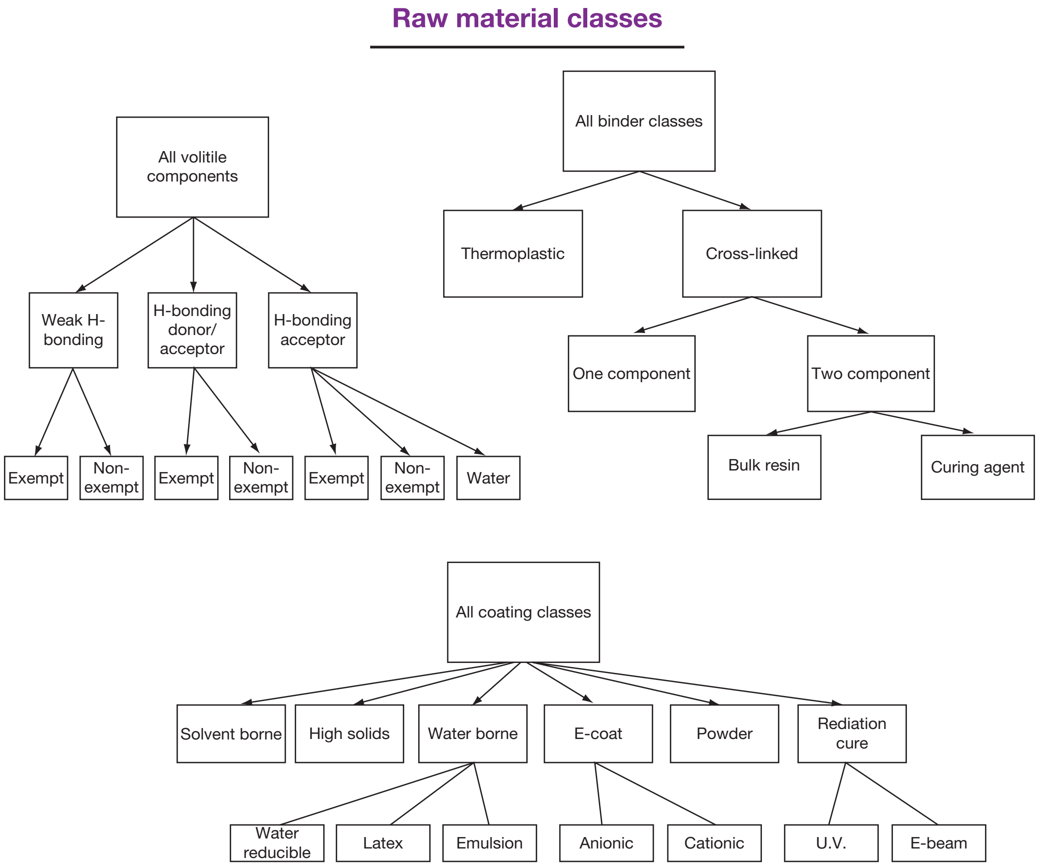


Figure 9 Alternate coating raw material database organization.

in the coating as a random two-phase (below the CPVC) and three phase (above the CPVC) composite. Figure 14 shows schematically the increase in permeability that occurs in a coating above the CPVC, while Figure 15 shows the sudden drop in film resistance measured by the low-frequency impedance modulus $|Z_0|$ or noise resistance, R_n, that occurs at the CPVC. Similarly, the film capacitance measured in an aqueous electrolyte will increase drastically above the CPVC because of water intrusion into voids and corrosion resistance, measured in accelerated testing salt spray, will increase drastically above the CPVC.[71] Thus, a coating formulated above the CPVC provides hardly any barrier protection and often gives poor adhesion in certain types of polymers. Primers can be formulated above the CPVC, if they are coated with a topcoat formulated below the CPVC. This gives a total coating system that does not have a porous structure open to water/electrolyte intrusion. This is often done with Zn-rich primers that are formulated near the CPVC.

The barrier properties of coating are ideally maximized at the CPVC, but in practice, it is known that voids sometimes appear in real coating systems below the CPVC.[1] These voids form in local areas of the coating where the local PVC exceeds the CPVC because of the nonuniform distribution of pigment and polymer throughout the coating film. This can be described by a parameter named coarseness (from Torquato),[4] used to analyze these results properly. It helps to interpret correctly what happens in films as the PVC approaches the CPVC.[74,75] A schematic of these effects, taken from calculations described in earlier work from this lab, is shown in Figure 16.

The interpretation of these data were based on an analysis of coatings as a random composite in which the local PVCs could vary from the calculated (global average) PVC as measured by the coarseness of the system. These variations could occur in coatings due to poor manufacture, film formation or application problems, or other processes in the coating that tend to separate the pigments from the polymer, such as flocculation in storage. Incorporating the coarseness parameter in the analysis, enables one to numerically predict the effect of poor, nonuniform distribution of particulate materials in a coating. The analysis also showed how such coarseness could affect many of the

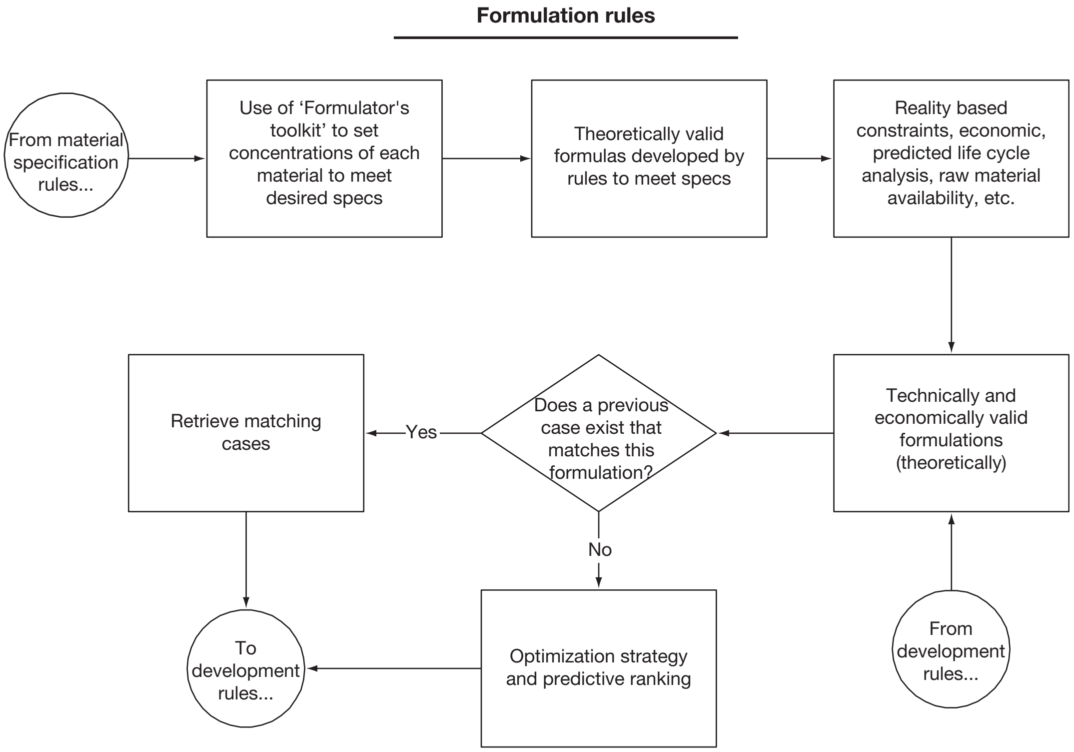


Figure 10 Raw materials choice flow process for coating design.

properties of coating films, especially those related to corrosion protection. These results helped to interpret the empirical observation that most corrosion-protective primer formulae, dependent on barrier effects as part of their protective properties, had Λ values of ~0.85. One would actually expect that these coatings would be formulated at $\Lambda \approx 1$ for maximum barrier protection, because one would assume that it would be the best value for corrosion protection. However, if one analyzes the onset of voids as a function of coarseness, one rapidly determines that there is a very small but finite probability for voids occurring above $\Lambda = 0.85$, but below this PVC value, the probability is very small. The margin of tolerance formulating at Λ values of ~0.85 given to the designer of primer barrier coatings is crucial for avoiding completely the onset of voids in the coating film.

There are no efficient experimental methods other than the manual interpretation of SEM cross-sections to estimate coarseness. A proper microview of the coating system is necessary to properly analyze the manifestations of coarseness throughout a film. We have been trying to use SEM photomicrographs for estimating coarseness, but a detailed three-dimensional characterization of pigment particle distribution in a paint film is necessary for an accurate estimate of coarseness.

4.11.6.3 Setting Formulation Goals

A coating is chosen for purchase, or designed/formulated, based on the requirements of the customer or as translated by sales/marketing and given to technical/research personnel. For example, corrosion-protective coatings often have a lifetime of performance measured by a specific accelerated test method in a specific set of conditions. An idealized list of specified properties for an organic coating is given in Table 3. These specifications could be considered in a design process, as shown in Figure 7.

The specifications for a coating are usually determined by the following:

1. Exposure environment(s) of use;
2. Properties of substrate – asset to be protected
   a. general chemical and mechanical properties of bulk substrate and its surface
   b. pretreatment of the substrate and resultant surface properties;
3. Desired lifetime of use.

The specifications can often be converted into the required properties of coating under the following classifications:

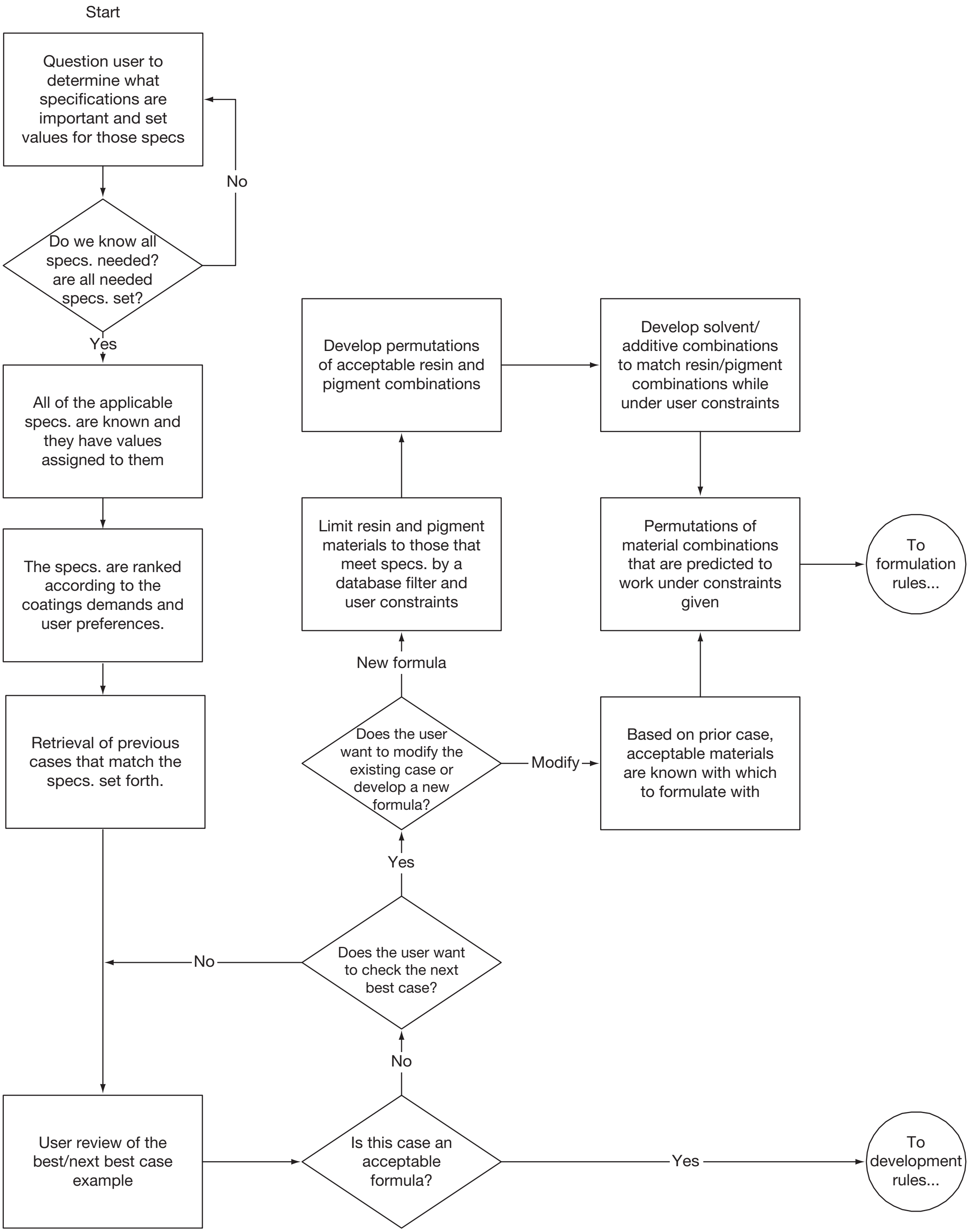


Figure 11 Flow process for coatings formulation with former formula for use as precedent and guide.

1. Diffusion and transport;
2. Thermal and mechanical;
3. Electrical;
4. Optical and color;
5. Chemical resistance;
6. Acid/base resistance;
7. UV resistance;
8. Degree of crosslinking;
9. Solvent and water resistance.

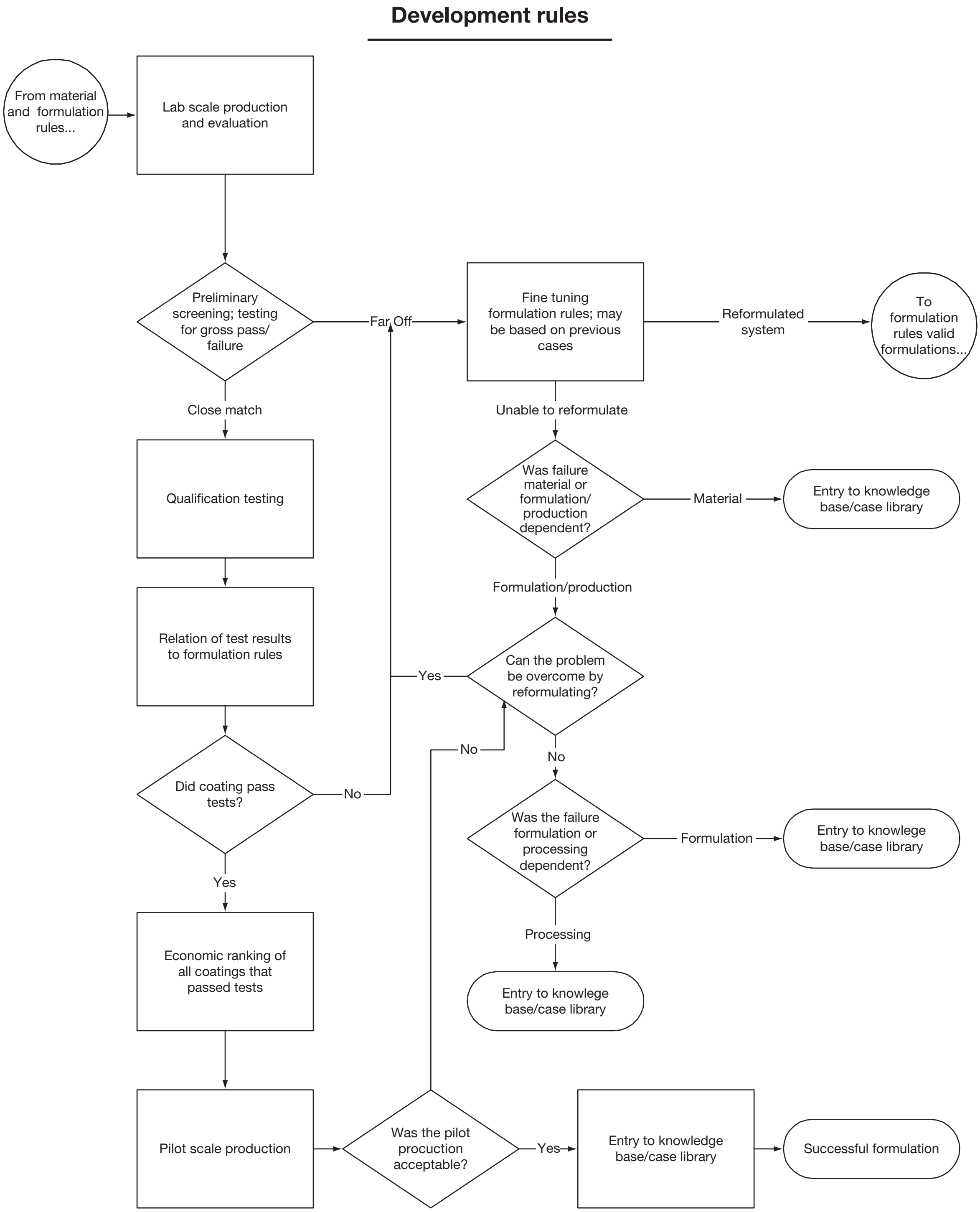


Figure 12 Development, testing, and pilot scale production flow process once an initial formula is proposed.

As described earlier, these requirements are converted into material properties, and material selections are made based on availability, material cost, and cost restrictions of the customer, subject to legal, toxicity, and ecological restrictions.

4.11.6.3.1 Use of combinatorial methods in coating design and choice

The new combinatorial methodologies developed for the pharmaceutical and electronics industries are now being applied to improving coatings.[76,77] These

Table 2 Paint properties affected by Λ, the reduced pigment volume concentration (PVC/CPVC)

- Gloss
- Flexibility (elongation)
- Tensile strength
- Color development (tint acceptance)
- Hiding – contrast ratio
- Block resistance
- Permeability
- Wet abrasion (scrubbability)
- Stain removal
- Corrosion resistance (salt spray resistance)
- Blistering
- Enamel holdout
- Penetration control over porous
- Density (specific volume)
- Durability
- Electrical resistance
- Cold crack resistance
- Dielectric constant
- Adhesion
- Dispersion

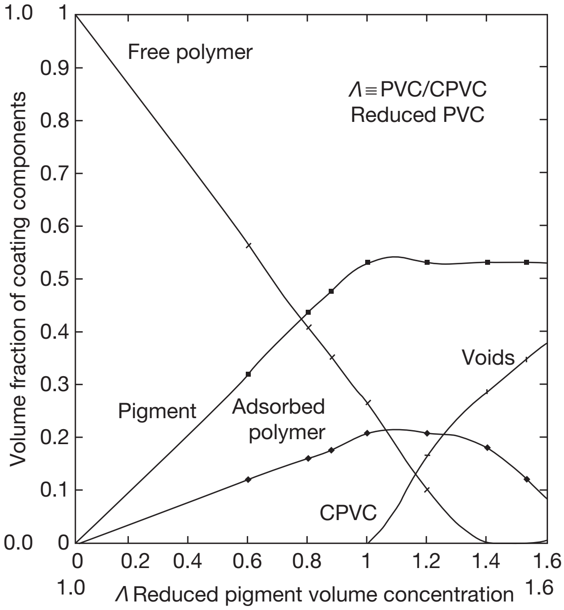
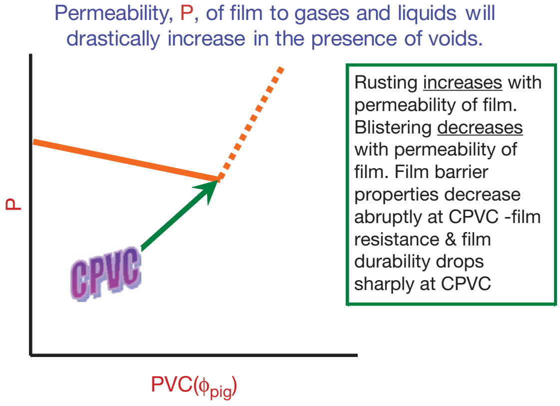


Figure 13 Coating film component variations with PVC.



Rusting increases with permeability of film. Blistering decreases with permeability of film. Film barrier properties decrease abruptly at CPVC -film resistance & film durability drops sharply at CPVC

Figure 14 Organic coating film permeability.

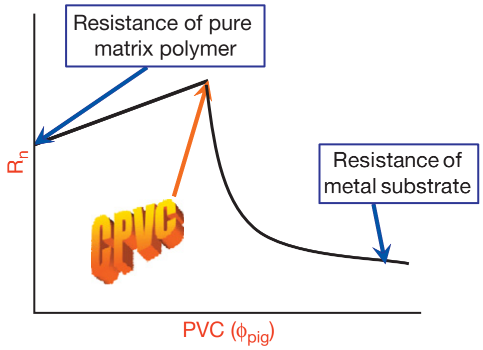


Figure 15 Film resistance as R_n or $|Z_0|$ or vs. PVC.

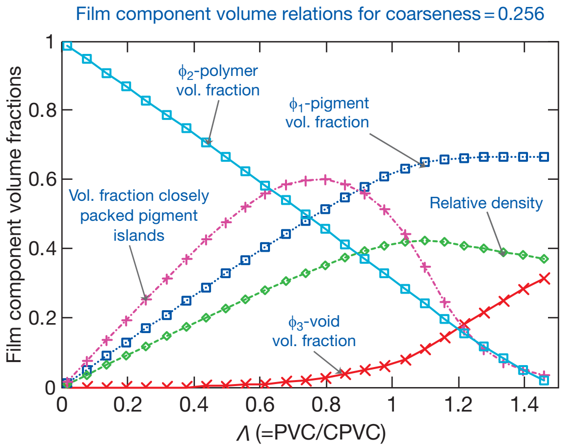


Figure 16 Film component volume relations with coarseness effects for CPVC = 0.66.

methods speed up considerably the time-consuming conversion of material requirements to material choice in the design of coatings and related materials. Combinatorial methods convert one-at-a-time serial methods of sample preparation and testing into parallel methods that, in the case of coating testing, convert single sample testing to 24-samples-at-a-time high-speed testing. For example, these methods have been used in a crude form to modify an automotive coating to one suitable for the corrosion protection of bronze statuary.[78] More recent developments have focused on the development of high throughput screening methods for testing[79,80] and designing corrosion-protective coatings.[81] Coupled with the database-driven material choice methods described earlier, the numerical methods available for polymer and pigment choice, combinatorial coating design, and testing will greatly accelerate the design and testing cycle for corrosion-protective organic coatings.

Table 3 Simplified coating specification list for coatings design

Issues determining coatings design/formulation coatings systems specifications/performance requirements
Cost
Number of layers (more than one layer ≡ system)
Topcoat properties – usually contain color and optical properties plus the barrier and chemical and UV resistance properties
Primer properties (usually contains corrosion resistance properties)
System physical properties including color and mechanical properties
System chemical resistance properties
System exposure resistance properties
Application method and flow properties

4.11.7 Coatings Design and Testing: Choosing the Final Formula

The final stages of coating design involve the examination of experimental formulations according to tests that have been chosen to determine whether the coating films resulting from a proper application of the prototype formulations meet the specifications for the new coating system. The type of tests performed often is discussed in the literature,[2,17,82] but no one set of specifications is agreed upon by all users. There have been many arguments about the validity of test methods to evaluate protective coating systems, including disagreements on whether cyclic or continuous exposure tests are more accurate and predictive. Many of these issues have been discussed in previous reports of this laboratory.[83]

The testing of corrosion protection is discussed in detail in earlier volumes of this series and will not be discussed in detail here. The steps in coating development are

1. Developing the prototype formula;
2. Converting formulation specifications to qualification tests;
3. Short-term lab testing;
4. High-throughput combinatorial testing;
5. Modifying the prototype formula;
6. Accelerated testing/lifetime prediction.

One can see how these steps fit in the schematic of Figure 12 on coating development and testing. As shown in Figure 12, no information from testing should ever be discarded or unrecorded.

As mentioned earlier, this laboratory has been working on metal-rich primer coatings for corrosion protection. A brief discussion of the testing involved in the Zn-rich subclass of such coatings will illustrate the type of corrosion-related testing done. There has been some recent work on lifetime of protection of Zn-rich primers,[84,85] but little has been done on characterizing quantitatively their performance or their lifetime of corrosion protection. Unfortunately, the science and technology of Zn-rich primers is assumed to be a 'mature' technology, to which little technical improvement can be made. This is definitely not true, as clearly indicated by the recent work of Marchebois *et al.*,[86] and Böhm and co-workers.[36] There is a need to re-examine Zn-rich coatings over steel substrates by the experimental and theoretical methods that we have developed for the examination of Mg-rich coatings over Al alloys.

The characterization tools previously used on metal-rich coatings for the active protection of metal substrates are as follows:

> Open Circuit Potential (OCP)(E_{corr}) measurements versus exposure time to verify electrochemical cathodic protection;
> Electrochemical Impedance Spectroscopy;
> Electrochemical Noise Studies;
> Weight Gain/loss;
> Optical Microscopy and local XRD;
> SEM, EDX, some local XPS for Zn reaction product ID.[32,33,37,84–86]

Little that is new in characterization methodology has been introduced for this class of coatings in recent years, and subsequently, little that is new in coating technology or product protection performance for this class of coatings has entered the marketplace recently. Specifically, very little data acquisition and analysis, focused on improving costing system performance or lifetime, has been described in the recent literature. Further, little has been done to acquire proper time series data for lifetime/durability prediction. There has been no true detailed modeling of Zn-rich coatings as a material system to assist material design based on advanced characterization. Surprisingly, in the face of their successful use in many areas of electrochemical science, there has been no inclusion of new local measurement techniques, especially scanning probe methods for the characterization and modeling of Zn-rich coating performance. No analyses of cyclic transport and no electrochemical data from drying cycles have been made as aqueous electrolyte required for data acquisition.

4.11.8 Summary and Conclusions

The design/formulation of a corrosion-protective organic coating is a very challenging design procedure, often involving 20–40 individual materials that must be properly chosen, mixed, packaged, and applied as a final coating to a metal substrate. The design procedure is quite complex, as also the formulation of the proper choice of matrix polymer and pigments of the corrosion-protective coating system. The basic information on such choices has been given, and the process of choosing raw materials has been described. A general bibliography on monographs and textbooks pertinent to corrosion-protective coating design is given.

References

1. Bierwagen, G. *J. Coatings Technol. Res.* March 2008; Online, 2007 Matiello Lecture.
2. Bierwagen, G. P.; Tallman, D. E. *Prog. Org. Coat.* **2001**, *41*, 201–217.
3. Bierwagen, G. P.; Fishman, R. S.; Storsved, T.; Johnson, J. *Prog. Org. Coat.* **1999**, *35*, 1–10.
4. Torquato, S. *Random Heterogeneous Materials;* Springer: New York, 2001; Chapter 1.
5. Bierwagen, G. P.; Hay, T. K. *Prog. Org. Coat.* **1975**, *3*, 28.
6. Bierwagen, G. P. *J. Coat. Technol.* **1992**, *64*(806), 71–75.
7. Bierwagen, G. P. *Prog. Org. Coat.* **1996**, *28*, 43–48.
8. Feliu, S. Jr.; Morcillo, M.; Bastidas, J. M.; Feliu, S. *J. Coat. Technol.* **1993**, *65*(26), 43–48.
9. Feliu, S. Jr.; Morcillo, M.; Bastidasand, J. M.; Feliu, S. *J. Coat. Technol.* **1991**, *63*(793), 31–34.
10. Szauer, T.; Miszczyk, A. In *Polymeric Materials for Corrosion Control*; Dicke, R. A., Floyd, F. L., Eds.; ACS Symposium Series 322; American Chemical Society: Washington, DC, 1986; Chapter 21.
11. Funke, W. In *Polymeric Materials for Corrosion Control*; Dicke, R. A., Floyd, F. L., Eds.; ACS Symposium Series 322; American Chemical Society: Washington, DC, 1986; Chapter 20.
12. Mayne, J. E. O. *Met. Finish. J.* **1966**, *12*(143), 437–441.
13. Thomas, N. L. *Prog. Org. Coat.* **1991**, *19*, 101–121.
14. Johnson, J, Ph.D. thesis; Department of Polymers & Coatings, North Dakota State University: Fargo, ND, May 2000.
15. Ashby, M. F.; Johnson, K. *Materials and Design;* Butterworth Heinemann-Elsevier Science: Oxford, UK, 2002.
16. Wicks, Z. W.; Jones, F. N.; Pappas, S. P.; Wicks, D. A. *Organic Coatings: Science & Technology*, 3rd ed.; John Wiley: New York, 2007; Chapter 34.
17. Koeleske, J. V. Ed. *Paint and Coating Test Manual: 14th Edition of the Gardner-Sward Handbook*; ASTM Manual Series MNL 17; ASTM: Philadelphia, PA, 1995.
18. Bierwagen, G.; Tallman, D.; Li, J.; He, L.; Jeffcoate, C. *Prog. Org. Coat.* **2003**, *46*, 148–157.
19. Kinsella, E. M.; Mayne, J. E. O.; Scantlebury, J. D. *Br. Polym. J.* **1971**, *3*, 41–43.
20. Allahar, K. N.; Su, Q.; Bierwagen, G. P. *Corrosion* **2008**, *64*, 860–870.
21. Dill, K.; Bromberg, S.; Stitger, D. *Molecular Driving Forces;* Taylor & Francis: New York, 2003; Chapter 33.
22. Bierwagen, G. P.; Jeffcoate, C.; Mills, D. J.; Li, J.; Balbyshev, S.; Tallman, D. E. *Prog. Org. Coat.* **1996**, *29*, 21–30.
23. Li, J.; Jeffcoate, C. S.; Biewagen, G. P.; Mills, D. J.; Tallman, D. E. *Corrosion* **1998**, *54*, 763–771.
24. Bierwagen, G.; Tallman, D.; Li, J.; He, L.; Jeffcoate, C. *Prog. Org. Coat.* **2003**, *46*, 148–157.
25. Allahar, K. N.; Hinderliter, B. R.; Bierwagen, G. P.; Tallman, D. E.; Croll, S. G. *Prog. Org. Coat.* **2008**, *62*, 87–95.
26. Thomas, N. L. *Prog. Org. Coat.* **1991**, *19*, 101–121.
27. Hare, C. In *Uhlig's Corrosion Handbook*; 2nd ed.; Review, R. W., Ed.; John Wiley: New York, 2000; Chapter 55, pp 1023–1038.
28. Felix, S.; Barajas, R.; Bastidas, J. M.; Morcillo, M.; Feliu, S. In *Electrochemical Impedance Spectroscopy, ASTM STP 1188*; Scully, J. R., Silverman, D. C., Kendig, M., Eds.; American Society for Testing and Materials (ASTM): Philadelphia, PA, 1993; pp 438–449.
29. Nanna, M. E.; Bierwagen, G. P. *J. Coat.Technol. Res.* **2004**, *1*, 69.
30. Battocchi, D.; Simões, A. M.; Tallman, D. E.; Bierwagen, G. P. *Corros. Sci.* **2006**, *48*, 1292–1306.
31. Battocchi, D.; Simões, A. M.; Tallman, D. E.; Bierwagen, G. P. *Corros. Sci.* **2006**, *48*, 2226–2240.
32. Panossian, Z.; Mariaca, L.; Morcillo, M.; Flores, S.; Rocha, J.; Peñ, J. J.; Herrera, F.; Corvo, F.; Sanchez, M.; Rincon, O. T.; Pridybailo, G.; Simancas, J. *Surf. Coat. Technol.* **2005**, *190*, 244–248.
33. Amirudin, A.; Thierry, D. *Prog. Org. Coat.* **1996**, *28*, 59–76.
34. Marder, A. R. *Prog. Mater. Sci.* **2000**, *45*, 191.
35. Brown, S. G. R.; Barnard, N. C. *Corros. Sci.* **2006**, *48*, 2291–2303.
36. Böhm, S.; Holness, R. J.; McMurray, H. N.; Worsley, D. A. In Eurocorr; 2000, Queen Mary and Westfield College, London, pp 10–14, September 2000.
37. Kalendová, A.; Kuckačová, A. *Macromol. Symp.* **2002**, *187*, 377–386.
38. Selvaraj, M.; Guruviah, S. *Prog. Org. Coat.* **1996**, *28*, 271–277.
39. Chen, W.-B. *et al. Appl. Surf. Sci.* **2002**, *187*, 1254–1264.
40. Schweitzer, P. A. *Paint and Coatings: Applications and Corrosion Resistance;* CRC-Taylor & Francis: New York, 2006.
41. Smith, L. M. Ed. *Generic Coatings Types: An Introduction to Industrial Maintenance Coating Materials*; SSPC 95-08; Technology Publishing: Pittsburgh, PA, 1996.
42. del Amo, B.; Romagnoli, R.; Vetere, V. F.; Hernandez, L. S. *Prog. Org. Coat.* **1998**, *33*, 28–35.
43. Sinko, J. *Prog. Org. Coat.* **2001**, *42*, 267–282.
44. Kendig, M. W.; Buchheit, R. G. *Corrosion* **2003**, *59*, 359–400.
45. Wang, H.; Presuel, F.; Kelley, R. G. *Electrochim. Acta* **2004**, *49*, 239–255.
46. Pommersheim, J. M.; Nguyen, T.; Zhang, Z.; Hubbard, J. B. *Prog. Org. Coat.* **1994**, *25*, 23–41.
47. Deya, C. G.; Romagoli, D.; del Amo, B. *J. Coat. Technol. Res.* **2007**, *4*, 167–175.
48. Kendig, M. W. In Proceedings of the 4th International Symposium on Aluminum Surface Science & Technology, Beaune, France, May 2006.
49. Provder, T.; Baghdachi, J. *Smart Coatings,* ACS Symposium Series, 957; American Chemical Society Press: Washington, 2007.
50. Lambourne, R.; Strivens, T. A. Eds. *Paint and Surface Coatings: Theory and Practice*, 2nd ed.; Woodhead: Cambridge, UK, 1999.

51. Goldschmidt, A.; Streitberger, H.-J. *The BASF Handbook on Basics of Coatings Technology;* Vincentz Network: Hannover, Germany, 2003.
52. Kehr, J. A. *Fusion Bonded Epoxy (FBE): A Foundation for Pipeline Corrosion Protection;* NACE: Houston, TX, 2003.
53. Chattopadhyay, D. K.; Raju, K. V. S. N. *Prog. Polym. Sci.* **2007**, *32*, 352–418.
54. Wicks, D. A.; Wicks, Z. W. *Prog. Org. Coat.* **2001**, *41*, 1–83.
55. Weiss, K. D. *Prog. Polym. Sci.* **1991**, *22*, 203–245.
56. Wang, D.; Bierwagen, G. P. *Prog. Org. Coat.* **2009**, *64*, 327–338.
57. Twite, R. L.; Bierwagen, G. P. *Prog. Org. Coat.* **1998**, *33*, 91–100.
58. Hare, C. H. *Paint Coat. Indust.* **1997**, *13*, 50–56.
59. Austin, M. J. *Raw Materials and Their Usage*; Surface Coatings, 3rd ed.; Vol. 1, Chapman & Hall, 1993; Chapter 25.
60. Kiil, S.; Johansen, K. D.; Weinell, C. E.; Pedersen, M. S. *Prog. Org. Coat.* **2002**, *45*, 423–434.
61. Chico, B.; Simancas, J.; Vega, J. M.; Granizo, N.; Díaz, I.; de la Fuente, D.; Morcillo, M. *Prog. Org. Coat.* **2008**, *61*, 283–290.
62. Amiuidin, A.; Barrear, C.; Hellouin, R.; Thierry, D. *Prog. Org. Coat.* **1995**, *25*, 339–355.
63. Zhang, X.; Wang, F.; Du, Y. *Surf. Coat. Technol.* **2007**, *201*, 7241–7245.
64. Moggridge, G. D.; Lape, N. K.; Yang, C.; Cussler, E. L. *Prog. Org. Coat.* **2003**, *46*, 231–240.
65. Perrin, X.; Merlatti, C.; Aragon, E.; Margaillan, A. *Prog. Org. Coat.* **2009**, *64*, 466–473.
66. Soera, W. J.; Minga, W.; Koringb, C. E.; van Benthem, R. A. T. M.; Mold, J. M. C.; Terryn, H. *Prog. Org. Coat.* **2009**, *65*, 94–103.
67. Ashby, M.; Johnson, K. *Materials and Design: The Art and Science of Material Selection in Product Design*; Elsevier Science: Oxford, 2002.
68. Bohl, A. H. Ed. *Computer Aided Formulation*; VCH Publishers: New York, 1990.
69. Wang, D.; Bierwagen, G. P. *Prog. Org. Coat.* **2009**, *64*, 327–338.
70. Pathak, S. S.; Sharma, A.; Khanna, A. S. *Prog. Org. Coat.* **2009**, *65*, 206–216.
71. Skerry, B. S.; Chen, C. T.; Ray, C. J. *J. Coat.Technol.* **1992**, *64*(806), 77–86.
72. Fishman, R. S.; Kurtze, D. A.; Bierwagen, G. P. *Prog. Org. Coat.* **1993**, *21*, 387.
73. Fishman, R. S.; Hill, E. S.; Storsved, T. K.; Bierwagen, G. P. *J. Appl. Phys.* **1996**, *79*, 729.
74. Fishman, R. S.; Kurtze, D. A.; Bierwagen, G. P. *J. Appl. Phys.* **1992**, *72*, 3116–3124.
75. Fishman, R. S.; Kurtze, D. A.; Bierwagen, G. P. *Prog. Org. Coat.* **1993**, *21*, 387–403.
76. Chisholm, B. J.; Webster, D. C. *J. Coat. Technol. Res.* **2007**, *4*, 1–12.
77. Chisholm, B.; Potyrailo, R.; Cawse, J.; Shaffer, R.; Brennnan, M.; Molaison, C.; Whisenhunt, D.; Flanagan, B.; Olson, D.; Akhave, J.; Saunders, D.; Mehrabi, A.; Licon, M. *Prog. Org. Coat.* **2002**, *45*, 313–321.
78. Shedlosky, T. J.; Huovinen, A.; Webster, D.; Bierwagen, G. In Metal 04: Proceedings of the International Conference on Metals Conservation, Canberra, Australia, 4–8 October 2004, p. 400.
79. Bonitz, V. S.; Hinderliter, B. R.; Bierwagen, G. P. *Electrochim. Acta* **2006**, *51*, 3558–3565.
80. Hie, J.; Bahr, J.; Chisholm, B.; Li, J.; Chen, Z.; Balbyshev, S.; Bonitz, V.; Bierwagen, G. *J. Comb. Chem.* **2008**, *10*, 704–713.
81. Chisholm, B. J.; Berry, M.; Bahr, J.; He, J.; Li, J.; Balbyshev, S.; Bierwagen, G. P. *J. Coat. Technol. Res.* **2009**.
82. Grundmeier, G.; Simöes, A. Corrosion and Oxide Films; Bard, A., Stratman, M., Eds.; *Encyclopedia of Electrochemistry,* Vol. 4 Wiley-VCH: New York, 2003; Chapter 5.4.
83. Bierwagen, G.; Li, J.; He, L.; Tallman, D. In *Proceedings of the 2nd International Symposium on Service Life Prediction Methodology and Metrologies, Monterey, CA, 14–17 November 1999*; Martin, J., Bauer, D., Eds.; ACS Symposium Series 805; ACS: Washington, DC, 2001; Chapter 14; pp 316–350.
84. Knudsen, O. Ø.; Steinsmo, U.; Bjordal, M. *Prog. Org. Coat.* **2005**, *54*, 224–229.
85. Abreu, C. M.; Izquierdo, M.; Merino, P.; Nóvoa, X. R.; Pérez, C. *Corrosion* **1999**, *55*, 1173.
86. Marchebois, H.; Savall, C.; Bernard, J.; Touzain, S. *Electrochim. Acta* **2004**, *49*, 2945–2954.

Further Readings

Ashby, M.; Johnson, K. *Materials and Design: The Art and Science of Material Selection in Product Design;* Elsevier Science: Oxford, UK, 2002.

Bierwagen, G. Ed. *Organic Coatings for Corrosion Control*; ACS Symposium Series 689; American Chemical Society: Washington, DC, 1998.

Bohl, A. H. Ed. *Computer Aided Formulation*; VCH: New York, 1990.

Fedrizzi, L. Terryn, H.; Simoes, A. Eds. *Innovative Pretreatment Techniques to Prevent Corrosion of Metallic Surfaces*; European Federation of Corrosion – Publication No. 54 Woodhead/CRC Press: Boca Raton, FL, 2007.

Martin, J. W.; Bauer, D. R. Eds. *Service Life Prediction: Methodology and Metrologies*; ACS Symposium Series 805; American Chemical Society: Washington, DC, 2001.

Scantlebury, D.; Kendig, M. *Advances in Corrosion Protection by Organic Coatings II;* Proceedings of the Electrochemical Society, Vol. 95–13; The Electrochemical Society: Pennington, NJ, 1995.

Sekine, I.; Kendig, M.; Scantlebury, D.; Mills, D. *Advances in Corrosion Protection by Organic Coatings III;* Proceedings of the Electrochemical Society, Vol. 94–41; The Electrochemical Society: Pennington, NJ, 1997.

Taylor, S. R. Isaacs, H. S.; Brooman, E. W. Eds. *Environmentally Acceptable Inhibitors and Coatings*; Proceedings of the Electrochemical Society; Vol. 95–16; The Electrochemical Society: Pennington, NJ, 1997.

Wicks, Z. W.; Jones, F. N.; Pappas, S. P.; Wicks, D. A. *Organic Coatings: Science & Technology* , 3rd ed.; John Wiley: New York, 2007.

Zarras, P.; Wood, T.; Richey, B.; Benicewicz, B. C. *New Developments in Coatings Technology;* ACS Symposium Series 962; The American Chemical Society: Washington, DC, 2006.

4.12 Mechanisms of Protection by Paints

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Glossary

D conduction The behavior of a paint film (or an area of a paint film) whose trends in conductivity follow directly the solution in which it is immersed.

Donnan effect Where species of a particular size or charge are unable to pass through a semipermeable membrane, an additional osmotic pressure is created across the membrane.

I conduction The behavior of a paint film (or an area of a paint film) whose conductivity follows inversely to the solution in which it is immersed.

Ionogenic Capable of forming ions; used especially of a molecule that can dissociate into fixed ions and mobile counterions

Isoelectric (point) The pH at which a particular molecule or surface carries no net electrical charge.

Zwitterion A chemical compound that is electrically neutral but carries formal positive and negative charges on different atoms.

Abbreviations

AC Alternating current
DC Direct current
PVC Pigment volume concentration
RH Relative humidity

4.12.1 Introduction

From time to time, astronomical estimates are made of the annual destruction of metals, particularly iron and steel, by corrosion. Paint is one of the oldest methods used for delaying this process. However, it is somewhat surprising that its protective action has only recently been systematically examined.

Since iron is the commonest structural material, the following discussion will be limited to the behavior of this metal. The general principles can readily be extended to nonferrous metals.

4.12.2 The Corrosion of Iron and Steel

Corrosion is essentially the conversion of iron into a hydrated form of iron oxide, that is, rust. The driving force of the reaction is the tendency of iron to combine with oxygen. It has long been known that iron is not visibly corroded in the absence of either water or oxygen. The overall reaction in their presence may be written as:

$$4Fe + 3O_2 + 2H_2O = 2Fe_2O_3 \cdot H_2O$$

When the supply of oxygen is restricted, the corrosion product may contain ferrous ions. The overall reaction can be broken down into two reactions, one producing electrons and the other consuming them:

$$4Fe = 4Fe^{2+} + 8e^- \quad \text{(anodic reaction)}$$

$$2O_2 + 4H_2O + 8e^- = 8OH^- \text{(cathodic reaction)}$$

Or, combining these:

$$4Fe + 2O_2 + 4H_2O = 4Fe(OH)_2$$

In the presence of oxygen, the ferrous hydroxide will be further converted into one of the forms of rust, for example, $Fe_2O_3{\cdot}H_2O$.

Ferrous hydroxide is soluble (9%) in pure water, but slight oxidation renders it appreciably less soluble. Thus, in the presence of water and oxygen alone, the corrosion product may be formed in close contact with the metal and attack will consequently be stifled. In the presence of an electrolyte such as sodium chloride, however, the anodic and cathodic reactions are modified, ferrous chloride being formed at the anode and sodium hydroxide at the cathode. These two compounds are highly soluble and not easily oxidized, so they diffuse away from the sites of formation and react at a distance from the metal surface to form ferrous hydroxide, or a basic salt, which then combines with oxygen to form rust with the regeneration of sodium chloride:

$$FeCl_2 + 2NaOH = Fe(OH)_2 + 2NaCl$$

$$4Fe(OH)_2 + O_2 = 2Fe_2O_3 \cdot H_2O + 2H_2O$$

Consequently, rust is formed at a distance from the metal, and so stifling cannot occur.

It follows that when iron rusts, the conversion is accompanied by a flow of electrons in the metal from the anodic to the cathodic regions and by the movement of ions in solution. This conclusion has been firmly established by Evans[1] and his coworkers, who have shown that in the case of a number of metals under laboratory conditions, the spatial separation of the anodic and cathodic zones on the surface of the metal was so complete that the current flowing was equivalent to the corrosion rate. In order to inhibit corrosion, it is necessary to stop the flow of current. This can be achieved by suppressing either the cathodic or the anodic reaction, or by inserting a high resistance in the electrolytic path of the corrosion current. These three methods of suppression are called cathodic, anodic, and resistance inhibition, respectively.

The effect of paint films on the cathodic and anodic reactions will now be considered and the factors which influence the electrolytic resistance of paint films will be discussed.

4.12.2.1 The Cathodic Reaction

The cathodic reaction in neutral solutions usually involves oxygen, water, and electrons:

$$O_2 + 2H_2O + 4e^- = 4OH^-$$

If a paint film is to prevent this reaction, it must be impervious to electrons; otherwise, the cathodic reaction is merely transferred from the surface of the metal to the surface of the film. Organic polymer films do not contain free electrons, except in the special case of pigmentation with metallic pigments; consequently, it will be assumed that the conductivity of paint films is entirely ionic. In addition, the films must be impervious to either water or oxygen, so that they prevent either of them from reaching the surface of the metal.

The rate of corrosion of unpainted mild steel immersed in seawater, found by Hudson and Banfield,[2] was found to be 0.089 mm year^{-1}. Hudson[3] obtained a similar average value for steel exposed to the open air under industrial conditions (0.051 mm year^{-1} at Motherwell and 0.109 mm year^{-1} at Sheffield). This rate of corrosion corresponds to the destruction of 0.07 g cm^{-2} of iron per year. Assuming that the corrosion product was $Fe_2O_3{\cdot}H_2O$, this rate of attack represents the consumption of 0.011 g cm^{-2} of water per year and 0.03 g cm^{-2} of oxygen per year.

4.12.2.1.1 Diffusion of water

The diffusion of water through paint films has been measured by various workers. The weight of water, which could diffuse through three clear vehicles and eight paint films, each 0.1-mm thick, at a relative humidity (RH) of 85–100%, has been calculated on the assumption that the water would be consumed as soon as it reached the metal surface, that is, the rate-controlling step was the rate of diffusion of water through the film, as shown in Table 1.[4,5]

By means of an ingenious instrument, which measured the 'wetness' of a painted surface, Gay[6] found that although the relative humidity of the atmosphere varies appreciably, this is not reflected in the behavior of paint films. He found that under normal conditions, paint films are saturated with water for about half of their life, and for the remainder, the water content corresponded with an atmosphere of high humidity; furthermore, the relative humidity of sea water is about 98%. It follows from Table 1 that the rate at which water passes through paint and varnish films is many times greater than the water consumed by an unpainted specimen exposed under industrial conditions or immersed in the seawater.

4.12.2.1.2 Diffusion of oxygen

The diffusion of oxygen through polymer films has been examined by a number of workers. Guruviah[5] measured the permeability to oxygen of films cast from five paints (Table 2) and compared the results with the corrosion rates of painted steel panels, when exposed to salt spray and humidity for 1000 h. He concluded that "the low corrosion rate could be explained by the low permeability to oxygen of the films"; however, when his values for the permeability are plotted against the corrosion, it is clear that this conclusion is without foundation.

The mass of oxygen, which could diffuse through unit area of a 0.1-mm thick film under a pressure gradient of 2 kPa of oxygen, has been calculated, and is shown in Table 2.[5,7,8] Baumann[9] has claimed that these figures are about 100 times too high, but

Table 1 Diffusion of water through paint films of thickness 0.1 mm

Vehicle	*Pigment*	*Rate of water consumed ($g\,cm^{-2}\,year^{-1}$)*	*Reference*
Glycerol phthalate varnish	None	0.825	4
Phenolformaldehyde varnish	None	0.718	4
Epoxy coal tar	None	0.391	5
Glycerol phthalate varnish	Flake aluminum	0.200	4
Phenolformaldehyde varnish	Flake aluminum	0.191	4
Linseed oil	Lithopone	1.125	4
Ester gum varnish	White lead/zinc oxide	0.122	4
Linseed penta-alkyd	Iron oxide, 15% PVC	0.840	5
Linseed penta-alkyd	Iron oxide, 35% PVC	0.752	5
Epoxypolyamide	Iron oxide, 35% PVC	1.810	5
Chlorinated rubber	Iron oxide, 35% PVC	1.272	5

Unpainted steel consumes water at a rate of 0.008–0.023 $g\,cm^{-2}\,year^{-1}$.

Table 2 Diffusion of oxygen through paint films of thickness 0.1 mm

Vehicle	*Pigment*	*Rate of water consumed ($g\,cm^{-2}\,year^{-1}$)*	*Reference*
Asphalt	None	0.053	7
Epoxy coal tar	None	0.002	5
Polystyrene	None	0.013	8
Polyvinyl butyral	None	0.027	8
Asphalt	Talc	0.039	7
Linseed penta-alkyd	Iron oxide, 15% PVC	0.003	5
Linseed penta-alkyd	Iron oxide, 35% PVC	0.003	5
Epoxypolyamide	Iron oxide, 35% PVC	0.002	5
Chlorinated rubber	Iron oxide, 35% PVC	0.006	5

Unpainted steel consumes oxygen at a rate of 0.020–0.030 $g\,cm^{-2}\,year^{-1}$.

this is because he compared the amount which could pass through in a day with that passing in a year. Haagen and Funke[10] concluded that the permeation of water was too great and that of ions too small to be the controlling factor and suggested that the rate controlling step was the rate of the diffusion of oxygen. However, if this were the case then painted steel upon exposure should corrode at a rate varying from that of unpainted steel to about a tenth of that value. Since painted steel upon exposure does not corrode immediately at this rate, it is concluded that the rate of the diffusion of oxygen is not the controlling factor.

The general conclusion drawn from these considerations is that paint films are so permeable to water and oxygen that they cannot inhibit corrosion by preventing water and oxygen from reaching the surface of the metal, that is to say they cannot inhibit the cathodic reaction.

4.12.2.2 The Anodic Reaction

The anodic reaction consists of the passage of iron ions from the metallic lattice into solution, with the liberation of electrons, which are consumed at the cathode by reaction with water and oxygen. There are two ways in which the anodic reaction can be suppressed:

(a) If the electrode potential of iron is made sufficiently negative, positively charged iron ions will not be able to leave the metallic lattice, that is, cathodic protection.

(b) If the surface of the iron becomes covered with a film impervious to iron ions, then the passage of iron ions into solution will be prevented, that is, anodic passivation.

4.12.3 Mechanisms of Paint Protection

4.12.3.1 Cathodic Protection

In order to make the potential of iron more negative, the iron must receive a continuous supply of electrons. As has already been pointed out, polymer films do not contain free electrons; there remains the possibility of obtaining these from a pigment. The only pigments which contain free electrons are metallic ones, and such pigments will protect iron cathodically if the following conditions are fulfilled:

(a) The metallic pigment must be of a metal less noble than iron, otherwise the iron will supply electrons to the pigment, which will be protected at the expense of iron.

(b) The pigment particles must be in metallic, that is, electronic, contact with each other and with the coated iron; if they are not, the movement of electrons cannot occur.

It has been shown[11] that zinc dust is the only commercially available pigment which fulfils both conditions. Paints capable of protecting steel cathodically can be prepared with zinc dust, provided that the pigment content of the dried film is of the order of 95 wt%; both organic and inorganic binders have been used, the latter being very useful when resistance to oil or organic solvents is required.

These paints are quite porous and function satisfactorily only in the presence of an electrolyte – for example, water containing a trace of salt, or acid – which completes the circuit formed by the two metals. It might be thought that the useful life of these paints is limited to the life of the electronic contact between the zinc particles, but this is not correct. Under normal conditions of exposure, the electrons supplied by the zinc to the steel are consumed at the surface of the steel by reaction with water and oxygen (cathodic reaction), with the formation of hydroxyl ions. Consequently, the surface becomes coated with a deposit of the hydroxides, or carbonates of zinc, calcium, or magnesium, which blocks the pores in the film and renders it very compact, adherent, and impervious. Thus, although metallic contact between the steel and the zinc dust particles is essential in the early stages of exposure, the paints provide good protection after that contact has been lost. Paints containing less zinc dust have been known for a long time, but as the zinc dust concentration is decreased, protection at scratch lines or at gaps in the coating decreases; however, such paints frequently afford good general protection owing to the formation of deposits (consisting of oxides and carbonates) on the metal at the base of the coating.

Recently, it has been pointed out that manganese satisfies both conditions since the oxide film around the particles contains ions in two states of oxidation, and it has been claimed that cathodically protective paints can be prepared with this pigment.[12] Exposure trials in this country have indicated that at an inland site their behavior is comparable with the zinc dust controls, but that they were inferior to zinc-rich paints under severe marine conditions. It has been suggested that they might be of interest where zinc was unsuitable owing to toxicity.[13]

4.12.3.2 Anodic Passivation

When a piece of iron is exposed to the air, it becomes covered with an oxide film. Upon immersion in water or solutions of certain electrolytes, the air-formed film breaks down and corrosion ensues. In order to prevent corrosion, the air-formed film must be reinforced with similar material, or a ferric compound, and there are two ways in which this may be achieved:

(a) The pigment may be sufficiently basic to form soaps when ground in linseed oil; in the presence of water and oxygen these soaps may autoxidize to form soluble inhibitive degradation products.
(b) The pigment itself may be an inhibitor of limited solubility.

4.12.3.2.1 Basic pigments

Typical pigments in this class include basic lead carbonate, basic lead sulfate, red lead, and zinc oxide.

It has been established that water becomes noncorrosive after contact with paints prepared by grinding basic pigments in linseed oil,[14] it was also shown that lead and zinc linoleates, prepared by heating the oxide with linseed oil fatty acids in xylene, behave in a similar way. Later, this observation was extended to the linoleates of calcium, barium, and strontium.[15]

Determinations have been made of the solubility of lead linoleate prepared in the absence of oxygen and extracted with air-free water.[16] Under these conditions, lead linoleate had a solubility of 0.002% at 25 °C, and the extract was corrosive when exposed to the air. However, when the extraction was carried out in the presence of air, the resulting extract contained 0.07% solid material and was noncorrosive. It was concluded that in the presence of water and oxygen lead linoleate yielded soluble inhibitive degradation products.

In order to obtain information regarding the composition of these degradation products, aqueous extracts of the lead soaps of the linseed oil fatty acids were analyzed, mainly by chromatography. The extracts contained formic acid 46%, azelaic acid 9%, and pelargonic acid and its derivatives 27%, the remaining 18% consisting of a mixture of acetic, propionic, butyric, suberic, pimelic, and adipic acids. It was shown that whereas the salts of formic acid were corrosive, those of azelaic and pelargonic acid were very efficient inhibitors.

Mayne and Ramshaw[17] have obtained information regarding the origin of these various acids by examining the degradation products of the lead soaps of the individual acids present in linseed oil. They found that it was only the unsaturated acids which degraded to give inhibitive materials, and that the lead soaps of linoleic and linolenic acid yielded in addition short-chain acids which were corrosive. He also examined the relative inhibiting powers of the lead, calcium and sodium salts of a range of mono- and dibasic acids in the pH range 4–6 at concentrations of 10^{-3} to 10^{-5} M.[18] Under these conditions the lead salts were always more efficient than the sodium and calcium salts, and the optimum efficiency occurred when both the mono- and dibasic acids had a chain length of 8–9 carbon atoms.

The mechanism of inhibition by the salts of the long-chain fatty acids has been examined.[19] It was concluded that in the case of the lead salts, metallic lead was first deposited at certain points and that at these points oxygen reduction proceeded more easily. Consequently, the current density was kept sufficiently high to maintain ferric film formation; in addition, any hydrogen peroxide present may assist in keeping the iron ions in the oxide film in the ferric condition, consequently the air-formed film is thickened until it becomes impervious to iron ions. The zinc, calcium, and sodium salts are not as efficient inhibitors as the lead salts and recent work has indicated that inhibition is due to the formation of ferric azelate, which repairs weak spots in the air-formed film. This conclusion has been confirmed by the use of ^{14}C-labelled azelaic acid, which was found to be distributed over the surface of the mild steel in a very heterogeneous manner.[20]

Zinc phosphate was introduced as an inhibitive pigment by Barraclough and Harrison,[21] and in the early tests, vehicles based on drying oils were used. Later, it was claimed[22] that it was an effective inhibitive pigment when used with all paint media in current use.

Variable results have been reported with this pigment and an examination of its inhibitive action[23] has led to the conclusion that under rural and marine conditions, where the pH of the rainwater is above 5, it behaves as an inert pigment owing to its limited solubility. However, in industrial and urban areas, where the pH of the rainwater may be in the region of 4 or lower, it is converted into the more soluble monohydrogen phosphate. This reacts, in the presence of oxygen, with the steel surface to form a mixture of tribasic zinc and ferric phosphates, which being insoluble protects the steel from further attack.

4.12.3.2.2 Soluble pigments

The most important pigments in this class are the metallic chromates, which range in solubilities from

17.0 to 0.00005 g l^{-1} as CrO_3.[24] An examination has recently been carried out of the mechanism of inhibition by chromate ions and it has been shown by chemical analysis of the stripped film, Mössbauer spectroscopy and electron microprobe analysis that the air-formed film is reinforced with a more protective material in the form of a chromium-containing spinel.[25] The situation is, however, complicated by the possibility that some chromates, particularly the basic ones, may inhibit through the formation of soaps. There is evidence that lead chromate can function in this way.

It has been found that red lead, litharge, and certain grades of metallic lead powder render water alkaline and inhibitive[14]; this observation has been confirmed by Pryor.[26] The effect is probably due to a lead compound, for example, lead hydroxide, in solution. Since, however, atmospheric carbon dioxide converts these lead compounds into insoluble basic lead carbonate, thereby removing the inhibitive materials from solution, these pigments may have only limited inhibitive properties in the absence of soap formation.

Work by Beckmann[27] indicated that lead hydroxide was only very slightly better as an inhibitor than sodium hydroxide, and the mechanism of inhibition is probably similar to that suggested for alkaline solutions.[28]

Owing to the low dielectric constant of organic vehicles, these pigments can ionize only after water has permeated the film; consequently, their efficiency is associated with the nature of the vehicle in which they are dispersed, a point which is sometimes overlooked when comparing the relative merits of chromate pigments.

4.12.3.3 Resistance Inhibition

It has been shown that paint films are so permeable to water and oxygen that they cannot affect the cathodic reaction, and that the anodic reaction may be modified by certain pigments. There are, however, many types of protective paints which do not contain inhibitive pigments. It is concluded that this class of paints prevents corrosion by virtue of its high ionic resistance, which impedes the movement of ions and thereby reduces the corrosion current to a very small value.

It is assumed that conduction in polymer films is ionic; it is difficult to see how it could be otherwise. The factors which break down the ionic resistance, or render it ineffective, will now be considered. The effective resistance of paint films may be influenced by ions derived from three sources:

(a) electrolytes underneath the film;
(b) ionogenic groups in the film substance;
(c) water and electrolytes outside the film, that is, arising from the conditions of exposure.

4.12.3.3.1 Electrolytes underneath the film

Atmospheric exposure trials, carried out in Cambridge, established the fact that when rusty specimens were painted in the summer, their condition, after some years' exposure, was very much better than that of similar specimens painted in the winter.[29] It was found that steel weathered in Cambridge carried spots of ferrous sulfate, deeply imbedded in the rust, and that the quantity of ferrous sulfate/unit area was very much greater in the winter than in the summer[30]; this seasonal variation was attributed to the increased sulfur dioxide pollution of the atmosphere in the winter, caused by the combustion of coal in open grates. It was concluded that there was a causal relationship between the quantity of ferrous sulfate and the effective life of the paint. It was suggested that these soluble deposits of ferrous sulfate short-circuit the resistance of the paint film, and since paint films are very permeable to water and oxygen, the ferrous sulfate will become oxidized and hydrolyzed with the production of voluminous rust, which will rupture the film at numerous points, thus giving rise to the characteristic type of failure seen on painted rusty surfaces.

It can be claimed that the problem of painting rusty surfaces is now understood. A method for estimating the ferrous sulfate content of any rusty surface has been put forward,[30] but the amount of ferrous sulfate which can be tolerated by various paints has not yet been established. Thus, it is a bad practice to apply paints to surfaces carrying electrolytes.

4.12.3.3.2 Ionogenic groups in the film substance

Ionogenic (ion-producing) materials may be present, in the form of electrolytes, in both the pigments and the vehicle. Their presence in the pigments may be eliminated by the selection of suitable raw materials by the paint manufacturer; though it does not concern us here, it is important to consider the possibility of the existence of ionogenic groups, such as carboxyl groups, in the polymer itself.

When paint films are immersed in water or solutions of electrolytes, they acquire a charge.

The existence of this charge is based on the following evidence. In a junction between two solutions of potassium chloride, 0.1 and 0.01 M, there will be no diffusion potential, because the transport numbers of both the K^+ and the Cl^- ions are almost 0.5. If the solutions are separated by a membrane equally permeable to both ions, there will still be no diffusion potential, but if the membrane is more permeable to one ion than to the other a diffusion potential will arise; it can be calculated from the Nernst equation that when the membrane is permeable to only one ion, the potential will have the value of 58 mV at 20 °C.

It is easy to measure the potential of this system and it has been found[31] that membranes of polystyrene, linseed oil, and a tung oil varnish yielded diffusion potentials of 43–53 mV, the dilute solution being always positive to the concentrated. Similar results have been obtained with films of nitrocellulose,[32] cellulose acetate,[33] alkyd resin, and polyvinyl chloride.[34]

This selective permeability is ascribed to the presence on the membrane of a negative charge, which is attributed to carboxyl groups attached to the polymer chains. Paint films can, therefore, be regarded as very large anions.

It has been shown that the charge influences the distribution of the primary corrosion products, and work[35] has indicated that the existence of carboxyl groups in the polymer film has an important influence on its behavior when immersed in potassium chloride solutions.

4.12.3.3.3 Water and electrolytes outside the film

Here, we are concerned with the effect of ions in the environment on the resistance of polymer films.

Kittelberger and Elm[36] measured the rate of diffusion of sodium chloride through a number of paint films. Calculations based on their results[31] showed clearly that the rate of diffusion of ions was much smaller than the rate of diffusion of either water or oxygen. Furthermore, they found that there was a linear relationship between the rate of diffusion and the reciprocal of the resistance of the film. This relationship suggests that sodium chloride is diffused through the membrane as ions and not as ion pairs, since the diffusion through the film of unionized material would not affect the resistance, because if a current is to flow, either ions of similar charge must move in one direction, or ions of opposite charge must move in opposite directions.

An examination has, therefore, been made of the effect of solutions of potassium chloride on the electrolytic resistance of films cast from a pentaerythritol alkyd, a phenolformaldehyde tung oil, and an epoxypolyamide varnish.[37,38] Potassium chloride was chosen because its conductivity is well known and unpigmented films were first examined in order to eliminate the complexities of polymer–pigment interaction.

The experimental procedure consisted of casting the varnish on glass plates by means of a spreader bar having a gap of 0.102 mm; this produced a wet film of thickness 0.051 mm that yielded a dried film of 0.025 mm. This standard thickness was used throughout and resistances are quoted in $\Omega\,cm^2$. The cast films were dried for 48 h in a glove box followed by a further 48 h in an oven at 65 °C.

The films were then soaked in water and removed from the plates. Portions were mounted in glass cells which were filled with potassium chloride solution; two Ag/AgCl electrodes were inserted into the limbs of the cells and the unit was placed in a thermostat. The resistance of the films was determined, from time to time, by connecting the cells in series with a known resistance and applying a potential of 1 V to the combination; the potential drop across the standard resistance was measured by means of a valve potentiometer.

When samples of about 1 cm^2 were taken from a single cast film of 100 × 200 mm^2 of a number of paint and varnish films, their resistances varied with the concentration of potassium chloride solution in one of two ways (**Figure 1**). Either the resistance increased with increasing concentration of the electrolyte (inverse or I conduction) or the resistance of the film followed that of the solution in which it was immersed (direct or D conduction). The percentage of I and D samples taken from different castings varied, but average values for a number of castings were 50% D for the pentaerythritol alkyd and the tung oil phenol formaldehyde varnishes, 57% for urethane alkyd, 76% for epoxypolyamide, and 78% for polyurethane varnishes.[39]

The effect of iron oxide, zinc oxide, and red lead on the percentage of D areas has been determined. Three vehicles were used, a pentaerythritol alkyd, a tung oil phenolic, and an epoxypolyamide.[40] In the case of iron oxide, the D areas increased with all the three vehicles; in contrast, zinc oxide had very little effect on the percentage of D areas. However, red lead when dispersed in the alkyd and tung oil vehicles behaved in a similar way to iron oxide, whereas red lead when dispersed in the epoxypolyamide vehicle had very little effect.

A careful examination has been made of the properties of I films when immersed in solutions of electrolytes. It was found that when a film of a pentaerythritol alkyd varnish was transferred from 0.001 to 3.5 N KCl its resistance rose, fell upon returning it to the 0.001 N KCl, rose again to the same high value when immersed in a sucrose solution isotonic with 3.5 N KCl and fell to the original value when returned to the dilute KCl solution (Figure 2). It was concluded that the changes in resistance were dependent only upon the available water in the solution and were associated, therefore, with the entry of only water into the varnish film.[37]

In contrast, D films followed the resistance of the solution in which they were immersed, and this behavior was originally explained by assuming that D films contained holes, or pores, filled with solution that controlled the resistance of the film. Thus, a typical value for the resistance of a D film in 3.5 M potassium chloride is $108\,\Omega\,\mathrm{cm}^2$ and if this resistance was due to a pore, then it would have a radius of about 50 nm. In order to test this explanation, the distribution of I and D areas in a given piece of film has been determined by means of a series of gaskets fitted into a dismountable cell.[41] It was found that I films were free from D areas, but in the case of the three vehicles examined, samples of D films always contained a mixture of I and D areas in an interlocking mosaic structure. It was concluded that those portions of the film having D properties were distributed over an appreciable area of the sample and not confined to a single area, as would have been the case had the sample contained a single pore.

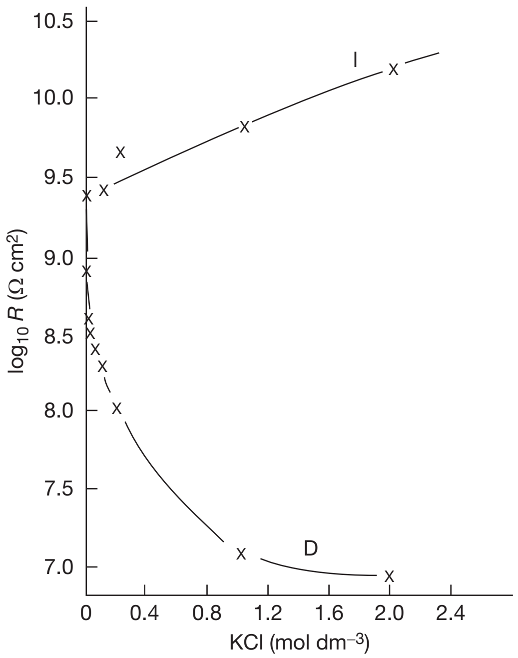

Figure 1 Relationship between the logarithm of the resistance of D and I films of a pentaerythritol alkyd paint, containing 6.1% iron oxide by volume, and the concentration of the potassium chloride solutions in which they were immersed. Reproduced from *Brit. Polym. J.* **1971**, *3*, 41.

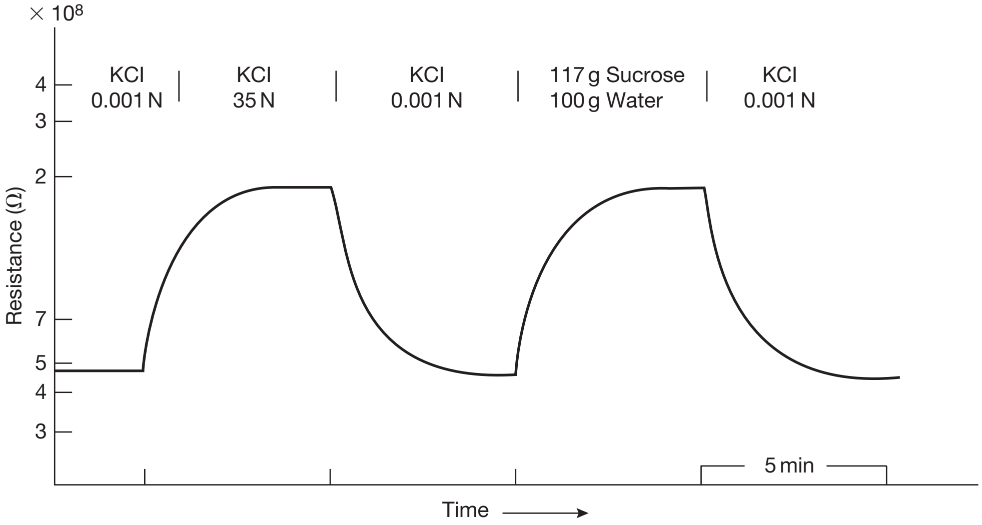

Figure 2 Relationship between the resistance of an I film (log scale) and the concentration of the solute. Reproduced from *Official Digest* **1970**, 34(452), 972–990.

It was concluded that D conduction cannot be attributed to the presence of pores, unless they were of molecular dimensions.

In general, the water uptake of D films tended to be higher than that of I films, but a more significant difference was shown by microhardness measurements. The results obtained with all the three vehicles showed that the D areas were significantly softer than the I areas and that the distribution of the hardness values corresponded to that of the resistances. It was concluded that these films have a very heterogeneous structure and that I and D areas are brought about by differences in cross-linking density within the film.

An investigation has been made of the factors that control I and D conduction and it has been found that the difference is only one of degree and not of kind.[42] Thus, if the varnish films are exposed to solutions of decreasing water activity, then the resistance falls with increasing concentration of electrolyte, but a point is eventually reached when the type of conduction changes and the films exhibit I-type behavior. It appears that D films can be converted into I films, the controlling factor being the uptake of water.

The discussion so far has been limited to the behavior of polymer films after immersion in potassium chloride solutions for only a short time. When varnish films were immersed in potassium chloride solutions for a month or more, a steady fall in resistance took place. Further experiments indicated that the effect was reversible and dependent on both the pH of the solution and the concentration of potassium chloride. It was concluded that an ion-exchange process was operative.[37]

In view of this, the properties of I films were examined after they had been subjected to increasing amounts of ion exchange.[38] In order to do this, detached films were exposed at 65 °C for 7 h to a universal buffer adjusted to a suitable pH and the resistance of the film measured at 25 °C in 3 M and 0.001 M potassium chloride. The results obtained with a pentaerythritol alkyd are shown in Figure 3 from which it can be seen that as the pH of the conditioning solution increased, the resistance of the film fell, until at a pH of about 7.5 when it suddenly dropped. The resistance of the film then followed that of the solution in which it was immersed, that is, it became a D-type film. Similar results were obtained with films of a tung oil phenolic varnish, although in this case the change-over point occurred at a higher pH, that is, about 9.

In the case of the epoxypolyamide varnish, however, as the pH increased the resistance of the film at first rose, then at about pH 8.8 it started to fall until at pH 11 the change-over in the type of conduction occurred. This suggests that the resin was acting as a zwitterion with an isoelectric point at about pH 8.8. Thus, before the isoelectric point, the membrane would be positively charged and an increasing concentration of hydroxyl ions would depress the ionization of the ionogenic groups; above the isoelectric point, the membrane would be negatively charged and ion exchange with potassium ions would take place. This conclusion was confirmed by diffusion potential measurements.

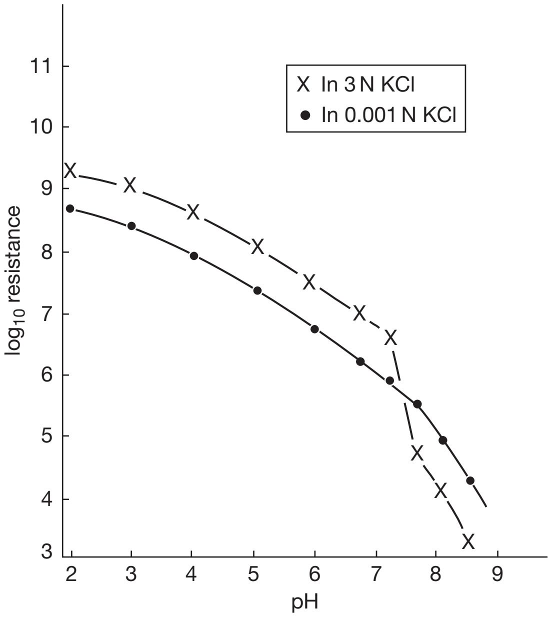

Figure 3 Variation of the resistance of I films (log scale) with the pH of the conditioning solutions.

In the case of all the three varnishes, after the ion exchange had taken place, a point was reached when the type of conduction changed from I to D. The change-over in the type of conduction was found to occur at the same pH as a fall in the temperature coefficient of resistance, and the lower value corresponded to that of the aqueous solution.

The phenomenon of ion exchange has been confirmed by chemical analysis.[43] Films were exposed to potassium chloride solutions of increasing pH, ashed and their potassium content determined by flame photometry. It was found that the potassium content of the films increased as the pH of the solutions rose until saturation was reached at a value which corresponded to that of the change-over in the mechanism of conduction. It was concluded that the change-over in the mechanism of conduction corresponded to the point at which the exchange capacity of the film had reached its limit.

Rothwell[44] found by resistance measurements that ion exchange occurred in films of eight unpigmented varnishes, and he confirmed this for pentaerythritol alkyd films by the determination of the uptake of radioactive potassium in the form of ^{42}KCl; however, his films, with one exception, were all D type.

Fialkiewicz and Szandorowski[45] examined the penetration of ^{90}Sr and ^{36}Cl ions through air-dried films of a styrenated alkyd pigmented with iron oxide over the range 10–60% PVC (pigment volume concentration) and found intense penetration of the strontium cations, but negligible penetration of the chloride ions.

Ulfvarson *et al.*[46] examined the ion exchange properties of free films of a soya alkyd, and later Khullar and Ulfvarson[47] extended the examination to clear films of 20 vehicles. They concluded that those binders with low ion-exchange capacities provided the best protection. In a later study,[48] they examined the relationship between ion-exchange capacity and corrosion protection of 22 paints based on three alkyd binders and concluded that ion exchange was not the dominating factor, but a secondary one. This conclusion was confirmed by van der Heyden,[49] who suggested that a process of ion exchange combined with diffusion of cations into the film was operative.

4.12.3.4 Physical Factors Affecting Resistance

4.12.3.4.1 Temperature

An examination has been made of the effect of temperature on the structural changes in polymer films produced from the three vehicles described earlier.[50] Three methods were used: dilatometry, water absorption, and ionic resistance. It was concluded that dilatometry was the most reliable method and water absorption is difficult to determine. Both methods use appreciable quantities of film, which contain both D and I areas. Resistance measurements, however, can be carried out on small areas of film and the relative properties of D and I areas studied.

It was established that significant changes in resistance took place at the transition temperature and consequently sharp changes in protective properties. The resistance always fell with an increase in temperature and this may provide an explanation for the fact that accelerated tests using the same corrosion cycle may not produce the same results if carried out at different temperatures.

4.12.3.4.2 Concentration of electrolyte

Myer and Sievers[51] applied the Donnan equilibrium to charged membranes and developed a quantitative theory of membrane selectivity. They expressed this selectivity in terms of a selectivity constant, which they defined as the concentration of fixed ions attached to the polymer network. They determined the selectivity constant of a number of membranes by the measurement of diffusion potentials. Nasini *et al.*[52] and Kumins[53] extended the measurements to paint and varnish films.

When the Donnan equilibrium is operative, the entry of ions into the membrane is restricted. Consequently, as the concentration of ions in the solution increases the resistance of the membrane remains constant until the concentration of ions in the solution reaches that of the fixed ions attached to the polymer network. At this point, their effect will be swamped and the movement of ions will be controlled by the concentration gradient.

Films of a pentaerythritol alkyd, a tung oil phenolic and an epoxy–polyamide pigmented with iron oxide in the range 5–7% PVC were exposed to solutions of potassium chloride in the range 0.0001–2.0 M.[54] It was found that in all cases, the resistance of the films steadily decreased as the concentration of the electrolyte increased. Since the resistances of the films were at no time independent of the concentration of the electrolyte, it was concluded that the Donnan equilibrium was not operative and that the resistance of the films were controlled by the penetration of electrolyte moving under a concentration gradient.

4.12.3.4.3 Film thickness

Varnishes prepared from the three standard polymers were cast on two thicknesses and the percentage of D areas compared with that obtained from the films produced by casting one thin coat, allowing it to dry and then casting a second coat on top.[39] Similar results were obtained from all the three varnishes and the results obtained with the epoxy–polyamide varnish are given in Table 3.

Table 3 Percentage of D areas on cast films epoxy-polyamide varnish

	Thickness (μm)	*% D-type*
Single coat	35–40	80
Single coat	75–80	50
Double coat	70–75	0–5

Earlier, it was shown that D type areas are relatively small; consequently, the chance of D areas overlapping each other is low. It follows that two coats of all the three varnishes, which are based on cross-linking polymers, are more effective in improving the resistance of the films than single coats of equal thickness.

4.12.3.4.4 Solvents

All the films discussed so far have been cast from paints or varnishes containing solvents. In order to examine the effect of solvents, films of a solvent-free epoxy–polyamine were cast, mounted in cells, and their resistances measured in dilute and concentrated potassium chloride solution.[55] All the films had I properties with resistances in the range 10^{10}–$10^{12}\,\Omega\,\mathrm{cm}^2$.

It appears that during the drying of paint or varnish films, the presence of solvent molecules interferes with the process of cross-linking; consequently, the films have a heterogeneous structure and films of improved protective quality arise when solvents are eliminated.

It is suggested that future work should be directed toward the pigmentation of solvent-free systems, either with inert pigments, when they would form coatings of high electrolytic resistance which would protect by the exclusion of ions, or as sealing coats applied over primers containing inhibitive pigments.

4.12.4 Prediction of Paint Performance

If protection by paints or varnish films is due to their ability to restrict the penetration of corrosive ions, then it follows that resistance measurements should form the basis of the prediction of their behavior. In 1948, Bacon *et al.*[56] measured the resistance of over 300 paint systems immersed in seawater using a direct current (DC) technique, and concluded that for good performance, coatings should have a resistance in excess of $10^8\,\Omega\,\mathrm{cm}^2$. Coatings having resistances in the range 10^6–$10^8\,\Omega\,\mathrm{cm}^2$ were found to be unreliable, and those of lower resistance behaved poorly.

It has frequently been suggested that during direct current measurements the specimens become polarized, consequently alternating current (AC) should be used. A comparison of DC and AC methods has been made and it was found that at a frequency of 1592 Hz and over the range 0.2–20 kHz, the values of the resistances were always lower when AC was used.[57]

The situation has now been clarified,[58] and it has been shown that, with AC, the values obtained are controlled by the capacitance until the frequency has fallen to about 1 Hz. It was shown that under these circumstances, in the absence of corrosion, the resistances of paint films measured by DC or AC were the same; furthermore, no polarization resistance was detected.

The conclusions are that when coatings have resistances greater than $10^8\,\Omega\,\mathrm{cm}^2$ (i.e., when corrosion is absent) then their resistances may be measured by either DC or AC. However, DC measurements can be made more quickly; they are easier to make and the apparatus is less costly. It has also been suggested that such measurements provide a basis for the prediction of performance. On the other hand, when corrosion starts, the AC should be used, since the values obtained can be resolved into two components, which provide a means of detecting and following the corrosion beneath the coating.

References

1. Evans, U. R. *The Corrosion and Oxidation of Metals*; Arnold: London, 1960; Chapter 21.
2. Hudson, J. C.; Banfield, T. A. *J. Iron Steel Inst.* **1946**, *154*, 229.
3. Hudson, J. C. *The Corrosion of Iron and Steel*; Chapman and Hall: London, 1940; p 66.
4. Edwards, J. D.; Wray, R. I. *Ind. Eng. Chem.* **1936**, *28*, 549.
5. Guruviah, S. *J. Oil Col. Chem. Assoc.* **1970**, *53*, 669.
6. Gay, P. J. *J. Oil Col. Chem. Assoc.* **1948**, *31*, 481.
7. Anderson, A. P.; Wright, K. A. *Ind. Eng. Chem.* **1941**, *33*, 991.
8. Davis, D. W. *Mod. Packag*. **1946**, *19*, 145–149.
9. Bauman, K. *Plaste Kautschuk* **1972**, *19*, 694.
10. Haagen, H.; Funke, W. *J. Oil. Col. Chem. Assoc.* **1975**, *58*, 359.
11. Mayne, J. E. O. *J. Soc. Chem. Ind.* **1947**, *66*, 93.
12. Kelkar, V. M.; Putambekar, S. V. *Chem. Ind.* **1964**, *1*, 315.
13. Wild, G. L. E. *Paint Technol.* **1966**, *30*, 9.
14. Mayne, J. E. O. *J. Soc. Chem. Ind.* **1946**, *65*, 196; **1949**, *68*, 272.
15. Mayne, J. E. O. *Oil Col. Chem. Assoc.* **1951**, *34*, 473.
16. Mayne, J. E. O.; van Rooyen, D. *J. Appl. Chem.* **1954**, *4*, 384.
17. Mayne, J. E. O.; Ramshaw, E. H. *J. Appl. Chem.* **1963**, *13*, 553.
18. Mayne, J. E. O.; Ramshaw, E. H. *J. Appl. Chem.* **1960**, *10*, 419.
19. Appleby, A. J.; Mayne, J. E. O. *J. Oil Col. Chem. Assoc.* **1967**, *50*, 897.
20. Mayne, J. E. O.; Page, C. L. *Br. Corros. J.* **1970**, *5*, 94; **1972**, *7*, 111, 115.
21. Barraclough, J.; Harrison, J. B. *J. Oil. Col. Chem. Assoc.* **1965**, *48*, 341.
22. Harrison, J. *Br. Corros. J.* **1969**, *4*, 55.
23. Burkill, J. A.; Mayne, J. E. O. *J. Oil. Col. Chem. Assoc.* **1988**, *71*, 273.
24. Sherman, L. R. *Official Digest* **1956**, *28*, 645.
25. Bancroft, G. M.; Mayne, J. E. O.; Ridgway, P. *Br. Corros. J.* **1971**, *6*, 119.
26. Pryor, M. J. *J. Electrochem. Soc.* **1954**, *101*, 141.

27. Beckman, P.; Mayne, J. E. O. *J. Appl. Chem.* **1971**, *10*, 417.
28. Gilroy, D.; Mayne, J. E. O. *Br. Corros. J.* **1966**, *1*, 161.
29. Mayne, J. E. O. *J. Iron St. Inst.* **1954**, *176*, 143.
30. Mayne, J. E. O. *J. Appl. Chem.* **1959**, *9*, 673.
31. Mayne, J. E. O. *Research, Lond.* **1952**, *6*, 278.
32. Sollner, K. *J. Phys. Chem.* **1945**, *49*, 47, 147, 265.
33. Meyer, K. H.; Sievers, J. F. *Helv. Chim. Acta.* **1936**, *19*, 665.
34. Nasini, A. G.; Poli, G.; Rava, V. In *Premier Congrès Technique International de Industrie des Peintures*, Paris, 1947; p 299.
35. Mayne, J. E. O. *J. Oil Col. Chem. Assoc.* **1957**, *40*, 183.
36. Kittleberger, W. W.; Elm, A. C. *Ind. Eng. Chem.* **1952**, *44*, 326.
37. Maitland, C. C.; Mayne, J. E. O. *Official Digest* **1962**, *34*, 972.
38. Cherry, B. W.; Mayne, J. E. O. In *First International Congress on Metallic Corrosion*, Butterworths, London, 1962; p 539.
39. Mills, D. J.; Mayne, J. E. O. *Corrosion Control by Organic Coatings*; NACE, 1981; p 12.
40. Mills, D. J.; Mayne, J. E. O. *J. Oil. Col. Chem. Assoc.* **1983**, *66*, 88.
41. Mayne, J. E. O.; Scantlebury, J. D. *Br. Polym. J.* **1970**, *2*, 240.
42. Kinsella, E. M.; Mayne, J. E. O. *Br. Polym. J.* **1969**, *1*, 173.
43. Cherry, B. W.; Mayne, J. E. O. In Second International Congress on Metallic Corrosion; National Association of Corrosion Engineers: Houston, TX, 1966; p 680.
44. Rothwell, G. W. *J. Oil Col. Chem. Assoc.* **1969**, *52*, 219.
45. Fialkiewicz, A.; Szandorowski, M. *J. Oil. Col. Chem. Assoc.* **1974**, *57*, 258.
46. Ulfvarson, U.; Khullar, M. L.; Wåhlin, E. *J. Oil. Col. Chem. Assoc.* **1967**, *50*, 254.
47. Khullar, M. L.; Ulfvarson, U. In *IX Congres Fatipec*, Fédération d'Associations de Techniciens des Industries des Peintures (FATIPEC): Brussels, 1968; Section 3, p 165.
48. Ulfvarson, U.; Khullar, M. L. *J. Oil. Col. Chem. Assoc.* **1971**, *54*, 604.
49. van der Heyden, L. A. In *XI Congres Fatipec*, Fédération d'Associations de Techniciens des Industries des Peintures (FATIPEC): Brussels, 1972; p 475.
50. Mayne, J. E. O.; Mills, D. J. *J. Oil. Col. Chem. Assoc.* **1982**, *65*, 138.
51. Meyer, K. H.; Sievers, J. F. *Helv. Chem. Acta* **1936**, *19*, 649.
52. Nasini, A. G.; Poli, G.; Rava, V. In Premier Congres Technique International de l'Industrie des Peintures et des Industries Associées, **1947**; p 299.
53. Kumins, C. A. *Official Digest* **1962**, *34*, 843.
54. Maitland, C. C.; Mayne, J. E. O.; Scantlebury, J. D. In Proceedings 8th International Congress on Metallic Corrosion, Dechema, Frankfurt, **1981**; p 1032.
55. Mayne, J. E. O. *Advances in Corrosion Protection by Organic Coatings*; Electrochemical Society PV, 1989; 89–13.
56. Bacon, R. C.; Smith, J. J.; Rugg, F. M. *Ind. Eng. Chem.* **1948**, *40*, 162.
57. Buller, M.; Mayne, J. E. O.; Mills, D. J. *J. Oil. Col. Chem. Assoc.* **1976**, *59*, 351.
58. Burstein, G. T.; Gao, G.; Mayne, J. E. O. *J. Oil. Col. Chem. Assoc.* **1989**, *72*, 407.

4.13 Temporary Protectives

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Abbreviations

VCI Volatile corrosion inhibitor

4.13.1 Introduction

There are many temporary protectives in the market and it would be impracticable to describe them individually. However, they may be classified according to the type of film formed, that is, soft film, hard film, and oil film; the soft film may be further sub-divided into solvent-deposited thin film, hot-dip thick film, smearing, and slushing types. All these types are removable with common petroleum solvents. There are also strippable types based on plastics (deposited by hot dipping or from solvents) or rubber latex (deposited from emulsions); these do not adhere to the metal surfaces and are removed by peeling. In addition, there are volatile corrosion inhibitors (VCI) consisting of substances, the vapor from which inhibits corrosion of ferrous metals. The types of temporary protectives in common use are given in Table 1.

4.13.2 Types of Temporary Protectives

4.13.2.1 Soft-Film Materials

Protectives that are deposited in the cold from a solvent usually consist of waxy substances such as lanolin or petrolatum mixtures dissolved in solvents such as white spirit. Films formed in this way are thinner than other soft films deposited by different methods. On the other hand, protectives applied by dipping the article in the hot molten material are usually based on petrolatum.

Corrosion prevention depends largely on the barrier provided by the film, but for improved protection, corrosion inhibitors such as sodium nitrite or benzoate may be added. The film may be relatively hard and waxy or quite soft like pharmaceutical petroleum jelly. Corrosion-inhibited petroleum-based waxes deposited from solvent find application for the supplementary protection of hollow sections of finished products. These waxes are applied by airless or air-assisted pressure-feed spraying techniques to clean and dry, but often painted, surfaces to provide increased protection against corrosion due to humid and corrosive atmospheres during both transit and use.

The smearing types of protective material usually consist of lubricating grease compositions, that is, blends of soaps and lubricating oil, but may be mixtures containing petrolatum, oil, lanolin or fatty material. They are softer than the hot-dip materials to permit cold application by smearing. Slushing compounds are a variant of the smearing types and possess some flow properties at room temperature. Thus, they can be brush applied and marks produced after application are reduced. Some materials contain solvent, so that they are free-flowing as applied, but stiffen when the solvent evaporates.

Table 1 Types of temporary protective in general use

Types of protective	*Typical ingredients*	*Method of application*	*Properties of film*
Solvent-deposited hard film		Dipping spraying, brushing	Solid, thin, tough, nonsticky, removable by wiping with solvent
(a) ordinary grade	(a) Plasticised bitumens, plasticised resins, white spirit, coal tar naphtha, chlorinated solvents		
(b) water-displacing grade	(b) As (a) above together with water displacing agents		
Solvent-deposited soft films		Dipping, spraying, brushing	Solid, thin, greasy, removable by wiping with solvent
(a) ordinary grade	(a) Lanolin, petrolatum, with and without specific corrosion inhibitors and antioxidants, white spirit, coal tar naptha, chlorinated solvents		
(b) water-displacing grade	(b) As (a) above together with water displacing agents		
Hot-dipping soft film	Petrolatum, lanolin, with and without specific corrosion inhibitors	Dipping in molten material	Solid, thick, waxy or greasy, removable by wiping with solvent or immersing in hot oil
Smearing	Metallic soap and mineral oil, soft petrolatum, lanolin (castor oil/lead stearate for rubber-containing components)	Smearing, brushing	Solid, thick, greasy, removable by wiping with solvent
Slushing	Metallic soap and mineral oil, oil-softened petrolatum, lanolin, small amounts of solvent	Smearing, brushing	As for smearing protective
Oil	Mineral oil, specific corrosion inhibitors and antioxidants	Dipping, rinsing, spraying	Liquid, thin, oily
Strippable			
(a) hot-dipping grade	(a) Ethyl celiulose, cellulose acetate butyrate, mineral oil, plasticiser, resins, stabilisers	(a) Dipping in molten material	(a) Solid, tough, nonadherent. Often leaves oily film with lubricating properties; film removed by stripping.
(b) cold-applied grade	(b) Vinyl copolymer resins, plasticisers, stabilisers, flammable or nonflammable solvents	(b) Spraying, dipping	(b) Solid, tough, nonadherent film, removed by stripping
Volatile corrosion inhibitor (V.C.I.)	Organic amino salts (e.g. dicyclohexylamine nitrite, cyclohexylamine carbonate)	From solution by spraying, as a powder by sprinkling, by wrapping with V.C.I. impregnated paper	Adsorbed, nonvisible film

4.13.2.2 Hard-Film Materials

These were developed to facilitate handling after treatment and to avoid contamination of adjacent components. The films are deposited in the cold and should be tough and neither sticky nor brittle. The deposited films may be plasticized polymer resins, bitumens, etc. which are varied according to the subsidiary properties required, such as transparency and color. The solvents used vary according to the solubility of the ingredients, drying-time requirements, flammability, and permissible toxicity in given circumstances. As with the soft-film solvent-deposited materials, the surface coverage is large, and for this reason, and because they can be applied at room temperature, hard and soft-film solvent-deposited protectives are widely used.

4.13.2.3 Oil-Type Materials

These are usually mineral oils of medium or low viscosity, which contain specific corrosion inhibitors and antioxidants. In spite of the relatively low protective properties of the fluid films, which are not nearly as great as those of the previously described solid films, these materials have an established field of use on the internal surfaces of tanks and assembled mechanisms, and where solid material or solvent cannot be tolerated.

4.13.2.4 Strippable Coatings

The most important of these to date are those applied by hot dipping. Many are based on polymer resins with comparatively high dipping temperatures (~190 °C). They rely mainly on the thickness (<2 mm) and toughness of the coatings for their extremely good protective properties. They have the added advantage of giving protection against mechanical damage so that little added packaging is required for transport. Reuse of the material is frequently possible. The disadvantages are the necessity for special dipping tanks and cost; the latter may, however, be offset by saving in packaging materials. Strippable films deposited from solvents in the cold are much thinner (0.05–0.25 mm) than those from the hot-dip materials and their protective properties are generally not nearly so effective.

Strippable coatings based on such polymer resins as vinyl, acrylic, and polyethylene are finding increasing favor for applying to finished products to protect them during transit. These coatings offer excellent temporary protection against moisture, chemicals, and weathering and some stand up well to such fabricating techniques as bending and deep forming. The coatings are easy to apply and some are removed simply by piercing the film and peeling it off, others by washing away by applying an alkaline solution or solvent.

4.13.2.5 Special Materials

4.13.2.5.1 Water displacing agents

These have been developed for special uses. For example, as petroleum-based materials harm natural rubber, greases based on castor oil are available for use on the steel parts of rubber bushes, engine mountings, hydraulic equipment components, etc. (but are not for use on copper alloys). Some soft-film solvent-deposited materials have water-displacing properties and are designed for use on surfaces which cannot be dried properly, for example, internal combustion engine cooling systems, boilers, etc.

An application of this type of fluid is assistance in the removal of ingested salt spray from jet aircraft compressors and the neutralization of corrosive effects. Other types of water-displacing fluids are claimed to have fingerprint neutralizing properties or to be suitable for use on electrical equipment. Some oil-type materials serve temporarily as engine lubricants and contain suitable inhibitors to combat the corrosive products of combustion encountered in gasoline engines.

4.13.2.5.2 Volatile corrosion inhibitors

Volatile corrosion inhibitors are a special type of protective, which when present as a vapor inhibit the corrosion of metals. They are generally used as an impregnant or coating on paper or synthetic film; as a powder, either loose or in a porous container; or in the form of a 5% (w/v) solution in nonaqueous solution (e.g., alcohol) with application by either swab or spray. Their effectiveness in preventing corrosion depends not only upon the inherent activity of the material but also upon their volatility and rate of release from the supporting medium. Being volatile, some form of enclosure is necessary for continued effectiveness, whether it is by the closing of orifices with bungs or overwraps when protecting internal surfaces, or by sealing the outer container for other packed stores. Volatile corrosion inhibitors should be used with caution in the presence of nonferrous metals which may be attacked, particularly in the presence of free water. Care should also be taken with painted surfaces and with some plastics and other organic materials which may become discolored or damaged.

4.13.3 Scope for Temporary Protectives

Temporary protectives against corrosion should be used only where removal is subsequently necessary for the fitting or the working of surfaces to which they are applied. For example, coatings are designed to protect packaged engineering materials against corrosion due to a humid atmosphere, in both rural and general industrial conditions, during transit and storage. Where conditions are severe, extra packaging may be required or, in the case of thick soft-film materials, extra thicknesses may be applied. The coatings are also often used to protect unpackaged spares during shelf storage.

In normal thicknesses, temporary protectives are unsuitable for outdoor exposure and they should be protected against gross liquid water by coverings or wrappings. The wax and grease-based thick-film materials will, however, give adequate protection outdoors if they are applied extra thickly. Protection cannot be expected if the surfaces remain in contact with waterlogged packing material.

Corrosion preventives should be applied to surfaces which are clean and dry or corrosion may well continue beneath the coating. Materials with special properties such as water displacement or the ability to neutralize fingerprints should not be used in place of drying and clean handling, but only where the application demands it.

4.13.4 Causes of Failure

In practice it is usually difficult to establish the reasons for failure as a number of factors may be simultaneously responsible, such as (1) application of the protective to dirty surfaces, (2) carelessness in application, (3) inherent inadequacy of the material, (4) exposure to unreasonably severe conditions, and (5) inevitable difficulties in application. Point (3) includes inadequacy not only in protective properties but, in the case of the hard-film materials, in certain physical properties, for example, the film may become brittle and flake when handled, may remain too sticky and become contaminated with dirt or adhere to the wrapping paper more strongly than to the surface to be protected, may age to form an insoluble material and become difficult to remove, or may not remain flexible and adherent at low temperatures. Point (4) includes, for example, the use of soft-film materials in hot conditions at temperatures too near to their melting point. As regards (5), it may be difficult to avoid thin places in the film arising from contact with other surfaces during the process of application, drying-off of the solvent, or cooling; when such thinning occurs, good surface-active properties are advantageous. In this connection, it may be pointed out that scraping in transit and stacking and local thinning due to grit, dirt, etc. are common; it follows therefore that shelf storage of unpacked items should be avoided if possible.

4.13.5 Application of Protectives

Application by dipping gives the most complete film, is the most economical in material, and is usually the quickest for large quantities of articles. This method should be chosen whenever possible. Spraying is the next best. Brushing and hand-smearing should be adopted only when dipping or spraying is not feasible.

During the dipping process, articles with recesses should be rotated in the bath so that air can escape. Dipping baths should be kept covered when not in use to prevent contamination and, in the case of solvent-containing materials, to prevent concentration by evaporation of the solvent, as this would lead to excessive film thicknesses and long drying times. The composition of a bath of solvent-containing material should be checked periodically. Unaided evaporation of the solvent from solvent-deposited films is usual, but the process can be speeded up by blowing air over the articles or by gentle warming; the heating, however, should not be excessive.

During hot-dipping, film thickness can generally be varied by altering the temperature of dipping and the duration of immersion. The molten material will first chill on to a cold article put in the bath, the solid coating bridging small crevices. This may give sufficient protection, but it may be desirable for the article to attain the temperature of the bath so that the material will fully penetrate into all the crevices, for example, between the ball and race of a rolling bearing. The article may then be withdrawn, allowed to cool and given a further dip to build up the film thickness.

4.13.6 Choice of Protective

Hard-film protectives can be applied to most types of single articles and are especially suitable in mass-production systems. They should not be applied to assemblies because the hard film is liable to cement mating surfaces together and considerable difficulty may arise in the removal of the protective film. This type of protective should be removed before the article is put into use.

The soft-film solvent-deposited type can be used broadly for the same purposes as the hard-film type. A grease-resistant wrapping is required as an inner wrapping (as for all soft-film types) in packaging. Grades of this material, consisting essentially of lanolin in a solvent, have been found to give better protection to packaged articles than some of the best available hard-film materials and are to be preferred for articles with very high precision surfaces. The film is usually dispersible in lubricating oil and it is therefore not so important to remove it from surfaces when an article comes into use except when it has become contaminated with grit and dirt.

The thick soft films produced by hot dipping are suitable for highly finished as well as normal machined surfaces. Grades with drop-points substantially higher than 50 °C are preferable for tropical storage as, otherwise, marked softening and possible thinning of the protective film are likely to occur. These films can be applied to many types of assemblies, the chief exceptions being assemblies with inaccessible interiors that cannot readily be blanked-off and fine mechanisms where any residue might interfere with the free movement of parts or their subsequent lubrication with low viscosity oil. These films can also be used on parts which might be affected by the solvent from the thin or soft film protectives, but they should not be applied to items having plastics or leather components.

Greases are usually applied by brush or smearing; the brush must be sufficiently stiff to give intimate contact with the surface yet not so stiff as to leave deep brush marks. Greases should not be melted and therefore cannot be applied by dipping or spraying; also, no attempt should be made to dissolve them in a solvent for application. They are particularly useful where only part of the surface of the item requires protection, because of the ease of application by cold smearing. They can be used in this way also in conjunction with solvent-deposited protectives for assemblies of a low degree of complexity, by coating screw threads and filling clearance spaces before dipping the article in the solvent-containing protective. Grease films can be made thick enough to give the desired level of protection. Wrapping is desirable to protect the very soft film. Removal before use is chiefly for the purpose of removing grit and dirt.

The slushing material finds its most useful application on big machinery requiring protection of large areas during storage or during intervals of idleness in machine shops. The effect of dust and dirt contamination should therefore be considered an important factor in assessing the quality of these materials.

The lower protective quality of oil-type materials largely restricts their use on internal surfaces of, for example, internal combustion engine cylinders, and gearbox and back-axle assemblies of motor vehicles. Such materials are widely used to fulfill the simultaneous functions of a protective and lubricating oil; for example, in machinery the protective can also serve as a lubricant during its initial period of use. The functions of corrosion inhibitor and hydraulic oil are also often combined. Oil-type materials are also used on small nuts, screws, and washers which cannot easily be protected by solid-film materials; in this case, protection must be reinforced by good packaging.

The hot-dip strippable coating is applicable when a high standard of protection from corrosion and mechanical damage is required, as on gauges and tools which so often have their working surfaces facing outwards. Assemblies must have orifices plugged so that molten material cannot penetrate during the dipping.

Volatile corrosion inhibitors are particularly useful when oil, grease or other adherent films are unsuitable. They should be used in conjunction with a primary wrap which should form as close an approach to a hermetically sealed pack as possible. They are widely used to provide protection to precision tools, moulds, and dies and also on a larger scale to car body components.

Further Reading

Protection of Metals from Corrosion in Storage and Transit, by Donovan, P. D.; Ellis-Horwood, (1986).
Guide to Temporary Corrosion Protectives, National Corrosion Service, National Physical Laboratory (2003).

4.14 Marine Paints

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Glossary

Term	Definition
Block	Modern ships are constructed in sections (called blocks). A typical block will contain 2000–3000 m^2 of steel which requires coating.
Block join-up	After construction and coating, the block is transferred to the building dock where it is welded to other blocks to produce the ship.
Boot top	Area on the outer hull, which is immersed when the vessel is loaded and is out of the water when the vessel is not carrying a load.
Fender damage	Fenders are applied on the side of docks to prevent the ship impacting with the dock wall.
Grit blasting	A high velocity jet of an abrasive material is directed at the steel substrate to remove rust and coating and to introduce a surface profile onto the steel substrate. The process can be automated (at Newbuilding) or manual.
Hydroblasting	Surfaces are treated with a high-pressure jet of water which is capable of removing coatings.
Slurry blasting	A variant on hydroblasting in which abrasive is added to the high-pressure water jet.
Ullage space	Space above the cargo (crude oil) and the top of the tank.

Abbreviations

FDA	Food and Drugs Administration
VLCC	Very large crude carrier

Symbols

T_g	Glass transition temperature

4.14.1 Introduction and Overview of the Marine Industry

Providing effective corrosion protection on ships and other marine structures presents a major challenge. The structure, which is normally constructed from mild steel, may be subject to continuous immersion, cyclic wet–dry exposure, and extremely aggressive environments, including many of the cargoes ships transport. Corrosion protection is primarily obtained through applying high-performance coatings that are specifically designed for use on the different vessel types and vessel areas.

The current world fleet comprises 94 936 vessels, of which 50 214 are cargo carrying.[1] The market is currently growing at 6.6% per annum. Market growth is primarily driven by the current high freight rates, major economic growth in Asia, increased demand for liquid natural gas (LNG) carriers, and regulations requiring the phasing out of single-hulled oil tankers by 2010. Table 1 shows the percentage of the world fleet by class of ship, in terms of both the number of ships and gross tonnage.[1]

This chapter primarily focuses on coatings for the high gross tonnage vessel types, because these represent the largest area of steel requiring protection, and therefore the largest coating volumes. The coating of smaller vessels, such as yachts and other marine structures, offshore platforms, etc., will not be considered in this chapter.

There are a number of distinct areas on ships as indicated in Figure 1: ballast tanks, underwater hull, cargo tanks (dry cargo, oil, chemicals), decks, topsides and superstructure, and the vessel interior. Each area presents different challenges to the coating system.

Table 1 World fleet by class of ship

Ship type	*Market % (by number of vessels)*	*Market % (by gross tonnage)*
Fishing vessels	25	2
Cargo carriers (including roro/ reefer/container ships)	25	28
Supply ships/tugs/dredgers	22	3
Tankers, product, and chemical	9	9
Bulk (dry cargo) carriers	8	28
Passenger vessels/Ferries	7	4
Tankers, crude oil	3	22
Liquid gas carriers	1	4

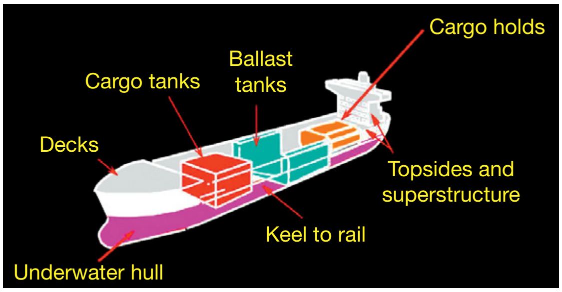

Figure 1 Different areas on a ship.

Table 2 shows the area of steel that requires coating for the different areas on the largest type of double-hull oil tanker, a VLCC vessel.

Over the last 20 years, there have been major changes in shipbuilding processes, ship operational procedures, and the marine coatings market, for example,

- Increase in Newbuilding shipyard productivity and reduction in vessel build times through the introduction of high-speed welding and cutting techniques, automation of certain fabrication processes and the adoption of block stage construction, and coating processes. To be compatible with the new shipyard procedures, coatings require fast cure/drying characteristics and flexible overcoating intervals.
- Changes in ship design and in-service operation. Examples include: (1) the move from single-hull to double-hull oil tankers, driven by major pollution incidents associated with damage to single-hull tankers (e.g., Exxon Valdez, MIT Erika); double-hull tankers have a significantly increased (at least 2 times) ballast tank area[2] as indicated in Figure 2, (2) the increased use of high-tensile steel in ship construction, and (3) increased cargo loading and unloading rates on bulk carriers.
- Environmental and health and safety issues together with changes in legislation have lead to

Table 2 M^2 of steel in the different areas on a VLCC tanker

Vessel area	*m^2 of steel*
Ballast tanks	235 000
Underwater hull	37 000
Boot top area	1600
Topsides	4300
Decks	21 800

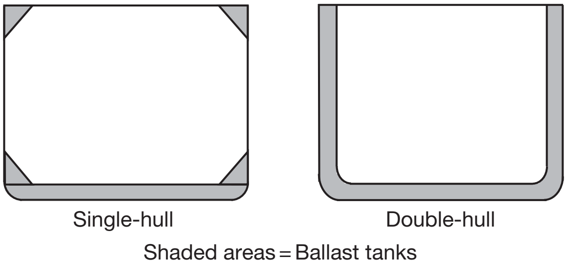

Figure 2 Ballast tanks on single-hull and double-hull oil tankers.

(1) a reduction in solvent emissions through the use of higher solids or waterborne coatings and (2) the gradual phasing out of a number of marine coating types, including coal tar epoxy anticorrosives and antifouling paints based on tin copolymers. The reduction in solvent emissions has increasingly resulted in a change from one pack thermoplastic to two-pack thermoset coatings.

- A trend toward higher performance coatings with a longer service life and a reduced frequency of coating maintenance, for example, the new International Maritime Organization (IMO) regulations relating to the coating of ballast tanks[3,4]; these regulations are intended to improve the corrosion protection obtained in this critical vessel area.

As a result, the types of coatings used in the marine market have changed significantly from the coating systems described in earlier reviews.[5,6]

Prevention of corrosion on ships is essential; corrosion is recognized as one of the key factors that contribute to the loss of vessels at sea. In 2006, 25 vessels accounting for 409 000 gross tones were lost at sea.[7] Corrosion reduces the steel thickness and structural integrity of the vessel. Studies have shown that the corrosion rates are highest in the ballast tanks[8] where steel losses in excess of 1 mm year^{-1} can be observed in uncoated tanks. Given the clear link between corrosion and vessel safety, ship operations are regulated by the classification societies who establish and apply technical requirements for the design, construction, and in-service survey of vessels. Ships and the coatings applied to ships are subject to regular surveys, and where the required remedial action, that is, the replacement of steel or the coating system, becomes mandatory in order for the vessel to be maintained in class. Class renewal/surveys are carried out every 1–5 years; this requires dry-docking of the vessel, which provides an opportunity to carry out major refurbishment of the coating system.

In addition to the benefits with regard to reduced corrosion, the application of coating systems, which provide effective long-term protection, is also important financially. The steel areas coated and the volume of paint applied to ships are significant. A VLCC tanker at Newbuilding will typically need >200 000 l of paint with a paint cost in excess of $1 million. Surface preparation and the application process further add to the costs. Although coatings are designed to have a long service, life breakdown does occur, and given that the average lifetimes of oil tankers and bulk carriers are 28 and 30 years, respectively, coating systems will need to be reapplied during the vessel's lifetime. At major refurbishment, the surface preparation costs, for noncomplex areas such as the underwater hull, are of the order of $8 m^{-2} (for an Sa2 blast), while application costs are typically $1 m^{-2}, highlighting the high costs associated with the application of marine coatings and the importance of specifying the correct coating systems.

4.14.2 Corrosion Breakdown of Marine Coatings and the Factors Influencing Coating Performance

Marine coatings are designed to provide different performance characteristics depending on the vessel type and vessel area:

corrosion protection (all vessel areas);
fouling control (underwater hull);
damage resistance (cargo holds);
chemical resistance (chemical tanks);
decorative effect (topsides, superstructure).

Although the primary attribute of many coatings is not corrosion protection, it is important to recognize that degradation and failure of the coating, for example, a cargo hold or chemical tank coating, will lead to conditions that result in corrosion of the steel substrate. The types of coatings used on different vessel areas and the specific modes of in-service failure associated with the coatings will be discussed in Section 4.14.4.

Considering the corrosion breakdown of coatings on ships, it is clear that there are a number of different failure mechanisms, including:

- *Through film breakdown*: Corrosion occurs through the film in the absence of any macroscopic defect. Breakdown is attributed to the presence of pores in the coating which act as pathways for the transport of ions to the coating–steel interface.[9,10] Academic studies[10,11] have clearly demonstrated that coatings do not act as effective barriers to oxygen and water transport and that ion transport normally determines the rate of corrosion.

  All coatings will contain microscopic pores and defects that are produced during the application, film formation, and coating ageing processes. However, the presence of pores does not mean that through film corrosion breakdown is inevitable as evident by the fact that marine epoxy–amine anticorrosive coatings can remain free from visual corrosion over a period of many years. The pore size and pore distribution are important factors as is the potential for the pores to become blocked with corrosion product, which retards the corrosion process. The onset of through-film corrosion after many years in-service is indicative of chemical or physical changes occurring in the coating, which reduce the coating's barrier properties and promote ion transport and corrosion breakdown.

- *Blistering:* Osmotic blistering of coatings, subject to full or periodic immersion, is due to the presence of water-soluble ionic contamination on the steel surface prior to coating application or soluble material present in the coating, which migrates to the coating–steel interface. Osmotic blisters are usually relatively small; larger blisters are produced by electroendosmosis, which can occur when the growing blister contains a pore. Anodic and cathodic blisters, associated with active corrosion cells, can also be observed.
- *Cathodic disbonding at areas of coating damage:* At sites of impact and abrasion damage where the coating is removed exposing the steel substrate, rapid corrosion takes place. The high pH environment associated with the cathodes in the corrosion cell has the potential to attack the coating–steel interface, leading to the loss of adhesion and disbonding of the coating. When cathodic protection systems are used, the rate of cathodic disbonding may increase as the entire defect will act as a cathode. The extent of disbonding can extend over significant distances, and where there are multiple sites of damage, this can result in complete disbonding of the coating. A number of factors have been shown to influence the rate of cathodic disbonding,[12] including the coating thickness, substrate type and pretreatment, type and concentration of electrolyte, oxygen concentration, potential at the cathode, and the temperature.
- *Rust jacking:* This type of failure is observed toward the end of the coating life. Where corrosion products are produced below the coating, the increase in volume of the rust, typically by a factor of 10, acts to lever the coating from the steel substrate as shown in Figure 3.

  Disbonding of the coating will further accelerate the corrosion process. A similar failure mode can be observed for the calcareous deposits produced at the steel–coating interface for coatings under cathodic protection.
- *Cracking of coatings:* This is now recognized as one of the potential early failure modes of anticorrosive coatings applied in ballast tanks.[13,14] Cracking, an example of which is shown in Figure 4, is primarily observed on welds, corners, stiffeners, and other structural areas where stress concentration occurs.

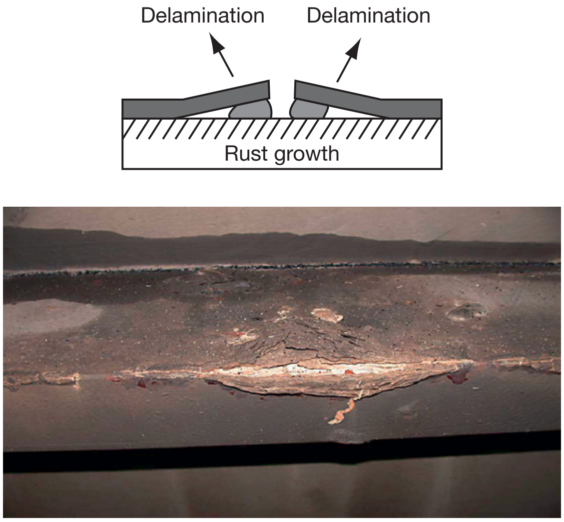

Figure 3 Rust jacking.

Figure 4 Cracking of coating in a ballast tank.

Once cracking has occurred exposing the steel substrate, rapid corrosion breakdown follows. A number of factors influence the cracking susceptibility of coatings, including the stresses and strains imposed on the ship structure during operation, the intrinsic mechanical properties (flexibility, etc.) of the coating, internal and thermal stresses developed in the coating, and the coating film thickness. Cracking can also be observed on the block join-up areas, which have been power tool prepared, suggesting that the surface profile on the steel and the coating–substrate adhesion are also important factors. However, a recent study of cracking on erection joint weld seams prepared to different standards found that the coating properties had the greatest influence on the cracking susceptibility.[15]

Cracking of ballast tank coatings appears to have increased on moving from single-hull to double-hull tankers. This potentially reflects the increased use of lower thickness high-tensile steel plates in double-hull tankers and the associated increase in the flexibility of the ship structure.[16]

In developing coatings and coating systems to provide long-term corrosion protection on ships, it is important to recognize that the coatings' composition and intrinsic performance characteristics are only two of the factors which will determine the in-service performance of the coating. The corrosion protection obtained will be influenced by:

1. The quality of the surface preparation prior to coating application. It is essential that contaminants, which may adversely affect the coating adhesion or lead to osmotic blistering, are removed. Potential contaminants include oils and grease, moisture, weld spatter, welding and cutting fume, corrosion products, and water-soluble salts. A range of surface cleaning procedures are available: solvent cleaning, abrasive blasting, water washing, hydroblasting, and power tool preparation. The appropriate technique or techniques are selected based on the nature of the contamination, the vessel area, and the conditions under which the surface preparation is carried out (there are major differences in the surface preparation procedures adopted at Newbuilding and Maintenance and Repair). Paint manufacturers normally recommend that the level of water-soluble salts on the steel surface is below 50 or 100 μg cm^{-2}, this is supported by a number of studies[17] noting that the salt type, coating type, and ship vessel area have an influence on the blistering characteristics, and several authors have proposed that the salt level should be significantly lower. The profile introduced onto the steel, by abrasive blasting or power tool cleaning, improves both the coating–substrate adhesion and the anticorrosive performance of the coated steel, particularly with regard to resistance to cathodic disbonding. The blast profile is determined by the type of blasting media selected and the standard of blast cleaning carried out; the latter is specified in a number of international standards as indicated in Table 3.

   Typical blast profiles, measured as the average peak to valley distance are 80–120 μm for steel grit and 50–70 μm for steel shot.[18]
2. Selection of the correct coating type. From a corrosion protection perspective, important characteristics are: good barrier properties, good adhesion to steel, mechanical properties and stress behavior required to minimize in-service cracking of the coatings, and environmental stability (resistance to degradation on long-term exposure). Given the highly alkali environments associated with corrosion cells and cathodic protection systems, the coating should be resistant to saponification. Epoxy–amine anticorrosives are currently the corrosion protection coatings of choice, particularly for vessel areas (underwater hull, ballast tanks) subject to permanent or periodic immersion.
3. Control of the application and cure conditions. In the marine market, it is not possible to control the environmental conditions, and coatings must be designed to be tolerant to application under a range of temperatures and humidities. Application at relatively high temperatures (>40 °C) can cause problems with excessive solvent loss during

Table 3 International standards for abrasive blasting

	NACE (National Association of Corrosion Engineers)	*Swedish Standard/ ISO SIS055900 (1967)*	*Japanese Shipbuilding Research Association – Standard 1984*
White metal (all milescale rust, foreign matter removed)	NACE #1	Sa3	JaSh3 or JaSd3
Near white metal (only traces of millscale, rust, foreign matter remain)	NACE #2	Sa2½	JaSh2 or JaSd2
Commercial blast (almost all millscale, rust, foreign matter removed)	NACE #3	Sa2	JaSh1 or JaSd1
Brush off blast (loose millscale, rust, foreign matter removed)	NACE #4	Sa1	–

Similar standards exist for hydroblasting, power tool, and hand tool preparation of the substrate.

spray application, which will adversely affect the flow characteristics of the applied paint and can result in poor coalescence of the paint droplets. Poor coalescence will potentially reduce the barrier properties of the coating and lead to early corrosion breakdown. For thermoset coatings, such as epoxy–amine systems, the rate of cure is significantly reduced as the temperature is lowered. If the coating enters service before an adequate degree of cure has been achieved, this can lead to early corrosion breakdown. So-called 'winter workable' epoxy–amine coatings have been developed, which are designed to cure rapidly at temperatures down to −5 °C. Although coatings are generally tolerant to variations in the relative humidity, it is important that the coatings are not applied onto steel surfaces where condensation has occurred. Paint application should not take place when the steel temperature is less than 3 °C above the dew point. Air flow and ventilation, which is particularly important when coating enclosed areas such as tanks, can have a significant impact on the rate of solvent loss from the coating. If the coating has a high level of retained solvent on service entry, this can have an adverse effect on the in-service performance.

4. Control of coating thickness. If the coating is underapplied, this will reduce the barrier properties and potentially lead to early corrosion breakdown. Overapplication of the coating, which frequently occurs when coating complex structures in confined areas, such as ballast tanks, can also have an adverse effect on performance. With increasing film thickness, the internal and environmental stresses developed in the coating will be higher, which increases the potential for cracking and loss of adhesion at the coating–steel interface. Overapplication will also increase the amount of retained solvent in the coating.

   The coating of edges presents a further problem. Due to the difficulty of spraying coatings onto the edges and the surface tension driven flow of the coating away from the edge, achieving the specified coating thickness is difficult and in-service corrosion breakdown of coatings is often observed at edges. This is shown in Figure 5.

   Several approaches to improve the edge protection can be adopted:

   - Changing the edge profile by grinding the edge.
   - Brush or roller application of stripe coats of the paint to the cut edge. Normal practice for coating cut edges in a ballast tank would be spray coat–stripe coat–spray coat–stripe coat. Stripe coating is also used to improve the coating thickness control on fillet welds.
   - Formulation of the coating to improve edge retention. This involves modifying the rheological characteristics of the paint to reduce the surface tension driven flow.

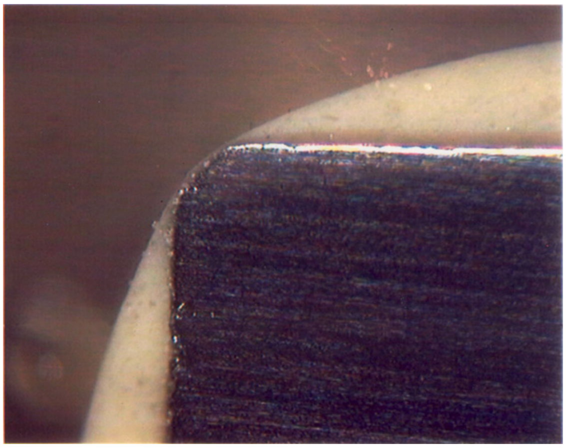

Figure 5 Flow of paint away from an edge.

5. Use of a cathodic protection system on vessel areas that are continuously or periodically immersed. Such systems are used on the underwater hull, ballast tanks, and in cargo holds, which are also ballasted. The cathodic protection system will significantly reduce corrosion of any exposed steel. At the exposed steel, the cathodic reaction produces hydroxide ions, which react with metal ions and CO_2 in the seawater to produce an insoluble calcareous deposit, which provides a degree of protection to the steel. It should be noted that cathodic protection systems in ballast tanks do not protect when the tank is empty, which typically accounts for 50–60% of the vessels operation. The cathodic protection system needs to be correctly designed and operated, as overprotection can in itself lead to coating breakdown through blistering and calcareous deposit jacking.
6. Effective maintenance of the coating. In vessel areas that are readily accessible to the ship's crew, coating breakdown due to corrosion can be routinely repaired. The ship operator will monitor the coating condition in other vessel areas and put in place a strategy to either repair or replace coatings that are showing a significant degree of breakdown. Major refurbishment of the coating may only be possible when the ship is in dry-dock.

4.14.3 Coating Processes in the Marine Market

4.14.3.1 Newbuilding

The fabrication and coating processes at Newbuilding have been designed to increase productivity, lower costs, and reduce the build time for new vessels.

Ships are primarily constructed from hot-rolled steel. During the steel manufacturing process, a relatively thick (20–50 μm) oxide layer, referred to as mill scale, is produced on the steel surface. As the mill scale is cathodic to the steel, rapid pitting corrosion is observed where there are breaks in the scale layer. It is therefore essential that the mill scale is fully removed prior to coating application. The steel is normally blasted with shot to an Sa2½ standard, using an automated rotary or wheel blasting unit.[19] The blast profile introduced on the steel should be less than 100 μm peak-to-valley, as a larger profile may lead to peak coverage issues when the low film thickness shop primer coating is applied. After blast cleaning, it is important to apply a protective coating, a shop primer, as soon as possible to avoid corrosion of the cleaned surface. In practice, the blasting and primer coating processes are carried out on the same automated pretreatment line and the coating application takes place immediately after blasting.

The shop primer coating, which is typically applied at 15–20 μm thickness, must have the following performance characteristics in order to meet the requirements of the shipyard:

- Dry rapidly to allow handling of the coated steel within 2–3 min.
- Provide effective corrosion protection of the steel during the ship fabrication process. As the build cycle varies in different shipyards, the corrosion protection period required is typically between 3 and 9 months. The low film thickness coating of shop primer is formulated to effectively follow the contours of the 50–100 μm profile on the steel introduced during the shot blasting process.
- Be compatible with high-speed cutting and welding processes and have no detrimental effect on the weld quality.
- Resistant to mechanical damage during fabrication.
- Overcoatable with the full range of marine coatings.

Historically, a number of different types of shop primers have been used: phenolic–polyvinylbutyral (PVB) primers, epoxy coatings pigmented with iron oxide, inhibitor pigments, or zinc and zinc silicate coatings. The current market is, however, dominated by solvent-borne zinc silicate shop primers; this reflects (1) the improved cutting and welding characteristics obtained through the use of an inorganic binder system and (2) the enhanced corrosion protection. The zinc pigment galvanically protects the steel substrate and the zinc corrosion products produced, while providing protection, act to block pores in the coating, leading to an increase in the coating barrier properties.[20] Solvent-borne zinc silicate shop primers are two-pack coatings based on a prehydrolyzed tetraethyl orthosilicate binder system, the cure of which is acid catalyzed.[19,21] Unlike the high-build zinc silicate anticorrosive coatings used in the protective coatings market, the amount of zinc in the coating is kept as low as possible, while maintaining effective corrosion protection; this is because zinc can have an adverse effect on the welding process. Coatings are normally formulated above the critical pigment volume concentration (CPVC) and the applied coatings are therefore porous. The shop primer coating is applied using automated airless or high-volume low-pressure (HVLP) spray processes.

Solvent emission legislation, particularly in Europe and the United States, is impacting on the use of the high solvent content (typically 650 g l^{-1}) zinc silicate shop primers. As it is difficult to formulate this type of product with higher solids, the Newbuilding shipyard has two options to reduce emissions: (1) to install solvent abatement equipment on the pretreatment line and continue to use the current solvent-borne products or (2) to move to an alternative low or zero solvent content shop primer. Although waterborne zinc silicate coatings are commercially available, the conventional formulations based on alkali silicate binders are unsuitable for use in the marine market because of their high water-soluble salt content and susceptibility to osmotic blistering when overcoated and immersed. New waterborne coatings, which overcome this limitation have recently been commercialized[22] or are under development. A further issue with the use of zinc silicate shop primers is the potential for the formation of zinc corrosion products (so-called white rust) on the coating surface. If overcoated, the corrosion products may produce a mechanically weak interface and adversely affect the in-service performance of the coating scheme. Normal shipyard practice is to carry out secondary surface preparation (sweep blasting with grit) to remove any white rust immediately prior to applying subsequent coatings. Certain solvent-borne zinc silicate shop primers have been formulated to produce low levels of white rust, which allows direct overcoating without the need for secondary surface preparation.

The shop-primed steel plates and bars are cut and welded to produce subassemblies, and eventually, blocks. In high-productivity shipyards, the application of the main epoxy anticorrosive system and many of the other coatings takes place at the block stage. In certain shipyards, 80–90% of the coatings can be applied at the block stage. A typical block from a VLCC tanker is shown in Figure 6.

Coating of the blocks is carried out indoors, allowing better control over the environmental conditions. Normal practice is to apply the full anticorrosive scheme, for example, 2×150 μm coats of epoxy plus stripe coating of welds and cut edges, followed by the cosmetic finish or antifouling paint. Coatings are airless spray applied. Although it is possible to apply different epoxy coatings onto different areas of the block, reflecting where the block will be positioned in the final ship construction, a current industry trend is the move to ‘universal primer’ coatings, which are designed for use on all areas of the ship, except certain specialist areas such as potable water and chemical tanks. The use of a universal primer simplifies the coating process, providing both time and cost savings. The coated blocks are subsequently transferred to the building dock where they are welded together. Prior to applying coatings to the block join-up areas, the steel surface has to be prepared. Grit blasting cannot be carried out due to concerns over damaging the coatings already applied to the block, so the join-up areas are manually prepared using power tools and associated techniques. Following construction of the ship, any remaining coatings are applied; chemical tank coatings are always applied postconstruction and many shipyards choose to apply the antifouling paint and finishes at this stage.

4.14.3.2 Maintenance and Repair

Although the cost of repairing coatings is relatively high, when the surface preparation, labor, and paint costs are considered, this cost is low in comparison with the cost of steel replacement, which would be required if extensive corrosion takes place.

Two different scenarios need to be considered: (1) major refurbishment of the vessel where the existing coating is either fully replaced or subject to significant repair and (2) on-board maintenance (OBM) where the ships crew carries out routine repair of the coating on those vessel areas (decks, superstructure, certain areas in ballast tanks) that are readily accessible.

At major refurbishment, the coatings used are essentially the same as those applied at Newbuilding. The surface preparation procedures are, however, significantly different

Figure 6 Block section from a VLCC.

- Due to the potential for high levels of salt contamination on the coating surface, thorough high-pressure water washing is essential prior to preparation of the surface.
- Although grit blasting continues to be widely used, concerns over the amount of dust (grit and removed coatings) released to the atmosphere have seen an increase in the use of hydroblasting and slurry blasting techniques.[19] Although hydroblasting is very effective at removing old coatings and cleaning corrosion pits, it is important to recognize that it does not introduce a new blast profile (the profile applied at Newbuilding is however retained) and the technique can also lead to flash rusting of the steel substrate.

Following the replacement of any heavily corroded steel, the removal of existing coatings, and surface preparation, the new coating scheme will be applied by airless spray. As at Newbuilding, stripe coating of cut edges and welds is essential.

The objectives of OBM are (1) to maintain the ship's appearance by periodically applying new finishes to the deck and superstructure and (2) to repair areas of coating breakdown and corrosion. Manual surface preparation, using power tools and discs, is carried out at sites of corrosion breakdown, but is generally confined to the areas of visible corrosion, leaving potential active corrosion cells under the intact coating. Finishes are normally applied directly over the existing coating scheme, which will be prepared by solvent degreasing (where required) and high-pressure water washing. One-pack alkyd finishes are widely used in this market and the application is by brush and roller. Alkyd and epoxy primers are used; these can be significantly different from the products used at Newbuilding and major refurbishment, and are designed to have improved surface tolerance (to damp and contaminated surfaces, residual rust, aged coatings) and for application under the variable environmental conditions encountered at sea. One important difference in the OBM market is that the coating systems used are not subject to any regulations on solvent emissions. Lower solids coatings can therefore be used in the OBM market.

4.14.4 Coating Selection for Different Vessel Areas

4.14.4.1 Underwater Hull

The coating system has two primary functions: (1) to provide effective corrosion protection on a vessel area that is subject to permanent sea water immersion and (2) to prevent the attachment of marine organisms to the hull; fouling increases the hull's roughness and significantly reduces the vessel's fuel efficiency. Corrosion protection is provided by a combination of a high-build epoxy anticorrosive (refer to **Section 4.14.4.2**) and cathodic protection, using either an impressed current system or sacrificial zinc or aluminum anodes. As previously discussed, the cathodic protection system must be correctly designed and installed to avoid overprotection issues, which can lead to premature breakdown of the coating.

Antifouling coatings are classified as either biocidal or nonbiocidal foul release systems.

The biocidal coatings contain pigments, such as copper oxide, copper thiocyanate, and copper metal, which in the presence of seawater, produce biocidal copper ions. Organic booster biocides are also introduced to further improve the antifouling performance, particularly against slimes and weeds. The use of biocides is increasingly subject to regulatory review in Europe[23] and it is likely that the range of biocides approved for use in marine antifoulings will reduce in the future. Biocidal antifoulings are further classified in terms of the binder type[24]:

- *Self-polishing copolymers (SPC):* At the coating–water interface, the binder undergoes controlled hydrolysis and is converted from a water-insoluble to a water-soluble polymer. The coating slowly dissolves and the dissolution process effectively maintains a constant rate of release of the biocide throughout the coating lifetime. The coating dissolution also reduces the coating roughness introduced during application and further improves the vessel's fuel efficiency. SPC antifoulings were originally based on acrylic copolymers of tributyltin-methacrylate; however, these coatings have now been phased out because of environmental concerns over the released tributyltinoxide (TBTO). Alternative binder systems based on metal (copper or zinc) acrylate and silyl ester polymers have recently been developed.
- *Controlled depletion polymers (CDP):* An intrinsically water-soluble material, normally gum rosin, is blended with a water-insoluble vinyl or acrylic polymer. The advantage of this coating type is the lower solvent content. However, CDP antifoulings do not show the smoothing effect observed for SPC coatings and the in-service lifetime of CDP coatings is normally limited to 3 years rather than the 5 years achievable from SPC coatings.

- *Hybrid coatings:* Rosin and a self-polishing copolymer are combined.

Typical coating schemes applied on the underwater hull are summarized in Table 4.

Biocidal antifouling coatings are one-pack solvent-borne coatings with solid volumes in the range 45–55% and typically contain up to 60 wt% biocidal pigments in the dry film.

The selection of the antifouling type and applied coating thickness is, in part, determined by the time period between dry-docking of the vessel, normally 2.5 or 5 years, depending on the classification society rules and the vessel activity. It is essential that the antifouling maintains effective performance throughout this period in-service.

At major refurbishment of the vessel, the underwater hull will either (1) be high-pressure washed, fully blasted, and recoated with both the anticorrosive and antifouling, or (2) be high-pressure washed, have areas of damage spot repaired, and a new coating of antifouling applied to the underwater hull.

Nonbiocidal foul release coatings were originally based on silicone elastomers.[25] The coatings are highly hydrophobic, low surface energy, low T_g materials, which present surfaces that are difficult to adhere to. If the coating remains static, fouling will occur; however, movement of the vessel causes release of the fouling. To be effective, the vessel should be operating at speeds in excess of 10 or 15 knots for >80% of its service life. As shown in Table 4, the silicone antifouling comprises a silicone tie coat and a silicone topcoat, the topcoat being modified with a silicone fluid to optimize the foul release characteristics. Due to the low surface energy of the silicone coating, the coating cannot be applied directly to the epoxy anticorrosive, so hybrid epoxy–silicone tie coats containing adhesion promoters are used to obtain effective adhesion. Recently introduced fluoropolymer topcoats offer a further enhancement in the antifouling performance.

Table 4 Typical coating schemes for the underwater hull

Antifouling coating type	*Coating scheme (dft)*	
Tin free SPC (60-month scheme)	Epoxy anticorrosive SPC antifouling	2×150 μm 3×125 μm
CDP (36-month scheme)	Epoxy anticorrosive CDP antifouling	2×150 μm 2×125 μm
Foul release coating	Epoxy anticorrosive Silicone tie coat Silicone or fluoropolymer finish coat	2×150 μm 1×100 μm 1×150 μm

Foul release coatings are more expensive, on a \$ m^{-2} basis, than the biocidal antifoulings. However, significant through life cost benefits can be obtained. Major refurbishment costs are reduced; the normal procedure is to carry out only touchup repair and apply a further thin coat of the topcoat every 5 years.

The amount of corrosion breakdown observed on the underwater hull is normally relatively low; this reflects the fact that (1) the submerged areas are not subject to mechanical damage, (2) the antifouling paint prevents marine organisms adhering to and potentially damaging/removing the coating, and (3) the hull is cathodically protected. Corrosion breakdown primarily takes place at the waterline, the so-called Boot-top area on the vessel, because of a combination of the repeated wet–dry cycling of the coating, UV exposure, and fender damage.

The use of copper or copper oxide (which contains low levels of copper metal) pigmented antifouling paints can lead to severe pitting corrosion on aluminum hull vessels.[26] As copper has a more positive electrochemical potential than does aluminum, if there are defects in the epoxy primer system, a galvanic cell will be set up with the aluminum hull acting as a sacrificial anode.

4.14.4.2 Ballast Tanks

The corrosion rates in ballast tanks, if left uncoated, are usually the highest of any vessel area.[8] This reflects the severity of the conditions experienced in ballast tanks, as the tank alternates between full immersion in seawater when in ballast and a high humidity environment when deballasted. The latter condition is more aggressive from a corrosion perspective, in part, because any cathodic protection system used in the ballast tanks will not be active. Ballast tanks are also subject to large variations in temperature, which can both accelerate corrosion and contribute to a premature breakdown of coatings through cracking and other processes. The increased ballast tank area in double-skin tankers and the structured complexity of the tanks, with many welds and edges, makes the effective protection of the tanks with coatings both essential and a major challenge. Figure 7 shows a typical area in a ballast tank.

It is important that coatings applied at Newbuilding provide long-term protection as the cost of replacing the coating is potentially financially prohibitive;

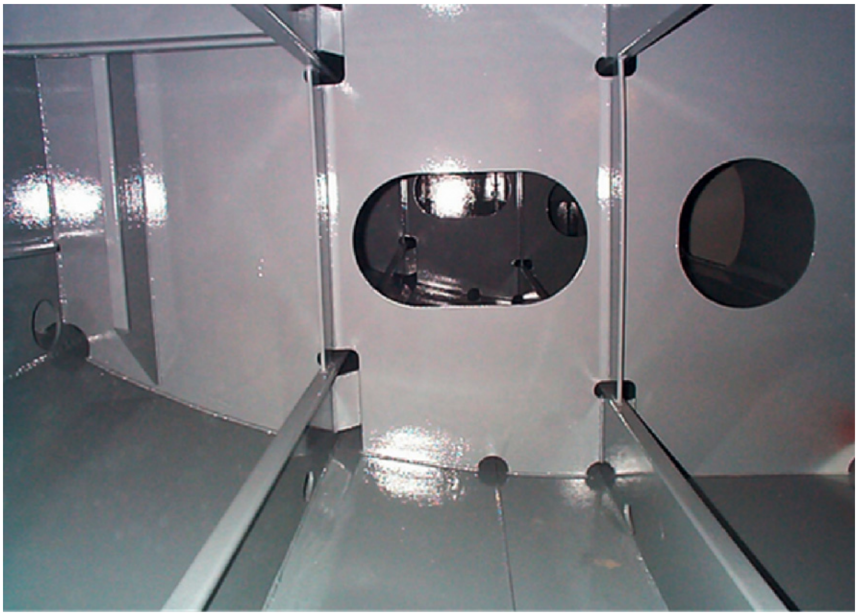

Figure 7 Interior of a typical ballast tank.

Mills[2] suggests that it would take 250 days and cost about $20million to fully recoat a VLCC tanker with 250 000 m^2 of ballast tanks. This issue is currently being addressed, at least in part, by the new IMO ballast tank coating standard for Newbuilding,[3,4] which defines procedures for the design of the coating systems, surface preparation, acceptable application conditions, and the inspection of the applied coating. A coating service life of 15 years is targeted, which means that major refurbishment of the ballast tank coating will normally still be required during the vessel's lifetime.

The coating systems used in ballast tanks are almost exclusively based on epoxy–amine resins. The coatings are relatively high solids ($\geq$70% volume solids), solvent-borne systems. This coating type has a number of characteristics: excellent barrier properties, good adhesion to steel and shop primer, resistance to hydrolytic and high pH degradation, and potential for rapid cure under ambient conditions, which make it particularly suitable for use in ballast tanks and as a universal primer applied at Newbuilding. Epoxy ballast tank coatings contain a relatively high loading of barrier pigments such as mica and talc. Corrosion inhibitor pigments are not used due to concerns over the potential for osmotic blistering. The coating is normally light colored to make in-service inspection and the detection of the onset of corrosion easier. A number of different types of epoxy–amine ballast tank coatings are available; all are based on aromatic, bisphenol A, or to a lesser extent, bisphenol F, epoxy resins:

- *Coal tar epoxy:* The epoxy–amine resin system is combined with a naturally occurring coal tar. A two-phase, heterogeneous, binder is produced, which is very hydrophobic. Although coal tar coatings have a long track record of providing excellent corrosion protection in ballast tanks, this type of product is currently being phased out due to (1) health and safety concerns over materials present in the coal tar, and (2) the dark color of the coatings.
- *Pure epoxy and modified epoxy coatings:* The distinction between the two coatings is that the modified epoxy coatings contain either (1) nonepoxy resins, for example, acrylate functional materials, which can react into the epoxy–amine binder, or more commonly, (2) nonreactive liquid or solid resins, typically hydrocarbons, which modify the properties of both the liquid and cured coating. A concern with the use of modified epoxy coatings is the potential for extraction of the nonreactive resin on long-term immersion. There has been considerable debate concerning the relative merits of pure and modified epoxy coatings,[27,28] the pure epoxy being claimed to have the better barrier properties and the modified epoxy improved tolerance to

application onto surfaces with reduced preparation. If correctly formulated, both coating types can provide good long-term anticorrosive performance.

- *Aluminum pigmented coatings:* The amount of aluminum flake pigment added to coatings has to be maintained at a relatively low level in the cured coating, typically less than 10 wt%, to avoid potential safety issues associated with the generation of sparks when the coating is subject to impact or abrasion. Aluminum pigmented epoxy coatings can provide excellent corrosion protection, and in particular, very good resistance to cathodic disbonding at defects. Although the lamellar aluminum flake pigmentation may improve the coating barrier properties, recent studies[29] have demonstrated that the aluminum pigment also reacts with the hydroxide ions produced at the cathodic sites in the corrosion cell.
- *Solvent-free epoxy coatings:* A recent development to address the increasing legislative restrictions on solvent emissions. To maintain an acceptable viscosity for application, the paints are normally formulated with a reduced level of pigmentation, may contain high levels of reactive or nonreactive diluents, and may require the use of heated application equipment.

A more detailed consideration of the coating chemistry and formulation guidelines can be found in other reference works.[30,31] In addition to epoxy–amine coatings, these references also discuss both the polyurethane and alkyd coating systems that are used on other vessel areas.

The epoxy–amine coatings are two-pack products, which are mixed immediately prior to application. Coatings are normally applied by airless spray. Typical coating schemes are indicated in **Table 5**.

Stripe coating of welds and cut edges, by brush or roller, is important if effective corrosion protection is to be achieved, and this is now a mandatory requirement in the new IMO coating regulations.[3,4]

Because of the wide range of temperatures experienced during application and cure of the coatings, for example, in Korean Newbuilding shipyards, paints are applied at temperatures as low as −5 °C, epoxy coatings are often formulated in ‘summer’ and ‘winter’ versions. The type of amine curing agent and level of catalyst are varied in order to obtain the rapid cure characteristics required by the shipyard.

Table 5 Coating schemes for ballast tanks

Coating type	*Coating scheme (dft)*
Coal tar epoxy	1×250 μm+stripe coat or 2×125 μm + 2 stripe coats
Modified and pure epoxy	2×125 or 2×150 μm + 2 stripe coats
Aluminum pigmented epoxy	2×125 or 2×150 μm + 2 stripe coats
Solvent-free epoxy	1×300 μm + 2 stripe coats

Cathodic protection systems based on sacrificial zinc or aluminum anodes are used in ballast tanks. The system is either installed at Newbuilding or can be introduced several years into the coating life; this largely depends on the vessel operator’s preference.

Other approaches to improve the corrosion protection in ballast tanks are also being considered, including the use of deoxygenation of the ballast water[32] and the use of gas inertion systems.[33] Neither of these approaches is considered as a replacement for the coating system, but they may enhance the coating performance.

Given that the average life expectancy of ships is in excess of 25 years, repair and/or replacement of the ballast tank coatings applied at Newbuilding will be required. The coating systems and schemes outlined in **Table 6** are also applied at Maintenance and Repair. Other more surface and damp-tolerant epoxy and one-pack vinyl coatings have also been developed for the OBM market. An IMO standard for the maintenance of ballast tank coatings is currently under discussion.

Future IMO regulations, due to be implemented from 2009, will require the treatment of ballast tank water to prevent the transport of marine organisms between different geographic locations in the ballast water. A number of different treatment technologies, including electrolysis, UV radiation, addition of chemicals, and deoxygenating, are currently being proposed. There are concerns that the water treatments could increase the corrosion rates in ballast tanks,[34] and testing of the new technologies in conjunction with ballast tank coatings is required.

4.14.4.3 Cargo Tanks

As indicated in **Table 1**, cargo tankers, which transport crude oil, account for 22% of the world fleet (considered as gross tonnage). Until recently, normal practice was to leave the cargo tanks uncoated, as the oil was considered to be a relatively inert material and the oil film remaining on the tank walls, on emptying the tank, provided a degree of corrosion protection.[5] However, corrosion was frequently observed in cargo tanks primarily at the top (the deck head) and on the floor (the tank top) of the tank, and the corrosion rates

Table 6 Coating systems for chemical and product tanks

Coating type	*Typical scheme (dft)*	*End use/potential limitations*
Epoxy–amine	2×125 μm or 3×80 μm or 3×100 μm	Primarily used for product carriage
Zinc silicate	1×100 μm	Cannot carry strongly acidic or basic cargos Unsuitable for carriage of vegetable oils
High-performance epoxy (epoxy–isocyanate)	3×90 μm	Chemical carriage Relatively low solids products
Epoxy phenolic	3×100 μm	Chemical carriage To obtain optimum performance the coating needs to be postcured

were typically 2–3 times higher than those expected for uncoated steel.[35] Corrosion breakdown was primarily attributed to[35]

1. the low level of water in the crude oil, which on storage, settles to produce a thin layer below the oil. The water can have a strongly acidic pH due to water-soluble materials, such as sulfates, present in the oil;
2. microbial-induced corrosion, particularly associated with acid-producing bacteria (APB) and sulfate-reducing bacteria (SRB); and
3. corrosive materials present in the ullage space above the crude oil. Gases such as hydrogen sulfide can be released from the oil. The inert gas system, which is used to prevent the buildup of oil vapor in the ullage space, contains sulfur dioxide and nitrous oxides as well as other impurities.[13]

Factors (1) and (2) lead to the corrosion of the floor of the tank and can result in severe pitting of the steel.

More general corrosion breakdown is observed on the deck head.

Changes in ship design have also contributed to the increased rates of corrosion. Double-skin tankers retain the heat of crude oil (certain heavy crude oils are loaded into the tank at 80–100 °C) more effectively than do the older single-skin tankers and the higher temperature will accelerate any corrosion processes. The increased use of high-tensile steels has resulted in more flexible ships and the increased flexing of the structure acts to loosen scale and rust on the deck head, exposing a new layer of steel to the corrosive environment.[36] Vessels constructed from thermomechanically controlled process (TCMP) steel can also show increased susceptibility to pitting corrosion.[35]

Given the corrosion issues observed in cargo tanks, coatings are now normally applied to the top and bottom 2–3 m of the tank. The rest of the tank is not coated with anything other than the low film thickness zinc silicate shop primer applied at Newbuilding. Coal tar epoxy coatings were very effective in cargo tanks due to their excellent acid resistance; however, this product type is being phased out due to health and safety concerns. Modified or pure epoxy–amine coatings, essentially the same coatings as applied in ballast tanks, are currently used in cargo tanks. The coating will be applied as a 2×125 or 2×150 μm film thickness scheme. The coatings provide long-term protection and will not normally be replaced during the vessel's 20–30 year lifetime. Proposed IMO regulations are expected to make the coating of the deck head and the top of cargo tanks mandatory at Newbuilding.[37] A potential amendment to the new regulations currently under discussion is the option of constructing the tank, or parts of the tank, from corrosion-resistant steels, which have improved resistance to the environments present in cargo tanks. The corrosion-resistant steel would not require coating.

4.14.4.4 Chemical and Product Tankers

Although crude oil carriage represents by far the largest sector of the cargo tanker market, there has been an increasing trend toward shipping refined oil products (aliphatic hydrocarbons, gasoline, diesel, aviation fuel) and chemicals (organic and inorganic chemicals, vegetable oils/animal fats). Coating of the tanks on chemical and product tankers is essential; certain cargoes can chemically attack the steel, and after carriage of a cargo, the tank will be subjected to a rigorous cleaning regime, using water and often acidic or basic cleaning chemicals. If corrosion occurred in the tank, the corrosion products could contaminate the cargo.

High-performance coatings are used in the chemical and product tanker market. The coatings must be resistant to the wide range of cargoes carried and impose minimum restrictions on the carriage of the subsequent cargoes. The coating should also exhibit low cargo absorption and/or any absorbed cargo should be rapidly desorbed during the venting and cleaning of the tanks between cargoes – this is important to avoid the absorbed cargo being desorbed into the next cargo, resulting in contamination. Obtaining good coating–substrate adhesion and accurate film thickness control are also essential; to achieve this, high-quality surface preparation and coating application are required. At Newbuilding, the chemical tank coatings are applied post vessel erection rather than at block stage, the entire tank is reblasted to an Sa2½ standard and the coating is applied under a defined range of environmental conditions (temperature, relative humidity).

As an alternative to coated tanks, the ship owner has the option of constructing the tanks from stainless steel. However, stainless steel is expensive, more difficult to fabricate and weld, and can still be attacked by certain chemicals (e.g., chlorides). As a result, most vessels use coated mild-steel tanks or a combination of mild and stainless steel tanks.

A number of different coating types can be used as shown in **Table 6**.

The selection of the coating is largely dependent on the chemicals that will be carried. The epoxy–amine coatings, which are of the pure epoxy resin type discussed in the ballast tank section, provide very effective protection against refined oil products and certain chemicals. Cargo absorption is, however, an issue. Zinc silicate coatings, which can be either solvent-borne or waterborne, offer excellent chemical resistance together with low cargo absorption and cross contamination. However, this type of coating cannot be used for strongly acidic or basic cargoes because of the potential for rapid dissolution of the zinc pigmentation. The high-performance epoxy and epoxy phenolic coatings are designed to have polymer networks with very high crosslink densities to reduce cargo absorption. The epoxy–isocyanate coatings are relatively low solids due to the requirement to use hydroxide functional epoxy resins for reaction with the isocyanate, and certain owners also have health and safety concerns over the use of isocyanates. As a result, the market has increasingly moved to using epoxy–phenolic coatings for the most demanding applications. The epoxy–phenolic coatings, which are relatively high cost in comparison with the epoxy–amine and zinc silicate systems, produce a high crosslink density through a 'dual cure' mechanism. The epoxy phenolic resin is partially cured with an amine and the residual epoxy functionality is homopolymerized using a suitable catalyst. The homopolymerization reaction primarily takes place at elevated temperature (60–100 °C), and prior to the carriage of certain cargoes, the epoxy phenolic coating needs to be postcured. Postcure can be via heating with hot-air blowers or applying hot water onto the coating through the tank cleaning system; alternatively, the carriage of heated cargoes can produce an effective postcure.

In addition to meeting the demanding performance requirements of the chemical and product tanker markets, the coatings should also be compliant with the appropriate regulations relating to the carriage of foodstuffs in contact with coatings. If the coating is not appropriately certified, it cannot carry certain cargoes.

Chemical tank coatings typically have to be replaced every 5–7 years. At Major Refurbishment, the tank is fully blasted to an Sa2½ standard and the coating system reapplied.

4.14.4.5 Cargo Holds

Bulk carrier vessels transport dry cargoes, primarily coal, iron ore, grains, and bauxite/alumina. In 2007, ~1800 million tones of cargo was transported worldwide and the market is growing at typically 4–5% per annum fuelled by the rapid industrial growth in China and other Far East countries. The coatings applied in cargo holds have to resist the mechanical damage caused by the hard angular cargoes and the conditions experienced during cargo loading and unloading and while the vessel is at sea. The holds are normally loaded by dropping the cargo, using a conveyor or mechanical grab, from above the deck height (typically 30 m from the deck to the bottom of the cargo hold), while unloading is by mechanical grab. These processes have the potential to produce significant impact damage of the coating, particularly on the coated shedder plates and hopper sides at the bottom of the hold. Further damage of the coating can be caused by the slow settlement of the cargo during transportation; this produces a gouging action on the coating applied to the vertical walls of the hold,[38] and to minimize the damage the coating should have excellent abrasion resistance. An example of settlement damage of coatings is shown in **Figure 8**.

Where coating damage occurs and the mild steel substrate is exposed, rapid corrosion will occur, particularly as (1) certain cargos, such as coal, contain

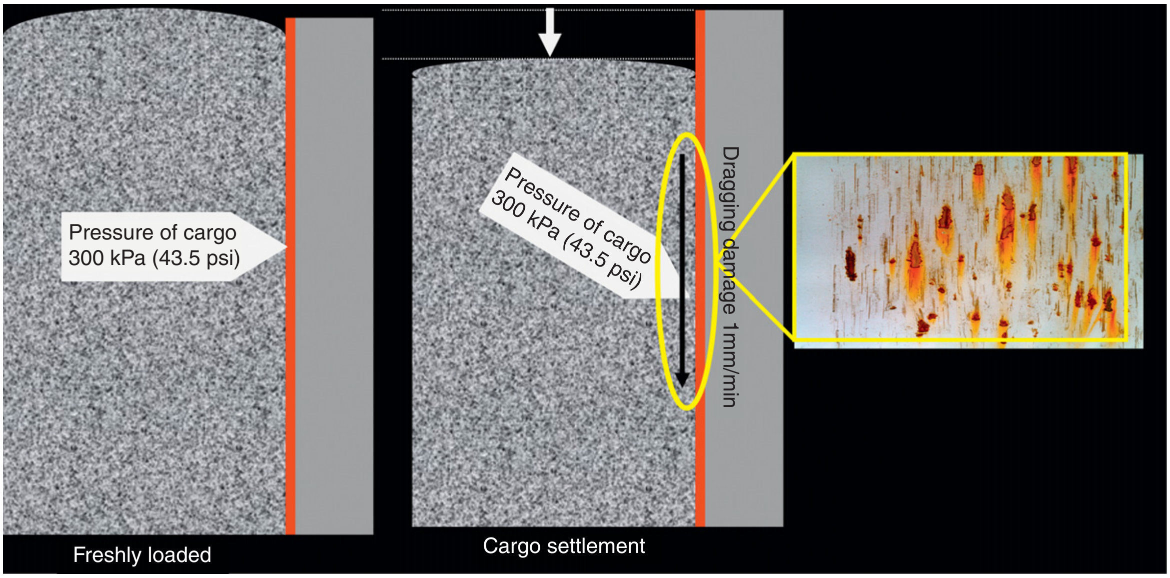

Figure 8 Settlement damage in a cargo hold.

Table 7 Coating systems for cargo holds

Coating type	*Typical specification (dft)*		
Abrasion resistant epoxy	2×150 μm	↑ Increasing performance	↑ Increasing cost
Pure epoxy	2×150 μm		
Modified epoxy	2×125 μm		
Alkyd	2×75 μm		

impurities that accelerate the corrosion process and (2) several of the cargo holds will be fully or partially ballasted during the normal operation of the vessel.

For the carriage of grain, the impact and abrasion issues are greatly reduced; however, any coating, which is in contact with grain, should comply with the appropriate food contact regulations, for example, should be FDA certified.

The different types of coatings used in the cargo hold market are summarized in Table 7. At Newbuilding or Major Refurbishment, the coatings are applied by airless spray.

Although high volumes of one-pack alkyd products are used, it is recognized that the coatings offer only limited damage resistance, and extensive, frequent, repair of the coating will be required if coal or iron ore are carried in the hold. The alkyd coatings are, however, FDA certified and therefore represent a cost-effective coating system for vessels that specialize in grain carriage. Two-pack pure and modified epoxy–amine coatings provide improved damage resistance and also have good intrinsic anticorrosive performance; the coatings are the same as those specified for use in ballast tanks and on the underwater hull. Hydrocarbon modification of the epoxy coating can have a detrimental effect on the damage resistance, while the aluminum pigmented pure epoxy–amine coatings are particularly resistant to gouging damage. The abrasion resistant epoxy–amine coatings contain a high loading of 'hard' pigments, such as bauxite and amorphous silica, and the polymer network is designed to provide excellent mechanical properties.

The coatings should develop good damage resistance shortly after application, including under the poor ventilation and low-temperature conditions frequently experienced in the bottom of the hold. Otherwise, high levels of coating damage may occur on loading and carriage of the first cargo. Avoiding over application of the coating and minimizing solvent retention are also important requirements.[39]

Epoxy–amine coatings provide effective damage resistance by transferring the impact energy through to the steel substrate. An alternative approach is to use a highly elastomeric coating, which absorbs the impact energy. High-build, solvent-free, polyurethane elastomer coatings are used, albeit to a limited extent in comparison with epoxy–amine coatings, to protect the shedder plates and hopper sides, which are subject to the high levels of impact damage. Polymer sheet linings, based on high-density polyethylene, can also be used to protect specific areas in the cargo hold; these lining materials have found applications on certain specialist self-unloaded vessels.

The in-service lifetime of the cargo hold coating will depend on the coating type, the cargos carried, and the amount of OBM of the coating carried out by the crew. Typical lifetimes are modified epoxy 3–5 years, pure epoxy 5–7 years, abrasion resistant epoxy 10–12 years.[38] At Major Refurbishment, the entire cargo hold will be reblasted to an Sa2 standard and the coating system reapplied. As previously discussed, a large amount of OBM can be carried out in cargo holds, for both the alkyd and epoxy–amine coatings types. The same coatings applied at Newbuilding and Major Refurbishment can be used for OBM; however, a range of more surface-tolerant epoxy coatings are also used.

A current trend in the bulk carrier market is an increase in the vessel cargo loading speeds used in certain countries. Loading rates of between 3000 and 17 000 tones per hour are being achieved. The new high-speed conveyor and loading systems can, depending upon the procedure adopted, fire the cargo at high speed against the coated walls of the hold, leading to increased damage of the coating on the forward and aft bulkheads. It is currently unclear whether the current high-performance hold coatings will provide effective long-term protection for vessels using the new high-speed loading procedures.

4.14.4.6 Other Vessel Areas

The preceding sections have focused on coatings for the vessel load carrying areas (cargo holds, cargo tanks, and chemical tanks) and the underwater hull and ballast tanks, which are critical areas with regard to fouling control and corrosion protection. There are a number of other areas on the vessel that also require coating: decks, topsides and superstructure, and internals. In general, the corrosion protection challenge in these areas is lower, reflecting the fact that the coated structure is not subject to permanent or periodic seawater immersion, or in extended contact with potentially damaging liquid or dry cargos. However, exposure to a marine atmosphere is one of the most aggressive nonimmersion corrosive environments and the coating system can also be subject to UV degradation, which may lead to both a loss of aesthetic appearance and cracking of the coating. If cracking occurs, it may reduce the corrosion protection provided.

A wide range of coatings, both anticorrosive primers and cosmetic finishes, are applied on these vessel areas and the coating scheme selected is often determined by a combination of (1) the conditions that the coating will experience, (2) the required in-service lifetime of the coating, and (3) the ship owner's coating preferences, including potential cost restrictions.

4.14.4.6.1 External decks

Coating systems for decks are required to provide damage and chemical resistance, cosmetic appearance, as well as effective corrosion protection. Representative coating schemes are indicated in Table 8.

Increasingly stringent solvent emission legislation has resulted in a phasing out or a significant reduction in sales volumes of the low solids chlororubber-based coatings and thermoplastic acrylic finishes, which were previously widely used in the marine market. High volumes of the relatively low-cost alkyd coatings are used on decks, including zinc phosphate pigmented primers; however, there is an increasing trend toward specifying higher-performance epoxy primer systems. The epoxy primers are of the pure and modified epoxy type discussed in Section 4.14.4.2. In general, the epoxy primers do not contain corrosion inhibitor pigmentation.

Significant differences are observed in the UV stability and durability of the different cosmetic finishes. Epoxy finishes undergo rapid UV degradation and chalking of the coating will be observed, while the more expensive polyurethane finishes

Table 8 Typical coating schemes for external decks

Coating system	*Scheme (dft)*
Alkyd primer + alkyd finish	2×75 μm primer + 40 μm finish
Epoxy primer + epoxy finish	2×125 μm primer + 50 μm finish
Zinc silicate + epoxy primer + epoxy finish	75 μm zinc silicate + 75 or 150 μm epoxy primer + 50 μm finish
Epoxy primer + polyurethane finish	2×125 μm primer + 50 μm finish
Epoxy primer finish	2×150 μm
Epoxy primer + one-pack thermoplastic acrylic finish	2×125 μm primer + 40 μm finish

have excellent long-term stability. Alkyd finishes also exhibit good durability, but can be prone to yellowing on long-term exposure.

If required, nonskid characteristics can be introduced into the deck coating by the addition of aggregate pigmentation, either present in the liquid coating or applied onto the wet coating, immediately following spray application.

At Newbuilding and Major Refurbishment, coatings will be applied by airless spray, while for OBM, which will regularly be carried out by the crew, roller and brush application is widely used.

4.14.4.6.2 Topsides and superstructure

The key performance requirements for the coating scheme are effective corrosion protection and good aesthetic appearance. As shown in Table 9, the typical coating schemes are similar to the schemes applied on decks.

Polysiloxane finishes, which provide excellent long-term durability, are being increasingly specified on vessels such as cruise liners where the aesthetic appearance is particularly important. The cost of the polysiloxane coating is higher than the other finishes used in the marine market.

4.14.4.6.3 Vessel interiors

The main coating requirement is cosmetic appearance. Low-cost, fast drying, alkyd primers often containing zinc phosphate anticorrosive pigmentation are normally applied typically at 1×75 μm dft. The primer will either be topcoated with 40 μm of an alkyd finish or wood veneers are attached over the primer. Waterborne one-pack acrylic primers and finishes have recently been introduced for use on vessel interiors. Although generally costlier than the alkyd system, the waterborne system provides significantly reduced solvent emissions.

Table 9 Typical coating schemes for topsides and superstructures

Coating system	*Scheme*
Epoxy primer + polysiloxane finish	2×100 μm primer + 100 μm finish
Epoxy primer + polyurethane finish	2×125 or 2×150 μm primer + 1×50 or 2×50 μm finish
Epoxy primer + epoxy finish	1×150 μm primer + 2×50 μm finish
Alkyd primer + alkyd finish	2×75 μm primer + 40 μm finish

For interior areas, such as the floor in the engine room, which may be exposed to more aggressive conditions, epoxy-based coatings will be specified.

A number of specialist coating systems have also been developed for use on decks, topsides, and the vessel superstructure:

- Low solar absorption (LSA) coatings, which are designed to reduce the amount of near-infrared radiation absorbed by the coating, thereby reducing the coating temperature. LSA coatings are widely used on military vessels where it is important to control the temperature of the electronic defense systems in the vessel interior. Use of LSA coatings can also reduce the air conditioning requirements on other vessel types. LSA is primarily achieved through the careful selection of the pigments used in the coating.[40]
- Finish coatings that reduce the level of rust staining on the topsides and superstructure, a major issue on cruise liners and other vessels. The coatings contain a chelating agent, which coordinates with the ferrous ions to produce a colorless product.
- Deck coatings for military ships, which are designed to resist the short duration high temperatures associated with vertical take-off aircraft.

4.14.5 Future Trends

Obtaining effective long-term corrosion protection in the marine industry represents a major challenge. High-performance coating systems have been developed, which provide both long-term protection, thereby reducing coating maintenance costs and meet the other requirements of the shipyards and ship owners – coatings compatible with shipbuilding processes, minimize the application time and costs, compliance with environmental regulations, etc.

The last 20 years have seen major changes in the marine industry, which have resulted in significant changes to the type of coating systems used to protect ships. Continued change in the ship construction processes, ship operational procedures, and environmental and industry regulations are envisaged and will require further development of the coating systems used in the marine market. Future trends may include:

- Further reduction in permissible solvent emissions driven by environmental legislation. Increased use of high-solids, solvent-free, and waterborne coating systems can be anticipated. It is important to recognize that, at present, waterborne coatings are not widely used in the marine market. This reflects (1) the temperature and humidity restrictions on the use of this type of product, (2) the higher cost, depending upon coating type, and (3) concerns over the anticorrosive performance and osmotic blistering susceptibility of waterborne epoxy anticorrosive coatings if used on areas subject to permanent or periodic immersion.

- Increasing health and safety concerns over certain materials used in marine coatings, for example, low molecular weight epoxy resins, amine curing agents, biocides, and isocyanates.
- A requirement for increased coating lifetimes in key vessel areas such as ballast tanks and cargo holds.
- Changes in the design of ships. The use of composite materials as a replacement for steel[41] and the use of steel–laminate–steel structural laminates[42] have recently been proposed. Aluminum is being increasingly used in the fast ferry market.
- Changes to the ship construction and Newbuilding coating processes. The use of higher-speed and alternative welding and cutting techniques, for example, laser welding.[43] The potential use of robotic coating application as a route to reduce application costs and improve the coating thickness control. Development of ultra fast drying anticorrosive coatings, which significantly reduce the time required to paint the blocks, which can be a major bottleneck in the ship construction process. For this last opportunity both modified epoxy and polyurea/polyurethane coatings are currently being investigated.[44,45]

References

1. Lloyds Register World Fleet Statistics 2006.
2. Mills, G.; Eliasson, J. Future Cargo and Ballast Tank Coatings – Forward Looking Technology SSPC October, 2003.
3. Performance standard for protective coatings for dedicated seawater ballast tanks of all types of ships and double side skin spaces of bulk carriers. 2006: SOLAS regulations II – 1/3-2 and regulation XII/6.3.
4. Howarth, D. *Asia Pacific Coatings J.* **2007**, 12–14.
5. Banfield, T. A. In *Corrosion, Corrosion Control*, 3rd ed.; Shrier, L. L., Ed.; 1994; Vol. 2; Section 14.7.
6. Lambourne, R. In *Paint and Surface Coatings, Theory and Practice,* 2nd ed.; Lambourne, R., Strivens, T. A., Eds.; 1999; Chapter 13 (The Painting of Ships).
7. World Shipyard Monitor Vol. 14 No 5; 2007 Clarkson Research Services.
8. Wang, G.; Spencer, J. S.; Olson, D. L.; Mishra, B.; Saidarasamoot, S.; Thuanboon, S. *Handbook of Environmental Degradation of Materials*; Myer, K., Ed.; 2005; Chapter 25 (Tanker Corrosion).
9. Nguyen, T.; Hubbard, J. B.; Pommersheim, J. M. *J. Coat. Technol.* **1996**, *855*, 45–56.
10. Greenfield, D.; Scantlebury, D. *J. Corros. Sci. Eng.* **2000,** *3,* Paper 5.
11. Mayne, J. E. O. *J. Oil and Colour Chem. Assoc. (JOCCA).* **1949**, *352*, 481–487.
12. Leidheiser, H.; Wang, W. *J. Coat. Technol.* **1981**, *672*, 77–84.
13. Eliasson, J.; Rauta, D.; Gunner, T. Ballast Water Tank Coatings of the Future, NACE Corrosion Conference 2005.
14. Song, E. H.; Lee, H. I.; Chung, M. K.; Park, C. S.; Lee, C. H.; Shin, C. S.; Lee, S. K.; Baek, K. K. NACE 61st Annual Conference and Exposition 2006, Paper 6015.
15. Park, C. S.; Son, S. M.; Shin, C. S.; Chung, M. K.; Baek, K. K. NACE 62nd Annual Conference and Exposition 2007, Paper 7004.
16. Koch, G. H.; Brongers, M. P. H.; Thompson, N. G.; Virmani, Y. P.; Payer, J. H. Corrosion Cost and Preventative Strategies in the United States, Office of Infrastructural Research and Development Federal Highway Administration, report no FHWA-RD-01-156 2001.
17. ISO/TR 15235:2001(E) Preparation of steel substrates before application of paint and related products – collected information on the effect of water soluble salt contamination.
18. Ward, D. NACE 62nd Annual Conference and Exposition Paper 7001, 2007.
19. Munger, C. G. Corrosion Prevention by Protective Coatings National Association of Corrosion Engineers, 1999.
20. Feliu, S.; Barajas, R.; Bastidas, J. M.; Marcillo, M. *J. Coat. Technol.* **1989,** (775), 63–70, 71–76.
21. Hare, C. H. Paint Film Degradation SSPC: The Society for Protective Coatings, 2001, Chapter 64.
22. International Coatings WO 00/55260 2000.
23. Biocide Products Directive in the European Union 98/8/EC.
24. Yebra, D. H.; Kill, S.; Dam-Johansen, K. *Biofouling* **2004**, 75–104.
25. Chambers, L. D.; Stokes, K. R.; Walsh, F. C.; Wood, R. J. K. *Surf. Coat. Technol.* **2006**, 3642–3652.
26. Woods Hole Oceanographic Institution Upper Ocean Process Group Technical Note 9508, 1995.
27. Callow, L. *Protective Coat. Eur.* **2001**, 20–24.
28. Alveberg, B. E.; Busklein, J. I.; Alveberg, J. J. *Protective Coat. Eur.* **2002**, 10–13.
29. Knudsen, O. O. PhD Thesis, Norwegian University of Science and Technology, 1998.
30. Muller, B.; Poth, U. *Coatings Formulation;* Vincentz Network GmbH & Co. KG: Hannover, 2006.
31. Hare, C. H. Protective Coatings Fundamentals of Chemistry and Composition, SSPC: The Society for Protective Coatings, 1998.
32. Lee, J. S.; Ray, R. I.; Little, B. J.; Lemieux, E. J. *Corrosion* **2005**, 12, 1173–1187.
33. Makoto, K.; Kobuchi, S. *Zairyo* **2000**, 11, 118–1192.
34. Dragsund, E.; Johannessen, B. O.; Anderson, A. B. *Protective Coat. Eur.* **2005**, 4–9.
35. Huang, R. T. International Workshop on Corrosion Control for Marine Structures and Pipelines, 9–11 February 1999, Galveston: Texas, USA.
36. Towers, R. *J. Protective Coat. Linings* March **2000**, 30–42.
37. MSC 82/23/4 proposal for a new SOLAS regulation II – 1/3–9, coating of cargo oil tanks of oil tankers.
38. Propeller Magazine (International Paint Publication) 2005 November, 13–15.
39. Parry, T. *J. Protective Coat. Linings* **2000**, 40–43.
40. Brady, R. F.; Wake, L. V. *Prog. Org. Coat.* **1992**, 1–25.
41. Dodkins, A. R. *Inst. Mech. Eng. IMechE C536/024* **1998**, 189.

42. Lloyds Register Special Report September 2000. A new concept for a new age – the sandwich plate system (SPS) for shipbuilding.
43. Zeyffarth, P.; Hoffman, J. *Laser Technol.* **2000**, 9–15.
44. Son, S. H.; Chang, M. K.; Kim, K. H.; Shin, C. S.; Baek, J. J.; Baek, K. K. Feasibility Evaluation of Rapid Cure Coatings for Ships Water Ballast Tanks PACE 2007, Dallas Convention Centre Feb 11–14 2007.
45. Kaznoff, A. I.; Evans, M.; Verbogt, J. The Future of Marine Coatings Technology in the US Navy, Marine Coatings Conference, 27–28 September 2006, SMM Fairgrounds Hamburg.

4.15 Coatings for Structures in Contact With the Ground

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Glossary

Bell hole Area of ground excavation around a pipeline that allows inspection and/or repair work to be carried out on the pipeline in a selective location.

Cup shot A sample of a liquid coating taken during the coating application usually in a plastic cup or similar receptacle. Once the liquid coating has fully cured, tests can be carried out to verify that the coating components have been mixed in the correct proportions.

Cut back When line pipe is coated, a small area at each end of the pipe is left free of protective coating so that adjacent sections of pipe can be welded together without the heat from the welding damaging the coating. The area of the joint (the field joint) is prepared and coated after welding.

Fusion-bonded epoxy (FBE) powder A protective coating supplied in powder form, containing both a base resin and a curing agent. The powder is stable at room temperature. When the powder is heated to within a certain temperature range, the powder melts and a chemical reaction takes place between the two components, which results in a complex stable polymer film.

Intelligent pig An electromechanical device which travels inside a pipeline measuring the pipe wall thickness.

LPG Liquid petroleum gas, that is, either liquefied butane or liquefied propane.

Off ratio Two-component coatings like epoxies and polyurethanes require the two components to be mixed in the correct ratio to achieve optimum performance from the finished coating. The correct mixing ratio is prescribed by the coating manufacturer with an appropriate tolerance. If the actual mixing ration is outside of the prescribed tolerance, that is, off ratio, then the optimum coating performance will not be achieved.

Pot life Protective coatings such as epoxies and polyurethanes are supplied to the applicator in two parts: a base and a curing agent. The two parts must be thoroughly mixed together before application in order for their corrosion protection qualities to be fully realized. Once the coating has been thoroughly mixed, the applicator has a finite time in which to apply it. This is known as the pot life. For many solvent-containing epoxies and polyurethanes, the pot life will be of the order of 1–2 h. For solvent free formulations, the pot life may be as short as 1–2 min, depending on the application temperature. If the coating is applied outside of the pot life, its protective qualities may be severely compromised.

Tenting Where discontinuities occur in the surface of a structure, for example at weldments, certain semirigid coating types, in particular cold-applied tapes, experience difficulty in conforming to the discontinuity. Instead, the discontinuity is bridged and a tent is formed at the location providing a weakness in the corrosion protection.

Abbreviations

HDPE High density polyethylene

4.15.1 Introduction

The most important types of steel structures affected by corrosion because of contact with the ground are: buried transmission pipelines and buried process piping networks, structural support piles, well casings, and above- and belowground storage tanks. A detailed discussion of the protective coatings applied to these structures is considered to be the best means of describing coatings for corrosion protection where steel is in contact with the ground.

The corrosivity of soil is determined by many factors, the principal ones being

- the soil type (sand, clay, chalk, carbonaceous, etc.)
- the degree of compaction,
- the water content and salinity,
- the oxygen content, and
- the extent and the prevalence of sulfate-reducing bacteria.

For buried steel structures, maintenance may be difficult or even impossible, and it is usually necessary to provide some form of corrosion protection in order for the structure to meet its design life. The corrosion protection will normally involve a protective coating often supplemented by cathodic protection. Protective coatings used on buried structures act as physical barriers, which isolate the structure from the surrounding environment. They must be sufficiently robust to withstand construction activities, including transportation to site, handling, and burial, and can vary in thickness from 500 μm to several millimeters. In service, the cathodic protection prevents corrosion from occurring at holidays in the coating, which result mainly from mechanical damage.

Improvements are continually being made to the quality of protective coating materials and to their methods of application. Nevertheless, it is virtually impossible to produce a protective coating that will protect 100% of the surface of a buried structure for the full design life at an economic cost. This is largely due to the skills required to apply these coatings successfully and the many opportunities, which exist for the coating to become damaged. The coating may suffer handling damage, during transportation to site and during construction. It may be penetrated by rocks during backfilling and by ground settlement following construction. Air–soil interfaces on partially buried items can be particularly vulnerable to mechanical damage. Some pipe coatings have been known to split because of the stressing of the coating in-service as a result of the repeated cycle of wetting and drying of the surrounding soil. All of these events inevitably result in isolated areas of bare metal being exposed to the possibility of soil corrosion. In the majority of cases, the combination of a protective coating with cathodic protection offers the best economic solution to soil corrosion. Therefore, protective coatings used on buried structures need to be compatible with cathodic protection.

Protective coatings used on buried structures may be divided into several generic types, namely

- liquid coatings (paint) applied manually by brush, by airless or conventional spraying, by roller, or by dipping;
- tape wrappings applied by hand or by wrapping machine;
- radiation cross-linked heat-shrinkable materials;
- reinforced coal tar or asphalt enamel coatings, applied in the factory or at site;
- fused (mostly epoxy) powder coatings applied by flock spray or fluidized bed, mainly under factory conditions; and
- multilayer coatings comprising a polyolefin outer layer applied on top of an adhesive with or without a fusion bonded epoxy (FBE) powder coating applied as a first coat. These are factory-applied coatings and their use is confined to pipelines.

The selection of the type of coating will be strongly influenced by the size and geometry of the item, the method of construction, and the operating conditions. For multiple items of the same geometry, such as sections of straight line pipe, factory application of the coating to individual pipe lengths on a continuous production line represents the most economical method of applying a protective coating. Numerous coatings have been developed, which lend themselves to this type of application, and will be dealt with in more detail later.

For single, large, or complex geometry items, such as storage tanks, buried piping networks at process sites, valves, etc., liquid coatings applied by spray, brush, or dipping (where size allows) represent the most practical solution.

For some applications, such as pipelines through marshland, or coastal inlets, the protective coating may be supplemented with an outer concrete compression coating to provide additional mechanical protection and negative buoyancy.[1]

For all coating types and methods of application, quality control at every stage is crucial to the long-term performance of the selected coating. The quality of surface preparation is arguably the single most important factor, which determines the lifespan of the coating (see Section 4.15.3). More will also be said about quality control in Section 4.15.7.

4.15.2 Properties Required of Coatings for Steel in Contact with Soil

The purpose of applying a coating to a buried structure is to prevent direct contact with the surrounding soil over the lifetime of the structure. With this requirement in mind, the characteristics required of a protective coating for buried steel are as follows:

1. *Ease of application:* It must be possible to apply the coating in the factory, the coating yard, or in the field at an economical rate, using the standard tools and equipment that are available.
2. *Resistance to handling damage:* It must be possible for the structural item to be handled reasonably quickly after the coating has been applied without damaging the coating. For liquid-applied materials, this means a short drying time.
3. *Good adhesion to the metal surface:* The coating must have an excellent bond to steel. To this end, some coating systems include specific primers to promote superior adhesion of the complete system to the substrate.
4. *Resistance to impact:* The coating must be able to withstand reasonable levels of impact without cracking, chipping, or disbondment.
5. *Resistance to abrasion:* Where relative movement between the coated item and the ground, or other structures is inevitable during construction, then the coating must have good abrasion resistance. This is particularly important in the case of driven piles and water or hydrocarbon well casings.
6. *Flexibility:* The coating must be flexible enough to withstand such deformation as may occur during construction, for example, during field bending or laying of pipe and during the lifting and placement of buried storage tanks, etc. The coating must also accommodate any expansion or contraction that may occur because of significant changes in environmental or operating temperatures.
7. *Resistance to soil stress:* Coatings on buried structures are often subject to very high shear stresses, due, for instance, to the contraction of clay soils during periods of very dry weather. The coating must be able to resist such stresses without suffering damage.
8. *Water resistance:* The coating should display a low rate of water absorption and be resistant to water or water–vapor transmission through it.
9. *High electrical resistance:* The coating must be an electrical insulator free of any significant amounts of electrically conductive material.
10. *Chemical and physical stability:* The physical properties of the coating must remain stable, showing negligible change under the prevailing operating conditions.

11. *Resistance to bacteria:* The coating must be resistant to the action of destructive effect of any bacteria in the soil.
12. *Resistance to marine organisms:* For structures buried in coastal areas, the coating should be resistant to penetration by marine organisms.
13. *Resistance to cathodic disbondment:* Where the coating is to be used in conjunction with cathodic protection, it must be resistant to the high levels of pH, which are generated at coating breaks, as the protective current flows to the exposed steel surface.

4.15.3 Preparation of Metal Surfaces

The single most important factor determining the lifespan of a protective coating is the quality of the surface preparation. Before applying a protective coating, it is essential to ensure that the surface is free from rust, mill scale, moisture, loose dust, grease, or any other form of surface contamination. The best time for achieving the optimum standard of surface preparation is when the item is new. Once significant corrosion has taken place, it is far more difficult to achieve the high standard of surface preparation required for coating longevity.

The first stage in the preparation process should be the complete removal of all dirt and grease using either a proprietary detergent–water solution followed by freshwater, or an organic solvent.[2] Once all grease and dirt have been removed, a number of surface preparation methods may be used to remove rust, mill scale, and old coatings as follows:

1. *Mechanical cleaning:* This includes the use of wire brushes or abrasive paper either handheld or mounted on rotary power tools, and scrapers, and needle guns. Although scrapers, wire brushes, and abrasive paper are able to remove loose rust and scale, they do not remove more adherent layers and tend to polish the steel surface. Protective coatings adhere best to surfaces that are contaminant-free and not smooth. They need to have a surface profile or anchor pattern in addition to being clean. Needle guns are more effective at removing tightly adherent rust and scale, but progress is slow and this form of surface preparation is impracticable for anything other than small areas.
2. *Dry abrasive blast cleaning:* The projection of small particles of hard nonmetallic particles, or steel shot or steel grit at metal surfaces, using compressed air or centrifugal wheels is an extremely efficient form of removing all rust, mill scale, and old coatings. Abrasive blasting is capable of leaving a very clean steel surface and a surface profile, which optimizes coating adhesion. The cost of attaining a very high standard of cleanliness is considerable, and careful consideration should always be given to specifying the correct level of abrasive blasting for the particular application.[3]
3. *Pickling:* Dipping in inhibited hydrochloric or sulfuric acid is a commonly used factory method of removing mill scale from steel, particularly in conjunction with hot phosphoric acid dipping (the Footner process). It is mainly used in the steel manufacturing industry and for the pretreatment of steel prior to the application of specialized coatings such as hot dip galvanizing and electrodeposits. It is rarely used as a method of surface preparation before the application of the types of protective coatings used on buried structures. Published specifications are available covering the pickling process.[4]

Before the application of any coating, the quality of the prepared surface should meet specific inspection requirements with regard to the visual appearance,[2] the degree of dust contamination,[5] and the surface profile.[6]

Both before and during surface preparation and coating application, it is necessary to ensure that condensation is not likely to occur to the detriment of the final protective coating quality.[7] Regardless of which method of cleaning is adopted, it is important to apply the first coating layer as soon as possible after the cleaning operation and before any deterioration in the prepared surface.

4.15.4 Specific Coating Material Types and Their Applicability

4.15.4.1 Liquid-Applied Coatings (Paint)

The earliest coating types used on buried steel were based upon coal tar or bitumen often blended with a volatile solvent. In the absence of the solvent, the coating material had to be heated until molten and then poured onto the steel surface or the item had to be coated by being dipped into a hot bath of the liquid coating. When blended with a volatile solvent, the coating could be applied at room temperature and dried by evaporation of the solvent, to leave a protective film on the steel surface. The solvent-blended coatings could be applied very simply by brush, or for smaller compact items, by dipping. Regardless of the coating type and the application method, the coatings were brittle and prone to mechanical damage. Significant improvements in mechanical properties were made by the addition of fillers, and in the case of coal tar coatings for pipelines, the inclusion of fabric reinforcement. More will be said about reinforced enamel pipeline coatings later.

Today, the most commonly used liquid-applied coatings for buried steel are based on two-component epoxy or polyurethane formulations.[8,9] Both types require thorough mixing of their two components before application. A chemical reaction takes place resulting in cross-linking of the molecules of the base resin by molecules of the curing agent. The fully cured coatings adhere rigidly to well prepared steel and are very resistant to mechanical damage. Until recently, epoxy and polyurethane formulations containing coal tar were very popular for protecting buried steel, such types having built up a strong reputation of long-term performance over many years because of the improved chemical resistance that coal tar imparts at reduced cost. However, health and safety concerns over the carcinogenic nature of the polycyclic aromatic compounds contained within coal tar and released during heating have led to a significant decrease in the availability of epoxy and polyurethane formulations containing this material in recent times.

Additional health and safety concerns over solvent emissions and the demand from customers for rapid curing have led to significant developments in epoxy and polyurethane coating technology. Solvent-free formulations now exist that satisfy health and safety legislation but require an enhanced degree of sophistication during application, due mainly to the short pot life of the mixed constituents. The principle method of application is by airless spray without any premixing of the two components. Instead, the two components are pumped separately to a mixing chamber just ahead of the spray gun to ensure that the short pot life of the fully mixed coating is accommodated. The curing rate can be further enhanced by thermostatically controlled heating of each separate component prior to mixing, with the final application temperatures being as high as 80 °C for some formulations. As a result, the coatings fully cure in a matter of hours, which is a major advantage for the applicator, as coated items can be handled a few hours after coating compared with several days for the solvent-based alternatives. The principal use of epoxy and polyurethane coatings is in the protection from soil corrosion of buried tanks and associated piping, and pipeline components such as thrust bore sections, field joints, preformed pipe bends, and valves. **Figure 1** shows several LPG storage tanks coated with a solvent-free coal tar polyurethane prior to encapsulation in a burial mound.

Liquid-applied epoxies and polyurethanes have also found use on above-ground storage tanks, specifically

Figure 1 Large LPG storage tanks externally coated with a solvent-free coal tar urethane awaiting burial.

on the undersides of the floor plates where the steel is in intimate contact with the tank mound. This is to help reduce the risk of under-floor corrosion, which can lead to perforation of the floor plates and the loss of product containment. Complete coverage of the undersides of the floor is not possible because of the method of construction. The plates can be coated prior to laying down the floor, but the edges have to be left bare to accommodate welding. Once welded in place, the undersides of the weldments are not accessible and have to be left bare. Nevertheless, the practice of painting the undersides of the plates before laying down the floor significantly reduces the area of bare metal in contact with the foundation mound and enhances the spread of protection from the cathodic protection system.

4.15.4.2 Cold-Applied Tapes

4.15.4.2.1 Petrolatum tapes

Petrolatum has, like lanolin, long been recognized as possessing corrosion preventative properties. Petrolatum tapes consist of a synthetic fabric carrier impregnated with petrolatum. Modern petrolatum formulations incorporate biocides to inhibit bacterial growth. The tapes are applied by hand over a soft petrolatum-based paste primer and are sufficiently conformable to accommodate irregular surfaces, such as flanges, large bolts, etc. They do tend to remain sticky to the touch long after application.

4.15.4.2.2 Pressure-sensitive tapes

Unlike petrolatum tapes, which possess corrosion-inhibitive properties, pressure-sensitive tapes rely entirely upon the prevention of the ingress of moisture to the metal surface to prevent corrosion. The tapes usually comprise a polyethylene or polyvinylchloride film of 0.25–0.5 mm thickness, with the inner surface coated with a thin layer of adhesive, often rubber-based. The adhesive is usually between 25 and 100-μm thick. They have minimal conformability and therefore cannot be used to wrap complex shapes. In addition, their resistance to mechanical damage and adhesion to steel are also limited. These tapes resemble those commonly used by electricians to bind electrical wiring and have limited use in corrosion protection applications other than as a temporary solution to a minor problem.

4.15.4.2.3 Laminated tapes

In a more general use as protective coatings for buried pipework are tape wrappings comprising a polyvinyl chloride or polyethylene carrier with a minimum thickness of 0.75 mm and an inner layer of a self-adhesive bituminous rubber compound with a minimum thickness of 0.8 mm.[10] These tape coating systems include a quick-drying primer with good adhesion to both the bituminous rubber compound and the prepared steel substrate. As with pressure sensitive tapes, laminated tapes have limited conformability and their use is mostly restricted to uniform cylindrical shapes such as buried pipe work. Laminated tapes are usually applied by hand or wrapping machine as a 55% minimum overlapping spiral, starting and ending with a double wrap and a neat square end. The application is easier and the performance is likely to be superior on smaller diameter pipe (<250 mm, say). During the application, care has to be taken to avoid tenting at weld seams, and where the weld cap is prominent, this may require the use of weld seam cover tape or proprietary mastic filler. Tenting may result in water channeling beneath the coating and localized corrosion of the substrate.

Laminated tape components are thermoplastic and the tapes have limited environmental and operating temperature resistance. Allowing tape-wrapped items to sit out in the hot sun prior to burial can result in distortion, disbondment, and blistering of the tape. Service at elevated temperatures may result in the movement of the tape wrapping relative to the coated item, exposing the substrate to soil corrosion.

4.15.4.3 Line Pipe Coatings

4.15.4.3.1 General

In the oil and gas industry, transmission pipelines are almost always of an all-welded construction. At the pipe mill, the pipe is manufactured in fixed lengths, usually 12 m, and is supplied to the pipeline construction site already factory coated to within several inches of the pipe ends. The coating cut-back is provided at each end in order to minimize damage to the coating from the heat generated during field welding operations. Once the field weld has been completed and inspected, the bare steel at the weld area and at the adjacent cut-back is cleaned and prepared (see Section 4.15.3), and a field joint coating is applied. The first 50–75 mm of the factory-applied coating is also prepared and the field joint coating overlapped onto it. Clearly, the factory coating and the line pipe coating have to be compatible and of a similar durability.

At the pipeline design stage, it is customary for the selection of an economic pipe wall thickness to be dominated by pressure containment considerations and any corrosion allowance is normally limited to a few millimeters at most. Thus, the integrity of the protective coating is paramount in ensuring the long-term integrity of the pipeline.

Figure 2 shows a schematic of the typical layout of a line pipe coating factory. The manufactured pipe enters the coating factory via the incoming pipe racks, and all dirt and grease are removed as the pipe passes through the washing unit. The pipe is then heated to typically 40–80 °C to drive off any residual moisture and ensure that the pipe temperature is maintained above the dew point throughout the ensuing surface preparation stage. The warm pipe enters an enclosed wheelabrator cabinet, where a mixture of steel shot and grit from a vertical hopper is propelled at high velocity on to the pipe surface via bladed wheels rotating at very high speeds. The steel shot, impacting on the surface with great force, breaks up the surface mill scale. The steel grit produces an angular surface profile on the pipe surface, which is necessary for optimum coating adhesion. After emerging from the cabinet, any surface debris, such as dust, spent grit, etc., is removed by vacuuming or brushing with stiff bristle brushes or a combination of the two. Debris is normally removed from the inside of each pipe by air blowing (not shown). Inspection racks are normally provided to permit inspection of the surface preparation quality before coating application.

Following the inspection and acceptance of the prepared surface, the pipe is transferred from the inspection racks onto a second conveyor system where a surface chemical pretreatment may be applied before further preheating and coating application. If chemical pretreatment is used, it usually involves the application of either a phosphate or chromate solution, sometimes, both in succession. The chemicals used are proprietary, being individually formulated for use with specific coating systems in line pipe coating plants.[11]

The specific example shown in Figure 2 involves the application of a three layer FBE–polyethylene coating, but the basic layout is typical of most modern line pipe coating factories. In the example shown in the figure, the prepared pipe is induction heated to the required temperature before the FBE powder is applied by electrostatic air spray. A polyethylene adhesive is then side extruded on to the FBE coating, followed by the side extrusion of the polyethylene outer coating.

The completed coating is cold water quenched to enable the coated pipe to be handled safely and

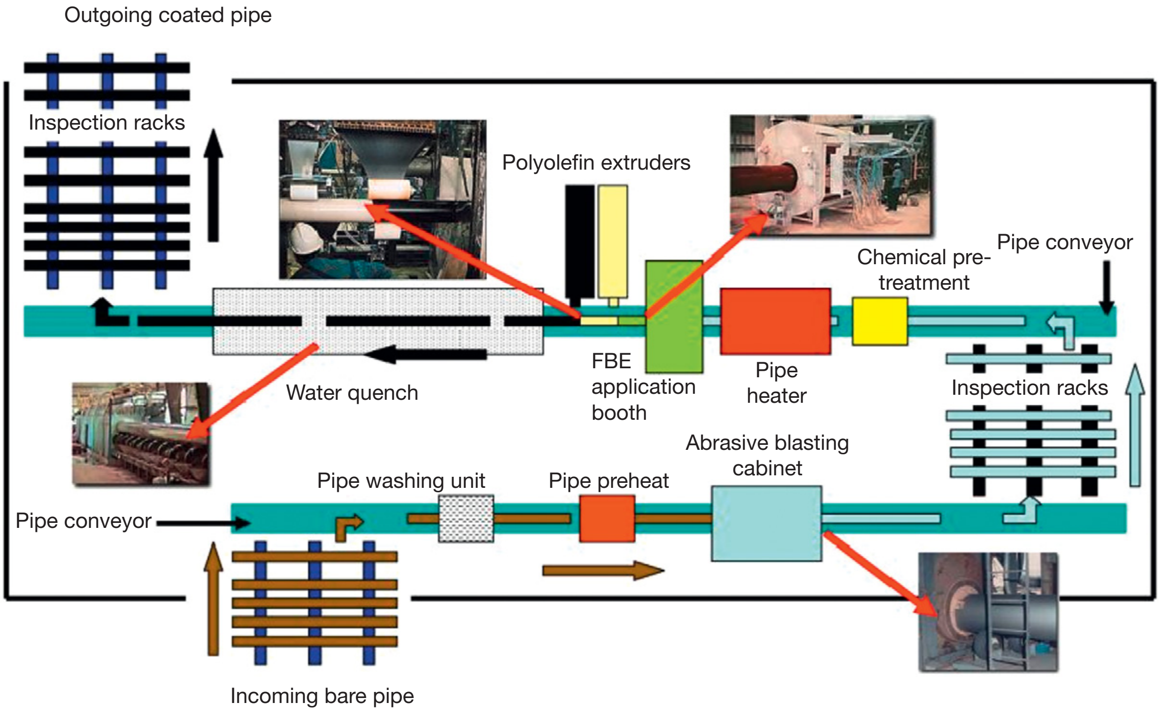

Figure 2 Schematic of a modern line pipe coating plant.

moved without damaging the coating. More will be said about this line pipe coating system later.

4.15.4.3.2 Coal tar and asphalt/bitumen enamels

Coal tar and bitumen were first used to protect pipelines from external corrosion in the 1870s. However, until the end of nineteenth century, these materials were not satisfactory as pipeline coatings, being, for the most part, brittle at low temperatures and soft and sticky at higher temperatures. Progressive developments included the incorporation of pulverized coal in coal tars and mineral fillers in both coal tar and asphalt coatings. These increased-viscosity formulations gave thicker films, but poorer wetting of the steel surface and necessitated the introduction of low-viscosity priming coats. The incorporation of reinforced glass inner wraps and asbestos felts, then to be replaced by the more modern glass fiber outer wraps, resulted in a much increased coating strength, and correspondingly, an enhanced protection against impact and soil stressing. Throughout all of the early developments, the importance of surface preparation on coating performance appears to have received little attention, the removal of oil and grease from the steel surface being the only major concern. Despite this apparent absence of rigorous substrate preparation, there are reports of coal tar enamel coatings on pipelines still being in good condition after more than 70 years in service. The early coatings were invariably applied on site using ‘over the ditch methods’ comprising various forms of line traveling equipment.

Only with the introduction of the more modern coatings, such as fusion bonded epoxies, in the early 1960s (see later), did the importance of good surface preparation and application under factory conditions to the consistency of asphalt or coal tar enamel coating performance become fully appreciated.

Hot-applied asphalt and coal tar coatings with their priming systems are now well classified, described, and specified in BS 4164:1967 (coal tar)[12] and BS 4147:1967 (bitumen),[13] but no guidance is given in these standards on the application procedure. The procedure commences with the application of a thin-film primer to the prepared pipe surface usually by spraying. Once the primer is dry, the hot molten enamel (200–240 °C) is poured over the rotating pipe. The hot enamel layer is immediately over wrapped with a continuous spiral of fibre glass inner reinforcement tape applied under just-sufficient tension to imbed the outer half of the still molten enamel layer. A second wrap or outer wrap of glass fiber preimpregnated with enamel is subsequently applied to produce a coating of 5 mm minimum thickness.[14,15]

Asphalt enamel coatings are generally regarded as inferior to coal tar enamel coatings because of their higher rate of water uptake and poorer mechanical strength, and this has resulted in the decline of the popularity of asphalt enamels in favor of coal tar over the past 30 years. Coal tar contains polycyclic aromatics, which are known carcinogens, and this has led to at least one major protective coating manufacturer’s removing coal tar completely from their protective coating formulations. For these reasons, the use of asphalt and coal tar enamel coatings on buried pipelines has largely been superseded by more modern alternatives described in the following sections.

4.15.4.3.3 FBE powder coatings

Fusion-bonded epoxy (FBE) powder, thermosetting resin, thin-film coatings were first used as standalone coatings on pipelines in the early 1960s. FBEs cure by chemical reaction of a curing agent with a base resin analogous to liquid epoxies, except that elevated temperatures (180–240 °C) are required for the chemical reaction to take place. Early formulations had poor flexibility and coated pipes could not be field bent. Over the next 20 years, developments in resin and curing agent formulations resulted in FBE coatings with improved flexibility without significant compromises in hot water and cathodic disbondment resistance.[16] Today, it is claimed that, there are in excess of 100 000 km of FBE-coated pipe installed throughout the world, mostly belowground. Originally developed as a single-coat system, typically 350–600-μm thick, more recent developments have included thicker dual-coating layer combinations. The main advantage of the dual-layer systems has been that they either increase the resistance to mechanical damage during transport and construction or improve the performance at high pipeline operating temperatures (>90 °C). As mentioned previously (see introduction to this section and **Figure 2**), FBE coatings have also become established as the primer layer in three-layer polyolefin coatings. A first layer of FBE enables polyolefin coating adhesion strengths of steel to be achieved, which are an order of magnitude higher than those possible without FBE. More will be said about polyolefin line pipe coating systems later.

One of the major advantages of FBE coatings is that they can be applied to line pipe, bends, fittings, and field joints, enabling just one coating system to be specified for the entire pipeline. This eliminates problems associated with the selection of the coating at field joints where, otherwise, two generically different coatings may have been applied to the parent line pipe on either side of the field joint, presenting significant coating compatibility problems.

FBE coatings are less forgiving of substandard surface preparation than are the reinforced enamel coatings, and a satisfactory long-term FBE coating performance is reliant upon a rigid adherence to established surface preparation and coating application procedures regardless of whether the coating is applied in the factory or the field.

The FBE application process is as follows: once the pipe surface preparation is complete, including chemical treatment (where specified), and the standard is acceptable, the pipe is induction heated to a temperature usually in the range 210–240 °C. The coating, which is in dry powder form, is electrostatically sprayed onto the rotating pipe using a number of low-pressure spray guns. The powder melts as it hits the hot pipe surface, thoroughly wetting the steel substrate. The axial and rotational speed of the pipe is carefully controlled to ensure that the correct coating thickness is applied using a set number of spray guns. Most FBE coating plants incorporate a reclaim system for collecting, cleaning, and recycling any surplus powder that has failed to make contact with the hot pipe. At such high substrate temperatures, the coating on the pipe cures within 1–2 min, and the coated pipe is immediately quenched, as it travels through a water cascade system. This allows the pipe to be handled and inspected very soon after the coating has been applied.

4.15.4.3.4 Polyolefin coatings

The early 1960s also saw the emergence of polyethylene as a commercial external pipeline coating system. Its inherent toughness was seen as the answer to the mechanical damage suffered by asphalt and coal tar enamel pipeline coatings, either during pipeline construction or in service. Poor or nonexistent grading of the pipeline trench backfill through rocky terrain can be particularly damaging for reinforced enamel coatings. The first polyethylene coatings were applied either as a powder by sintering or by hot extrusion as a film over a soft mastic adhesive. Neither of these application methods resulted in satisfactory adhesion of the coating to the steel substrate. In the case of the latter, the adhesive was brittle at temperatures close to 0 °C, and its viscosity was drastically reduced above 50 °C enabling the outer polyethylene sleeve to move relative to the pipe. Furthermore, the early grades of polyethylene were difficult to extrude and the coatings would suffer shrink back from the pipe ends, following application. The differential expansion rates between polyethylene and steel could also result in the crimping of the field joint coating at the joints, and the early polyethylene films also suffered environmental stress, cracking in service. Improvements in the grade of polyethylene used plus the development of a hard ethylene copolymer adhesive gave better adhesion quality and a more robust coating. A two-layer polyethylene/rubberized asphalt adhesive external pipeline coating system (yellow jacket®) is still used in the United States and Australia.[17]

A major break through in the adhesive bonding of polyethylene to steel came in 1982 with the advent of the three-layer FBE–polyethylene pipeline coating system. The development of a polyethylene copolymer that could cross link with FBE during the gel stage of the epoxy application process enabled peel adhesion strengths between polyethylene and steel to be obtained of a magnitude, perhaps never envisaged before.[18] As the FBE powder hits the hot pipe, it melts and becomes gel-like for a finite time, which is governed by the applied FBE powder coating thickness and the pipe temperature. For a typical FBE powder, the gel time can vary from 5 to 60 s depending upon these variables. Hence, the speed of the pipe plus the proximity of the extruders to the FBE application chamber must be carefully adjusted to ensure contact between the FBE in gel form and the polyolefin copolymer, and cross-linking between the two. The application process for three-layer polyethylene is shown in **Figure 2**. The application procedure for the FBE first layer is identical to that described earlier for standalone FBE coatings. The extrusion temperatures for the polyethylene adhesive and the polyethylene outer coating are normally in the ranges 190–210 °C and 200–240 °C, respectively. The FBE coating thickness is controlled by the number of electrostatic spray guns and the lateral and rotational speed of the pipe. For the polyethylene adhesive and top coat, the thickness is also governed by the speed of the pipe and also the width settings on the extruders. Typical specified individual layer thicknesses are FBE 75–350 µm, adhesive 400–600 µm, and top coat 1.5–2.5 mm.

The full coating system is cold water quenched to allow early handling and inspection.

An extension of this technology to polypropylene followed in 1989, and with it, the development, for the first time, of a coating with the ability to perform satisfactorily at operating temperatures up to 125 °C.[19] By comparison, the upper operating temperature limits for FBE–polyethylene coatings are normally in the range 70–80 °C. The factory coating application process for three-layer polypropylene is almost identical to that for three-layer FBE–polyethylene shown in Figure 2.

Three-layer coating systems combine the good adhesion of FBE to steel, with the enhanced mechanical and environmental degradation resistance of the modern thermoplastic polyolefins.

4.15.4.4 Field Joint Coatings

4.15.4.4.1 General

Before the advent of factory coating application to line pipe, asphalt and coal tar enamel coatings were applied on site over or adjacent to the pipeline trench. This meant that the field joints were not, in themselves, a specific concern, as the coating could be applied in a more or less continuous manner to long sections of welded pipe along the pipeline way before burial. It was only when these coating materials began to be applied to individual lengths of pipe under factory conditions that field joints became a subject of attention. At first, the field joints on coal tar and asphalt enamel factory-coated line pipe were coated in a manner analogous to the coating of the line pipe, that is, using hot enamel and fabric reinforcement applied as a full circumferential wrap. This archaic procedure has been largely superseded over the last 30 years by the application of cold-applied synthetic rubber adhesive backed PVC or polyethylene tapes (see Section 4.15.4.2.3), radiation cross-linked heat shrink sleeves (see Section 4.15.4.4.3), or liquid-applied coal tar modified two-pack epoxies and polyurethanes (see Section 4.15.4.4.2).

Liquid epoxies and polyurethanes, cold-applied tapes, and radiation cross-linked shrink sleeves have all been used to coat the field joints on FBE and two- and three-layer polyethylene-coated line pipe in recent times.

Three-layer FBE–polypropylene coatings are usually selected for the line pipe coating where a high resistance to mechanical damage is required and the operating temperature exceeds that, which can be handled satisfactorily by any of the alternative line pipe coating systems available and previously described. Correspondingly, it is usual to specify an analogous FBE–polypropylene coating system for the field joints in order to ensure that the performance of the field joint coating approaches that of the line pipe coating.

Driven by a need to achieve consistent field joint coating quality at economic production rates, the pipeline coating industry has made significant technological developments in field joint coating procedures in the last 20 years. Modern application methods necessitate the use of induction coils and invertors, fluidized beds, thermostatically controlled heaters, automated spray, or wrapping equipment plus diesel generators to provide the necessary power. All of the equipment needed is containerized and the containers are mounted on lorries or caterpillar-tracked vehicles, see Figure 3.

4.15.4.4.2 Liquid-applied field joint coatings

The major developments in solvent-free two-pack liquid epoxy and polyurethane coating technology

Figure 3 Typical field joint coating spread, including weatherproof shelters.

have already been mentioned in Section 4.15.4.1. These materials are widely used as field joint coating materials and are regularly applied using automated spray equipment of the type shown in Figure 4. The temperature of the separate components is thermostatically controlled inside furnished containers. The separate components travel to the spray head mounted on the carriage via a thermally insulated umbilical. A mixing chamber located just before the spray head ensures thorough mixing before application. A third process line in the umbilical allows the mixing chamber and spray head to be flushed with solvent to prevent them from becoming blocked between successive spray applications. During spraying, the spray head rotates around the pipe first in one direction and then in the other a sufficient number of times, depending upon the required coating thickness.

4.15.4.4.3 Radiation cross-linked heat shrink sleeves

The standard radiation cross-linked heat shrink sleeve comprises an expanded polyethylene backing with a heat-sensitive adhesive and is applied either over a steel surface primer or directly on to the field joint area. Heat is applied both before and after the application of the sleeve and care must be taken to ensure that the heating process does not damage the parent coating on either side of the field joint. Careful fitup and controlled uniform heating are essential to ensure uniform shrinkage and to avoid bubbling and blistering of the sleeve during the shrinking process. Although an open flame torch is the preferred method of both pre- and postheating by most applicators, induction heating provides a superior method of ensuring a uniform heat distribution at the preheat stage.

As with cold-applied tape wrappings, the components of polyethylene heat shrink sleeves remain thermoplastic after application, and their service temperatures are therefore limited.

In addition to their use on asphalt and coal tar enamel factory-coated pipe, heat shrink sleeves have also been used at field joints on FBE and two- and three-layer polyethylene-coated line pipe.

Recent developments have included an expanded polypropylene version for use with three-layer FBE–polypropylene factory-coated line pipe at high service temperatures (>60 °C). The application of this latter product requires a much higher heat input to the field joint area both before and following sleeve fitup but provides significantly improved levels of adhesion to both the pipe and the polypropylene factory coating at elevated service temperatures.

4.15.4.4.4 FBE powder coatings

Reference has already been made to the use of FBE as a field joint coating material for FBE-coated line pipe. The field application of FBE is similar, in most respects, to the factory application in that an induction coil is used to heat the field joint area to the required temperature (210–240 °C) before the powder coating is applied by low pressure air spray. The process requires a substantial amount of portable equipment, including a hinged induction coil (see Figure 5) and inverter and a fluidized bed, from which the airborne powder is conveyed to the

Figure 4 Application of a two-pack solvent-free liquid coating to field joints on large diameter pipe.

Figure 5 An induction coil being lowered into place over a prepared field joint on a large diameter pipe.

application jig. The application equipment comprises a hinged cylindrical frame, which fits around the field joint area and contacts the pipe via a number of wheels (see Figure 6). The frame is motorized so that it can be rotated around the pipe, first in one direction and then the other. The FBE powder is sprayed onto the hot pipe from a low-pressure air spray head mounted on the frame as the frame rotates around the pipe.

4.15.4.4.5 FBE–polypropylene

The introduction of the three-layer FBE–polyolefin coatings initially created a dilemma for field joint coating system specifiers as a few, if any, of the traditional field joint coating systems mentioned earlier adhere to polyolefin surfaces to a totally satisfactory degree, particularly at operating temperatures above ~40 °C. Correspondingly, the last 5–10 years have seen considerable development activity on behalf of the field joint coating specifiers and application contractors, to produce a field joint coating with the ability to match the performance of and be compatible with three-layer FBE–polypropylene line pipe coating.[20] As a result, six different field joint coating systems have been used. They may be summarized as follows:

1. Sintered polypropylene copolymer.
2. Coextruded polypropylene sheet.
3. Injection molded polypropylene.
4. Flame sprayed polypropylene copolymer.
5. Coextruded polypropylene tape.
6. Polypropylene heat shrink sleeve.

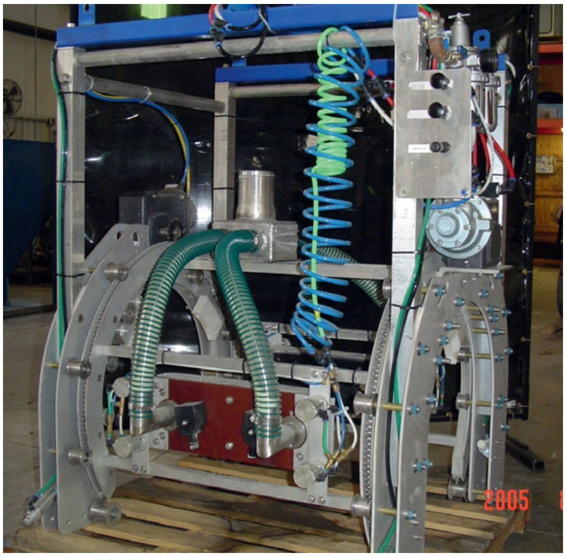

Figure 6 A typical coating application frame used for the application of FBE powder coatings at field joints. Courtesy by Offshore Joint Services, Houston, TX.

With the exception of the polypropylene heat shrink sleeve, which is described earlier, all of these systems incorporate the application of FBE as the first coating layer in the manner described earlier. This is followed immediately by a sprayed layer of polypropylene copolymer adhesive powder usually from a second coating head mounted on the FBE coating frame (see Figure 6). As with the factory application of three-layer FBE–polyolefins, the polypropylene copolymer must be applied within the gel time of the FBE powder in order to ensure adequate chemical cross-linking and a good chemical bond between the two. It is the subsequent and final step in the field joint coating procedure that differentiates between each of the first five polypropylene field joint coating types listed.

1. The sintered polypropylene copolymer field joint coating application method involves the buildup of the copolymer coating, by flock spraying as a dry powder, making use of the residual heat in the field joint to melt, and coalesce the copolymer particles. As polyolefins have a low thermal conductivity, the total coating thickness that can be achieved is limited usually to less than 1 mm without the application of additional external heat in between successive copolymer powder applications. In addition, the final copolymer layer may be porous because of a lack of fusion between adjacent particles of powdered polyolefin, which have failed to reach their melt temperature.

2. In the coextruded polypropylene sheet method, the field joint area is wrapped with a sheet of polypropylene–polypropylene adhesive coextruded sheet. Preheating of the sheet is required as is further heating of the field joint area to ensure good fusion between the sheet and the flock-sprayed layer of adhesive applied previously. Sealing of the longitudinal and circumferential edges of the sheet by plastic extrusion welding is also required, using a polypropylene consumable, see Figures 7 and 8. Although this method is capable of giving a sound field joint coating with properties equivalent to those of the line pipe coating, it is time consuming to apply it correctly. It has been superseded by a second generation extruded polypropylene copolymer sheet, which is capable of bonding directly to the field joint area, the line pipe coating, and itself. This can be applied as a complete wrap, overlapping the factory coating circumferentially and itself axially, and avoiding the need for extrusion welding.
3. The injection molding of polypropylene at field joints has been considered for buried pipelines, but to date, has been used exclusively on offshore pipelines. It requires bulky and sophisticated equipment to both melt the polypropylene and pump it into the mold, which fits around the field joint area, see Figure 9. It consumes a lot of energy and is expensive compared with the alternative systems available. Nevertheless, it gives an extremely robust field joint with properties almost identical to the factory coating on the line pipe.
4. Of all of the polypropylene field joint coatings that have been developed, flame spraying is perhaps the most versatile as, in addition to field joints, it can also be used to coat fittings and preformed bends at a wide range of coating thicknesses. During flame spraying, the polypropylene copolymer powder is blown through the center of a circular gas flame under inert-gas pressure. The pressure of the inert gas propels the heat-softened polypropylene particles toward the substrate. The softened particles impact on the pipe surface coalescing with themselves and the existing layer of copolymer adhesive, see Figures 10 and 11. The application is a highly skilled process, as the heat input to the substrate and the sprayed powder need to be carefully controlled in order to buildup the coating thickness without compromising the quality of the coating. Too much heat can result in a reduction in the long-term environmental stability of the finished coating.
5. The coextruded polypropylene tape is the most recent development and is an extension of the

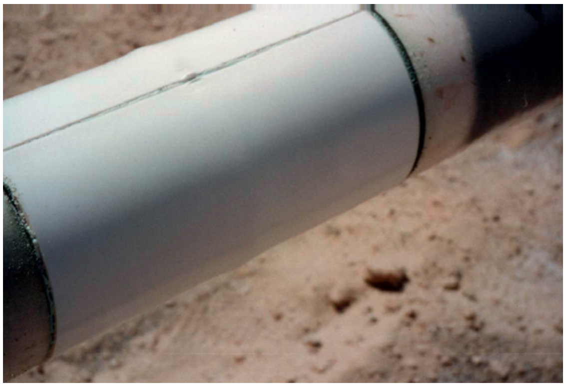

Figure 7 Coextruded polypropylene sheet in place over the field joint.

Figure 8 Final appearance after plastic welding at the horizontal and circumferential seams.

Figure 9 Injection molded polypropylene field joint coating application to pipe test pieces.

Figure 10 Flame spray application of polypropylene to pipeline field joints inside a weatherproof shelter.

Figure 11 Close up of flame spray polypropylene application trial. Note the completed trial field joint coating in the foreground.

coextruded sheet method. Being more flexible than the sheet, it is applied to the field joint as a spiral wrap in the same way as a cold-applied tape. Good adhesion between successive spirals of the tape, between the tape and the pipe, and between the tape and the line pipe coating requires preheating of the pipe and the tape, and postheating of the applied wrapping. An example of the automated polypropylene tape application equipment is shown in Figure 12.

Figure 12 Spiral wrapping of polypropylene coextruded tape.

4.15.5 Pipeline Coatings for Thermal Insulation

In certain circumstances, it may prove necessary for a buried pipeline to be thermally insulated. The justification for thermal insulation will be determined by the nature of the product being transported and/or the condition the product needs to be in, at the point of delivery. For multiphase hydrocarbon flow lines, flow assurance may well be the major concern. Maintaining the product temperature above a certain level will ensure that neither wax deposition nor hydrate formation will jeopardize the product flow rate over the projected lifespan of the project. For gas pipelines, the gas delivery specification may include a minimum temperature to be maintained to avoid liquid drop out and attendant problems with fluid handling at the reception facilities.

It is a common misconception that applying a thermal insulation system will also prevent external corrosion of the pipe. In practice, thermal insulation systems are invariably breached by moisture, resulting in localized corrosion rates well in excess of those to be anticipated if no thermal insulation system were in place. In addition, with thermal insulation, any applied cathodic protection is unlikely to be effective because of the high electrical resistivity of the thermal insulation. It is a good engineering practice, therefore, to ensure that steel pipelines are protected using one of the coating systems previously described, before thermal insulation is applied.

The most commonly used thermal insulation systems for buried piping usually employ polyurethane foam as the insulant with an outer protective layer. This outer layer needs to be mechanically robust as polyurethane foam has a low compressive strength and is easily damaged. A well established factory application system used for district heating purposes comprises a high-density polyethylene (HDPE) outer pipe arranged concentrically over the transmission pipe using spacers.[21] The annular space between the two pipes is filled with blown polyurethane foam. Temporary end caps ensure that the foam is not lost from the open ends of the HDPE pipe. At the field joints, the continuity of the thermal insulation must also be ensured. Various field joint insulation systems have been employed using some preformed polyurethane foam half shells with either heat shrink sleeves or cold-applied tapes to provide the outer protection for the foam. Because of the problems resulting from poor half shell fitup and correspondingly difficult field application procedures, track records with such systems have been indifferent, leading to severe corrosion in some cases. The use of such systems is difficult to justify on pipelines carrying hazardous products such as hydrocarbons.

A novel line pipe insulation system developed for a gas transmission pipeline in the early 1990s comprised of an FBE powder protective coating, 50–150 mm of polyurethane foam and an 8-mm poured polyurethane outer coating.[22] Using advanced polyurethane foam and liquid polyurethane application technology, each 12-m length of line pipe was first coated with FBE, then thermally insulated and the insulation was sealed. The insulation application process resulted in a tapered insulation profile at each end with an outer layer of solid polyurethane providing mechanical protection and a complete seal at the foam–coated pipe interface, see Figure 13. During pipeline construction, the field joints were coated with FBE in the traditional manner (see earlier) and then thermally insulated using preformed foamed polyurethane half shells fitted around the joint area, and then fully encapsulated in liquid polyurethane pumped into suitably sized molds; see Figure 14.

Figure 13 Thermally insulated line pipe awaiting pipeline construction.

Figure 14 Moulded thermally insulated field joints.

4.15.6 Pipeline Coating Rehabilitation

The decision to refurbish an external coating on an ageing, but still required, buried pipeline will normally be determined by an analysis of the results from a combination of the following: the leak history investigation, aboveground nonintrusive surveys (e.g., cathodic protection status), wall thickness measurements using intelligent pigs, and direct visual inspection of the condition of both the coating and pipe surface at a representative sample of bell holes. In many instances, the cost of excavation, pipe repairs and external coating refurbishment, and reburial will be prohibitive when compared against partial or total pipeline replacement. From a production standpoint, the consequences of taking the pipeline out of service for extended periods of time also need to be addressed.

Once the decision to refurbish the pipeline has been reached, the selection of the equipment needed for the removal of the old coating, for repairs to the pipe and for surface preparation and new coating application, has to be made at an early stage. This is so that questions regarding the extent of pipe excavation can be addressed and sufficient clearance can be provided around the pipe for all of the required equipment to function fully as intended.

Proprietary line travel equipment exists for refurbishing external coatings on long continuous pipeline sections. This equipment incorporates separate devices for the removal of old coatings, abrasive blasting of the steel surface, and application of the new coating. Preference should be given to the use of equipment that captures removed coating materials and spent abrasives for disposal, in accordance with local government legislation. Such equipment will often require a greater clearance around the pipe than usually required with manual methods of coating removal, surface preparation, and coating application.

The removal of old coatings will require one or more equipment types – scrapers, high-pressure water jetting (≤20 000 psi), abrasive blasting, etc., depending on the coating type and its condition. For optimum performance from the new coating, the final stage in the surface preparation process should be abrasive blasting. The ideal surface condition is one that complies with grade Sa2.5 in accordance with the visual standard in ISO 8501–1. An angular surface profile with minimum amplitude of 50μm is an additional advantage. Although some coating material suppliers would claim this requirement to be unnecessary,[23] careful consideration of the pipeline operating conditions, diameter, and projected further life is required before this advice is to be considered viable.

Protective coatings used for the refurbishment of old pipelines include all of those considered in the previous sections of this chapter with the exception of FBE powder and two- and three-layer polyolefins. The application of these coatings employs too high a level of sophistication to be practical on a scale larger than applicable to field joints only.

Today, liquid-applied epoxy and polyurethanes, mainly solvents-free (see Section 4.15.4.1) tend to be the coatings most regularly chosen for pipeline coating rehabilitation, as these provide superior mechanical damage resistance particularly at elevated temperatures (≥50°C), and the potential for longer-term external corrosion protection when compared with the alternatives available.[24,25] However, where partial refurbishment of existing coatings is to be carried out, over short sections such as at bell holes, for example, considerations of compatibility with the existing coating, or materials availability, for example, may justify the use of one of the different generic alternatives available.[26]

4.15.7 Quality Control During Coating Application

As with all protective coatings, the lifespan of those used to protect buried steel will be greatly enhanced by close attention to quality control during surface preparation and coating application. The cost of excavation and reburial on top of surface preparation and coating application emphasize the need to ensure that the risk of premature coating failure is avoided.

The cornerstone of good quality is the coating specification. The specification should define the following:

1. What exactly is to be coated in terms of the boundary limits and interfaces with other work.
2. The responsibilities of the different parties involved in the work, not just those actually carrying out the surface preparation and the coating application. This includes those responsible for ensuring that the specification is followed and all quality control activities are completed, which is usually the coating contractor, the supplier(s)/manufacturer(s) of the coating materials and those responsible for rectifying any damage caused during handling and transportation.
3. The reference standards to which the work is to be carried out, including all quality control measurements and test procedures.
4. The specific materials to be used, both for surface preparation and coating application and the number and thickness of each coat.
5. All quality control measurements and tests, their frequency, and the results to be achieved.

The location where the work is to be carried out may well have a significant bearing upon the specification. Surface preparation and coating application in the factory have the major advantages over site work of (1) being independent of the weather and (2) not being confined to daylight hours, as power and light are normally readily available. Equipment can be more easily maintained and testing and inspection can be more sophisticated and rigorous compared with work on site. The specification should recognize the conditions under which the work is to be carried out and the constraints imposed accordingly.

Quality control tests during surface preparation should include visual assessments of the surface condition both before and after preparation. Visual standards are available against which to compare the surface of the prepared item before application of the first coat.[3] Inspection of the surface should also include the assessment of dust[5] and where items to be coated have been stored in coastal areas, the level of salt contamination.[27] For abrasive blasted surfaces, quality control tests should include the measurement of the surface profile.[6]

Quality control tests on applied coatings should always include as a minimum coating thickness,[28] holiday detection,[29] and adhesion. There are several standard test methods available for determining the adhesion quality of thin-film coatings of limited flexibility.[30–32] For thicker, more flexible coatings, such as polyolefins, the quality of the adhesion is best determined using the peel adhesion test.[17] All of these standard adhesion test methods are destructive, requiring coating repairs at the test site. Thus it is often more convenient for coated test samples to be prepared in an identical manner so that the quality of the adhesion can be determined without incurring coating repairs on the work item. Such test samples can also be used to determine the resistance of the coating to cathodic disbondment.[17,18]

With multicomponent solvent free liquid-applied coatings such as polyurethanes and epoxies, it is also good practice to take cup shots of the mixed material at various stages during the coating application process. This is to verify that a consistent mixing ratio is being achieved within the coating manufacturer's recommended tolerances throughout the coating application process. The physical properties of the fully cured samples can be subjected to gravimetric analysis, hardness, tensile strength measurements, etc., to verify that the optimum mixing ratio is being achieved. This type of testing is particularly useful where the coating is being applied, using automated equipment such as that shown in **Figure 4** where there is a risk of the material going off ratio due to a component malfunction.

FBE powder coatings require a minimum substrate temperature for the coating to fully cure and provide optimum corrosion protection. It is therefore a standard practice to remove small samples of the applied coating from the substrate in order to confirm that full cure has been achieved. The removed coating samples are examined using a differential scanning calorimeter (DSC).[33] This equipment is able to determine the thermal characteristics of the coating, in particular, the glass transition temperature, from which the degree of cure can be ascertained.

It is very common for structures manufactured from steel and buried underground to have a design life in excess of 30 years. A sound coating selection process, good surface preparation, and coating application practice supported by a rigorous quality control system are necessary at construction if such aspirations are not to prove unrealistic.

References

1. National Association of Pipe Coating Applicators. Bulletin 18–99. Application Procedures For Concrete Weight Coating Applied by the Compression Method to Steel Pipe http://www.napca.com/
2. Steel Structures Painting Council. Specification SP1 Solvent Cleaning. http://www.sspc.org/
3. International Standards Organisation. ISO 8501–1: Preparation of Steel Substrates Before Application of Paints and Related Products.
4. Steel Structures Painting Council Specification SP8 Pickling. http://www.sspc.org/
5. International Standards Organisation. ISO8502–3: Preparation of steel substrates before application of paints and related products – Tests for the assessment of surface cleanliness – Part 3: Assessment of dust on steel surfaces prepared for painting. (Pressure sensitive tape method.)
6. International Standards Organisation. ISO 8503–1: Preparation of Steel Substrates Before Application of Paints and Related Products – Surface Roughness Characteristics of Blast-Cleaned Steel Substrates Part 1: Specifications and Definitions for ISO Surface Profile Comparators for the Assessment of Abrasive Blast-Cleaned Surfaces.
7. International Standards Organisation. ISO 8502–4: Preparation of steel substrates before application of paints and related products – Tests for the assessment of surface cleanliness – Part 4: Guidance on the estimation of the probability of condensation prior to paint application.
8. BS EN 10289: Steel tubes and fittings for onshore and offshore pipelines – External liquid applied epoxy and epoxy-modified coatings.
9. BS EN 10290: Steel tubes and fittings for onshore and offshore pipelines – External liquid applied polyurethane and polyurethane-modified coatings.
10. ANSI/AWWA C209: Cold Applied Tape Coatings for Special Sections, Connections and Fittings for Steel Water Pipelines.
11. Bates, C. R. 15th International Conference on Pipeline Protection Proceedings, Aachen, Germany, 29–31 October. BHR Group Limited, The Fluid Engineering Centre, Cranfield, Bedfordshire, UK, 2003; p 33.
12. BS 4164: 1967: Specification for coal tar-based hot-applied coating materials for protecting iron and steel, including a suitable primer.
13. BS 4147: 1967: Specification for bitumen-based hot-applied coating materials for protecting iron and steel, including suitable primers where required.
14. National Association of Pipe Coating Applicators. Specification and Plant Coating Guide 1-65-94 thru 17–98. http://www.napca.com/
15. ANSI/AWWA C203: Standard for coal tar protective coatings and linings for steel water pipelines – Enamel and tape – Hot applied http://www.awwa.org/
16. Neal, D. *Fusion Bonded Epoxy Coatings. Application and Performance*; Harding & Neale: Texas, 1997.
17. CAN/CSA Z245.21-02: External Polyethylene Coating For Pipe (System A) http://www.csa.ca/contact/
18. CAN/CSA Z245.21-02: External Polyethylene Coating For Pipe (System B) http://www.csa.ca/contact/
19. Waterton, K. C.; Woolf, L.; Fowler, C. M.; Palmer, A. C. NACE Canadian Region Western Conference Proceedings; Calgary: Alberta, February, 1990; pp 20–22.
20. Fairhurst, D.; Willis, D. *J. Prot*. Coat. Linings 1997.
21. Socotherm/Socologstor. Adria, Italyhttp://www.socotherm.com/
22. Gower, S.; Fairhurst, D. *Oil Gas J* **1992**, *219*(8), 49–63.
23. Weber, T. J. 15th International Conference on Pipeline Protection Proceedings; Aachen, Germany, Oct 29–31; BHR Group Limited, The fluid Engineering Centre. Cranfield: Bedfordshire, UK, 2003; pp 337.

24. Norman, D.; Swinburne, R. 13th International Conference on Pipeline Protection Proceedings, Edinburgh, UK, Sep 29–Oct 1; BHR Group Limited, The fluid Engineering Centre. Cranfield: Bedfordshire, UK, 1999; pp 199.
25. John, R. 15th International Conference on Pipeline Protection Proceedings, Aachen, Germany; Oct 29–31 Papers presented at 15th International Conference on Pipeline Protection. BHR Group Limited: Cranfield, 2003; pp 331.
26. NACE Technical Committee Report Item No 24202: Coatings for repair and rehabilitation of the external coatings on buried steel pipelines July 1999.
27. ISO 8502–6: Preparation of steel surfaces before application of paints and related products – Tests for surface cleanliness – Part 6: Sampling of soluble impurities on surfaces to be painted – Bresle Method.
28. ASTM B499: Test method for measurement of coating thickness by the magnetic method: Nonmagnetic coatings on magnetic basis metals.
29. ASTM G62–87: Standard test methods for holiday detection in pipeline coatings.
30. ASTM D 6677: Standard test method for adhesion by knife.
31. ASTM D3359: Standard test method for measuring adhesion by tape test.
32. ISO 4624: Paints and varnishes – Pull-off test for adhesion.
33. CAN/CSA Z245.20–06: External Fusion Bonded EpoxyCoating For Steel Pipe (System A) http://www.csa.ca/contact/

4.16 Inspection of Paints and Painting Operations

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Abbreviations

BSI British Standards Institute
ICorr UK Institute of Corrosion
ISO International Standards Organisation
NACE National Association of Corrosion Engineers

4.16.1 Introduction

It is not always easy to apply the concepts of quality control, which have become routine on coating production lines, to new steel structures. In many steelwork fabrication shops, much of the day-to-day throughput does not require a high-performance paint system to be applied. For most major new constructions, however, a protective coating system is needed to ensure the best possible corrosion protection. It is for these types of project that painting inspection is an essential requirement. The full performance of any protective coating system will only be realized if it is applied to a well prepared surface, under suitable environmental conditions. The paint system must have good adhesion to the substrate and must be free from defects. Each individual coat must also be applied at the correct film thickness. For most protective coating projects, therefore, the skill and diligence of the blasters and sprayers involved will determine whether a particular paint system will provide the long-term corrosion protection required or fail prematurely. Inspection of both surface preparation and each stage of paint application by a suitably trained, and preferably independent, painting inspector is the best way to ensure that the protective coating of new constructional steelwork or the maintenance painting of an existing asset is successful. The primary purpose of painting inspection, therefore, is to ensure that the coating specification is met fully by the contractor, on time and, wherever possible, on budget. Inspection is never a substitute for adequate supervision, nor is it a satisfactory way of overcoming the shortfalls of a badly written specification.

4.16.2 Duties of the Painting Inspector/Types of Inspection

4.16.2.1 Introduction

The duties of a painting inspector will be determined by the scope of his engagement. As a minimum, the inspector will check and report that all elements of the coating schedule have been completed satisfactorily.

The painting inspector's duties will usually extend beyond this, however, to ensuring that the specification, as written, is met fully and that, if any deficiencies in workmanship are discovered, they are brought to the attention of the client at the earliest possible moment. It is important to note that a painting inspector has no power to order work to stop, unless the power has been delegated to him, which is unlikely.

For the high-performance protective coating systems specified today, some projects will require the maximum level of surface preparation and will benefit from continuous inspection at every stage. For many minor painting programs, however, less intensive inspection may be adequate. It is the responsibility of the client to determine the appropriate level of inspection needed and to make provision accordingly. One of the following three possible levels of inspection is usually selected:

- *Full inspection:* The inspector is on site throughout the project to witness that preparation and painting work complies with the requirements of the specification, at all times. Work is inspected at each stage of the program and only when formal approval has been given is the next coat of the paint system applied, for example. For the largest projects, more than one inspector may be needed.
- *Intermittent inspection:* The inspector is not on site at all times and observes work in progress at agreed intervals. Intermittent inspection is, by its nature, less costly than full inspection, but is also less complete.
- *Occasional inspection:* The inspector observes the initial work by the applicator and agrees the standard to be achieved for subsequent work. He then returns to site infrequently to inspect the work done and to check that the agreed standard of application has been maintained. Although the cost savings that can result on inspection are considerable, the overall benefit to the client technically is very much reduced.

The level of inspection chosen will be determined, most often, by the nature of the project and the complexity of the protective coating work involved. A strong case for full inspection on a minor maintenance painting program, therefore, or a relatively undemanding new construction project can rarely be made.

4.16.2.2 Inspection Records and Reports

The compiling of adequate inspection reports is an important aspect of a painting inspector's duties. Inspection reports not only provide a record of progress on a contract, but also become a source of useful information when maintenance painting is due. In the event of an unexpected coating failure, an investigation into the cause can often be moved forward more quickly, when access to inspection records can be provided.

The painting inspector will usually complete a daily inspection record and provide a weekly summary report. The inspector's daily and weekly records will be issued to the client and may also be circulated to other interested parties, as required. The permanent record of progress provided by the inspector will be retained on file by the client and, subsequently, will become an integral part of the archived project documentation. A daily paint inspection report will usually include, as a minimum, information on

1. The general weather conditions and the local ambient temperature, relative humidity, dew point, and steel temperature.
2. The location of the work area that day and the number of blasters and painters involved.
3. Whether surface preparation work is being undertaken and, if so, the condition of steel surface before and after preparation, together with details of the method of surface preparation used.
4. Whether paints are being applied and, if so, the product reference and the batch number of each paint coating, together with a note on their method of application.
5. While inspecting, a description of the inspection methods and instruments used, together with the results obtained.
6. Whether the requirements of the specification have been met fully in the areas inspected and, if not, the nature and extent of any noncompliance.

4.16.2.3 Additional Inspection Services

Most specialist providers of painting inspectors will usually offer a number of additional services, when required, including

1. Constructive comments on the coating specification, wherever appropriate, to alert the client to any ambiguities, inaccuracies, or omissions.
2. A preliminary discussion on the painting contractor's proposed method of working and any foreseen health and safety hazards.
3. Liaison with the paint manufacturer directly on the coating products selected and any critical requirements for their successful application.
4. The drafting and presentation of an inspection schedule, setting out precisely how and at what stages of the coating program, inspection will be carried out and reported.

5. Where there is a requirement for precontract inspection of the blast cleaning and painting contractor's facilities and equipment, specialist providers of painting inspection will usually offer this preliminary service as well.

The purpose of a precontract inspection at works is to confirm that the facilities are adequate and that the equipment that will be used has been well maintained and is currently in good working order. The cleanliness of the paint shop and the tidiness of the paint store can often give a telling indication of the seriousness with which the workforce takes the surface preparation and protective coating of steelwork.

The purpose of a precontract inspection on site is to ensure that any scaffolding and access platforms needed will provide safe access to the work, that compressors are in good working order, that any temporary sheeting needed will be effective and that extraction equipment is available to remove solvent vapors and dust particles.

4.16.2.4 The Importance of Precontract Discussions

Precontract discussions involving the client, the main contractor, the steel fabricator, the painting contractor and, in particular, the painting inspection company can be invaluable, as they provide a forum in which potential problems with the program, as a whole, can be 'ironed out' before any work on the project commences. Precontract discussions enable agreement to be reached on, for example

1. Any features of the design that, if not modified, may be difficult to coat successfully.
2. Arrangements and facilities for the testing of materials, including coatings.
3. The measures to be adopted to reduce coating damage during handling, transport, and subsequent erection on site.
4. The chain of authority to be followed in cases of difficulty or disagreement.

When the minutes of such discussions are recorded accurately, they can serve as a useful adjunct to the contract.

4.16.3 The Training and Certification of Painting Inspectors

The protective coating of constructional steelwork has advanced technically in recent years, and as a consequence, industry pressure for the development and provision of programs of formal training and certification of painting inspectors has increased. Initiatives over the last two decades, in both the United Kingdom and the United States, first to certificate painting inspectors and then to provide enabling training programs have culminated in the Institute of Corrosion's (ICorr) Painting Inspector Scheme in the United Kingdom and the National Association of Corrosion Engineers' (NACE) Coating Inspector Training and Certification Scheme. For both of these now well established certification schemes, candidates attain initially a Level 1 Certificate. With further study and verifiable work experience, inspectors can then progress to Level 2 and, ultimately, to Level 3 certification. For many high-profile, new construction projects and for programs of critical coating maintenance on important assets, the use of NACE- or ICorr-certificated painting inspectors has become very much the preferred option.

4.16.4 Specific Aspects of Inspection

4.16.4.1 Initial Inspection of Liquid Paints and Blast Cleaning Abrasives

Supplies of the liquid paints specified for a project and the blast cleaning abrasives to be used for surface preparation should be checked by the painting inspector initially to ensure that they are of the correct type, that they are being stored correctly, and that they have been supplied in sufficient quantities to allow surface preparation and paint application to proceed smoothly. For some projects, it may be a requirement of the inspection contract for tests on the paints to be performed, in a laboratory, to a predetermined schedule. In this event, the inspector may be required only to take the liquid samples needed for the testing program and forward them to the test house. Typically, the routine checks made by a painting inspector on liquid paints delivered to a steel fabricator's works, or to site, for a project will include the following:

1. Checking that the paints delivered correspond to the coating products specified, for example, manufacturer, product type, product name, and color.
2. Checking that the paints delivered are of the correct type for the method of application to be used, for example, spraying grade or brushing grade.
3. Checking that the paint store does not suffer from extreme temperatures and is both safe and secure.

Typically, the temperature inside the paint store should be above +3 °C and below +30 °C.

4. Checking that the paints have been delivered in sufficient quantities for the amount of steelwork to be coated (and, if not, that further supplies can be obtained quickly when needed).

The painting inspector should record the batch numbers and expiry dates of all paints held in the store. The subsequent withdrawal of paint, when coating work commences, should then be controlled and monitored by the inspector to ensure that the stocks are always rotated properly and that the paint used is always well within its shelf life.

When cans of paint are opened for use, the inspector will observe that they are first mixed thoroughly and that any settlement, if found, can be reincorporated into the bulk of the paint easily and satisfactorily. For two-pack paints, the inspector will observe that the base and hardener are always mixed together in the correct proportions and that any induction period before application is observed. The inspector will also ensure that any two-pack paints that cannot be applied within their pot life are discarded.

In cold weather conditions, it may be necessary to add small amounts of solvents to paints in order to lower their viscosity for spraying. Whenever any addition of thinners are made to the paints, the inspector will normally note the additions being made and ensure that they do not exceed, in percentage terms, the recommendations given by the manufacturer. Guidance on the preparation of samples of paints and coatings for testing and their subsequent examination may be found in BS EN ISO 1513.[1]

When abrasive blast cleaning is the method of surface preparation used, the inspector may be required to carry out checks on the abrasive itself. The extent of inspection of an abrasive will be determined by the requirements of the specification. As a minimum, however, it would be usual to check that the abrasive is of the correct type, for example, steel grit, steel shot, or copper slag, that it is of the correct particle size, and that it is dry. In the unlikely event that either the purity or the cleanliness of the abrasive is in doubt, then tests may be needed to determine, for example, the presence of foreign matter and the presence of water-soluble contaminants.

Guidance on test methods for metallic blast-cleaning abrasives may be found in BS EN ISO 11125[2] and guidance on test methods for nonmetallic blast-cleaning abrasives may be found in BS EN ISO 11127.[3]

4.16.4.2 Inspection of Surface Preparation

The primary objective of surface preparation is to produce a clean surface to which the first coat of a paint system will adhere well. For protective coating systems on steelwork, an inspector may be asked to examine the initial condition of the steel surface and then to examine the condition of the steel surface after preparation for painting. He will usually inspect prepared surfaces for physical cleanliness, chemical cleanliness, and surface roughness (profile) by visual assessment and appropriate test methods. Constructional steelwork is prepared for painting, most often, by abrasive blast cleaning, hand- and power-tool cleaning, or high-pressure water jetting. Fabrication of the steelwork is likely to have involved both cutting and welding operations.

Inspection of the surface preparation of steelwork prior to painting has been assisted greatly by the development of relevant national standards over the past 40 years; most notably in Sweden, the United Kingdom, and the United States. These national standards have led, in more recent years, to the publication of four series of International (ISO) Standards. In the United Kingdom, these multipart ISO Standards have been issued by BSI as BS EN ISO 8501–8504. The second edition of a general introduction to these BS EN ISO Standards, BS 7079,[4] provides a concise overview of their scope and content. The inspector's working standards for the surface preparation of steelwork are laid out in Parts 1 to 4 of BS EN ISO 8501.

BS EN ISO 8501-1 specifies a series of rust grades and preparation grades (subsequent degrees of visual cleanliness) for uncoated steel surfaces. The various rust and preparation grades are defined by written descriptions and by photographs that are representative examples. There are twenty eight photographs in total. Four rust grades of uncoated steel, designated A, B, C, and D and three series of preparation grades, designated Sa, St, and Fl, according to the method of surface preparation used, are described and illustrated.

For abrasive blast cleaning (Sa series), four preparation grades are designated as follows:

- Sa 1 Light blast-cleaning;
- Sa 2 Thorough blast-cleaning;
- Sa 21/2 Very thorough blast-cleaning;
- Sa 3 Blast-cleaning to visually clean steel.

For hand- and power-tool cleaning (St series), two preparation grades are designated as follows:

- St 2 Thorough hand- and power-tool cleaning;
- St 3 Very thorough hand- and power-tool cleaning.

For flame cleaning (Fl), there is only one preparation grade, namely

- Fl Flame cleaning.

BS EN ISO 8501–1 is an important inspection tool. It enables the inspector to compare the appearance of uncoated steel, and the same steel after it has been prepared for painting by one of these methods, with internationally agreed written descriptions and representative photographic examples.

A number of different abrasives may be used to blast clean steelwork. If the abrasive used is nonmetallic, dark in color, and becomes embedded in the surface profile, it can alter the visual appearance of the surface finish. In contrast, some hard, metallic abrasives can create an apparently darker surface finish as a result of shadows in deep-sided pits. To assist the inspection of such surfaces, a further six photographic examples of such effects have been included in BS EN ISO 8501-1, as an informative annex.

BS EN ISO 8501-2:2001 complements BS EN ISO 8501-1, and in a similar way, provides written descriptions and representative photographic examples of steel surfaces after the localized removal of previous paint coatings. BS EN ISO 8501-2 provides detailed guidance on the visual inspection of surface preparation in, for example, a maintenance painting program where the complete removal of all previously applied coatings may not be required.

Welds, cut edges, and minor imperfections in steelwork are often starting points for corrosion. Inspection of the surface preparation of these areas, prior to paint application, is assisted by BS EN ISO 8501-3. The standard defines three preparation grades for making steel surfaces with imperfections suitable for application of paints and related products. For each grade, requirements for the preparation of commonly found imperfections are tabulated and are also illustrated with line drawings.

While dry abrasive blast cleaning, and to a lesser degree, low-pressure water/abrasive blast cleaning are still used widely for the surface preparation of steelwork, the use of high-pressure water jetting has increased in recent years, as it offers an effective method of removing rust, previous coatings, foreign matter, and water-soluble contaminants, all at the same time.

BS EN ISO 8501-4 is a new standard that has been developed to stand alongside BS EN ISO 8501-1 and provide a comparable tool for the visual assessment and inspection of initial surface conditions, preparation grades and flash rust grades on steelwork prepared for the application of paints and related products by high-pressure water jetting. The preparation grades are again defined by written descriptions and photographs that are representative examples within the tolerances of each grade, as described in words. There are 23 photographs in total.

Specifically, five initial surface conditions are defined, three of which are applicable to degraded paint coatings and two of which are applicable to damaged prefabrication primers. Three preparation grades for each initial surface condition, after partial or full removal of previous paint coatings by high-pressure water jetting, indicate the degree of cleaning required. Three grades of flash rusting of the steel surface that develop when high-pressure water jetting is the method of preparation used are also specified.

4.16.4.3 Inspection of Surface Profile

Preparation of steelwork by abrasive blast cleaning not only removes surface contaminants, such as rust and mill scale, but also introduces a surface profile. The magnitude of the surface roughness (peak-to-trough height) that results when this is the method of surface preparation selected will be determined by the particle size of the abrasive used and the air pressure at the nozzle. Measurement of surface profile and checks each day on the air pressure at the nozzle of the blast cleaning equipment being used will form part of the inspector's duties on many contracts. Ensuring that the specified surface profile is achieved is important. If the profile is too low, the adhesion of the coating may be compromised. If the profile is too high, there is a danger that the tallest peaks will not be covered adequately by the coating and so will corrode in service.

Surface comparators are used most commonly today by inspectors for assessing the grade of surface profile on steel surfaces. In parts 1–4 of BS EN ISO 8503, the requirements for these comparators are specified and two laboratory procedures for their calibration are defined. BS EN ISO 8503 is in five parts, and in part 5, an alternative method of measuring surface profile on site with the aid of replica tape and a micrometric gauge is defined.

Two surface profile comparators have been specified in BS EN ISO 8503: Reference Comparator 'G' is for grit-blasted surfaces and Reference Comparator 'S' is for shot-blasted surfaces. Each comparator has four segments (numbered 1–4) each of a peak-to-trough height defined by nominal values and associated tolerances. For Comparator ‘G’, for example, the nominal values and tolerances are as follows:

Segment	*Nominal reading (μm)*	*Tolerance (μm)*
1	25	3
2	60	10
3	100	15
4	50	20

‘Fine’, ‘medium’ and ‘coarse’ profiles are then defined, as follows:

- Fine: Profiles equal to segment 1 and up to but excluding segment 2;
- Medium: Profiles equal to segment 2 and up to but excluding segment 3;
- Coarse: Profiles equal to segment 3 and up to but excluding segment 4.

In use, the inspector compares the blast-cleaned surface to be graded visually with the segments on the appropriate comparator and determines whether the work surface is ‘fine,’ ‘medium,’ or ‘coarse.’ This relatively simple approach to grading surface profile is generally adequate.

Many specifications continue to rely on the final inspection of the blast-cleaned surface as the procedure for acceptance. This approach is reasonable as long as the blast-cleaning equipment used has been well maintained and is functioning satisfactorily. When problems do arise with the equipment, however, the inspector may be required also to check the air pressure at the blasting nozzle and the quality of the compressed air emitted. The checks required are simple and can be performed quickly.

In order to check the air pressure at the nozzle of the blast-cleaning equipment, the hypodermic needle of a special pressure gauge is inserted into the blasting hose, close to the nozzle, and the pressure is measured. The small hole made in the hose by the hypodermic needle seals quickly when the needle is withdrawn and the subsequent operation of the hose is not compromised. Typically, the air pressure required at the nozzle is 80–100 psi (550–690 kPa).

The compressed air itself must be clean and dry, in order not to contaminate the blast-cleaned steel surface. The quality of the compressed air can only be checked by the inspector, with the abrasive supply switched off. A clean white cloth (or filter paper) placed in front of the nozzle allows the inspector to see unwanted water and oil contaminants. If any contamination is found, the inspector will then require the contractor to check his equipment and rectify the problem.

4.16.4.4 Inspection of Steel Surfaces for Chemical Cleanliness

For steelwork that will be coated and then exposed, in service, to aggressive industrial and marine environments, the chemical cleanliness of the steel is of equal importance to the physical cleanliness of the surface and the surface roughness. The BS EN ISO 8502 Series of Standards addresses this requirement and defines field and associated laboratory test methods to determine both the physical and chemical surface cleanliness of steel substrates before application of paints and related products. There are currently nine parts to the 8502 Standard.

The test methods in 8502 describe suitable field procedures for the extraction of soluble ferrous salts and the analysis, on site, of the extract for the presence of ferrous ions, chloride ions, and sulfate ions. In the case of chloride ions, a procedure intended only for use in the laboratory is also provided. The field test methods include the use of ion-detection tubes for chlorides, measurement of conductivity for water-soluble salts, and measurement of turbidity for water-soluble sulfates. There is also a field test method for the refractometric determination of moisture; guidance on estimating the probability of condensation on a steel surface and a simple procedure, involving the use of pressure-sensitive tape, to determine whether a steel surface prepared for painting is free from dust and debris.

While it may be a requirement for an inspector to test steel surfaces for the presence of soluble ferrous salts after preparation for painting, it may not be necessary for him/her to determine whether soluble ferrous salts, when found, are chlorides or sulfates, for example. In such situations, the potassium ferricyanide test, first described in British Standard Code of Practice 5493,[5] is still often relied upon. For this test, an area of the blast-cleaned steel surface is moistened with distilled water, and when the surface is almost dry, a test paper that has been impregnated previously with a dilute aqueous solution of potassium ferricyanide is placed on the steel surface. Deep blue spots (a Prussian blue complex is formed) develop quickly on the yellow test paper wherever ferrous salts are detected. The test method is qualitative and very sensitive. It provides an easily conducted pass/fail procedure for routine site inspection work.

4.16.4.5 Monitoring of Ambient Conditions

An important aspect of the inspection of both surface preparation and paint application is the monitoring of ambient conditions. Specifications may require abrasive blast cleaning to be carried out under ambient conditions that will ensure that the freshly blast-cleaned surface will not deteriorate quickly and will be preserved until paint can be applied a few hours later. Specifications may also require paint to be applied only under defined ambient conditions.

The painting inspector will normally monitor the air temperature, the steel temperature, and the relative humidity, two or three times during the working day. On some projects, continuous measurement of air temperature and relative humidity may be provided by the client and the data logged electronically. For most projects, however, the monitoring of ambient conditions remains the duty of the inspector. Typically, a painting inspector will use a whirling hygrometer to determine the relative humidity and also to measure the air temperature. A contact thermometer will be used to measure the surface temperature of the steel. From the relative humidity, the dew point will then be calculated and recorded.

Specifications will usually require that steel temperatures should be at least 3 °C above the dew point, in order to avoid the possibility of moisture condensing on the work surface during preparation and painting operations. Relative humidity not greater than 85% and ambient air temperature not less than 4 °C are also usually prescribed. Ambient conditions outside these limits or deteriorating weather conditions that, it can be anticipated, will lead quickly to rainfall or relative humidity and air temperature outside the prescribed limits will be reasons for the inspector to advise the painting contractor to cease blast cleaning and painting.

4.16.4.6 Inspection during Paint Application

Monitoring paint application is an important aspect of a painting inspector's duties. The inspector will record climatic conditions; ensure that the paint is applied in accordance with that specified; and note that the correct method of application is being used. Application methods will depend on the type of coating product, the nature of the substrate, and the surface area to be painted. For most constructional steelwork, the method of paint application will be airless spray.

Paints almost always need to be mixed before being applied, to ensure that there has not been any settlement of pigment in the can. In the case of two-pack paints, thorough mixing of base and hardener, in the correct proportions, is essential. Thinning of some paints may also be needed prior to spray application, especially in colder winter months. The inspector will ensure that all of these procedures are carried out correctly and at the appropriate times.

A primer needs to cover the entire surface profile of the steel substrate and each coat of the paint system applied subsequently needs then to cover all areas completely and needs to be as uniform as possible in thickness. During paint application, therefore, the inspector may wish to measure the wet-film thickness of paint being applied. He should need only to make such checks infrequently, when the work is progressing smoothly, as the painters themselves should be checking wet-film thicknesses regularly as they proceed. Simple measurements with a wet-film thickness comb gauge are all that is required.

As the paint application progresses from primer to intermediate coats and finish, the inspector will ensure that each over-coating interval stated on the paint manufacturer's technical data sheet is observed and that any particulate contamination on intermediate painted surfaces, should it occur, is removed and is not painted over. The diligence of the painting inspector during the paint application phase of a project will influence, to a significant extent, the potential of the paint system ultimately to achieve its expected level of performance in service. A good rapport with the painting supervisor is always beneficial during this phase of the work program.

4.16.4.7 Inspection after Paint Application

When the paint system has been built up satisfactorily and has cured, the painting inspector can progress to the final phase of his inspection duties. Key requirements such as total dry film thickness, adhesion between individual coats, and curing of the paint system, as a whole, will all now need to be checked and reported. In addition, the inspector may be required to check the coating system for freedom from pinholes and to conduct other specific tests, if required by the client.

Methods for the measurement of paint film thickness are described in BS EN ISO 2808.[6] The procedure for checking nominal dry-film thickness is usually agreed between the inspector and his client.

Unless agreed otherwise, individual dry-film thicknesses of less than 80% of the nominal dry film thickness will not be acceptable. Values between 80% and 100% of the nominal dry-film thickness are acceptable, provided that the overall average value is equal to or greater than the nominal dry-film thickness. It is usually recommended that the dry-film thickness of a coating should not exceed three times the nominal film thickness.

These guidelines give the inspector a framework in which to analyze his/her results and to define any areas where coatings have been found to be either too thin or too thick. It is generally not the case that 'thicker is better.' Excessively thick films of paint and coatings will usually sag and may take an excessively long time to achieve full cure.

Good adhesion of the primer to the substrate and good adhesion of subsequent coats one to another is a prime requirement of a protective coating system and will usually be checked by the painting inspector. Guidance on cross-hatch adhesion tests is provided in BS EN ISO 2409[7] and guidance on pull-off adhesion tests is provided in BS EN ISO 4624.[8] As all adhesion testing is destructive, the inspector will not carry out more adhesion tests than required. On many painted surfaces, a simple St Andrews Cross cut with a sharp knife will give a good indication of poor paint adhesion and prompt the inspector to investigate further.

The full properties of a protective coating system will not be achieved if the paints have not cured properly. An inspector will usually use a solvent-rub test to determine whether, or not, a coating has achieved a full cure. Methyl ethyl ketone is the solvent used most often. Any softening or loss of coating during the test indicates an incomplete cure.

In addition to specific coating tests, an inspector will also examine painted surfaces visually for good coverage, uniformity of color, and for obvious defects such as sagging, wrinkling, and pinholes. The absence of pinholes is particularly important where protective coating systems are required to provide chemical resistance and barrier properties. Checks for the presence of pinholes can be made by the inspector with a low-voltage or a high-voltage pinhole detector, as appropriate. High-voltage pinhole detectors need to be used with caution and understanding. If the voltage is set too high, there is a risk that the instrument will introduce small holes in the coating rather than detecting them.

4.16.5 Concluding Remarks

The demand for well trained, certificated painting inspectors has increased in recent years, as the importance of thorough surface preparation has been recognized fully and advances in paint technology have led to the introduction of new generations of protective coating systems. Painting inspection can not only provide quality control throughout a painting contract but also ensure that the specification is met and that the client's expectations for robust corrosion protection are delivered.

References

1. BS EN ISO 1513: *Paints and Varnishes: Examination and Preparation of Samples for Testing*; British Standards Institution: London, 1995.
2. BS EN ISO 11125: *Preparation of Steel Substrates before Application of Paints and Related Products: Test Methods for Metallic Blast-Cleaning Abrasives*; British Standards Institution: London, 1997.
3. BS EN ISO 11127: *Preparation of Steel Substrates before Application of Paints and Related Products: Test Methods for Non-Metallic Blast-Cleaning Abrasives*; British Standards Institution: London, 1998.
4. BS 7079: *General Introduction to Standards for Preparation of Steel Substrates before Application of Paints and Related Products*; British Standards Institution: London, 2008.
5. BS 5493:1977: *Code of Practice for Protective Coating of Iron and Steel Structures against Corrosion*, Appendix G. British Standards Institution: London, 1977. [Obsolescent, Superseded largely by BS EN ISO 12944].
6. BS EN ISO 2808: *Paints and Varnishes: Determination of Film Thickness*; British Standards Institution: London, 2007.
7. BS EN ISO 2409: *Paints and Varnishes: Cross-Cut Test*; British Standards Institution: London, 2007.
8. BS EN ISO 4624: *Paints and Varnishes: Pull-Off Test for Adhesion*; British Standards Institution: London, 2003.

4.17 Paint and Coating Failures and Defects

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4.17.1 Coating Failures and Defects

Coatings can be very complex materials and their principal constituents are resin, tinting pigments (colorants), and solvent. Other ingredients can be extender pigments (fillers), nonreactive diluents, thixotropes, curing agents, catalysts, film forming agents, etc. Not all coatings will contain all of the different types of ingredients, but most are complex mixtures that have to be carefully formulated to satisfy the design and performance criteria. The percentage by weight of a particular ingredient will vary between the type of coating and the supplier of the coating.

The coatings, single pack, two pack, or three pack, are mixed in the correct proportions for the two and three pack materials prior to application as a thin film by various methods. The application can take place at different levels of surface preparation under a wide range of environmental conditions that can vary from one part of a structure to another.

The applied coating after curing would be expected to retain its cosmetic qualities and perform and protect the substrate from the general elements such as variable levels of heat, cold, and humidity as well as wind, rain, sunlight, and oxygen. Coatings may also be subject to special conditions such as immersion in seawater or chemicals such as a specialist tank lining.

Considering all the variables, it is inevitable that some coatings fail earlier than anticipated. Coating defects may also be expected; however, this may not necessarily lead to a coating failure. For example, alligatoring may be considered as a coating defect, but the system will still perform, and therefore, this defect does not necessarily constitute a coating failure.

In general terms, a coating failure can be related to formulation deficiencies, application problems, inadequate surface preparation, or external factors such as exposure to an environment to which it is not resistant. Coating failure is not always attributed to a single source, and often a number of contributing factors have to be considered in evaluating the breakdown mechanism. Coating defects normally fall into three categories: those arising during application such as sagging and cissing, those arising after application but prior to service entry such as blushing and wrinkling, and those appearing after entry into service such as chalking.

Probably the most common reasons for coating failure are inadequate surface preparation in terms of applying the coating to a lower standard of preparation than it was designed for, inadequate correction of steel defects, and inadequate removal of soluble salts. The coating failure could therefore be attributed to poor workmanship and/or incorrect specification requirements.

Application-related failures are common, particularly in the industrial and marine coatings industry where basic application faults, such as inadequate film thickness, misses, lack of stripe coating, incorrect over coating times, and inadequate curing times and temperatures prior to entry into service, frequently lead to early coating failure.

Coating selection is important; many coating failures being related to improper coating selection for the specific environment to which it would be exposed, that is, the use of a product for a purpose for which it was not designed. Environments can also change with time, a prime example being tank linings on chemical carriers where variables of different cargoes, different temperatures, and tank cleaning on a cyclic basis place great stress on the coating system.

No matter how carefully a coating is formulated, laboratory testing is relied upon, to a great extent, to simulate in-service conditions and the results, together with those from field trials, are used to evaluate the coating prior to launch. Laboratory testing, however, cannot cover all of the in-service variables, and in addition, has to be of an accelerated nature; hence, only long-term use of the product is likely to highlight any formulation problems.

The following examples of coating failures and defects have been chosen to illustrate how coatings can fail prematurely or exhibit application defects. The photographs are examples only, as the type of failure or defect could manifest itself in a different way. It is not intended to make the reader an instant 'paint expert,' as the establishment of a failure mechanism is often difficult because of the number of potential contributory factors.

4.17.1.1 Adhesion Failure (Delamination/Flaking)

Description: Flaking, generally accepted as the detachment of the paint system from the substrate, and delamination, used to describe intercoat detachment in a multicoat system, are both forms of adhesion failure where a coating has failed to adhere to the substrate or the underlying paint coating.

Probable causes: Adhesion failures can be as a result of either internal stress alone or internal stress plus the exacerbating effect of one or more other factors. The contributory factors could be related to formulation, inadequate surface profile, surface contamination, exceeding overcoating times, application to a glossy paint surface, amine bloom, incorrect surface preparation, and differential expansion/contraction of the paint coating and the substrate, particularly in the painting of timber.

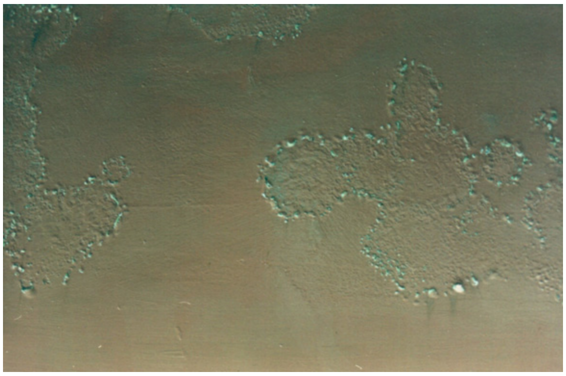
4.17.1.2 Alligatoring (also Known as Crocodiling)

Description: Very large (macro) checking or cracking that resembles the skin of an alligator or crocodile. Cracks may penetrate to the undercoat, but generally not down to the substrate.

Probable causes: Internal stresses in the coating where the surface shrinks faster than the body of the paint film. Can be caused by excessive film thickness and limited paint flexibility and on paint systems having a flexible undercoat with a hard topcoat.

4.17.1.3 Aluminum Corrosion

Description: Blistering and/or lifting of the paint coating because of the formation of aluminum corrosion products under the paint.



Probable causes: Pinholes in the coating, porosity of flame-sprayed aluminum, or insufficient coating thickness.

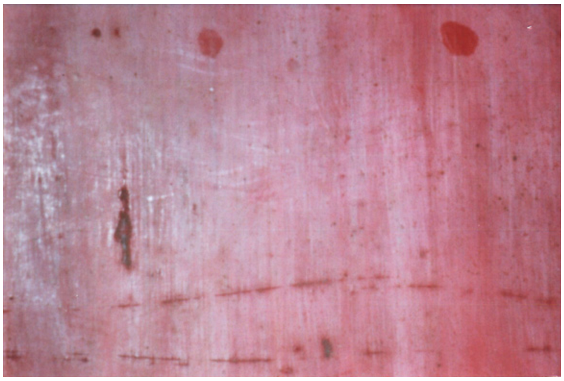
4.17.1.4 Bittiness

Description: Film contaminated by particles of paint skin, gel, flocculated material, or foreign matter, which project above the paint surface to give a rough appearance. The term *Peppery* is used when the bits are small and uniformly distributed.

Probable causes: The main cause is contamination within or on the surface of the paint film by paint skin, gelled particles, airborne sand and grit, or contamination from brushes or rollers.

4.17.1.5 Bleaching (also see Fading)

Description: Total loss of the color of a coating.



Probable causes: Bleaching due to weathering or chemical attack.

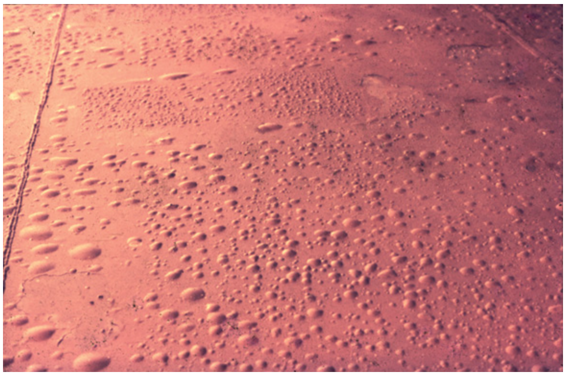
4.17.1.6 Bleeding (also Called 'Bleed Through')

Description: Staining of a paint film by diffusion of a soluble, colored substance from the underlying paint to give undesirable discoloration or staining. Very often, this is seen where bitumen or tar-based products are overcoated with alkyd-based or other conventional topcoats. It can also occur with emulsion paints.

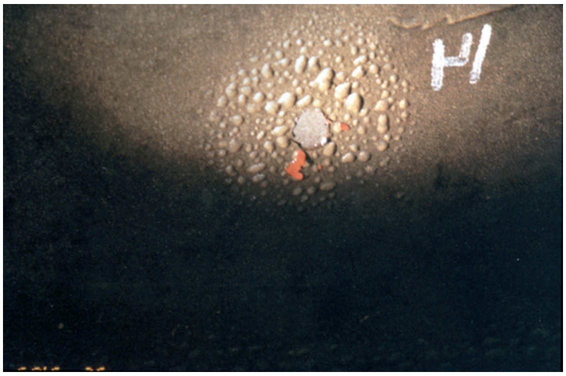
Probable causes: 'Bleed through' is generally a full or partial redissolving of the previous coat and can happen when strong solvents are used in the topcoats.

4.17.1.7 Blistering

Description: Dome-shaped projections in the dry paint film through local loss of adhesion from the underlying surface. The blisters may contain liquid or gas, or may be dry.

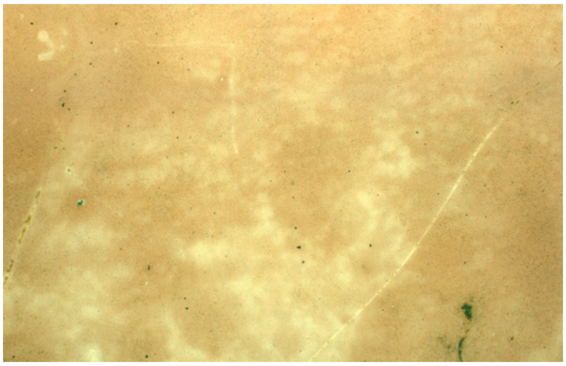


Probable causes: Osmotic blistering is commonly associated with the presence of soluble salts, soluble pigments, retained solvents, or the absorption and retention of low molecular weight water-miscible solvents, typically from the carriage of chemical cargoes. Nonosmotic blistering, commonly described as cathodic blistering, is often seen as a circular pattern of blisters around a coating defect where the substrate is exposed. Nonosmotic blistering can also occur due to a cold-wall effect producing condensation. Where coatings are used with cathodic protection, hydrogen production is possible and the resultant hydrogen vapor pressure could produce blisters.



4.17.1.8 Bloom (Blush)

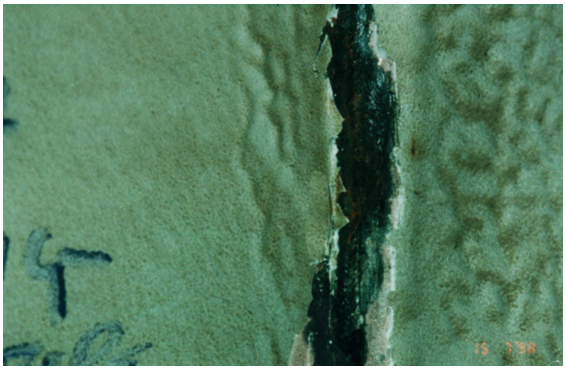
Description: A hazy deposit on the surface of the paint film, resembling the bloom on grape resulting in a loss of gloss and a dulling of the color.



Probable causes: Paint film exposed to condensation or moisture during curing (common phenomenon with amine-cured epoxies). Incorrect solvent blends can also contribute to blooming.

4.17.1.9 Bridging

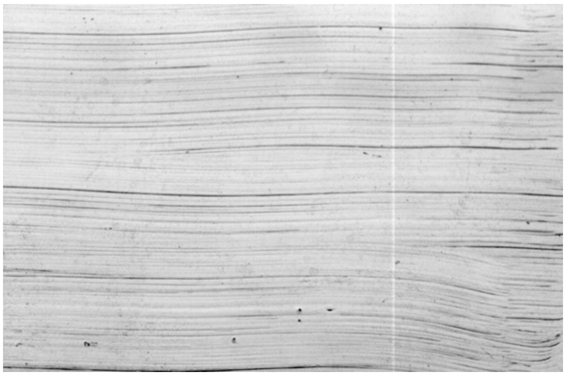
Description: The covering over of unfilled gaps such as cracks or corners with a film of the coating material. This causes a weakness in the paint film, which may crack, blister, or flake off.



Probable causes: Poor application, high-viscosity paint, or failure to brush paint into corners and over welds.

4.17.1.10 Brush Marks (also Laddering, Ladders, or Ropiness)

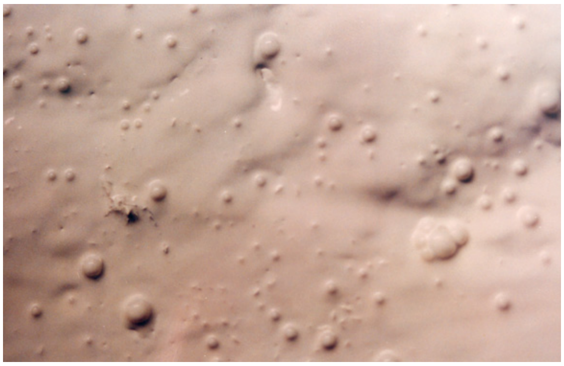
Description: Undesirable ridges and furrows that remain in a dry paint film after brush application where the paint film has not flowed out. May be found as a cross-hatch pattern (laddering) where alternate coats have been applied in opposite directions. Pronounced brush marks are known as ropiness.



Probable causes: Viscosity of material may be too high for brush application, incorrect thinners used in the paint, inadequate mixing, or poor application technique. Two-pack paints may have exceeded their application pot-life.

4.17.1.11 Bubbles or Bubbling

Description: Bubbles within a paint film appear as small raised blisters and may be intact or broken to leave a crater. They are found in excessively thick paint films, especially if spray applied, and also with roller application. This defect should not be confused with blistering.



Probable causes: Trapped air/solvent within the coating, which is not released before the surface dries. They are also associated with factory-applied coatings where application is by dipping, electrodeposition, or roller coating.

4.17.1.12 Chalking

Description: A friable, powdery layer on the surface of a paint film, often associated with a change of color or fading. Chalking rates vary with pigment concentration and choice of binder, and are a known characteristic of certain paints for example, amine- or amide-cured epoxy paints.

Probable causes: The deterioration of the paint binder on exposure to weathering and/or UV light, leaving a powdery layer of underbound pigment at the surface.

4.17.1.13 Checking (also see Cracking)

Description: Fine cracks that do not penetrate to the substrate. Some checking can be so minute that it is impossible to see without magnification.

Probable causes:	Typically, a formulation and/or a specification problem where the paint has limited flexibility. Surface stresses are developed, which cause the surface of the paint film to become brittle and crack.

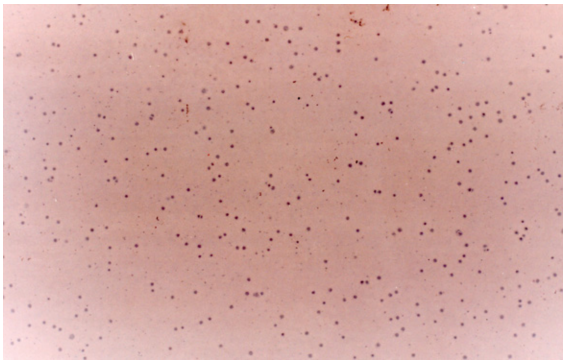
4.17.1.14 Cheesiness (Soft Coating)

Description:	The coating remains soft, even after a prolonged drying time.

Probable causes:	Wrong mixing ratio for two-pack paints, too low a drying/curing temperature, or excessive solvent retained within the coating.

4.17.1.15 Cissing (also Referred to as Crawling)

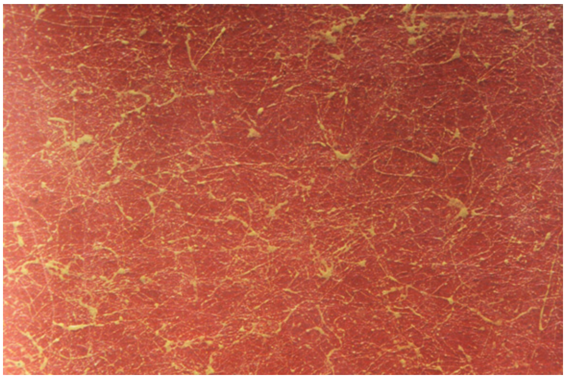
Description:	Surface breaks in a wet paint film, where the paint has receded to expose the underlying substrate, because the paint is unable to wet-out the substrate. The individual areas involved can be very large.



Probable causes:	Surface contamination by either moisture or foreign matter such as oil, grease, silicone, etc. and is also known to happen when incorrect solvent blends have been used.

4.17.1.16 Cobwebbing

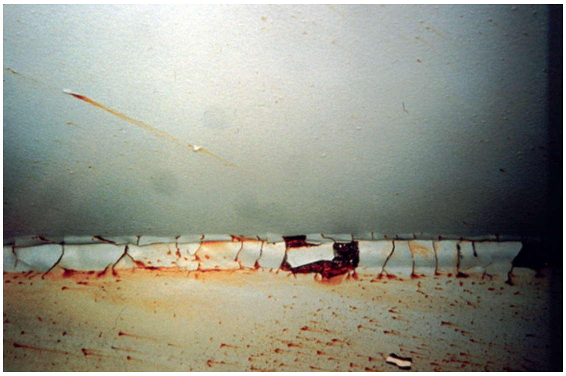
Description:	The production of fine filaments instead of normal, atomized particles when some solutions of high-molecular weight polymers are sprayed.



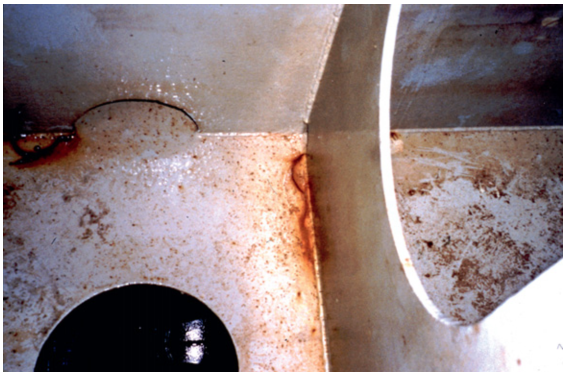
Probable causes:	Too high a viscosity with some types of polymer solutions.

4.17.1.17 Cracking (also see Alligatoring and Checking)

Description:	Paint coatings with visible cracks, which generally penetrate to the substrate. Cracking comes in several forms and ranges from minor cracking to severe cracking.

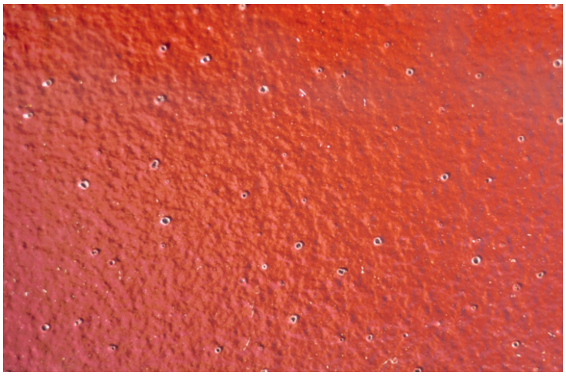


Probable causes:	Cracking is generally related to internal stress within the body of the coating. Factors involved in cracking are formulation, high film thickness, thermal cycling, substrate geometry, substrate movement, ageing, absorption/desorption of water or chemicals, and inadequate surface profile. One or more contributory factors exacerbates the internal stress in the coating.



4.17.1.18 Cratering

Description:	The formation of small bowl-shaped depressions in the paint film, which are not to be confused with cissing.



Probable causes:	Trapped air bubbles that have burst to leave small craters as the coating dries and the coating has had insufficient time to flow out as a uniform film.

4.17.1.19 Crowsfooting (also see Wrinkling)

Description:	The development of small wrinkles in the paint film, which occur in a pattern resembling that of a crow's foot.

Probable causes:	Usually due to the surface drying rapidly to form a skin, which then wrinkles as the solvent slowly evaporates from the soft, underlying paint layer.

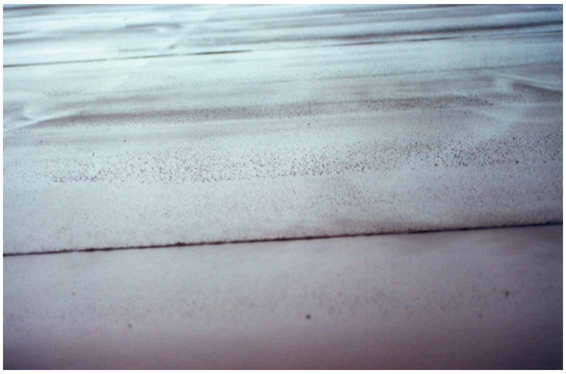
4.17.1.20 Delamination (also see Adhesion Failure and Flaking)

Description:	Loss of adhesion between coats of paint.

Probable causes:	Provided compatible paint materials have been used, delamination defects are generally related to contamination between coats, including amine bloom, exceeding overcoat times, or application to a glossy surface.

4.17.1.21 Dryspray (also see Overspray)

Description: Rough and uneven finish to the surface of the paint film where the particles are insufficiently fluid to flow together and are often poorly adhered.



Probable causes: Incorrect spray application, for example, gun distance. Also associated with fast drying products and too high an application temperature.

4.17.1.22 Efflorescence

Description: The formation of a white (powdery) substance on the substrate of concrete, brick, masonry, and plaster, or on the surface of the paint. The efflorescence, which comes from the migration of salts, can lift the paint from the substrate where impermeable films are involved.

Probable causes: Soluble salts within the substrate. Moisture brings the salts to the surface of the substrate, resulting in coating adhesion failure, or they deposit on the coated surface where more porous films are involved.

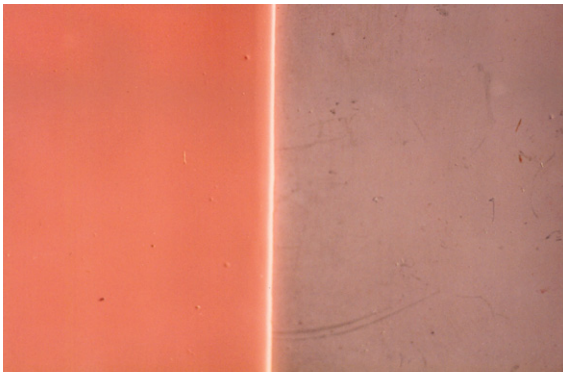
4.17.1.23 Erosion

Description: Selective removal of paint films from areas of high spots.

Probable causes: The wearing away of the paint film by various elements such as rain, snow, wind, sand, etc. and found to be more prominent on brush applied coatings because of the uneven finish.

4.17.1.24 Fading (also see Bleaching)

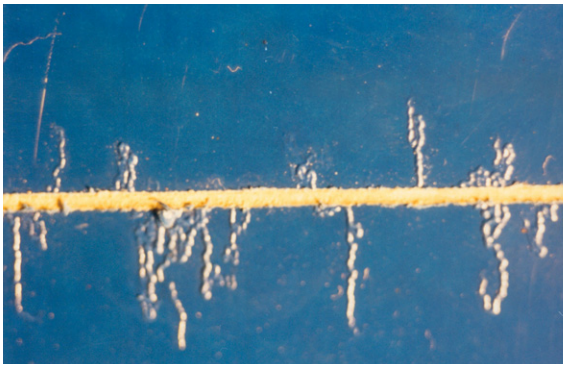
Description: Gradual decrease in the color of the paint when exposed to sunlight/weather, which tends to occur more rapidly in the presence of moisture and may be accompanied by a loss of gloss. In some situations, it may resemble chalking but without the powdery surface.



Probable causes: Incorrect pigmentation, the use of organic pigments, atmospheric contamination, or a porous substrate.

4.17.1.25 Filiform (Corrosion)

Description: Random threads of corrosion that develop beneath thin lacquers and other coating films from a growing head or point. Often seen on old ‘tin’ food cans with thin electroplating, but also seen on painted aluminum and other surfaces.



Probable causes: Contamination on the metallic substrate or damage to the coating, which allows a corrosion cell to develop at the tip and advance under the coating.

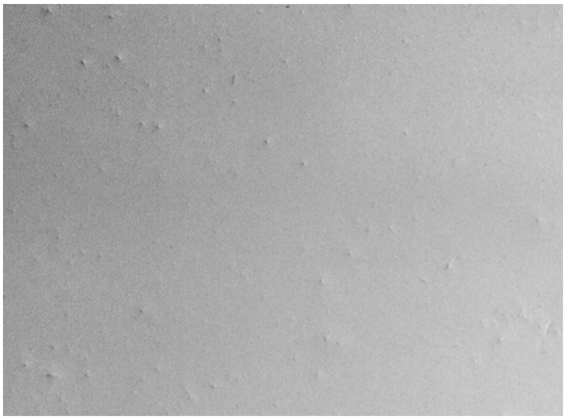
4.17.1.26 Flaking (also see Delamination and Adhesion Failure)

Description: A form of adhesion failure where the paint flakes from the substrate, which is a familiar sight on wood substrates and on galvanizing.

Probable causes: Incorrect paint system used. Either none or incorrect pretreatment used for certain substrates such as nonferrous or galvanized. May also be attributed to differential expansion and contraction of paint and substrate, for example, wood, and can be the result of the ageing of the paint system.

4.17.1.27 Flocculation

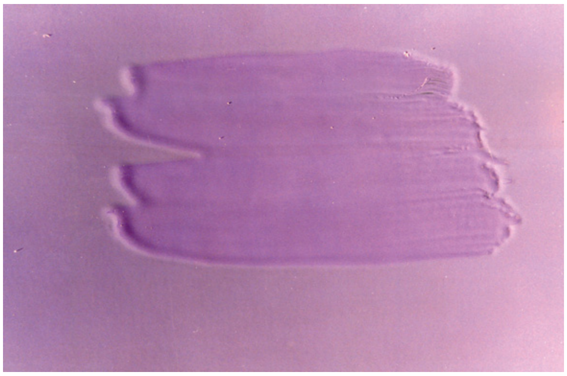
Description: The development of loosely coherent pigment agglomerates in a coating material.



Probable causes: Nonuniform pigment dispersion, which results in the pigments forming agglomerations, arising from the use of unsuitable thinners, inadequate mixing, or inappropriate surfactants.

4.17.1.28 Flooding (also see Flotation)

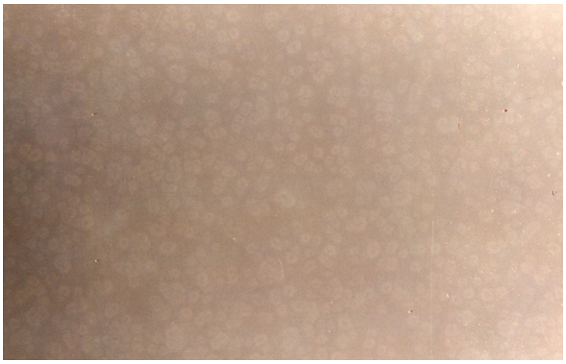
Description: A defect that appears soon after application due to pigment separation, the visual appearance being a change of color where the affected area dries to a different shade than that of the remainder of the surface.



Probable causes:	Pigment separation and settlement.

4.17.1.29 Flotation (also see Flooding)

Description:	Occurs in colored materials containing mixtures of different pigments and closely resembles flooding, although a mottled or streaky effect is produced when the different pigments separate.



Probable causes:	The mottled effect, which is visible to the eye, is caused by the separation of the different colored pigments and may also result from the addition of excessive thinners.

4.17.1.30 Grinning (also see Grinning Through)

Description:	The underlying surface is visible through the paint film due to inadequate hiding power of the coating material. It is sometimes called grinning-through and is often seen where dark colors are overcoated with lighter colors.

Probable causes:	Low film thickness of topcoat, poor opacity and covering power of topcoat, or strong color of the penultimate coat.

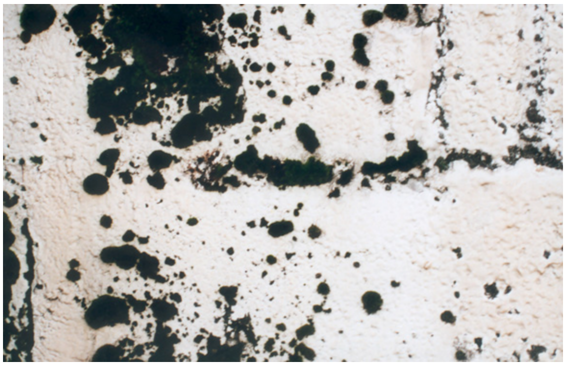
4.17.1.31 Grit Inclusions

Description:	Particles of grit and dust embedded within or adhering to the surface of the coating system.

Probable causes:	Failure to remove used blast cleaning abrasive from the surface prior to the application of the paint. Contamination of the wet primer or undercoat with abrasive from other blast-cleaning operations, wind blown grit particles adhering to the topcoat, or poor housekeeping.

4.17.1.32 Growth (on the Surface of Paint Film)

Description:	Growth and attachments of natural organisms to the surface of finished products, which vary in form, size, and lifespan, for example, algae, mosses, etc.



Probable causes:	Generally, natural organisms within moist, wet, or immersed conditions. Growth may continue after attachment.

4.17.1.33 Incorrect Coating System

Description:	An unsuitable or incompatible coating system has been used that results in rapid failure.

Probable causes:	The use of incompatible or unsuitable coating materials.

4.17.1.34 Impact Damage (Star Cracking)

Description:	Cracks that radiate from a point of impact.

Probable causes:	Impact damage to a relatively brittle coating, which is often seen on glass fiber reinforced plastics.

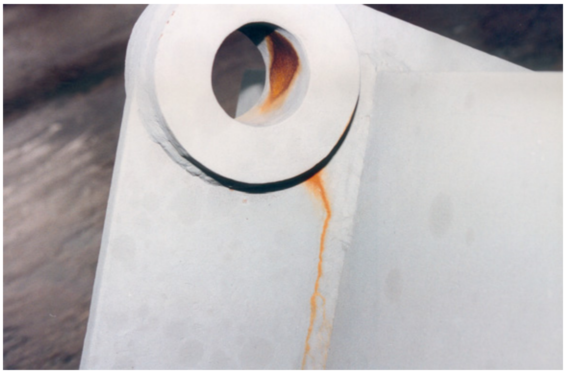
4.17.1.35 Lamination or Shelling (of Cast Iron)

Description:	The photograph shows flaking or shelling of sections of cast iron from the surface that has been overpainted, which has led to subsequent rust staining.

Probable causes:	Failure to remove or treat delaminated sections prior to the application of the coating system.

4.17.1.36 Misses/Skips/Holidays

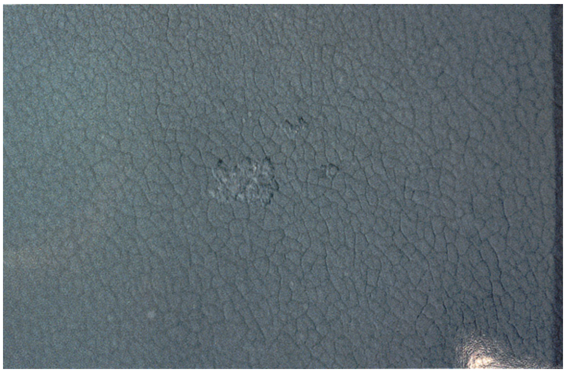
Description:	Exposed areas of substrate or previous coat when the intention was to coat the entire area. Could be confined to a single coat in a multicoat paint system.



Probable causes:	Poor application techniques or a lack of quality control, or both.

4.17.1.37 Mud Cracking

Description:	The dried paint film has the appearance of a dried-out mud bath where the cracks can vary in size and amount, but form a network of cracks.



Probable causes: Generally, overapplication of heavily pigmented primers such as inorganic zinc silicates or water-based coatings, although it can occur with other systems that are thickly applied.

4.17.1.38 Orange Peel (also Known as Pock-Marking)

Description: The uniform pockmarked appearance, in particular, of a sprayed paint film, in which the surface of the paint film resembles the skin of an orange.

Probable causes: Failure of the paint film to flow out. Usually caused by poor application techniques or by incorrect solvent blend.

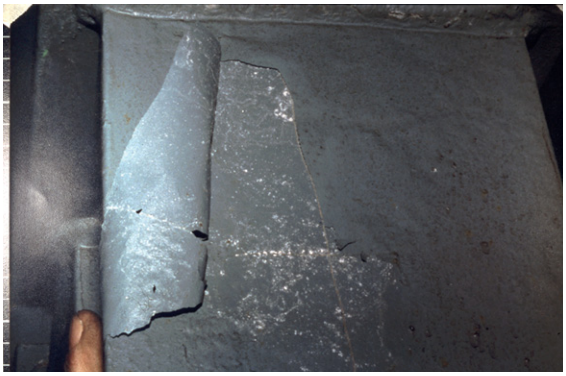
4.17.1.39 Overspray (also see Dry spray)

Description: Small particles of paint adhering to the surface of the previous dry coat, generally adjacent to the area being sprayed, and often appears as a pebbly surface, similar to dry spray.

Probable causes: Particles of wet paint falling outside of the spray pattern, too rapid a solvent evaporation, or spray application under windy conditions.

4.17.1.40 Peeling (also see Flaking)

Description: Similar to flaking, although peeling tends to involve soft and pliable coatings that can be pulled away from, or spontaneously flake away from the substrate or from between coats because of loss of adhesion.



Probable causes: Peeling is due to a reduction in bond strength of the paint film because of inadequate surface preparation, contamination, or incompatibility of coats.

4.17.1.41 Pinholes

Description: The formation of minute holes in the wet paint film during application and drying due to air or gas bubbles that burst giving rise to small craters or holes, which fail to coalesce before the film dries.

Probable causes: Solvent or air entrapment within a paint film, which is a common problem when coating porous substrates such as zinc-filled primers, zinc silicates, and metal-sprayed coatings. Pinholes can also be caused by incorrect spray application or incorrect solvent blend.

4.17.1.42 Rain Damage – Water Spotting

Description: Craters and water marks on the surface of the paint film, caused by rain or heavy condensation.

Probable causes: Rain falling on a freshly painted surface causes craters and/or water marks to form on the surface before it has hardened sufficiently.

4.17.1.43 Rippled Coating

Description: A rippled effect on the surface of the paint.

Probable causes: Strong wind blowing across the surface of wet paint causes it to ripple and this occurs on the underside; the ripples can hang down in the form of small stalactites. Can also be caused by poor application techniques.

4.17.1.44 Runs or Sags (also Described as Curtains or Wrinkles)

Description: The downward movement of paint that appears soon after application to vertical surfaces because of excessive paint application and appears as tears, or in severe situations, it may be described as curtains.

Probable causes: Overapplication of paint, addition of excessive thinners, lack of or wrong curing agent, and in extreme circumstances, could be a formulation problem.

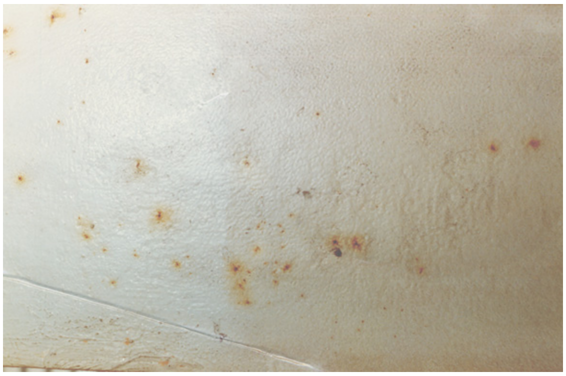
4.17.1.45 Rust Rashing (to Thermal Spray Coating)

Description: Spots of rust develop within the pores of sprayed metal coating, similar to rust spotting of a paint film.

Probable causes: A phenomenon that can develop on aluminum thermal-sprayed coatings soon after application when moisture is absorbed into the metal coating and reacts with the ferrous substrate. Early sealing with an appropriate coating prevents such events.

4.17.1.46 Rust Spotting (also Referred to as Rash Rusting)

Description: Fine spots of rust that appear on a paint film, usually a thin primer coat, which frequently starts as localized spotting, but rapidly spreads over the surface.



Probable causes: Where the rust spotting emanates from the substrate, low film thickness, pinholes, and defects in the steel such as untreated laminations, or too high a surface profile causing penetration of peaks through a paint film are probable causes. Where the rust spotting does not penetrate to the substrate, it is probably from the metallic contamination of a coated surface by ferrous grinding debris.

4.17.1.47 Rust Staining

Description: A red/brown staining on the surface of the paint.

Probable causes: Water run-off from a rusty surface adjacent to a soundly coated surface. Rust staining occurs when the rust is wetted-out and contaminated water runs over and discolors other items or locations. It is usually more of an eyesore than a defect where the coating itself may not be defective, only stained.

4.17.1.48 Saponification

Description: The coating appears to be soft and sticky, and can occur as sporadic isolated spots or as an overall effect.

Probable causes: Chemical breakdown of the binder, for example in alkyd and oleo resinous paints by reaction with alkali. Commonly seen when these types of paint are used on concrete or cement render.

4.17.1.49 Settlement

Description: A term used to describe the settlement of pigment/solid in a liquid prior to application, occurring during paint storage. Settlement, which occurs after mixing and during application, can result in a variation in color in different areas.

Probable causes: Old stock, heavily pigmented paint, wrong formulation, or contamination of product. Can be a problem with zinc-rich primers.

4.17.1.50 Solvent Lifting (also see Wrinkling)

Description: Eruption of the surface of the paint film by wrinkling and blistering, which leads to a weak surface and ultimate coating breakdown.

Probable causes: Incompatible paint system used, topcoats with a strong solvent blend can attack underlying coatings with a weaker solvent blend, or overcoating before the previous coat has adequately hardened.

4.17.1.51 Solvent Popping

Description: Solvent bubbles on the surface of the paint film soon after application.

Probable causes: Incorrect solvent blends, porous surfaces, or wrong environmental conditions.

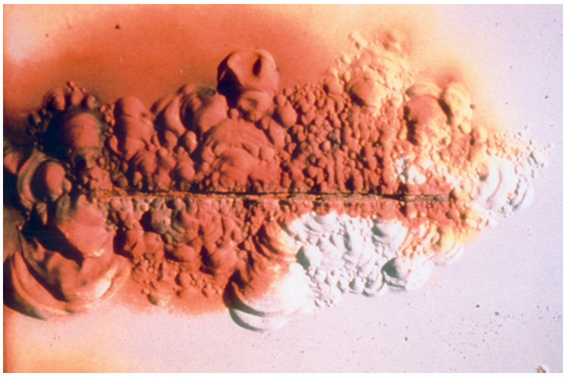
4.17.1.52 Tackiness

Description: Soft surface film of the applied coatings. Although, beyond the

	wet and liquid stage, the paint film remains as a tacky and soft surface, sometimes only apparent on touching.
Probable causes:	There are various reasons why paint will remain tacky, including overthickness, addition of excessive thinners, incorrect, insufficient, or lack of curing agent, low drying/curing temperature, or the use of coating beyond its shelf life.

4.17.1.53 Undercutting

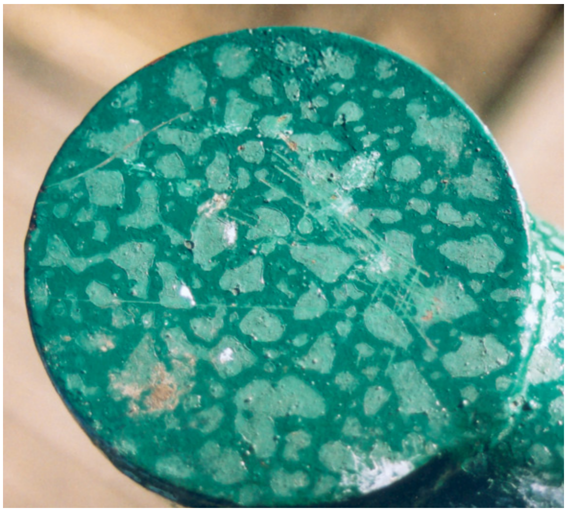
Description:	Corrosion beneath a paint film. Corrosion travels beneath the paint film and lifts the paint from the substrate, and in severe cases, can show as flaking, cracks, and exposed rust.



Probable causes:	The application of paint to a corroded substrate and/or rust creep from areas of mechanical damage and/or missing primer coats. Can be found in areas of poor design or access where inadequate preparation and coating thickness were applied and could also be due to a lack of maintenance.

4.17.1.54 Water Spotting (also see Rain Spotting)

Description:	The spotty appearance of the paint film caused by drops of water on the surface, which remains after the water has evaporated. The effect may or may not be permanent.



Probable causes:	Rain drops falling on to a wet paint film, leaving permanent marks, or falling on a freshly dried but hard surface where after the water has evaporated, marks may be seen, which can be rubbed off.

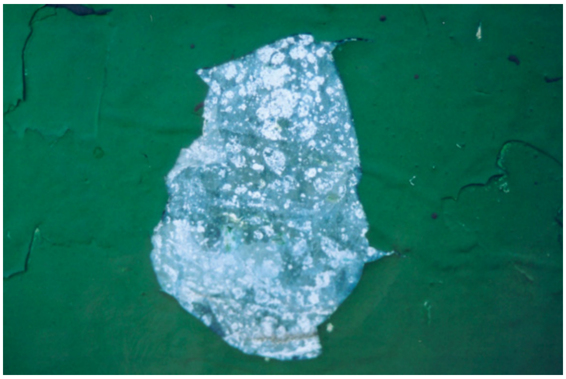
4.17.1.55 Wrinkling/Rivelling (also see Crowsfooting)

Description:	The development of wrinkling in the paint film during drying, appearing as wrinkling, swelling, and blistering of the coating.

Probable causes:	Usually due to the initial formation of a surface skin with solvent-based paints and related to shrinkage stress as the lower area of the film cures after the top surface. Can arise from overcoating before the previous coat has adequately hardened and swelling of the coating from reaction with solvent.

4.17.1.56 Zinc Carbonates

Description:	The loss of adhesion to galvanized surfaces and blistering of paint on a galvanized surface.



Probable causes:	White rust or carbonates on the surface of galvanizing prior to the application of the paint coating. Corrosion of zinc under the paint surface.

For a full and comprehensive range of definitions, see BS EN ISO 4618: Paints and Varnishes.

Terms and definitions for coating material, general terms, and BS 2015 glossary of paint and related terms.

Reference

Fitz's Atlas of Coating Defects. Fitzsimons, Weatherhead, and Morgan ISBN 0 9513940 2 9.

4.18 Principles of Cathodic Protection

V. Ashworth

This article is a revision of the Third Edition article 10.1 by V. Ashworth, volume 2, pp 10:3–10:28, © 2010 Elsevier B.V.

Abbreviations

AC Alternating current
BS British Standard
DC Direct current
emf Electromotive force
EN European Norm
NACE National Association of Corrosion Engineers
SRB Sulfate-reducing bacteria

Symbols

E Potential
E° Equilibrium potential
E_a Anodic potential
E_c Cathodic potential
E_{corr} Corrosion potential
I Current
I_a Anodic current
I_c Cathodic current
I_{corr} Corrosion current
I_{lim} Limiting current
IR Ohmic drop (equivalent to a voltage)
R Resistance
η Overpotential

4.18.1 Historical Background

In recent years, it has been regarded as somewhat passé to refer to Sir Humphry Davy in a text on cathodic protection. However, his role in the application of cathodic protection should not be ignored. In 1824, Davy presented a series of papers to the Royal Society in London,[1] in which he described how zinc and iron anodes could be used to prevent the corrosion of copper sheathing on the wooden hulls of British naval vessels. His paper shows a considerable intuitive awareness of what are now accepted as the principles of cathodic protection. Several practical tests were made on vessels in harbor and on seagoing ships, including the effect of various current densities on the level of protection of the copper. Davy also considered the use of an impressed current device based on a battery, but did not consider the method to be practicable.

The first 'full-hull' installation on a vessel in service was applied to the frigate HMS Samarang in 1824. Four groups of cast iron anodes were fitted, and virtually perfect protection of the copper was achieved. So effective was the system that the prevention of corrosion of the copper resulted in the loss of the copper ions required to act as a toxicide for marine growth, leading to increased marine fouling of the hull. Since this led to some loss of performance from the vessel, interest in cathodic protection waned. The beneficial action of the copper ions in preventing fouling was judged to be more important than preventing deterioration of the sheathing. Cathodic protection was therefore neglected for 100 years, after which it began to be used successfully by oil companies in the United States to protect underground pipelines.[2]

It is interesting that the first large-scale application of cathodic protection by Davy was directed at protecting copper rather than steel. It is also a measure of Davy's grasp of the topic that he was able to consider the use of two techniques of cathodic protection, namely sacrificial anodes and impressed current, and two types of sacrificial anode, namely zinc and cast iron.

4.18.2 Electrochemical Principles

4.18.2.1 Aqueous Corrosion

The aqueous corrosion of iron under conditions of air access can be written as

$$2Fe + O_2 + 2H_2O \rightarrow 2Fe(OH)_2 \qquad [1]$$

The product, ferrous hydroxide, is commonly further oxidized to magnetite (Fe_3O_4) or a hydrated ferric oxide (FeOOH), that is, rust.

It is convenient to consider separately the metallic and nonmetallic reactions in eqn [1]:

$$2Fe \rightarrow 2Fe^{2+} + 4e^- \qquad [2]$$

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \qquad [3]$$

To balance eqns [2] and [3] in terms of electrical charge, it has been necessary to add four electrons to the right-hand side of eqn [2] and to the left-hand side of eqn [3]. However, simple addition and rationalization of eqns [2] and [3] yield eqn [1].

We conclude that corrosion is a chemical reaction [1] occurring by an electrochemical mechanism (eqns [2] and [3]), that is, by a process involving electrical and chemical species. **Figure 1** is a schematic representation of aqueous corrosion occurring at a metal surface.

Equation [2], which involves consumption of the metal and release of electrons, is termed an anodic reaction. Equation [3], which represents consumption of electrons and dissolved species in the environment, is termed a cathodic reaction. Whenever spontaneous corrosion reactions occur, all the electrons released in the anodic reaction are consumed in the cathodic reaction; no excess or deficiency is found. Moreover, the metal normally takes up a more or less uniform electrode potential, often called the corrosion or mixed potential (E_{corr}).

4.18.2.2 Cathodic Protection

It is possible to envisage what might happen if an electrical intervention was made in the corrosion reaction by considering the impact on the anodic and cathodic reactions. For example, if electrons were withdrawn from the metal surface, it might be anticipated that reaction [2] would speed up (to replace the lost electrons) and reaction [3] would slow down, because of the existing shortfall of electrons. It follows that the rate of metal consumption would increase.

By contrast, if additional electrons were introduced at the metal surface, the cathodic reaction would speed up (to consume the electrons) and the anodic reaction would be inhibited; metal dissolution would be slowed down. This is the basis of cathodic protection.

Figure 2 shows the effect on the corrosion reaction shown in **Figure 1** of providing a limited supply of electrons to the surface. The rate of dissolution

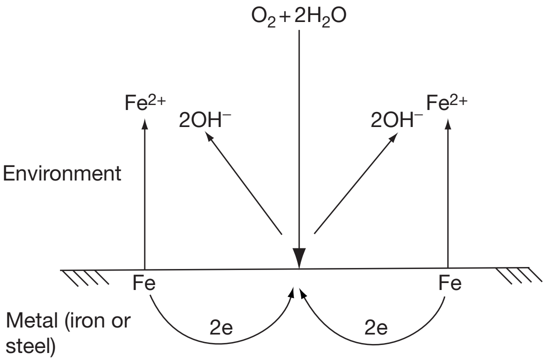


Figure 1 Schematic illustration of the corrosion of steel in an aerated environment. Note that the electrons released in the anodic reaction are consumed quantitatively in the cathodic reaction, and that the anodic and cathodic products may react to produce $Fe(OH)_2$.

slows down because the external source rather than an iron atom provides two of the electrons. Figure 3 shows the effect of a greater electron supply; corrosion ceases since the external source provides all the requisite electrons. It should be apparent that there is no reason why further electrons could not be supplied, when even more hydroxyl (OH^-) ion would be produced, but without the possibility of a concomitant reduction in the rate of iron dissolution. Clearly, this would be a wasteful exercise.

The corrosion reaction may also be represented on a polarization diagram (Figure 4). The diagram shows how the rates of the anodic and cathodic reactions (both expressed in terms of current flow I) vary with electrode potential E. Thus, at E_a, the net rate of the anodic reaction is zero and it increases as the potential becomes more positive. At E_c, the net rate of the cathodic reaction is zero and it increases as the potential becomes more negative. (To be able to represent the anodic and cathodic reaction rates on the same axis, the modulus of the current has been drawn.) The two reaction rates are electrically equivalent at E_{corr}, the corrosion potential, and the corresponding current I_{corr} is an electrical representation of the rate of the anodic and cathodic reactions at that potential, that is, the spontaneous corrosion rate of the metal. That is, at E_{corr} the polarization diagram represents the situation referred to above; namely, that when spontaneous corrosion occurs, the rate of electron release equals the rate of electron consumption, and there is no net current flow although metal is consumed, and meanwhile the metal exerts a single electrode potential.

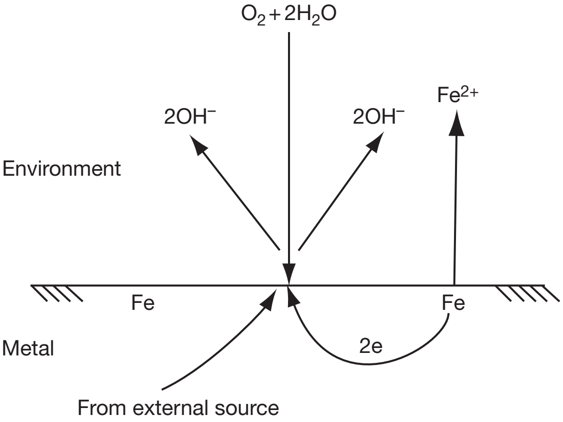


Figure 2 Schematic illustration of partial cathodic protection of steel in an aerated environment. Note that one of the anodic reactions shown in Figure 1 has been annihilated by providing two electrons from an external source; an excess of OH^- ions over Fe^{2+} now exists at the surface.

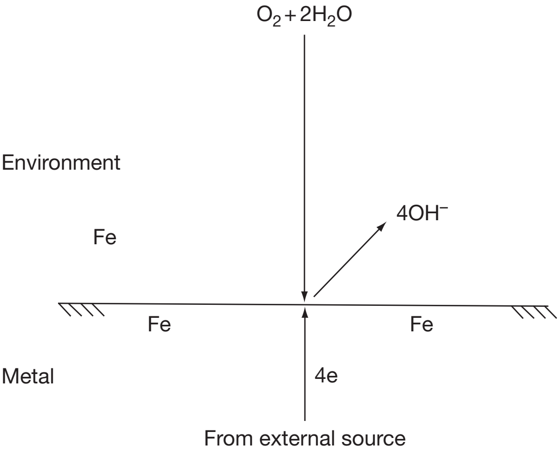


Figure 3 Schematic illustration of full cathodic protection of steel in an aerated environment. Note that both anodic reactions shown in Figure 1 have now been annihilated, and there is an accumulation of OH^- at the surface.

To hold the metal at any potential other than E_{corr} requires that electrons be supplied to, or be withdrawn from, the metal surface. For example, at E', the cathodic reaction rate I'_c, exceeds the anodic reaction rate I'_a, and the latter does not provide sufficient electrons to satisfy the former. If the metal is to be maintained at E', the shortfall of electrons given by $(|I'_c| - I'_a)$ must be supplied from an external source. This externally supplied current serves to reduce the metal dissolution rate from I_{corr} to I'_a.

At E_a, the net anodic reaction rate is zero (there is no metal dissolution) and a cathodic current equal to I''_c must be available from the external source to maintain the metal at this potential. It may also be apparent from Figure 4 that, if the potential is maintained below E_a, the metal dissolution rate remains zero ($I_a = 0$), but a cathodic current greater than I''_c must be supplied; more current is supplied without achieving a benefit in terms of metal loss. There will, however, be a higher interfacial hydroxyl ion concentration.

4.18.2.3 Oxygen Reduction

In illustrating the corrosion reaction in eqn [1], the oxygen reduction reaction [3] has been taken as the cathodic process. Moreover, in Figures 1–4, oxygen reduction has been assumed. While there is a range of cathodic reactions that can provoke the corrosion of a metal (since to be a cathodic reactant, any particular species must simply act as an oxidizing

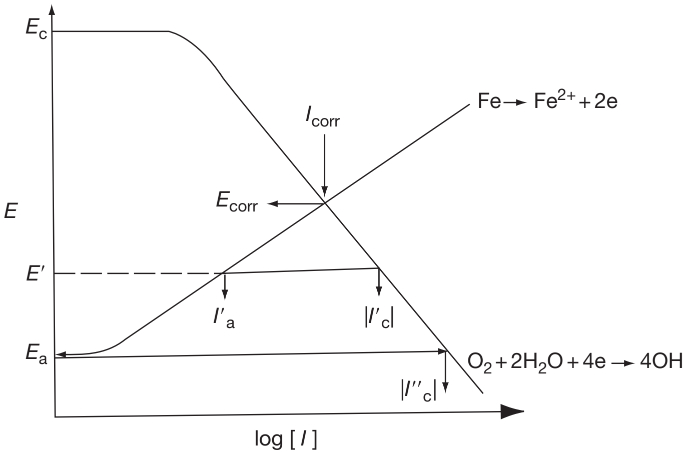


Figure 4 Polarization diagram representing corrosion and cathodic protection. A corroding metal takes up the potential E_{corr} spontaneously and corrodes at a rate given by I_{corr}. If the potential is to be lowered to E', a current equal to ($|I'_c| - I'_a$) must be supplied from an external source; the metal will then dissolve at a rate equal to I'_a.

agent to the metal), the most common cathodic reactant present in natural environments is oxygen. It is for this reason that the oxygen reduction reaction has been emphasized here.

When corrosion occurs, if the cathodic reactant is in plentiful supply, it can be shown both theoretically and practically that the cathodic kinetics are semilogarithmic, as shown in Figure 4. The rate of the cathodic reaction is governed by the rate at which electrical charge can be transferred at the metal surface. Such a process responds to changes in electrode potential, giving rise to the semilogarithmic behavior.

Because oxygen is not very soluble in aqueous solutions (~10 ppm in cool seawater, for example), it is not freely available at the metal surface. As a result, it is often easier to transfer electrical charge at the surface than for oxygen to reach the surface to take part in the charge transfer reaction. The cathodic reaction rate is then controlled by the rate of arrival of oxygen at the surface. This is often referred to as mass transfer control. Since oxygen is an uncharged species, its rate of arrival is unaffected by the prevailing electrical field and responds only to the local oxygen concentration gradient. If the cathodic reaction is driven so fast that the interfacial oxygen concentration is reduced to zero (i.e., the oxygen is consumed as soon as it reaches the surface), the oxygen concentration gradient to the surface reaches a maximum and the reaction rate attains a limiting value. Only an increase in oxygen concentration or an increase in flow velocity will permit an increase in the limiting value. The cathodic kinetics under mass transfer control will be as shown in Figure 5.

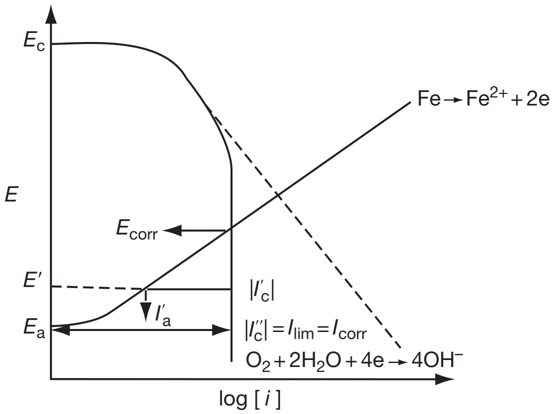


Figure 5 Polarization diagram representing corrosion and cathodic protection when the cathodic process is under mass transfer control. The values of E_{corr} and I_{corr} are lower than when there is no mass transfer restriction, that is, when the cathodic kinetics follows the dotted line.

Figure 5 demonstrates that, even when semilogarithmic cathodic kinetics is not observed, partial or total cathodic protection is possible. Indeed, Figure 5 shows that the corrosion rate approximates to the limiting current for oxygen reduction (I_{lim}), and the current required for protection is substantially lower than when semilogarithmic cathodic behavior prevails.

4.18.2.4 Hydrogen Evolution

In principle, it is possible for water to act as a cathodic reactant with the formation of molecular hydrogen:

$$2H_2O + 2e^- \leftrightarrows H_2 + 2OH^- \quad [4]$$

Indeed, in neutral solutions, the corrosion of iron with concomitant hydrogen evolution deriving from the reduction of water is thermodynamically feasible. In practice, this cathodic reaction is barely significant because the reduction of any oxygen present is both thermodynamically favored and kinetically easier. In the absence of oxygen, the hydrogen evolution reaction at the corrosion potential of iron is so sluggish that the corrosion rate of the iron is vanishingly small.

Nevertheless, hydrogen evolution is important in considering the cathodic protection of steel. Although hydrogen evolution takes little part in the corrosion of steel in aerated neutral solutions (see Figure 6), as the potential is lowered to achieve cathodic protection, it plays a larger, and eventually dominant, role in determining the total current demand. This too is demonstrated in Figure 6 where, it must be remembered, the current supplied from the external source at any potential must be sufficient to sustain the total cathodic reaction, that is, both oxygen reduction and hydrogen evolution reactions at that potential. It will be seen that to lower the potential much below E_a entails a substantial increase in current and significantly more hydrogen evolution.

4.18.3 Methods of Applying Cathodic Protection

There are two principal methods of applying cathodic protection, namely the impressed current technique and the use of sacrificial anodes. The former includes the structure as part of a driven electrochemical cell, and the latter includes the structure as part of a spontaneous galvanic cell.

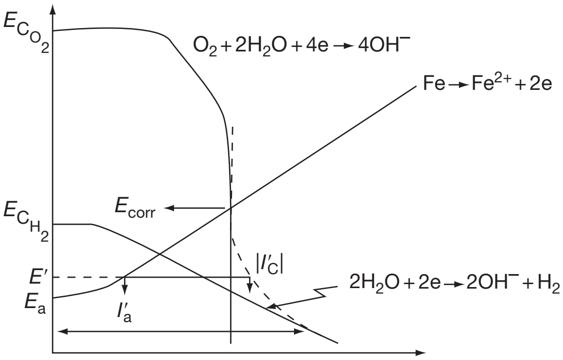


Figure 6 Polarization diagram showing the limited role hydrogen evolution plays at the corrosion potential of steel in aerated neutral solution, the larger role in determining cathodic protection currents, and the dominant role in contributing to current requirements at very negative potentials. The dotted line shows the total cathodic current due to oxygen reduction and hydrogen evolution.

4.18.3.1 Impressed Current Method

Figure 7 illustrates the use of an external power supply to provide the cathodic polarization of the structure. The circuit comprises the power source, an auxiliary or impressed current electrode, the corrosive solution, and the structure to be protected. The power source drives a positive current from the impressed current electrode through the corrosive solution and onto the structure. The structure is thereby cathodically polarized (its potential is lowered), and the positive current returns through the circuit to the power supply. Thus, to achieve cathodic protection, the impressed current electrode and the structure must be in both electrolytic and electronic contact.

The power supply is usually a transformer/rectifier that converts AC power to DC. Typically, the DC output will be in the range 15–100 V and 5–100 A, although 200 V/200 A units are not unknown. Thus, fairly substantial driving voltages and currents are available. Where mains power is not available, diesel or gas engines, solar panels, or thermoelectric generators have all been used to provide suitable DC.

It will be seen that the impressed current electrode discharges positive current, that is, it acts as an anode in the cell. There are three generic types of anode used in cathodic protection, namely consumable, nonconsumable, and semiconsumable. The consumable electrodes undergo an anodic reaction that involves their consumption. Thus, an anode made of scrap iron produces positive current by the reaction

$$Fe \rightarrow Fe^{2+} + 2e^-$$

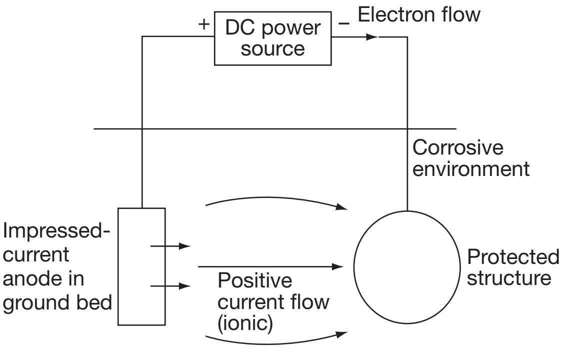


Figure 7 Schematic diagram of cathodic protection using the impressed-current technique.

The ferrous ions then enter the environment as a positive current carrier (although in practice the current will be carried in the environment by aqueous ions such as Na^+ and Cl^-. Since the dissolving anode must obey Faraday's law, it follows that the wasting of the anode will be proportional to the total current delivered. In practice, the loss for an iron anode is approximately $9\,kg\,A^{-1}\,year^{-1}$. Thus, consumable anodes must be replaced at intervals, or be of sufficient size to remain as a current source for the design life of the protected structure. This poses some problems in design because, as the anode dissolves, the resistance it presents to the circuit increases. More important, it is difficult to ensure continuous electrical connection to the dissolving anode.

Nonconsumable anodes sustain an anodic reaction that decomposes the aqueous environment rather than dissolves the anode metal. In aqueous solutions the reaction may be

$$2H_2O \rightarrow O_2 + 4H^+ + e^-$$

or in the presence of chloride ions

$$2Cl^- \rightarrow Cl_2 + 2e^-$$

Anodes made from platinized titanium or niobium belong to this category.

Because these anodes are not consumed faradaically, they should not, in principle, require replacement during the life of the structure. However, to remain intact, they must be chemically resistant to their anodic products (acid and chlorine) and, where the products are gaseous, conditions must be produced that allow the gas to escape and not interfere with anode operation. This is particularly true of the platinized electrodes because they can operate at high current density ($>100\,A\,m^{-2}$) without detriment, but will then produce high levels of acidity ($pH < 2$) and large volumes of gas. Ground-bed design (the way in which the anode is installed) is therefore crucial.

Although the anodes are described as nonconsumable, they do suffer some loss of the thin (~ 2.5–$10\,mg\,m^{-3}$) platinized coating. This loss, which unfortunately has become known as the wear rate although there is no question of the loss being due to mechanical wear, is usually small, related to the total current passed, and increased if the applied current has an AC component. Typically, values for the loss rate are $8\,mg\,A^{-1}\,year^{-1}$ for platinized titanium, which may be increased 10-fold if an AC component of $<100\,Hz$ is present. Negative-going current spikes, such as may be induced by a poorly designed thyristor switching device, even given otherwise clean DC, can produce a 100-fold increase in the rate of loss.

The semiconsumable electrodes, as the name implies, suffer rather less dissolution than Faraday's law would predict and substantially more than the nonconsumable electrodes. This is because the anodic reaction is shared between oxidizing the anode material (causing consumption) and oxidizing the environment (with no concomitant loss of metal). Electrodes made from silicon–iron, chromium–silicon–iron and graphite fall into this category.

Table 1 gives a brief summary of the behavior of some impressed current anodes, and protection by impressed current is discussed in more detail elsewhere.

4.18.3.2 Sacrificial Anodes

Using the impressed-current technique, the driving voltage for the protective current comes from a DC power source. The sacrificial anode technique uses the natural potential difference that exists between the structure and a second metal in the same environment to provide the driving voltage. No power source is employed. Moreover, the dissolution of the second metal, that is, the sacrificial anode, provides the source of electrons for cathodic polarization of the structure. Thus, while the impressed-current anode may be more noble or more base than the protected structure because the power source forces it to act as an anode, the sacrificial anode must be spontaneously anodic to the structure, that is, be more negative in the galvanic series for the given environment. Thus, in principle, zinc, aluminum, or magnesium could be used to protect steel, and iron to protect copper. Figure 8 illustrates the use of a sacrificial anode for cathodic protection.

In practice, pure metals are never used as sacrificial anodes. There are a variety of reasons for this, which includes the need for

1. a reliable, reproducible and negative operating potential for the anode;
2. a high and reproducible capacity ($A\,h\,kg^{-1}$) for the anode;
3. uniform dissolution of the anode so that all metal is consumed usefully in providing cathodic protection and not wastefully by mechanical loss;
4. freedom from any loss of activity by the anode due to passivation.

For these reasons, alloying elements appear in all the commercial anodes, and very careful quality control

Table 1 Impressed-current anode materials

Material	*Consumption rate or operating current density*	*Notes*
Consumable:		
Scrap iron	~ 9 kg A^{-1} year^{-1}	Cheap: suitable for buried or immersed use
Cast iron	<9 kg A^{-1} year^{-1}	Cheap; buried or immersed use; carbon skeleton reduces consumption
Semiconsumable:		
Silicon cast iron (Fe–14Si–(3 Mo)	5–50 A m^{-2} (in freshwater or soil)	Buried or immersed use; consumption (<1 kg A^{-1} year^{-1}); Mo reduces consumption in seawater
Graphite	2.5–10 A m^{-2}	Consumption rate very much less than steel or cast iron (<1 kg A^{-1} year^{-1}); chloride ions reduce consumption
Nonconsumable:		
Lead alloys:		
1. Pb–6Sb–1Ag	$<$50–200 A m^{-2} (in seawater)	PbO_2 film restrains consumption
2. Pt-activated	$<$50–500 A m^{-2} (in seawater)	PbO_2 film protective
Platinized Ti, Ta, or Nb	<1000 A m^{-2} (consumption)	Discontinuities in Pt coat protected by oxide film on subtrate; sensitive (<100 Hz) AC ripple in DC or negative current spikes causing electrode consumption; maximum operating potential with Ti substrate: 9 V

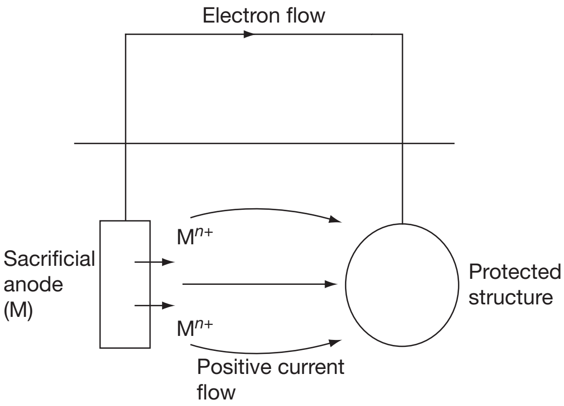


Figure 8 Schematic diagram of cathodic protection using sacrificial anodes. In practice, the anode, which will be mounted on a steel core, can be attached directly to the structure.

is required to keep disadvantageous tramp elements (notably iron and copper) below defined threshold levels. Many anode failures can be attributed to poor production quality control. A guide to minimum quality standards has been produced.[3]

Table 2 gives electrochemical properties for various generic anode types. It will be apparent that the driving voltages that are available from sacrificial anodes are substantially less than those available from power sources. At best, an anode will produce 1 V to steel, whereas an impressed current power source may produce up to 100 V.

A more detailed treatment of cathodic protection by sacrificial anodes is provided elsewhere in this book.

4.18.4 Proof of Protection

4.18.4.1 Steel

Figure 4 demonstrates that the rate of dissolution of iron (or any other metal) decreases as the potential is made more negative. Figure 6 shows that the current required to reach any given potential below the corrosion potential (E_{corr}) will vary according to the composition of the corrosive solution. Thus Figure 6 shows that, in the absence of oxygen, the current requirement would be low, but would increase to a value approximating to the limiting current in its presence. Moreover, since the limiting current can be increased by increasing the oxygen concentration or the solution flow rate, the current required for protection will change predictably with change in either of these parameters.[4] It follows that the current required to prevent corrosion completely (i.e., in principle to achieve E_a) will vary according to the environment and the environmental dynamics. As a consequence, there is no single current that will assure protection in all cases. Current supplied is not, therefore, an unequivocal indication of the effectiveness of protection.

By contrast, it appears from Figures 4 and 6 that a potential measurement would be more reliable: specifically, that E_a (the equilibrium potential for the

Table 2 Typical sacrificial anode compositions and operating parameters

Alloy	*Environment*	*Operating voltage vs. Ag/AgCl/seawater (V)*	*Driving voltage*[a] *(V)*	*Capacity (Ah/kg)*
Al–Zn–Hg	Seawater	−1.0 to −1.05	0.20–0.25	2600–2850
Al–Zn–In	Seawater	−1.0 to −1.10	0.20–0.30	2300–2650
Al–Zn–In	Marine sediments	−0.95 to −1.05	0.15–0.25	1300–2300
Al–Zn–Sn	Seawater	−1.0 to −1.05	0.20–0.25	925–2600
Zn[b]	Seawater	−0.95 to −1.03	0.15–0.23	760–780
Zn[b]	Marine sediments	−0.95 to −1.03	0.15–0.23	750–780
Mg–Al–Zn	Seawater	−1.5	0.7	1230
Mg–Mn	Seawater	−1.7	0.9	1230

It is often important to control impurities and especially Fe, Cu, Ni, and Si, although a controlled Si concent is essential to some aluminum alloys.

[a] The driving voltage to bare steel, that is, protection potential of steel–anode operating potential.

[b] US Military Specification.

iron/ferrous-ion electrode given a suitably low ferrous ion concentration) would always represent the achievement of full protection for iron.

Almost without exception, all the accepted criteria for full cathodic protection of iron are based on a potential measurement. The various recommended practices published by the U.S. National Association of Corrosion Engineers (NACE) give six criteria for full protection.[5–11] The current British Standard Code of Practice[12] gives one. These are summarized in Table 3. Only the first three are useful; the remaining ones are of dubious value or expressions of pious hope.

The most widely accepted criterion for protection of steel at room temperature (the protection potential) in aerobic conditions is –0.85 V with respect to a Cu/$CuSO_4$ reference electrode. In anaerobic conditions, –0.95 V (versus Cu/$CuSO_4$) is the preferred protection potential because of the possible presence of active sulfate-reducing bacteria (SRB).

Various limitations on the most negative potential that may be imposed during cathodic protection are often quoted for high-strength steels (typically –1.0 V versus Cu/$CuSO_4$ for steels in the 700–800 MPa tensile strength range). The restriction is to limit the evolution of hydrogen at the structure and thereby prevent hydrogen absorption with the possibility of embrittlement of the steel, possibly leading to fracture. The consequence is that the useful window of potential in which the steel can operate is severely restricted, especially under anaerobic conditions.

It must not be assumed that the protection potential is numerically equal to the equilibrium potential for the iron/ferrous-ion electrode (E_a). The standard equilibrium potential ($E°$) for the iron/ferrous-ion is –0.440 V (versus the standard hydrogen electrode). If the interfacial ferrous ion concentration when corrosion ceases is approximately 10^{-6} M, then according to the Nernst equation, the equilibrium potential (E_a) is given by

Table 3 Cathodic protection criteria: after British Standard Code of Practice[12] and NACE Recommended Practices[5–11]

1. ≤ −0.85 V w.r.t Cu/$CuSO_4$ with current applied but minimizing *IR* error
2. Negative shift ≥300 mV when current applied
3. Positive shift ≥100 mV when current interrupted
4. More negative than beginning of Tafel segment of cathodic polarisation (*E* – log *I*) curve
5. A net protective current in the structure at former anodic points
6. Polarize all cathodic areas to open circuit potential of most active anode areas

$$E_a = E^\circ + \frac{2.303}{2F} RT \log(a_{Fe^{2+}})$$

where $a_{Fe^{2+}}$ is the activity or thermodynamic concentration of the ferrous cation, R is the gas constant, F is Faraday's constant, and 2 represents the number of units of charge transferred (i.e., the doubly charged ferrous ion). Thus, E_a = –0.62 V versus the standard hydrogen electrode or –0.93 V versus Cu/$CuSO_4$. This is a value substantially more negative than the accepted protection potential (–0.85 V).

A simple calculation based on the solubility product of ferrous hydroxide and assuming an interfacial pH of 9 (due to the alkalization of the cathodic surface by reaction [3]) shows that, according to the Nernst equation, at –0.85 V (versus Cu/$CuSO_4$), the ferrous ion concentration then present is sufficient to permit deposition of the hydroxide ion. It appears that the ferrous hydroxide formed may be protective, and that the practical protection potential (–0.85 V), as opposed to the theoretical protection potential ($E_a = -0.93$ V), is governed by the thermodynamics of precipitation and not those of dissolution.

It is also worth noting that the exact achievement of the so-called protection potential is not essential to excellent corrosion control. Figures 4–6 show the anodic kinetics as semilogarithmic in character. Behavior approaching this is observed in practice for steel in many environments. Thus, the first increment of negative potential shift will reduce the anodic dissolution rate substantially. A second equal shift will be 10 times less effective and will require the application of very much more current. A third equal shift will be 10 times less effective again. That is, the dissolution rate decreases asymptotically as the full protection potential is approached; a small shortfall in cathodic polarization is not, therefore, disastrous. By contrast, the current required to achieve the protection potential, and more particularly to exceed it, is often very substantial and may increase exponentially. There may often be good economic reasons for permitting a minor shortfall of polarization.

4.18.4.2 Other Metals

In principle, all metals may be protected by cathodic protection. In practice, it is not always relevant, either because the metals are, to all intents and purposes, naturally immune to corrosion (the noble metals) and often not used as engineering materials or, being base metals, they are well protected by the spontaneous formation of a passive film in aqueous solution (aluminum or a stainless steel, for example).

Copper-base alloys will corrode in aerated conditions. It is, therefore, sometimes appropriate to consider cathodic protection. It becomes particularly relevant when the flow rates are high or when the design of an item causes the copper to be an anode in a galvanic cell (e.g., a copper alloy tube plate in a titanium-tubed heat exchanger). Corrosion can be controlled by polarization to approximately –0.6 V (versus $Cu/CuSO_4$) and may be achieved using soft-iron sacrificial anodes.

Some metals are amphoteric: that is, they form simple cations (in acid solutions) and soluble oxyanions (in alkaline solution); only in the mid-pH range is a protective film stable. Since cathodic protection produces alkali at the structure's surface, it is important to restrict the polarization, and thereby the amount of hydroxyl ion produced, in these cases. Thus both lead and aluminum will suffer cathodic corrosion under cathodic protection if the potential is made excessively electronegative.

Many passive metals suffer pitting attack when aggressive ions (usually chloride) enter the system. It is possible to forestall pitting, or to stop it once started, using cathodic protection. It is not necessary to polarize to the protection potential of the metal; a negative shift of 100 mV from the natural corrosion potential in the environment will often be sufficient. This technique has been applied to various stainless steels and to aluminum.[13] The philosophy is not unlike that applied to rebar in concrete.

Where there is a perceived risk of crevice corrosion, cathodic protection can often be used to prevent its initiation. Once more, a 100-mV cathodic polarization will usually prove sufficient. However, it is doubtful whether cathodic protection can arrest crevice corrosion once started and, despite claims to the contrary, whether it could be effective in arresting stress-corrosion cracking. The problem lies in the fundamental difficulty of forcing cathodic current into an occluded area.

Some recommended protection potentials for other metals are given in Table 4.

Table 4 Recommended protection potentials for other metals[12]

Metal	*Protection potential (V vs. $Cu/CuSO_4$)*
Lead	−0.6
Copper-base alloys	−0.5 to −0.65
Aluminum	
Positive limit	−0.95
Negative limit	−1.2

4.18.4.3 Steel in Concrete

Concrete is a very benign environment for steel so long as its natural pH remains high and no aggressive species enters. The low corrosion rate experienced by the steel is due to the formation of a protective passive film. There are a number of circumstances that allow chloride ions to enter reinforced concrete. When these ions reach the reinforcing bar (rebar), they may cause localized corrosion damage to it, with consequent cracking or even spalling of the concrete. The result is both unsightly and potentially dangerous. Impressed-current cathodic protection has been used to overcome the problem, and significant beneficial effects have been claimed.[14–16]

The proof of protection is more difficult to establish in this case for two reasons. First, the object is to restore passivity to the rebar and not to render it virtually immune to corrosion. Second, it is difficult to measure the true electrode potential of rebars under these conditions. This is because the cathodic-protection current flowing through the concrete produces a voltage error in the measurements made (see below). For this reason, it has been found convenient to use a potential decay technique to assess protection rather than a direct potential measurement. Thus, a 100-mV decay of polarization in 24 h once current has been interrupted has been adopted as the criterion for adequate protection.[17] It will be seen that this proposal does not differ substantially from the decay criterion included in **Table 3** and recommended by NACE for assessing the full protection of steel in other environments. Of course, in this case, the cathodic polarization is intended to inhibit pit growth and restore passivity, not to establish effective immunity.

4.18.4.4 Potential Measurements

It is clear that to ensure adequate protection of a structure under cathodic protection, it is necessary to measure its electrode potential. This can be achieved only by using a reference electrode placed in the same environment as the structure and measuring the emf of the cell so formed. Since the electrode potentials of different types of reference electrode vary, it is clear that the measured emf will also vary according to the particular reference electrode used. It follows that the potential measured must always be recorded with respect to the reference electrode deployed, which must always be stated.

The protection potential for a given metal is numerically different according to the reference electrode used. Thus the protection potential for iron in aerobic environments is

–0.85 V versus $Cu/CuSO_4$;
–0.80 V versus Ag/AgCl/seawater;
–0.77 V versus Ag/AgCl/1 M KCl;
–0.84 V versus Ag/AgCl/0.1 M KCl;
–0.55 V versus standard hydrogen electrode.

It is fundamental that a reference electrode should have a stable and reproducible potential. Not all reference electrodes are suitable for all environments or circumstances. For example, a $Cu/CuSO_4$ electrode is suitable for use in soil, but should never be used in seawater or on concrete. Contamination of the electrode can occur, which will produce serious changes in the reference potential.

The Ag/AgCl/seawater electrode should be used only in seawater since the electrode is merely a Ag/AgCl element that provides a known stable reference potential when immersed in clean seawater. Immersion in any other chloride-containing fluid will produce a different reference potential depending on the chloride concentration present in the environment. Only if appropriate allowance is made for the particular chloride content present, will the potentials measured be reliable. Commercial Ag/AgCl electrodes are available in which the element is encapsulated within an environment containing a fixed chloride content. The electrodes are very stable and suitable for short-term use in fluids containing any concentration of chloride or no chloride ions at all. They are not suitable for continuous immersion in fluids in which the chloride concentration of the encapsulation will change with time as a result of chloride leaching (e.g., in distilled water) or chloride ion ingress (e.g., in seawater).

Finally, calomel electrodes (and particularly hydrogen electrodes) are not suitable for field measurements because they are not sufficiently robust. The calomel electrodes are, however, essential for calibrating the field reference electrodes. Saturated KCl calomel electrodes are the most suitable because there is then no doubt about the reference potential of the calibrating electrode. Lack of adequate calibration is a common cause of cathodic protection system mismanagement.

Incorrect potential measurement technique leads to another management problem. If the potential of a freely corroding metal is measured, the values recorded will remain constant wherever the reference electrode is placed in the environment. If the same metal is under cathodic protection, the positioning of the reference electrode is crucial. This is because the cathodic protection current flowing through the corrosive environment produces an electric field gradient as the current I flows through the environment of resistance R. Thus, when the reference electrode is placed remote from the metal surface, the measured potential comprises the true electrode potential of the metal and the potential difference in the environment between the metal and the reference electrode due to the electric field. As the reference electrode is moved closer to the metal surface, less of the electric field is included in the measurement and the potential of the metal appears more positive (**Figure 9**). That is, with current flowing, a remote reference electrode ensures measurement of a more negative potential for the metal (it appears better protected than it is), while the closer the reference electrode is placed to the

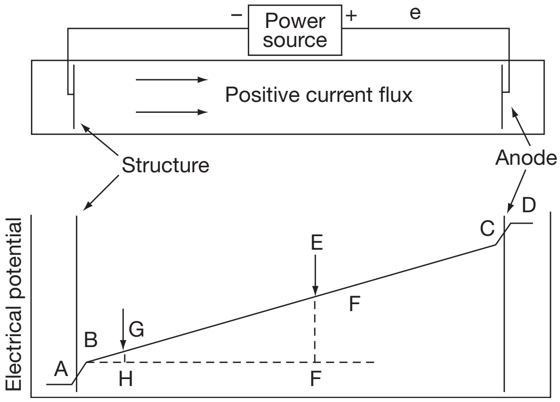


Figure 9 Diagram illustrating the source of the *IR* error in potential measurements on a cathodically protected structure. BA is the absolute electrode potential of the structure; CD is the absolute electrode potential of the anode; and CB is the field gradient in the environment due to cathodic protection current flux. A reference electrode placed at E will produce an *IR* error of EF in the potential measurement of the structure potential. If placed at G, the error will be reduced to GH. At B there would be no error, but the point is too close to the structure to permit insertion of a reference electrode. If the current is interrupted, the field immediately becomes as shown by the dotted line, and no IR is included.

metal, the more positive, and more reliable, the measurement becomes.

The deviation from the correct potential value by inclusion of the field gradient in the measurement is often called the *IR* error, and it must be minimized in assessing the state of polarization of a cathodically protected structure. The recommended protection potentials all assume no significant *IR* error in the measurement.

It is desirable to measure the potential of a structure without an *IR* error. It is not always possible to place the reference electrode close to the structure to minimize the *IR* error but it can be achieved using the so-called instant-off technique. The technique relies on the fact that when the current is interrupted, the *IR* effect, being ohmic, dissipates immediately but the polarization decays much more slowly. Thus, if the current is switched off and the potential is measured immediately, the *IR*-free polarized potential of the structure can be measured. Where the cathodic protection system uses multiple power sources, it is necessary to switch off all the units simultaneously if true *IR*-free conditions are to be achieved.

In an impressed-current cathodic protection system, the power source has a substantial capacity to deliver current and it is possible to change the state of polarization of the structure by altering that current. Thus, effective control of the system depends on credible potential measurements. Since the current output from any given anode is substantial, the possibility of an *IR* error, which may reach many hundreds of millivolts in any potential measurements made, is high. Thus the instant-off technique (or some other means of avoiding *IR* error) is essential to effective system management.

By contrast, a cathodic protection system based on sacrificial anodes is designed from the outset to achieve the required protection potential. If this is not achieved in practice, there is no control function that can be exercised to improve the situation. Some remodeling of the system will be required. Moreover, the current from each current source (the sacrificial anodes) is modest so that field gradients in the environment are not significant. It is at once clear that potential measurements are less significant in this case and instant-off measurements are neither necessary nor possible.

4.18.5 Current Requirements

It was indicated earlier that the cathodic current is a poor indicator of adequate protection. While, to a first approximation, the protection potential is a function of the metal, the current required for protection is a function of the environment and, more particularly, of the cathodic kinetics it entails. From Figure 4, it is apparent that any circumstance that causes the cathodic kinetics to increase will cause both the corrosion rate and the current required for full (I''_c) or partial ($|I'_c| - I'_a$) protection to rise. For example, an increase in the limiting current in Figure 5 produced by an increase in environmental oxygen concentration or in fluid flow rate will increase the corrosion rate and the cathodic protection current. Similarly, if the environment is made more acidic, the hydrogen evolution reaction is more likely to be involved in the corrosion reaction and it also becomes easier and faster; this too produces an increased corrosion rate and cathodic current demand.

In short, the current demand for cathodic protection varies according to the aggressiveness of the corrosive environment. It is for this reason that cathodic protection finds its greatest application where the pH is close to neutral. The more acidic environments entail a current output that rapidly becomes uneconomical. The more alkaline environments prove less aggressive to the structure and therefore often do not justify cathodic protection.

4.18.6 Coatings and Cathodic Protection

Coatings (e.g., paints) applied to metal surfaces can be extremely effective in containing the corrosion of the substrate in many environments. This is particularly true for steel in natural environments. However, no freshly applied coating is entirely free from defects and so there will always be small areas which are exposed directly to the corrosive environment. It is possible to reduce, but not eliminate, these defects by paying attention to workmanship. In practice, it becomes increasingly expensive to achieve fewer and fewer defects because of the need for high-grade inspection as well as the detection and repair of individual defects.

Large structures, even in near-neutral pH environments, require a considerable current for cathodic protection. As a result, structure coatings are an almost mandatory requirement when cathodic protection is contemplated. The coating then provides the major part of the protection, and the cathodic protection provides the protection at the coating defects. This apparently ideally complementary behavior occurs because the coating defects represent a low resistance path, and therefore a preferred route, to the structure, for the cathodic protection current. It is now apparent that the coating does not need to achieve total surface coverage and the cathodic protection system must deliver only a fraction (often less than 1%) of the current that would be required to protect a bare structure. Figure 10 shows schematically that there is an optimum combination of coating quality and cathodic protection that minimizes the cost of protecting a structure.

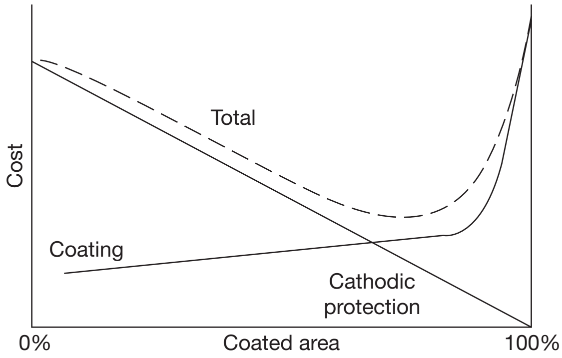


Figure 10 Schematic diagram illustrating the economic benefit of the conjoint use of coating and cathodic protection. The increasing cost of coating as the coating is made progressively more defect free is shown; the corresponding cost of applying cathodic protection to the holidays decreases. The dotted line shows the total cost, and that there is overall benefit in using a good coating reinforced by cathodic protection.

A coating deteriorates chemically and mechanically during its lifetime. This leads to a progressive increase in both the number of defects and the current required to protect the steel as they occur. Fortunately, each new defect represents a new low-resistance path and the cathodic protection current will flow to it to provide protection. Of course, this means that the cathodic protection system as installed must have sufficient reserve to provide this necessary extra current. This is readily accommodated in an impressed-current system where, if correctly designed, the voltage output can be increased to provide the requisite current. It is rather more difficult in the case of a sacrificial anode system because, as the anodes get smaller (by dissolving sacrificially), they are not capable of delivering more current. Thus increasing current demand develops alongside decreasing current availability. Of course, it is possible to provide anodes capable of delivering substantially more current initially in order to be able to provide sufficient current for later demand. This entails anodes operating in their early life at low current densities, which has sometimes been known to result in anode passivation and failure to deliver any significant current when it is needed.

Notwithstanding this latter difficulty, cathodic protection is usually applied to coated structures. Thus, ships, many piers and jetties, and virtually all buried pipelines are coated when cathodic protection is applied. Liquid storage tanks standing on sand or bitumen sand often have the underside of their base plate under cathodic protection. Here coating is often omitted, but this is more often due to ignorance of the designer than a conscious decision not to coat. Only offshore oil production platforms, particularly in the North Sea, are cathodically protected but often deliberately uncoated. There are two reasons for this. First, these structures are almost all protected using sacrificial anodes and it is easier to design for a more or less constant current demand than for an increasing current demand in these systems. Second, the construction of the platforms is made against a tight schedule; any weather conditions that prevented completion of coating would involve launching a platform with an incomplete coating and insufficient anodes to protect the now partially coated structure. It is certainly true that the first platforms in the North Sea were coated and cathodically protected. However, at that time the only reliable marine anodes were based on zinc alloys which entailed a heavy weight penalty (because they have a low capacity) and there was thus a pressing need to reduce anode weight by coating.

4.18.7 Calcareous Deposit

It has been noted that the total current required to protect large structures can be substantial even in mildly corrosive environments. In seawater, for example, an initial current in the region of 200 mA m^{-2} for bare steel might well be required in the North Sea. This is because the relatively high oxygen concentration and the tide and wave action all contribute to a facile cathodic reaction. Fortunately, this current diminishes with time. The reason for this is the protective scale on the steel surface, which forms during cathodic protection by decomposition of the seawater.

During cathodic protection, the dissolved oxygen is reduced to produce hydroxyl ions:

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$$

causing an increase in the pH at the interface. Seawater contains carbonate and bicarbonate ions that are in a pH-dependent equilibrium with one another:

$$HCO_3^- \rightarrow CO_3^{2-} + H^+$$

The higher the pH of the seawater, the greater will be the proportion of carbonate ions present (since as the pH increases, so the H^+ concentration decreases, thereby moving the equilibrium to the right). It follows that at a surface under cathodic protection, the hydroxyl ion produced has the effect of increasing the local carbonate ion concentration.

Seawater also contains calcium ions which form an insoluble carbonate with carbonate ions:

$$Ca^{2+} + CO_3^{2-} \rightleftharpoons CaCO_3$$

An increase in carbonate-ion concentration moves the equilibrium in favor of calcium carbonate deposition. Thus, one secondary effect of cathodic protection in seawater is the production of OH^-, which favors the production of CO_3^{2-}, which in turn promotes the deposition of $CaCO_3$. Cathodically protected surfaces in seawater will often develop an aragonite ($CaCO_3$) film. This film is commonly referred to as a calcareous deposit.

Similarly, the seawater contains magnesium ions which can react with the hydroxyl ion directly to form magnesium hydroxide:

$$Mg^{2+} + 2OH^- \rightarrow Mg(OH)_2$$

Thus, brucite, $Mg(OH)_2$, is also commonly found on surfaces under cathodic protection in seawater. Because more hydroxyl ions (higher pH) are required to cause magnesium hydroxide to precipitate, the magnesium is virtually always found in the calcareous deposits associated with calcium.[18]

The practical consequences of these events are that, once the calcareous film has formed, a cathodic current density at least an order of magnitude lower than that required to protect bare steel is needed to maintain protection. Although temporary damage to the film (e.g., storm action) may create a temporarily increased current demand, the film soon repairs and the lower current demand is restored. There is, however, a danger in excessive cathodic polarization: hydrogen is evolved at the steel surface, which, as it emerges, can itself disrupt the film mechanically. Since hydrogen continues to be produced so long as there is excessive polarization, there is continuing mechanical damage to the film and a more or less permanent increase in the cathodic current required for protection.

On the basis of laboratory experiments, it is widely believed, but there is little field evidence to prove, that high initial cathodic current densities promote the development of thinner, more compact, and more protective calcareous deposits. If this could be proved, some reduction in the sacrificial anode burden on a structure might be possible. As a result, some attention has been paid to the possibility of designing cathodic protection systems capable of delivering a high initial current with a view to reducing the total lifetime current required to attain and maintain protection. In general, this approach has involved proposals to use a limited number of high-current-output magnesium alloy sacrificial anodes to reinforce the anode burden (usually aluminum alloy) installed to provide long-term protection. It remains to be seen whether this is, or could be, successful.

4.18.8 Potential Attenuation in Impressed-Current Systems

An impressed-current cathodic protection system circuit comprises an anode, the power source, the structure, and the environment in which it is placed. In addition, there are electrical connections between the power source and the anode and between the power source and the structure (at the so-called negative drain point). The voltage available from the power source is used to polarize the anode and the structure and to overcome the electrical resistance of the environment and the metallic circuit, including that of the structure itself. It follows that the overall circuit resistance to various parts of a very large structure will differ and, where the resistance is higher, the voltage available for polarization of the structure will be lower. Thus, on large structures protected by a limited number of anodes, some lateral variation in the level of polarization is to be expected. This variation of potential is referred to as attenuation. Given that to ensure full protection the structure should everywhere be polarized at least to the protection potential, some part of it must be polarized to a greater extent. We have seen that more polarization requires more cathodic current. In the interest of economy, it is important to minimize attenuation as far as possible. One practical way to achieve this is to use a protective coating and thus limit the total current in the circuit. It may then still prove desirable to use more than one anode groundbed to render the attenuation less extreme. To pursue this latter course, it is helpful to have some assessment of the likely level of attenuation that will be experienced on a given structure.

No exact mathematical analysis of potential attenuation for all structures has yet been developed. Some indicative analysis has been achieved for a buried pipeline,[19] which is perhaps the simplest case.

In making the analysis, it is assumed that the anode groundbed is remote from the pipeline. That is, the length of the pipeline in question stands in what is virtually a uniform anode field, as shown in **Figure 11**. Since the electrical potential on the soil side is constant, any electrical potential change in the pipeline metal due to current flow within it reflects an equal electrode potential change at the pipe–soil interface. The change is also numerically equal to the cathodic overpotential, that is, the shift in electrode potential from the spontaneous corrosion potential.

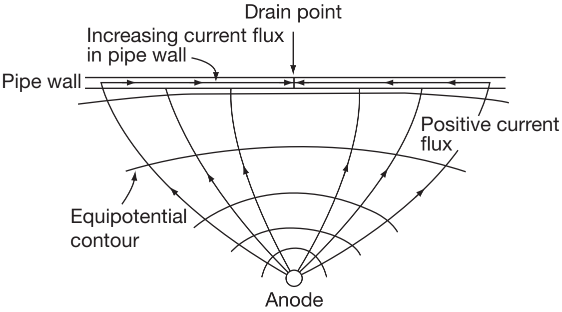


Figure 11 Schematic diagram showing an impressed-current anode installed in a groundbed remote from a pipeline. The positive current produces a field gradient in the soil, but the gradient tends to zero close to the line, producing a uniform lateral electrical potential on the soil side.

We assume that the current enters the pipeline from the soil side through defects in the coating and returns to the power source via the line and one of the drain points, as shown in **Figure 12**. If the total current in the pipeline at a point a distance x from a drain point is I_x, then the change in current per unit length at x is the current entering at x:

$$\frac{\mathrm{d}I_x}{\mathrm{d}x} = -2\pi r i_x \qquad [5]$$

where r is the radius of the pipeline and i_x is the current density entering at x.

The electrical potential change along the pipeline at x is

$$\frac{\mathrm{d}\varphi_x}{\mathrm{d}x} = -R_{\mathrm{L}} I_x$$

where ϕ_x is the electrical potential at x and R_{L} the resistance of the metallic pipeline/unit length. However, since the rate of electrical potential change is equal to the rate of change of overpotential, given a remote groundbed, it follows that

$$\frac{\mathrm{d}\eta_x}{\mathrm{d}x} = -R_{\mathrm{L}} I_x \qquad [6]$$

where η_x is the overpotential and is the difference between the actual potential at x and the free corrosion potential of the metal.

From eqns [5] and [6]:

$$\frac{\mathrm{d}^2\eta_x}{\mathrm{d}x^2} = R_{\mathrm{L}}(2\pi r i_x) \qquad [7]$$

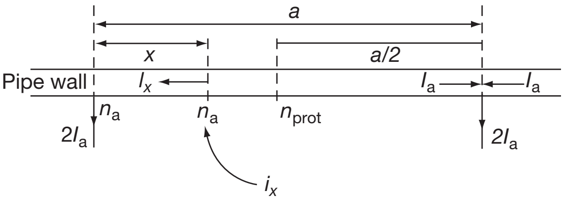


Figure 12 Schematic representation of a pipewall subject to cathodic protection (see text). η_x = overpotential at x; η_a = overpotential at $x = 0$; η_{prot} = overpotential at $x = a/2$; I_x = current line at x; i_x = current density entering line at x; I_a = current in line at $x = 0$ from one side of drain point ($2I_a$ = total current drain); a = distance between the drain points.

Now, when i_x is small, the polarization of the pipeline is approximately directly proportional to the true current density (i'_x) at the holidays in the coating. Thus

$$\eta_x = k' i'_x \qquad [8]$$

Also,

$$i'_x = \frac{i_x}{f}$$

where f is the fraction of the surface covered by holidays in the coating and is inversely proportional to the resistance of the coating/unit area (z).

Thus

$$\eta_x = k' i'_x = \frac{k' i_x}{f} = K i_x z \qquad [9]$$

where K is a constant that depends on the nature of the structure to be protected and the properties of the soil.

From eqns [7] and [9]:

$$\frac{\mathrm{d}^2\eta_x}{\mathrm{d}x^2} = R_\mathrm{L}\left(\frac{2\pi r}{Kz}\right)\eta_x \qquad [10]$$

The solution to eqn [10] for an infinite pipeline, that is, when $\eta_x = 0$, $x = \infty$ and when $\eta_x = \eta_a$, $x = 0$, is

$$\eta_x = \eta_a \exp\left[-\left[\frac{2\pi r R_L}{Kz}\right]^{1/2} x\right] \qquad [11]$$

However, if the pipeline has multiple drain points separated by distance a, and the aim is that the pipeline electrode potential should just reach the protection potential at the mid-point ($x = a/2$), then $\eta_x = a/2$ is equal to η_{prot} (the overpotential required just to achieve the protection potential). At $x = a/2$, the current in the line is zero and $(\mathrm{d}\eta_x/\mathrm{d}x)_x = a/2$ is also zero. Thus

$$\eta_x = \eta_\mathrm{prot} \cosh\left[\left[\frac{2\pi r R_\mathrm{L}}{Kz}\right]^{1/2}\left[x - \frac{a}{2}\right]\right] \qquad [12]$$

and

$$\eta_x = \eta_\mathrm{prot} \cosh\left[-\left[\frac{2\pi r R_\mathrm{L}}{Kz}\right]^{1/2} \frac{a}{2}\right] \qquad [12a]$$

The current in an infinite pipeline is obtained by differentiating eqn [11] and substituting into eqn [6]:

$$I_x = \left[\frac{2\pi r R_\mathrm{L}}{Kz}\right]^{1/2} \frac{\eta a}{R_\mathrm{L}} \exp\left[-\left[\frac{2\pi r R_\mathrm{L}}{Kz}\right]^{1/2} x\right] \qquad [13]$$

The drainage current (i.e., $2I_x = 0$) is therefore

$$2\left[\frac{2\pi r R_\mathrm{L}}{Kz}\right]^{1/2} \frac{\eta_a}{R_\mathrm{L}} \qquad [13a]$$

This analysis is far from exact since it assumes a remote groundbed, uniform soil resistivity, and uniform defect density in the coating. At best, it demonstrates that attenuation is likely to follow an exponential decay and that it will be less severe for larger diameter pipes than for smaller diameter ones. The problem is more difficult to solve for more complex structures (e.g., congested pipeline networks) and especially so for marine installations where the development of the calcareous deposit introduces the possibility of temporal variations in attenuation.

The question of attenuation is not significant in the case of sacrificial anode protection systems where the individual source outputs are small.

4.18.9 Summary

Cathodic protection is a long-established and proven technique for protecting metals from corrosion. While in principle it may be used to protect any metal in an aqueous environment, in practice it is used mainly to protect carbon steels in natural environments such as water, soil, and sand. Other metals often do not require protection because they do not corrode significantly under these circumstances. More aggressive environments render cathodic protection less attractive because of the substantial cost of providing the requisite current. Nevertheless, cathodic protection is applied to a vast area of metal on structures such as buried pipelines, ships, piers and jetties, oil production platforms, and liquid storage tanks. More recently, the protection of reinforcing bar in concrete has received attention. Cathodic protection is therefore of great technological significance.

There are two methods of applying cathodic protection, namely using an impressed current or a sacrificial anode. The former requires a source of DC power, but is then capable of delivering large voltages (<100 V) and currents (<100 A). A sacrificial anode operates independently of a source of DC power but only delivers a voltage of about 1 V and a current that will rarely exceed 5 A. The relative advantages of the two methods largely derive from these differences.

Cathodic protection benefits from its conjoint use with a coating on the structure; the current required for protection is reduced. However, in seawater, the application of the technique encourages deposition of protective salts which to some extent achieves the same objective.

Since cathodic protection, if operated correctly, can prevent the corrosion of a metal entirely, it is unique among all the methods of corrosion control.

References

1. Davy, H. *Philos. Trans. Roy. Soc.* **1824**, *114*, 151, 242,328.
2. Scherer, L. F. *Oil Gas J.* **1939**, *38*(27), 179.
3. *Metallurgical and Inspection Requirements for Cast Sacrificial Anodes for Offshore Applications*; SP 0387–2006; NACE: Houston, TX, 2006.
4. Ashworth, V. *Hot Risers: Managing the Corrosion Problem*; Oyez: London, 1979.
5. *Recommended Practice: Control External Corrosion on Underground or Submerged Metallic Piping Systems*, SP 0169–2007; NACE: Houston, TX, 2007.
6. *Recommended Practice: Internal Cathodic Protection Systems in Oil Treating Vessels*, SP 0575–2007; NACE: Houston, TX, 2007.
7. *Cathodic Protection of Pipeline Transportation Systems – Offshore Pipelines*; ISO 15589-2: 2004 (also ANSI/NACE SP 0607–2007), ISO: Geneva, 2004.
8. *Corrosion Control of Submerged Areas of Permanently Installed Steel Offshore Structures Associated with Petroleum Production*, SP 0176–2007 NACE: Houston, TX, 2007.
9. *Recommended Practice: Cathodic Protection of Pulp and Paper Mill Effluent Clarifiers*, RP-0181–2001; NACE: Houston, TX, 2001.
10. *Recommended Practice: Corrosion Control of Underground Storage Tank Systems by Cathodic Protection. Control of External Corrosion on Metallic Buried, Partially Buried or Submerged Liquid Storage Systems*, RP 0285–2002; NACE: Houston, TX, 2002.
11. *Recommended Practice: Application of Cathodic Protection of External Surfaces of Well Casings*, SP 0186 (2007); NACE: Houston, TX, 2007.
12. *Cathodic Protection: Part 1: Code of Practice for Land and Marine Applications* (formerly CP 1021). BS 7361: Part 1: 1991; BSI: London, 1991.
13. Dees, D. D. In Corrosion/87; NACE: Houston, TX, 1987; Paper no. 73.
14. Stratfull, K. F. *Corrosion* **1959**, *15*(6), 65.
15. Stratfull, R. F. *Transport. Res. Rec. (USA)* **1974**, *500*, 1.
16. Anderson, G. H. In Proceedings of the Conference on Cathodic Protection of Reinforced Concrete Bridge Decks NACE: Houston, TX, 1985.
17. European Standard, *Cathodic Protection of Steel in Concrete*, BS EN 12696: 2000; BSI: London.
18. Yague-Murillo, O. Ph.D. Thesis, Victoria University of Manchester, England, 1983.
19. Uhlig, H. H. *Corrosion and Corrosion Control*; Wiley: New York, 1971.

Further Reading

BS EN12473: General principles of cathodic protection in sea water
BS EN12495: Cathodic protection for fixed offshore structures
BS EN12696: Cathodic protection of steel in concrete
BS EN12954: Cathodic protection of buried or immersed metallic structures: General principles and applications for pipelines
BS EN13173: Cathodic protection for steel offshore floating structures
BS EN13174: Cathodic protection for harbor installations
BS EN13509: Cathodic Protection measurement techniques
BS EN13636: Cathodic protection of buried metallic tanks and related piping
BS EN14505: Cathodic protection of complex structures
BS EN15257: Cathodic protection – Competence levels and certification of cathodic protection personnel

4.19 Sacrificial Anodes

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Abbreviations

ASTM American Society for Testing and Materials
DNV Det Norsk Veritas
FSA Flame sprayed aluminum

Symbols

E Anode consumption rate
L Anode lifetime
M Mass of single anode
N Total number of anodes
U Utilisation factor of anode
W Total mass of all anodes

4.19.1 Principles of Operation

When two different metals are immersed in the same electrolyte, they will usually exhibit different electrode potentials. If they are connected by an electronic conductor, there will be a tendency for the potentials of the two metals to move toward one another; they are said to mutually polarize. The polarization will be accompanied by a flow of ionic current through the solution from the more negative metal (the anode) to the more positive metal (the cathode); therefore, electrons will be transferred through the conductor from the anode to the cathode. Thus, the cathode will benefit from the supply of electrons in that it will dissolve at a reduced rate; it is said to be 'cathodically protected.' Conversely, in supplying electrons to the cathode, the anode will be consumed more rapidly and will act as a 'sacrificial anode.'

From the above discussion, it is clear that, for an anode material to offer sacrificial protection, it must have an open-circuit potential that is more negative than that of the structure being protected (the cathode). The extent of protection experienced by the cathode will depend on the potential it attains. This is dependent on the electrochemical properties of the anode which in turn are governed by its composition and the environment to which it is exposed.

4.19.1.1 Applications of Sacrificial Anodes

The first recorded work on the application of sacrificial anodes was in the 1820s when Sir Humphrey Davy and his assistant Michael Faraday's work for the Royal Navy was reported in Philosophical Transactions of the Royal Society.[1–3] Their work centered on the reduction of the corrosion of copper sheets attached to the wooden hulls of naval vessels. Davy identified that the corrosion was associated with differences in potential across the sheets of copper and, especially, where adherent corrosion products were present. By attaching pieces of zinc wire to a coil of copper wire, Davy demonstrated the process of sacrificial anode cathodic protection; he expanded this to larger scale trials and, finally, to full-scale trials on the HMS Sammarang and the Carnbrea Castle using anodes of cast iron.

When iron hulls became more common later in the nineteenth century, zinc sacrificial anodes were used to reduce corrosion; however, impurities, particularly iron, in the then commercially available zinc resulted in the formation of adherent nonconducting corrosion products of zinc on the anodes, which stifled the protection current flow and reduced the driving potential to unacceptable level.

Examples of the application of sacrificial anodes include ship, hulls and ballast tanks, offshore oil and gas drilling rigs, production platforms semisubmersibles and support facilities, underwater pipelines, underground pipelines, buried structures, harbor piling and jetties, floating dolphins, buoys, lock gates, and submerged concrete structures. There are many other uses including a large range of industrial equipment in which the surfaces are in contact with corrosive electrolytes, for example, heat exchangers, pump impellers, and vessel internals.

4.19.2 Sacrificial Anode Basics

4.19.2.1 Anode Operating Potential, Protection Potential, and Driving Voltage

The operating potential of an anode material is its potential when coupled with the structure under protection (i.e., the closed-circuit potential). Since commercial anode materials are formulated to suffer only limited polarization, under most conditions of exposure, the operating potential approximates to the open-circuit potential. Indeed, any substantial difference ($>50\,\mathrm{mV}$) between these two potentials questions the suitability of the anode in the particular environment. For this reason, the open-circuit potential is usually used in design calculations wherein the operating potential is more precise but generally unknown at the time when the design is undertaken.

The protection potential refers to the potential at which experience shows that corrosion of a metal

Table 1 Anode potentials of various alloys used in cathodic protection

Alloy	*Anode potential (V vs Ag/AgCl/ Seawater)*	*Max anode capacity (A h kg^{-1})*
Al–Zn–Hg	−1.0 to −1.05	2830
Al–Zn–Sn	−1.0 to −1.05	2600 (heat treated)
Al–Zn–In	−1.05 to −1.15	2700
Zn–Al–Cd	−1.05	780
Mg–Mn	−1.70	1230
Mg–Al–Zn	−1.50	1100–1230

will cease. Different materials have different potentials (Table 1). Occasionally, a less negative potential will be specified because some degree of corrosion is permissible. It should be noted that in a mixed metal system, the protection potential for the most base metal is adopted although the designer should take into account any deleterious effect that over protection may have on the nobler component and the need to supply excessive current if it is an efficient cathode. The cathodic protection of mixed metal systems can be a complex subject and is discussed in detail later in the chapter.

The driving voltage is the difference between the anode operating potential and the potential of the polarized structure to which it is connected. For design purposes, the driving voltage is taken as the difference between the anode open circuit potential (unless there are data on how the anode material will actually behave) and the required protection potential of the structure.

4.19.2.2 Anode Capacity and Anode Efficiency

The anode capacity is the total coulombic charge (current × time) produced by the unit mass of an anode as a result of electrochemical dissolution. It is normally expressed in ampere hours per kilogram (A h kg^{-1}); however, the inverse of anode capacity, that is, the consumption rate (kg A^{-1} year^{-1}), is also sometimes used.

The theoretical anode capacity can be calculated according to Faraday's law. From this, it can be shown that 1 kg of aluminum should provide 2981 Ah of charge. In practice, the realizable capacity of the anode is less than the theoretical value. The significance of the actual (as opposed to the theoretical) anode capacity is that it is a measure of the amount of cathodic current an anode can give. Since anode capacity varies among anode materials, it is the parameter against which the anode cost per unit anode weight should be evaluated.

The anode efficiency is the percentage of the theoretical anode capacity that is achieved in practice:

$$\text{Anode efficiency} = \frac{\text{Anode capacity}}{\text{Theoretical capacity}} \times 100\%$$

Anode efficiency is of little practical significance and can be misleading. For example, magnesium alloy anodes often appear to have an efficiency of around 50%, while for zinc alloys, the value exceeds 90%; it does not follow that zinc alloy anodes are superior to those based on magnesium. Efficiency will be encountered in many texts on sacrificial anode cathodic protection.

4.19.2.3 Anode Requirements

The fundamental requirements of a sacrificial anode are to impart sufficient cathodic protection to a structure economically and predictably over a defined period, and to eliminate, or reduce to an acceptable level, corrosion that would otherwise take place.

In view of the above criteria, the following properties are prerequisites for the viability of a sacrificial anode[4,5]

1. The material must have a potential more negative than the potential at which corrosion ceases on the material being protected (i.e., the anode must exhibit a driving potential relative to the protected cathode). Thus, for steel, which is considered protected at potentials more negative than 0.8 V negative to the silver chloride seawater reference electrode, the driving voltage must be capable of overcoming the ohmic resistances of the anode cathode and the electrolyte in order to make the anode deliver the protection current. In practice this means a driving potential of at least 0.2 V more negative than the metal to be protected.
2. The driving potential of the anode must be stable with respect to time and must be predictably affected by the passage of current, that is, the anode material must have known and have acceptable polarization characteristics.
3. The anode material must have adequate capacity; that is, it must deliver an adequate and predictable number of ampere hours for every kilogram consumed.
4. The alloy must be capable of being formed by simple and economical processes into shapes in which it may be used, and it must have adequate

mechanical strength to remain in the desired form throughout its designed life.

5. The alloy must be commercially viable; that is, it must be capable of being produced in significant quantities (the world production of sacrificial anodes runs into many tens of thousands of tons per annum) and sold at a price that is acceptable to the users.

4.19.3 Sacrificial Anode Materials

While cathodic protection can be used to protect most metals from aqueous corrosion, it is most commonly applied to carbon steel in natural environments (waters, soils, and sands). In a cathodic protection system, the sacrificial anode must be more electronegative than the structure. There is, therefore, a limited range of suitable materials available to protect carbon steel. The range is further restricted by the fact that the most electronegative metals (Li, Na, and K) corrode extremely rapidly in aqueous environments. Thus, only alloys based on magnesium, aluminum, and zinc are viable possibilities. These metals form the basis of the three generic types of sacrificial anodes.

In practice, with one minor exception (pure zinc), the commercially pure metals are unsuitable as sacrificial anode materials. This is because they fail to meet one or more of the prerequisites outlined above. For each basis metal, alloying elements are added to ensure more acceptable properties.

Table 2 gives a list of the more important anode materials by broad categories, and some indication of their operating parameters. It is clear that there are major differences in performance between one generic type and another. Thus, the magnesium alloys have very negative operating potentials and are therefore able to provide a large driving voltage for cathodic protection; zinc and aluminum alloys are more modest in this respect. Aluminum alloys, by contrast, provide a substantial current capacity which is more than twice that available from the zinc and magnesium alloys. It might appear that this implies that if the driving voltage is the most important feature in a given cathodic protection system (e.g., when there is a need for short-term high currents or a high resistivity to overcome), then magnesium alloys are to be preferred, but if a high capacity is required (e.g., steady delivery of current over a long life), aluminum alloys would be better. In practice, selection is significantly more complicated, and the topic is discussed in more detail in later sections.

Table 2 Typical basis material composition requirements for anode alloys

99.90% Magnesium		*99.99% Zinc*	
Cu	0.02 max	Pb	0.003 max
Mn	0.01 max	Cu	0.001 max
Sn	0.01 max	Cd	0.003 max
Ni	0.001 max	Fe	0.002 max
Pb	0.01 max	Sn	0.001 max
Others	0.05 max	Zn	99.99 min
Mg	99.90 min		
99.85% Aluminum (P0610)		*99.90% Aluminum (P0506)*	
Fe	0.10 max	Fe	0.06 max
Si	0.06 max	Si	0.05 max
Cu	0.003 max	Cu	0.003 max
Ni	0.003 max	Ni	0.003 max
Cd	0.002 max	Cd	0.002 max

Even within a generic type of alloy, there are significant performance differences. Thus, for example, Al–Zn–In alloys provide a higher driving voltage but a lower current capacity than Al–Zn–Hg alloys. Once a decision to use a generic type of alloy has been made, these apparently small differences in performance may become important in the final selection.

Alloying additions are made to improve the performance of an anode material.[5] Of equal importance is the control of the levels of impurity in the final anode, since impurities (notably iron and copper) can seriously adversely affect anode performance. Careful quality control of the raw materials used and the manufacturing process adopted is essential to sound anode production.

An intimate knowledge of the factors influencing the operation of sacrificial anodes and design parameters is essential if a full appreciation of how best to select an anode and achieve optimum performance is to be realized. The following considerations deal with those factors, which ultimately determine anode performance.

4.19.4 Factors Affecting Anode Performance

4.19.4.1 Alloy Composition

The constituent elements of anode materials, other than the basis metal, are present as a result of either being impurities in the raw materials or deliberate alloying additions. Impurity elements can be deleterious to anode performance; therefore, it is necessary to control the quality of the input materials in order to achieve the required anode performance. Since this will usually have an adverse impact on costs, it may be desirable to tolerate a level of impurities and to overcome their action by making alloying additions. Alloying elements may also be added for other reasons, which are important to anode production and performance.

In general, sacrificial anode alloy formulations are proprietary and may be covered by patents. The patent documents are often very imprecise when they relate to compositions that will produce effective anodes and quite inaccurate in ascribing the function to a given alloying element. While the commercial literature is more specific when it relates to compositions, it rarely details the purpose of an alloying addition. In discussing alloy composition here, the treatment derives from the technical literature and is necessarily a broad-brush account. The reader is referred to the wealth of literature published over the past 50 years, for example, as reviewed by Googan.[6]

4.19.4.2 Impurities

One important feature of an anode alloy is that it should dissolve with a capacity approaching the theoretical value. That is, all the electrons released by the metal dissolving should be transferred to the structure to support the cathodic reaction there, and should not be wasted in local cathodic reactions on its own surface.

In all the generic types of sacrificial anode alloys, the presence of iron is found to be deleterious. This is because an intermetallic compound formed between it and the basis metal proves to be a good cathode. Its presence-*c* will result in a substantial lowering of the capacity of an anode. Moreover, the presence of this cathodic material will often raise (make less negative) the anode operating potential and may, in the limit, promote actual passivation. Thus, the driving force available from the anode is reduced or completely destroyed. For example, when the solid solubility of iron in zinc (~14 ppm) is exceeded, the anode operating potential becomes more positive. This has been attributed to the formation of $Zn(OH)_2$ around intermetallic precipitates of $FeZn_{13}$.[7] The presence of iron has a similar adverse effect in aluminum[8] and magnesium[5] alloys.

There are two ways of avoiding the iron problem: to control the iron added with the basis metal or to sequester the iron in some way to render it ineffective. In practice, it is not possible to permit more than a limited iron content because sequestering is only economic and practicable within defined limits. The wider availability of electrolytically smelted zinc with iron levels around 20 ppm means that iron is no longer an issue in the production of zinc anodes. The same is true for aluminum as world demand for higher purity ingot for the electronics industry means that aluminum with a notional purity of 99.85% is readily available with less than 0.08% iron and 99.90% with iron levels selectable at below 0.05%.

Other heavy metal impurities (especially copper and nickel) have similar adverse effects on all generic alloy types. In their case, sequestering has not proved successful, and control of input quality is used to keep their concentration acceptably low.[5] It is important that these impurities are specified at the time of selecting a supplier as what is a deleterious impurity to one application may be a beneficial ingredient to another; for example, levels of nickel in aluminum sourced in the Middle East were not considered relevant for most applications but resulted in significant reduction in capacity when used for anode production. Similarly, naturally occurring levels of gallium present in aluminum feedstock sourced in the United States for the development of Al–Zn–Si–In alloys contributed to the activation process, but when the alloy was licensed for production in the United Kingdom, locally sourced aluminum did not have the gallium impurity, and it had to be deliberately added to achieve the desired properties.

4.19.4.3 Alloying Additions

We have seen that the adverse effect of impurities can, within limits, be controlled by alloying additions. Thus, silicon and aluminum are added to zinc and manganese to magnesium, to counter the effect of iron.

Additions are made for other purposes, all of which aim to improve the performance of the anode. These include lowering the anode operating potential to increase the driving voltage, avoiding passivation, increasing the anode capacity, improving the dissolution morphology, modifying the mechanical properties of the dissolution product to promote detachment, and improving the mechanical properties of the anode.

Table 3 lists some common zinc anode alloys. In three cases, aluminum is added to improve the uniformity of dissolution and thereby reduce the risk of mechanical detachment of undissolved anode material.[5] Cadmium was traditionally added to encourage the formation of a soft corrosion product that readily crumbles and falls away so that it cannot accumulate to hinder dissolution[7]; however, its use is now restricted due to environmental concerns. The Military Specification[9] material was developed to avoid the alloy

Table 3 Standard zinc anode alloys

Alloy Component (wt%)	*ASTM B4 18-88 Type I*	*ASTM B 418-88 Type II*	*US Mil Spec A 18001 K*	*DNV Elevated temp*
Al	0.10–0.50	0.005 max	0.10–0.50	0.10–0.20
Cd	0.025–0.07	0.003 max	0.025–0.07	0.03–0.06
Fe	0.005 max	0.0014 max	0.005 max	0.002 max
Cu	0.005 max	0.002 max	0.005 max	0.005 max
Pb	0.006 max	0.003 max	0.006 max	0.006 max
Si	–	–	–	0.125 max
Others(total)	0.1 max		0.10 max	–
Zn	Remainder	Remainder	Remainder	Remainder
o/c potential Ag/AgCl/ seawater	−1.05 V	−1.05 V	−1.05 V	−1.05 V
Capacity (A h kg^{-1})	780	780	780	780

Table 4 Proprietary aluminum anode alloys

Alloy Component (wt%)	*Al–Zn–In*	*Al–Zn–Sn*	*Al–Zn–Hg*
Fe	0.12 max	0.13 max	0.08 max
Si	0.05–0.20	–	0.11–0.21
Zn	2.0–6.5	4.0–6.0	0.35–0.5
Hg	–	–	0.035–0.050
In	0.01–0.02	–	–
Sn	–	0.1	–
Cu	0.006 max	−.01 max	0.006 max
Ti	0.02 max	0.02 max	0.02 max
Others	0.02 max	0.02 max	0.02 max
o/c potential Ag/AgCl/ seawater	−1.10 V	−1.10 V	−1.05 V
Capacity (A h kg^{-1})	2700	Variable	2830

passivating as a result of the presence of iron.[5] It later became apparent that this material suffered intergranular decohesion at elevated temperatures (>50 °C) with the result that the material failed by fragmentation.[10] The material specified by Det Norske Veritas[11] was developed to overcome the problem: the aluminum level was reduced under the mistaken impression that it produced the problem. It has since been shown that decohesion is due to a hydrogen embrittlement mechanism,[12] and that it can be overcome by the addition of small concentrations of titanium.[13] It is not clear whether the titanium acts as a getter for hydrogen or simply serves to refine the grains and increase the grain boundary area thereby diluting the embrittlement effect. It is claimed that recently developed alloys with magnesium additions are also resistant to intergranular attack at elevated temperatures.[5,10]

Although aluminum is a base metal, it spontaneously forms a highly protective oxide film in most aqueous environments; that is, it passivates. Consequently, it has a relatively noble corrosion potential and is then unable to act as an anode to steel. Low level mercury, indium, or tin additions have been shown to be effective in lowering (i.e., making more negative) the potential of aluminum; they act as activators (depassivators). Each element has been shown to be more effective with the simultaneous addition of zinc. Zinc additions of up to 5% lower the anode operating potential, but above this level, no benefit is gained. Below 0.9% zinc, there is little influence on the performance of aluminum anodes.[5] Table 4 lists a number of the more common commercial alloy groups.

The best capacities in seawater are obtained from alloys containing zinc and mercury, but this is achieved at the expense of a somewhat more noble operating potential. Higher zinc additions at around 5% result in an alloy highly tolerant of burial in seabed muds. Mercury has become associated with environmental issues and is now seldom used in offshore applications. Zinc and indium additions give a less noble operating potential but are associated with a lower capacity. In practice this effect on the operating potential can be quite significant. The driving voltage between Al–Zn–Hg (open circuit/operating potential −1.05 V) and steel (protection potential −0.80 V) is 0.25 V. The use of Al–Zn–In provides a 20% increase in the driving voltage and thereby the possibility of a higher current output from equal sized anodes. Thus, both alloys have important advantages and disadvantages.

The Al–Zn–Sn alloys require careful solution heat treatment in their production to achieve optimum properties. Inevitably, this leads to more expense, longer production times, and a need for greater quality control. The advent of the alloys containing mercury or indium rendered these alloys very much less attractive. Magnesium additions (0.1–2.0%) to Al–Zn–In alloys have been made, but it is not known whether this was a deliberate addition to improve a particular property or because the starting point for alloy development was an existing structural alloy. These materials can harden with age and hence suffer reduced ductility; since this can subsequently lead to longitudinal cracking of the anodes, they should not be cast in thin sections or stored at elevated temperatures (full sun in hot climates). Higher levels of magnesium (up to 8%), while improving strength and casting characteristics, incur the disadvantage of a reduced capacity.

Both titanium and boron can be added as grain refiners to ensure small grain size and hence high surface area grain boundaries.[14] This reduces the risk of preferential attack at grain boundaries and promotes more uniform dissolution. This effect also results in an alloy that is less susceptible to 'hot shortness.'

Typical proprietary magnesium anode materials are given in Table 5. Magnesium anodes comprise two distinct types, the Mg–Mn and Mg–Al–Zn alloy systems. Addition of up to 1.5% manganese to high-purity magnesium yields a material with an operating potential of –1.7 V versus Ag/AgCl/seawater. The Mg–Mn alloys therefore exhibit very high driving potential and thus find application in particularly resistive environments. Mg–Al–Zn anodes have an operating potential (−1.5 V versus Ag/AgCl/seawater) 200 mV above that of the Mg–Mn alloys. This is very favorable in view of problems with overprotection. Thus, they are more popular in typical environments than the Mg–Mn alloys. The alloys also contain manganese, which is added to overcome the deleterious effects of iron.[5] Alloying additions of aluminum, zinc, and manganese to magnesium serve to improve the anode capacity and reduce the operating potential, compared with that of pure magnesium. There is, however, no difference between the capacity of Mg–Mn and Mg–Al–Zn anodes. Mg–Al–Zn alloys are called 'high purity' when produced from virgin magnesium to distinguish them from a series of alloys developed after the Second World War when large amounts of magnesium alloy scrap were available.

Table 5 Proprietary magnesium anode alloys

Alloy Component (wt%)	*Mg–Mn (Galvomag®)*	*Mg– Al– Zn (high purity)*
Cu	0.02 max	0.02 max
Al	0.01 max	5.3–6.7
Si	–	0.10 max
Fe	0.03 max	0.003 max
Mn	0.5–1.3	0.15 min
Ni	0.001 max	0.002 max
Zn	–	2.5–3.5
Sn	0.01 max	–
Pb	0.01 max	–
o/c potential vs. Ag/AgCl/seawater	–1.7	–1.5
Capacity Ahrs/kg	1230	1230

4.19.4.4 Metallurgical Factors

In producing anodes, the production method must not compromise the benefits of alloy formulation. A number of undesirable anomalies can occur during production, which may detract from the desired anode properties. Some of these anomalies are discussed below. A detailed account of finished anode requirements can be found elsewhere.[11,15]

Although most anodes are made by gravity casting, some are made by continuous or semicontinuous casting or extrusion. The method of casting affects the physical structure of the anode. That is, the associated cooling process will influence the segregation or distribution of alloying constituents. In some cases, it is undesirable to permit segregation since this may lead to preferential attack at grain boundaries. However, it is believed that segregation of activating elements during cooling benefits the performance of some alloys. This mechanism is a suggested explanation for the mercury- and indium-rich phases round on the surfaces of aluminum anodes.[13] The increased surface concentrations of these elements aid activation and are therefore beneficial.

Significant porosity within the anode is an indicator of the presence of dissolved gasses in the molten alloy and is an indicator of poor foundry practice and should be a cause for rejection and further investigation. The inclusion of extraneous matter, as a consequence of unclean foundry practices, may increase the tendency to fragmentation.

Cracking of anodes during casting is, in some cases, unavoidable due to the stresses imposed by cooling particularly those occurring between the cooling contracting anode and the mould heating and expanding. The problem is more common in Al–Zn–Hg anodes and less common when continuous or semi-continuous casting is used. Longitudinal cracks cannot be accepted, as these will lead eventually to mechanical loss of material. A greater tolerance to transverse cracks can be exercised although foundry practice and the use of grain refinement additions can minimize their occurrence. For example, one quality specification permits an anode completely supported by the insert to have transverse cracks of unlimited length and depth provided that there are no more than ten cracks per anode and their width does not exceed 5 mm.[15] This is somewhat arbitrary but emphasizes the point that cracks that threaten anode integrity are of greatest importance.

The anode material must stay firmly attached to the steel insert, which is necessary to conduct the current from the anode so that the structure remains effective, throughout its design life. Consequently, surface preparation of the insert prior to casting to ensure a sound bond with the anode material is essential. Voids at the insert–anode material interface are undesirable, as these will also affect the bond integrity. Dry blast cleaning to near white metal at the time of casting is the usual preparation for aluminum alloy anodes,[15] and coating by hot dip galvanizing or electrogalvanizing is used for inserts of zinc or magnesium anodes. Zinc coating of inserts for aluminum anodes must not be used as the coating enables the molten alloy to dissolve the insert.

4.19.4.5 Environmental Factors

The conditions of environmental exposure play a key role in determining anode performance. Indeed, specific environments often preclude, or necessitate, the use of particular anode materials.

This section is not intended to deal with those environmental factors that influence cathodic current demand (e.g., oxygen availability or the presence of calcareous deposits) but those that directly affect the performance of the anodes.

Temperature is of particular importance to the performance of anodes, especially when anodes are buried. Anodes may often be used to protect pipelines containing hot products. Thus, temperature effects must be considered. Al–Zn–In anodes experience greatly reduced capacity in open seawater at temperatures above 70 °C[16] (down to 1200 $\mathrm{A\ h\ kg^{-1}}$ at 100 °C) and in seabed muds in excess of 50 °C[16,17] (900 $\mathrm{A\ h\ kg^{-1}}$ at 80 °C). At elevated temperatures, passivation of both aluminum alloys and pure zinc can occur.[18] Considerable improvement in performance (capacity, and to a lesser extent operating potential) has been claimed for a range of modified Al–Zn–In anode materials containing a deliberate alloying addition of silicon.

Zinc anodes have also experienced problems at elevated temperatures in saline mud, suffering intergranular decohesion at approximately 70 °C.[19] Later work by the same authors showed the threshold for damage to be ~50 °C. The material is not recommended above 40 °C[10] although special zinc based materials for temperatures exceeding 50 °C have been developed.[11] Pure zinc, which does not suffer intergranular decohesion, will passivate under these conditions. It is claimed that newly developed Zn–Al–Mg anodes will perform satisfactorily at elevated temperatures.[10] Nevertheless, Al–Zn–In anodes have been specified for operation above 50 °C.[10] Furthermore, steps are now taken to ensure that the anode design prevents anode material being exposed to elevated temperatures under buried conditions.

It must be observed that most anode testing and development for use at elevated temperatures both in laboratories and in the field has been under isothermal conditions, and it is often erroneously assumed that the anode temperature is that of the product, whereas the anode is probably at a significantly lower temperature but is operating under high heat transfer conditions and that consideration should be given to placing a thermal barrier between the anode and the structure to minimize both temperature and heat transfer effects.

The presence of H_2S (from bacterial activity in anaerobic saline mud, for example) can result in a significant decrease (16%) in capacity and loss of operating potential for Al–Zn–In anodes.[17]

Environmental resistivity and chloride content will affect anode performance. Aluminum alloy anodes require the presence of chloride ions to prevent passivation. Land-based applications generally provide insufficient chloride levels for this purpose. Consequently, aluminum alloy anodes predominantly find application in marine environments although some water produced from oil or gas wells is both saline and hot, and aluminum anodes find application in corrosion protection in vessels handling these fluids. The capacity and operating potential, of aluminum alloy anodes in particular, illustrated in **Figures 1 and 2**, are dependent on the degree of salinity. With reducing salinity, the anode capacity will decrease and the operating potential rise. This becomes increasingly significant below 10–20% seawater strength and is important for design in estuarine conditions. Passivation of aluminum zinc indium alloy anodes may occur as a consequence of electrolyte stagnation, particularly, if the anode is immersed in silt or sand; zinc and Al–Zn(5%)–Hg perform reasonably under these conditions.

The capacity of an anode is dependent on the anode operating current density.[16] To some extent, it will be governed by its environment but, in part, is within the control of the design. Certainly, wholly unsuitable current densities can usually be avoided

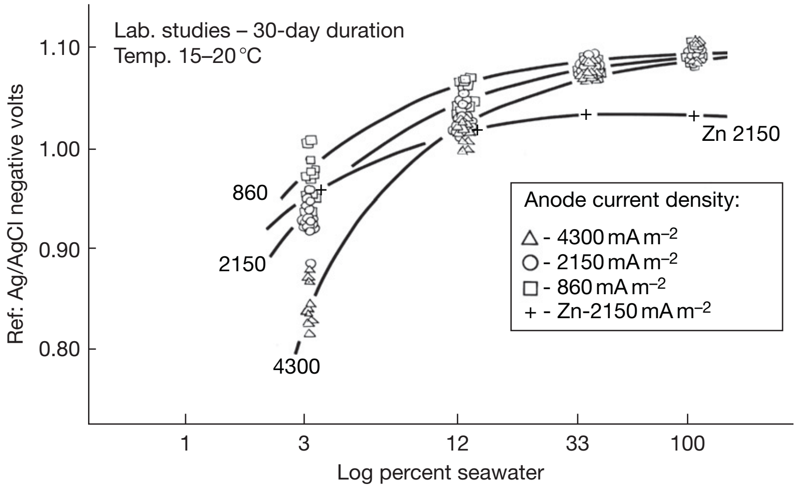

Figure 1 Electrochemical potential of aluminum and zinc anodes as a function of salinity and current density.

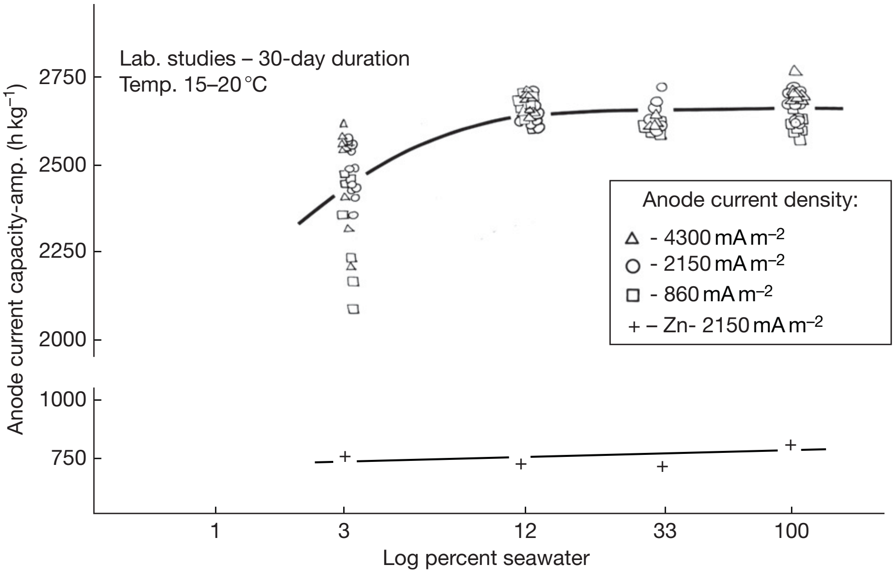

Figure 2 Capacity of aluminum and zinc anodes as a function of chloride ion concentration and current density.

by correctly sizing the anodes. At lower operating current densities, some anodes exhibit reduced capacity; this is shown in Figure 3. Long periods of low operating current density can lead to passivation. This may result in failure to activate when the current demand increases (as can occur with anodes on coated structures when the coating deteriorates).

4.19.5 Selecting the Appropriate Anode Material

It is desirable to choose an anode material with the lowest cost per ampere hour of current supplied. However, the choice is often governed by other constraints and frequently becomes a compromise.

4.19.5.1 Zinc

Of all the anode materials, zinc is arguably the most reliable. It has, with few exceptions, reliable electrochemical performance; the exceptions lie within the area of high temperature operation. Zinc provides the lowest driving voltage of the generic alloy types. It is therefore unsuitable in highly resistive soils, except possibly as a ribbon, and in low salinity waters. However, an operating potential of −1.05 V versus

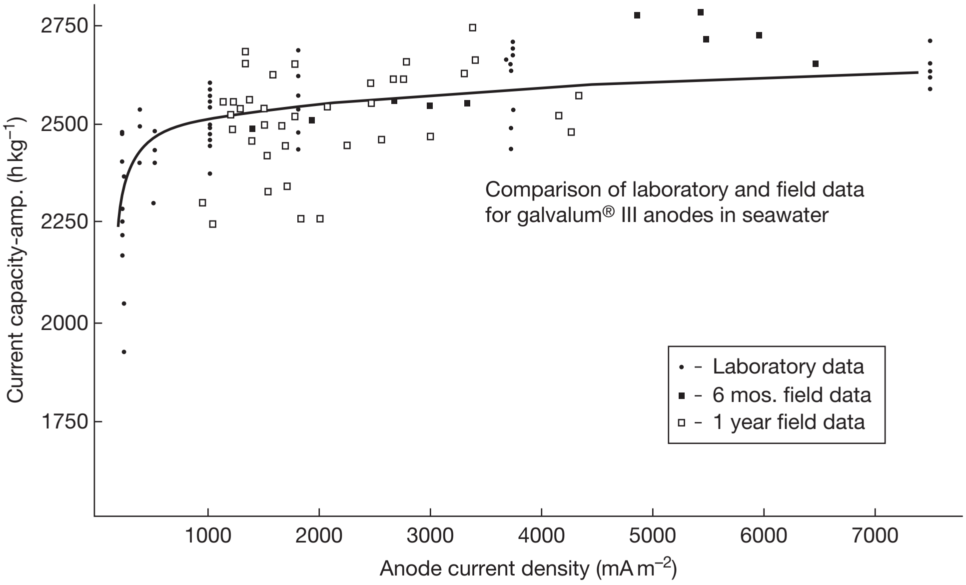

Figure 3 Capacity of an aluminum anode as a function of current density in seawater.

Ag/AgCl/seawater cannot lead to overprotection, which is an advantage where concerns for coating disbondment and hydrogen damage of high strength steel (>700 MPa) exist.[11]

Zinc anodes have a poor capacity (780 A h kg^{-1}) compared with aluminum (>2500 A h kg^{-1}) although with its much higher density equivalent life anodes are frequently of similar dimensions. However, zinc is not susceptible to passivation in low chloride environments or as a consequence of periods of low operating current density. The reliable operational characteristics of zinc often outweigh the apparent economic attraction of aluminum, which can passivate under such conditions. At the time of writing, raw zinc costs about half the price of aluminum, which can significantly contribute to enhancing the appeal of zinc.

Zinc anodes do not find application at temperatures in excess of 50 °C. Zn–Al–Cd alloys suffer intergranular decohesion, and high purity zinc will passivate. Zinc anodes are not predominant in onshore or offshore applications, but they find use under both conditions. The use of zinc anodes on fixed structures in the North Sea is now proscribed under EU regulation (Paris Convention).

4.19.5.2 Aluminum

The great attraction of aluminum anodes is their very high capacity, over three times that of zinc. They are attractive from a cost point of view and also offer substantial weight savings, which can be of great importance (e.g., offshore structures wherein the float-out weight is of paramount importance and the cost of increased weight of anodes can be many times the cost of the anodes and their installation).

Aluminum anodes comprise essentially three generic types: Al–Zn–In, Al–Zn–Hg, and Al–Zn–Sn. Since Al–Zn–Sn alloys have largely been superseded, they will not be discussed further. Indium and mercury are added to aluminum to act as activators, that is, to overcome the natural passivation of aluminum. Despite this, aluminum anodes are not suitable for low chloride environments, which would lead to passivation. These anodes are therefore not used for land-based applications (although examples of use in environments such as swamps do exist). Similarly, their use in low chloride aqueous environments such as estuaries must be viewed with caution.

Traditionally, the technical choice between Al–Zn–In and Al–Zn–Hg anodes is influenced by their respective operating potentials and capacities; however, more recently the environmental concerns have restricted the use of mercury-containing anodes. Where an additional driving voltage is required (such as in seabed mud), Al–Zn–In anodes may be preferred to ensure adequate structure polarization. Alternatively, a lower driving potential may be acceptable where the additional capacity (and hence weight saving) is the predominant factor; this favors Al–Zn–Hg anodes.

Aluminum anodes are less constant in their electrochemical characteristics than zinc. This presents no major problem provided the designer is aware of their properties. They suffer from reduced capacity and increased operating potential (and hence risk of passivation) with increasing temperatures above approximately 50 °C, decreasing salinity (**Figure 2**) and decreasing operating current density (**Figure 3**).

Aluminum alloys are susceptible to thermite sparking when dropped on to rusty surfaces. Consequently, their use may be subject to restrictions. For example, in ships' tanks where explosive gases or mixtures of gases can accumulate, the weight of the anode and the height at which it is suspended are strictly controlled. This is because thermite sparking is dependent on the kinetic energy of the anode released on impact, should it fall.

4.19.5.3 Magnesium

Magnesium anodes are of two generic types, Mg–Mn and Mg–Al–Zn. Both alloy systems have a high driving voltage and therefore find application in high resistivity environments: soils and fresh, or brackish waters, for example. The Mg–Mn alloy is useful in particularly resistive environments (up to 6000 Ω cm) as a result of an available driving voltage 200 mV greater than Mg–Al–Zn anode. Because magnesium is nontoxic, its use is permissible in potable water systems wherein the conductivity is low.

The high driving voltage may, however, result in overprotection. Combined with relatively poor capacity (1230 $\mathrm{A\,h\,kg^{-1}}$) and high unit cost, these disadvantages mean that magnesium rarely finds application in subsea environments where alternatives are available. Despite this, Mg–Al–Zn anodes have been used in seabed mud and for rapid polarization of structures (in ribbon form).

The susceptibility of magnesium to thermite sparking when dropped onto rusty surfaces precludes its consideration for applications involving a spark hazard, for example, tankers carrying inflammable petroleum products.

4.19.6 Anode Testing

Tests or sacrificial anode materials are generally conducted for three reasons: for screening (or ranking), performance information, and quality control. The application of sacrificial anodes for the protection of structures requires the development of suitable anode materials for the exposure environment.

1. Screening tests enable the rapid selection of materials that show potential as candidates for the given application. These tests may typically use a single parameter (e.g., operating potential at a defined constant current density) as a pass/fail criterion and are normally of a short duration (usually hours) with test specimen weights of the order of a few tens or hundreds of grams. The tests are not intended to simulate field conditions precisely and often include cutting samples from larger castings and surface preparation to give uniformity/across tests.
2. Performance testing is long term (months to years). Once a potentially attractive formulation has been identified, it is usual to produce detailed data on its performance and behavior as an anode material under the anticipated exposure conditions. For this reason, the test should mirror as closely as possible the expected operating conditions, or where practicable be conducted in the field. Large specimens (tens or hundreds of kilograms) in the as cast condition would be used for these tests.
3. Quality control tests are intended to detect produced materials that deviate from manufacturing specifications, and thus may result in questionable performance. This area of anode testing has probably been the subject of more debate and controversy than any other. The anode alloy is usually subjected to chemical analysis usually by spark emission spectroscopy, which is the primary quality control check. The preparation of samples for this testing, especially if small samples from the melt or samples that are cut from a full anode are to be used, must be validated to ensure that analysis is not corrupted by surface preparation. The risk is reduced if the analytical technique uses dissolution of the sample when surface preparation is irrelevant.
4. Exposure testing has generated a whole industry of quite dubious value to the final product. It was first developed to act as a quality check on the efficacy of solution heat treatment of Al–Zn–Sn alloy anodes when a simple capacity test based on measurement of hydrogen evolved under impressed current was used as a go or no-go acceptance test. Samples, heat treated alongside full sized anodes, were tested overnight. Unfortunately, the results were expressed in the same units as anode capacity, and electrochemical testing has now been mandated to do a job that was never intended, that is, to confirm the actual long-term performance of full sized anodes in service. The use of short-duration (hours or days) tests on small samples, which have had some form of surface treatment not typical of

full-sized anodes, in which the test conditions attempt to reflect the environment of operation, for example, using artificial seawater for a marine application, cannot and never will reflect full-scale operation. In more than 30 years of experience, this author has not heard of a single instance in which a sensible sized anode (>10 kg) made from a correctly formulated alloy has failed to deliver electrochemical performance as expected. Conversely, the examples of small-scale tests on samples giving erratic results are legion, and the subsequent contractual and so called scientific wrangles have contributed nothing to corrosion control.

4.19.7 Cathodic Protection System Design

4.19.7.1 Design Parameters

Before a satisfactory cathodic protection system using sacrificial anodes can be designed, the following information has to be available or decided upon:

1. the area of the steelwork to be protected;
2. the type of coating, if any, that is to be used;
3. the cathodic current density;
4. cathodic protection system life.

While the data given here is general guidance for many situations, detailed guidance will be given in classification society or client rules, and these will take precedence and may change based on the experience gained in actual operation.

4.19.8 Area of Steel Requiring Protection and Coating Considerations

The area of bare steel to be protected is usually calculated from drawings and knowledge of the actual structure and must account for all electrically continuous steelwork exposed to the electrolyte. Steelwork not specified in drawings and subsequently overlooked is a common cause of underdesign. In one classic example, the current drain to the conductors of an offshore production platform was ignored with near disastrous consequences and a requirement for a gigantic retrofit program. In practice, the area is usually taken assuming the steel surfaces to be flat without corrugations, indentations, or surface roughness. An allowance for uncertainties in real area is normally involved.

Many structures, especially pipelines, are coated. Thus, the presented area far exceeds the area of steel to be protected, which is restricted to uncoated areas and holidays in the coating. It is therefore good practice to assume an arbitrary level of coating breakdown for coated areas to obtain the area of metal requiring cathodic protection. During installation of larger diameter subsea pipelines (>8 in. dia), pipe sections are prepared in 40 ft lengths onshore where coating integrity can be rigorously controlled; however, field joints are often made under severe constraints as the pipe is prepared to go over the stinger. It is therefore often assumed that these field joints will fail, and 2.5% coating loss is used as the basis for design

$$\text{Area to be protected} = \frac{\text{Presented area} \times \%\ \text{breakdown}}{100}$$

Breakdown will vary through the life of a structure with the result that the area requiring protection will change. Various estimates of coating breakdown have been made, and Table 6 provides an example based on a single coat epoxy coating system on blast cleaned steel exposed to seawater, for example, a subsea completion structure. Table 6 reasonably assumes a rate of breakdown that varies with time; this will be much greater for fully exposed surfaces compared, for example, to pipeline coatings which may be overlaid with several centimeters of reinforced concrete which are then trenched into the seabed, as are shown alongside. A ships hull may be expected to lose 10–20% or even more of its coating system in a relatively short period dependant on operating location. The significance of the area of steelwork is that the greater the area, the greater the weight and/or the area of anode material required for protection.

4.19.9 Cathodic Current Densities for Protecting Steel

Examples of current density requirements for the protection of steel (to achieve a steel potential of –0.8 V

Table 6 Guidance on coating breakdown for offshore structures

Steel structures fully exposed simple epoxy coating			
Lifetime (years)	Coating breakdown %		
	Initial	Mean	Final
10	2	7	10
20	2	15	30
30	2	25	60
40	2	40	90
Pipeline with glass fiber/bitumen and 70-mm reinforced concrete weight coat			
40	1	2.5	5

Table 7 Guidance on current density for cathodic protection of bare steel

Location	*Current density* *($mA\,m^{-2}$)*		
	Initial	Mean	Final
Northern North Sea	180	90	120
Southern North Sea	150	90	100
Arabian Gulf	130	70	90
Indian Ocean	130	70	90
Australia	130	70	90
Brazil	130	70	90
West Africa	130	70	90
Gulf of Mexico	110	60	80
Indonesia	110	60	80
Saline mud	25	20	15

versus Ag/AgCl/seawater) are given in Tables 7. It should be realized that the current demand of a structure will be influenced by, *inter alia*, temperature, degree of aeration, flow rate, protective scales, burial status, presence of bacteria, and salinity.

It is important that the correct current density requirement is assigned for design purposes. If too high a value is used the structure may be overprotected and anode capacity wasted. On the other hand, if too small a value is used it will mean that the protection system will not achieve its design life.

4.19.10 System Life

Cathodic protection systems may be designed with a life as short as 1 year or more than 40 years. The greater the time of protection, the greater the mass or anode material that is required.

Intermittent exposure and local conditions need to be considered also. The ballast or storage tanks of ships will experience periods of complete submergence and partial coverage, and may at times be empty. Similarly, the wetted areas of offshore structures may be governed by tidal and seasonal variations. Local requirements must therefore be considered in order to achieve the optimum amount of anodic material to achieve the life of the system.

4.19.10.1 Calculating the Weight and Number of Individual Anodes

Firstly, the total weight of anode required to protect the structure for its projected life is calculated. This is given by:

$$W = \frac{i_{av} A l \times 8760}{C}$$

where W is the total mass of anode material (kg); A, the structure area to be protected (m^2); i_{av}, the mean structure current density demand ($A\ m^{-1}$); l, the design life in years (1 year = 8760 h); and C is the anode capacity ($A\ h\ kg^{-1}$).

Obviously, the total weight of the anode material must be equal to or be greater than the total weight, W, calculated above. Similarly, each anode must be of sufficient size to supply current for the design life of the cathodic protection system. The anodes must also deliver sufficient current to meet the requirements of the structure at the beginning and end of the system's life. That is, if current demand increases (as a result of coating breakdown, for example), the output from the anodes should meet the current demands of the structure.

4.19.10.2 Anode Size and Shape

In practice, while there is often an extensive range of suitable anode sizes to select from, economics may dictate a bespoke anode for a project depending on its precise requirements. Computer programs are used to optimize (minimize) the number of anodes required to satisfy the often conflicting protection requirements. The cost of the anode insert in a platform anode may be close to that of the anodic material, and the cost of lifting, welding, etc. is substantially more than that of the anode. Furthermore, after a set of moulds has been used to produce several thousand anodes, they will probably only be fit for recycling.

The current output from an anode will depend on its resistance, which will be a direct function of shape and size. Generally, larger anodes will have a higher current output. Anodes of the same weight but differing shape can have different outputs because the surface area to weight ratio will not be equal for all possible dimensions. Thus, for a given weight of anode, the shape will offer a degree of flexibility when considering current output.

4.19.10.3 Anode Output

Anode output is the current available from the anode under the design conditions. It will depend on the shape of the anode, the resistivity of the environment, the protection potential of the structure, and the anode operating potential. It is defined as:

$$I = \frac{[E_2 - E_1]}{R}$$

I is the anode output (A); E_1, the operating potential of the anode (V); E_2, the protection potential (V); and R is the anode resistance (Ω).

The protection potential of steel in aerobic environments is taken as –0.80 V (versus Ag/AgCl/seawater).

4.19.10.4 Anode Resistance

Table 8 lists some of those formulae suitable for the calculation of anode resistance, R, under submerged conditions. Some are based on earth resistance effects and modifications of the formulae used in the design of electrical earthing systems, while others are purely empirical. Similar formulae exist for anodes in buried conditions. These have been extensively researched and reviewed.[20–24]

To calculate the anode resistance, a knowledge of the environmental resistivity is required. For submerged anodes, the water resistivity can be obtained from graphical representations such as in Figure 4, provided that the temperature and water density are known. However, field data are preferable, and, in the case of soils that can have widely varying resistivities, they are essential.

4.19.10.5 Anode Life

Having calculated the resistance, and hence the current output, the anode life, L, is checked by the calculation:

$$L = \frac{MU}{IE}$$

where L is the effective life of anode (years); M, the mass of single anode (kg); U, the utilization factor, for example, 0.75–0.80 for bracelet anodes and 0.95 for platform anodes; E, the consumption rate of the anode (kg A^{-1} year^{-1}) (inverse of capacity in suitable units); and I is the anode output (A).

Table 8 Table of anode resistance formulae DnV RP B401

Anode type	*Resistance formula*
Long slender stand-off[a,b] $L \geq r$	$R_a = \frac{\rho}{2\pi L}\left(\ln\frac{4L}{r} - 1\right)$
Short slender stand-off[a,b] $L < 4r$	$R_a = \frac{\rho}{2\pi L}\left[\ln\left\{\frac{2L}{r}\left(1 + \sqrt{1 + \left(\frac{r}{2L}\right)^2}\right)\right\} + \frac{r}{2L} - \sqrt{1 + \left(\frac{r}{2L}\right)^2}\right]$
Long flush-mounted[b] L ≥ 4 width and L > 4 thickness	$R_a = \frac{\rho}{2S}$
Short flush-mounted, bracelet and other types	$R_a = \frac{0.315\rho}{\sqrt{A}}$

[a] The equation is valid for anodes with minimum distance 0.30 m from protection object. For anode-to-object distance minimum 0.15 m the same equation may be applied with a correction factor 1.3.
[b] For noncylindrical anodes: $r = c/2\pi$ where c(m) is the anode cross-sectional periphery.
Source: DnV RP B401 (2005) – Recommended practise for cathodic protection design.

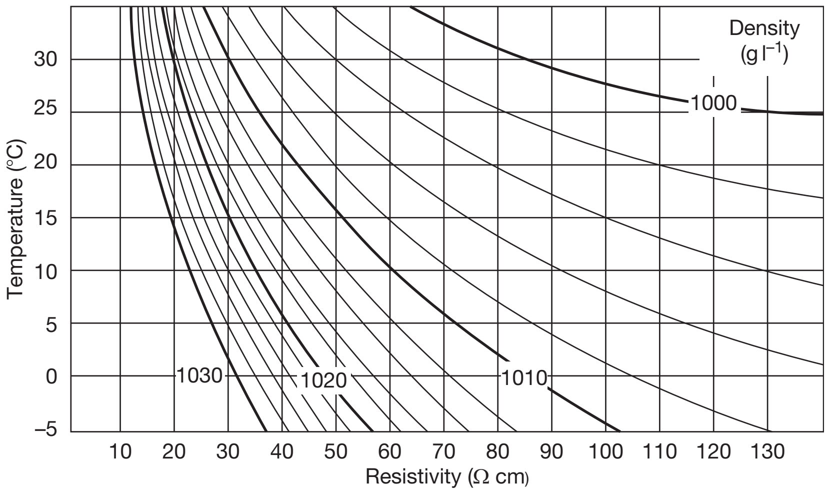

Figure 4 Resistivity as a function of specific gravity for seawater/fresh water mixtures.

U is purely a function of anode geometry and is the fraction of anode material consumed when the remaining anode material cannot deliver the current required or the anode can no longer be supported by its insert.

Excessive anode life is of no benefit. If the calculated life is unsuitable a different anode size and/or shape should be considered. However, this may not always be possible, especially for short-life, coated structures, when dimensional constraints on the anodes may be imposed.

4.19.10.6 Number of Anodes

The total number of anodes, N, is calculated from:

$$N = \frac{Ai_{\mathrm{ay}}}{I}$$

This calculation should yield a practicable number of anodes; that is, 10 or 10 000 anodes are both clearly unacceptable for the distribution of protection. On an offshore oil production platform, $N \times M$ must be equal to, or greater than, the total weight or anode material, W, required.

It is also useful at this point to consider the limitations imposed by the production processes and the actual application of the anode. For a platform anode, hypothetically, the anode could be almost as long as the water depth, but first such an anode would have such a large mass and consequently inertia that it would be unlikely to survive the installation or piling processes and would be torn off. Using a stronger insert and attachment configuration would result in such a large diameter core relative to the body cross section that the anode material could reasonably be expected to split longitudinally during the solidification and subsequent cooling. Some of these could be overcome by semicontinuous casting rather than horizontal gravity casting. However, this process, originally developed for production of extrusion ingots still, has the limitation of the depth of the pit into which the casting is discharged and the lifting equipment servicing it. In order to minimize the likelihood of some or all of these, for all practical purposes, the maximum core diameter of a platform anode is 150 mm, and for this to be cast into an anode, the cross section would have to give at least 100-mm depth of cover of the anodic material over the insert. While some foundries design a small cross-section taper over the length of the anodes, others use very heavy preheated wall moulds and inserts (or both) to minimize anode mould interaction. Unless the mould/insert is heated to the casting temperature of the anode alloy, the mould and insert will continue to expand as the anode solidifies and contracts, and transverse cracking of the anode becomes more probable. Grain refinement increases the high strength of the alloy, but there are limits to how much can be done. Typically, a maximum anode length of 3 m and a maximum weight of 500 kg have been imposed as practical limitations. Bracelet anodes for submarine pipelines are often sized to match a weight coating thickness where there is no weight coating. The thinner the anode, the lesser the impact as it goes over the stinger during laying. Many of the same limitations that applied to platform anodes also apply to bracelets although thin wall moulds and water cooling have assisted reducing anode thickness where necessary. Bracelet diameters are governed by pipe diameters and thickness by laying or coating considerations, but they are unlikely to be viable at more than 1.5 m long and 400 kg in weight. Needless to say, some readers will be able to quote examples of anodes larger than those implied here, but they will be few and far between and almost certainly associated with some special circumstance; for example, a very large platform anode mounted on a sea bed sled or a bracelet designed to be mounted on a large pipe to be retrofitted to a platform to compensate for a shortfall in the original design.

It can be difficult to achieve both the exact current output and precise weight of anode material simultaneously although, as mentioned previously, the use of iterative calculation by a computer program can optimize this. Where a compromise is necessary, both must at least match design requirements.

A check to ensure that the anodes will deliver sufficient current to protect the structure at the end of the design life should be conducted. This entails calculating the expected anode output at the end of its life and checking that it meets the demands of the structure. Generally, the output is calculated using a modified resistance based on an anode that is 90% consumed.

4.19.10.7 Anode (End Current) Distribution

It is evident that a greater number of anodes distributed over the structure will improve current distribution. However, aside from the unacceptable cost incurred by attaching excessive numbers of anodes, an anode must continue to function throughout the life of the structure and must, therefore, be of sufficient size to meet the design life. A very large number of heavy anodes is clearly impracticable and uneconomic.

It is essential to ensure adequate current distribution such that all of the exposed structure remains protected; particularly important, for example, for the nodes of an offshore steel structure. Similarly, over-protection should be avoided. Thus, sacrificial anodes need to be distributed to ensure that the protection potential over the whole structure is achieved.

The proximity of the anodes to structures is also important. For example, if the sacrificial anodes are placed on or very close to the steel pipework in soil, then the output from the face of the anodes next to the steelwork can be severely limited. Alternatively, in high conductivity environments, corrosion products may build up and wedge between the anode and the structure. The resulting stresses can lead to a mechanical failure of the anode. On the other hand, when anodes are located at an appreciable distance from the steelwork, part of the potential difference will be consumed in overcoming the environmental resistance between the anode and cathode.

Complex computer models are now available to assist in defining the optimum anode distribution.[25]

4.19.10.8 The Anode Insert

The anode insert must be strong enough to support the weight of the anode and must be capable of being welded, or mechanically fixed to the cathode.

It should be appreciated that the attachment may be required to withstand the launching and pile driving of a steel jacket for offshore applications.

Consideration must be given to the ease and speed of anode fixing, as this is a significant part of the total installation cost. The methods of fixing anodes to flat, vertical or horizontal surfaces are relatively well known and simple. The methods of fixing anodes to curved surfaces of pipelines and immersed structures are more complex, and generally require more steel insert. Figure 5 shows typical anodes in common use offshore on jackets and pipelines.

While catalogues of proprietary platform anodes often show a wide variety of attachment arrangements involving tube, angle, channel, and other sections, it must be remember that most anodes are attached to structural tubular members of a stressed structure subject to significant cyclic forces during installation, piling, and service (wave impacts). The welds between anode insert and structure have to be designed to avoid fatigue failure; not only will this involve, in most cases, the doubler plates of a metal compatible with both anode and structure but also full penetration welds that are subject to most stringent inspection (probably radiography) and the avoidance of stress raisers, meaning that only all tubular inserts are likely to be acceptable. Bracelet anodes are usually clamped around the pipe with little or no welding between inserts, and pipe steel electrical connection is achieved by a low temperature connection process such as copper thermite welding or pin brazing with a very small contact area, but even then usually to an expendable doubler plate.

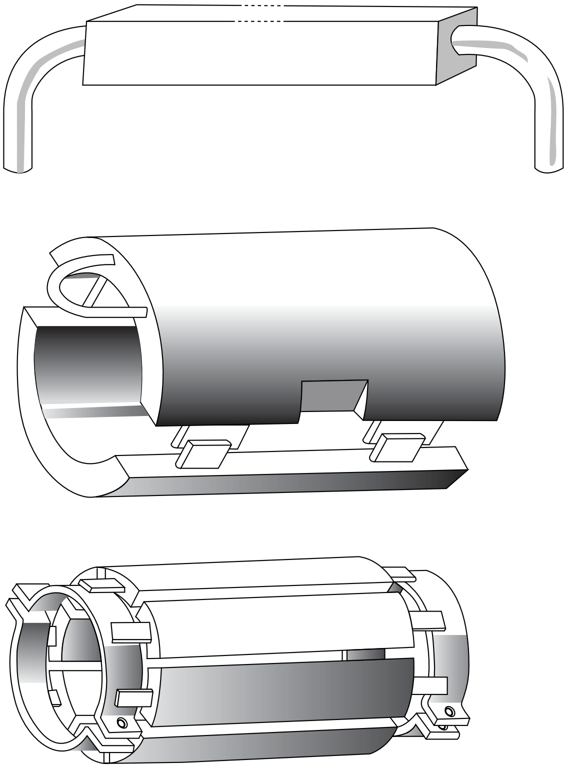

Figure 5 Typical anodes in common use offshore on jackets and pipelines.

4.19.10.9 Utilization Factor

This component of anode design calculation is worthy of serious consideration as too often a figure of 0.9 or 90% is used for platform anodes and 0.75–0.85 or 75–85% for bracelets without understanding where it originates from. Essentially, the utilization factor reflects how much of the net weight of an anodes delivers useful cathodic protection before it becomes structurally unstable and (literally) falls to pieces. Examination of long thin anodes, which are cast on tubular inserts, towards the end of their life reveals that the attack on the original rectangular cross section approaches a final circular appearance.

Moreover, the attack is preferential towards the ends of the anode such the overall appearance approximates to a traditional 'cigar' shape while it remains supported by the insert. Anodes with a stand-off at least 300 mm from the structure being protected in open seawater are unlikely to be seriously affected by proximity and corrode nonuniformly. Anodes installed close to the structure should have an inert nonconducting coating (coal tar epoxy) on the face closest to the structure to minimize preferential attack on the close face and the possibility of anode corrosion products building up behind the anode and forcing it off. This is of particular importance for bracelet or hull anodes and much less so for platform anodes.

For pipeline or hull anodes, the distance through the anode that the insert is placed directly influences the utilization factor since; if, for example, the insert is in the centre of the anode mass, the utilization factor will be 0.5 or 50%; if it were on the front face, the U/F would theoretically be zero and on the back face, 1.0, although none of these would be practical. Thus, if the insert is 75% of the depth of the anode from the front face, then the utilization factor is likely to approximate to 75%. Ingenious designs of insert involving a backing plate with a mesh embedded in the back face of the anode material in order to approach a U/F of 1.0 have been patented but are not in common use.

4.19.10.10 Backfills for Anodes

When zinc or magnesium anodes are used for cathodic protection onshore,[25–28] they are usually surrounded by a backfill, which decreases the electrical resistance of the anode. Small anodes are usually surrounded with backfill in bags and large anodes are usually surrounded with a loose backfill during installation. The backfill prevents the anode coming into contact with the soil and suffering local corrosion, thus reducing the capacity. By surrounding the anodes with a backfill, the combination of the anode with soil salts is reduced, and this helps prevent the formation of passive films on the anode surface.

The effect of the backfill is to lower the circuit resistance and thus reduce potential loss due to the environment. The additive resistances of the anode/backfill and backfill/soil are lower than the single anode/soil resistance. Backfills attract soil moisture and reduce the resistivity in the area immediately round the anode. Dry backfill expands on wetting, and the package expands to fill the hole in the soil and eliminate voids.

For use in high resistivity soils, the most common mixture is 75% gypsum, 20% bentonite, and 5% sodium sulfate. This has a resistivity of approximately 50 ohm cm when saturated with moisture. It is important to realize that carbonaceous backfills are relevant to impressed current anode systems and must not be used with sacrificial anodes. A carbonaceous backfill is an electronic conductor and noble to both sacrificial anodes and steel. A galvanic cell would therefore be created causing enhanced dissolution of the anode, and eventually corrosion of the structure.

4.19.11 Other Considerations

4.19.11.1 Calcareous Scale

A consequence of cathodic protection in seawater is the formation of a protective calcareous scale.[29] The increased local pH at the steel surface caused by hydroxyl production (a product of the cathodic reaction) favors the deposition of a mixed scale of $CaCO_3$ and $Mg(OH)_2$. This scale is beneficial since it is protective and nonconducting, thus reducing the cathodic current density. Ensuring a high current density in the early period of operation will encourage calcareous scale deposition and thus reduce the current requirements in the long term.

The build-up of calcareous deposits is a complex topic. Very high current densities will not necessarily result in the most protective scale. In the extreme, hydrogen evolution may rupture the scale resulting in reduced protection. An optimum current density will exist, and this should be recognized.

4.19.11.2 Combined Alloy Anodes for Rapid Structure Polarization

Combined (or binary) alloy sacrificial anodes have been developed.[30] An aluminum anode, for example, might have attached to it a short-life supplementary magnesium anode, or anodes, for quick polarization of the structure. The overall reduction in structure current requirements is claimed to result in an anode weight saving of 35–50%. This derives from the increased current output from the anode early in its operating life, giving rise to a relatively protective calcareous scale, which then reduces the current demand for protection later in life.

4.19.11.3 Flame Sprayed Aluminum

The use of flame sprayed aluminum (FSA) with a silicon sealer paint has been applied to protect high-strength steel tension legs of a North Sea production facility.[32] The FSA system primarily acts as a very effective barrier coating. In addition, the coating has significant anodic capability and aluminum corrosion products serve to plug coating defects. The sealer, although reducing the anodic current output, serves to increase the service life of the FSA coating. This coating system is subject to strict control of application procedures.

4.19.11.4 Protection of High-Alloy Steels

High-alloy pipeline steels (e.g., austenitic–ferritic or duplex) have been used where the product stream demands materials with better corrosion resistance than carbon steel. In practice, the external corrosion resistance of these materials cannot be guaranteed, so cathodic protection is employed to protect areas which may be subject to corrosion.

Concern about hydrogen damage has lead to much debate regarding limits for protection potentials of high-alloy steels. However, it is thought that under normal seawater service and cathodic protection conditions, these materials will not be adversely affected provided that the microstructure has at least 40% of austenite present. This latter point is of particular importance to welds and their heat affected zone where careful control of heat input is necessary to maintain a favorable microstructure.

The latter part of this chapter has dealt with the design considerations for a sacrificial anode cathodic protection system. It has outlined the important parameters and how each contributes to the overall design. This is only an introduction and guide to the basic principles of cathodic protection design using sacrificial anodes and should be viewed as such. In practice, the design of these systems can be complex and can require experienced personnel who will have to not only satisfy the needs of the protection system but also the client and the classification body, and not all of these are mutually compatible.

References

1. Davy, H. *Philos. Trans. Royal Soc. (London)* **1824**, *114*(1), 117.
2. Davy, H. *Philos. Trans. Royal Soc. (London)* **1824**, *114*(2), 242.
3. Davy, H. *Philos. Trans. Royal Soc. (London)* **1825**, *115*(2), 328.
4. Crundwell, R. F. In NACE Corrosion 82, Houston TX, March 1982; Paper no. 166.
5. Crundwell, R. F. In *Cathodic Protection Theory and Practice*, 2nd International Conference, Stratford upon Avon, June 1989.
6. Googan, C. G. Ph.D. Thesis, Institute of Science and Technology, University of Manchester, 1979.
7. Salleh, M. M. B. H. Ph.D. Thesis, University of Manchester, 1978.
8. Klinghoffer, O.; Linder, B. In NACE Corrosion/87, San Francisco, CA, March 1987; Paper no. 59.
9. US Military Specification MIL-A-18001 K, 1991.
10. Jensen, F. O.; Torleif, J. In Corrosion/87, San Francisco, CA, March 1987; Paper no. 72.
11. Det Norske Veritas Recommended Practice, Cathodic Protection Design, RP B401. 1986, revised 1993, revised 2005.
12. Ahmed, D. S.; Ashworth, V.; Scantlebury, J. D.; Wyatt, B. S. *Br. Corros. J.* **1989**, *24*, 149.
13. Ashworth, V. Private communication.
14. Lennox, T. J.; Peterson, M. H.; Groover, R. E. *Mater. Protect.* **1968**, *7*(2), 33.
15. NACE Standard Recommended Practice RP0387-87, Metallurgical and Inspection Requirements for Cast Sacrificial Anodes for Offshore Applications; NACE: Houston, TX, 1990.
16. Schreiber, C. F.; Murray, R. W. In Corrosion/88; St. Louis, March 1988; Paper no. 32.
17. Schreiber, C. F.; Murray, R. W. *Mater. Perform.* **1981**, *20*(3), 19.
18. Houghton, C. J.; Ashworth, V. *Mater. Perform.* **1982**, *21*(7), 20.
19. Ashworth, V.; Googan, C. G.; Scantlebury, J. D. *Br. Corros. J.* **1979**, *14*(1), 46.
20. Dwight, H. B. *Electrical Engineering*; 1936, *Vol. 55*, 1319–1328.
21. Sunde, E. D. *Earth Conduction Effects in Transmission Systems*; Van Nostrand: New York, NY, 1949.
22. Cochran, J. In Corrosion 82, Houston, TX, March 1982; Paper no. 169.
23. Nisancioglu, K. In Corrosion 84; New Orleans LA, April 1984; Paper no. 255.
24. Morgan, J.H. *Cathodic Protection*, 2nd ed.; NACE: Houston, TX, 1987
25. Nisancioglu, K. In *Cathodic Protection Theory and Practice,* 2nd International Conference, Stratford upon Avon June 1989.
26. Osborn, O.; Robinson, H. A. *Corrosion* **1952**, *8*, 114–129.
27. Craven, D. *The Protected Gas Service*; Institution of Gas Engineers: Cardiff, 1969.
28. Peabody, A. W. *Control of Pipeline Corrosion*; NACE: Houston, TX, 1971.
29. Evans, T. E. In *Cathodic Protection Theory and Practice,* 2nd International Conference, Stratford upon Avon June 1989.
30. Schreiber, C. F.; Reding, J. T. In Corrosion/90; Las Vegas, NV, April 1990; Paper no. 381.

4.20 Impressed-current Anodes

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Glossary

Backfill A material having preferred properties, such as conductivity, noncorrosiveness, etc., and that is emplaced around an anode in order to enhance its performance.

Groundbed The location of one or more buried anodes in, for example, soil, mud, etc.

Abbreviations

AC alternating current
ASTM American Society for Testing and Materials
BS British Standard
DC direct current
DSA Dimensionally stable anodes
HSI High-silicon iron
MMO Mixed metal oxides

4.20.1 Introduction

The ideal anode for impressed-current cathodic protection (CP) would be capable of passing the required current into the environment, at a low operating overpotential, with insignificant loss of material with time. The first application of impressed-current systems used steel anodes which were Faradaically consumed during operation. Later anodes replaced such metal dissolution with the evolution of oxygen or chlorine, depending on the composition of the environment. The lower anode dissolution rate associated with such evolution then depends on the properties of the surface film produced (usually an oxide) and its resistance to the evolved oxidizing gases. Thus, the oxygen evolved on graphite forms some carbon dioxide consuming some of the carbon in the process. Lead and silicon iron anodes rely on the formation of an insoluble but conductive oxide film allowing current to pass while significantly reducing, but not eliminating, metal loss.

This reduction in anode consumption because of oxide formation is most efficient on platinum, where the loss rate is of the order of 1.0–10 μg A^{-1} h^{-1}. Further reductions in dissolution rate have come with the development of the most recent anode materials, which effectively dispense with the underlying dissolving metal by using a coating consisting solely of oxides (e.g., mixed metal oxides, MMO), supported on an anodically inert substrate (titanium). Even at high currents, these anodes are consumed at a rate which can be as much as an order of magnitude less than that seen on platinum. These latter materials probably represent the ultimate to be achieved in anode performance.

The various types of materials which have been, or are, used as anodes in impressed-current systems may be classified as follows:

- Ferrous materials: steel, cast iron, iron, stainless steel, high-silicon iron, high-silicon molybdenum iron, high-silicon chromium iron, magnetite, ferrite.
- Lead materials: lead–antimony–silver, lead with platinum alloy microelectrodes, lead/magnetite, lead dioxide/titanium, lead dioxide/graphite.
- Carbonaceous materials: graphite, carbon, coke breeze, conductive polymer, conductive paint.
- Precious metals and oxides: platinum, platinized titanium, platinized niobium and tantalum, mixed metal oxide-coated titanium, titanium oxide-based ceramics.

Each group is discussed in detail in the following sections, while the final sections briefly describe those that are presently employed in common CP scenarios.

4.20.2 Ferrous Materials

4.20.2.1 Steel

One of the earliest materials to be used in impressed current CP was carbon steel. Although it has severe limitations, it has sometimes been found to be cost effective in situations where steel scrap is available in suitable quantities and geometry, and it is only in such situations where its use would now be considered. Steel anodes have found particular use in seawater, with a surprising variety of forms being reported to have been utilized, for example, pipes, piling, machinery, rails, and even obsolete ships which have not been economic to salvage. When used as an anode, the consumption rate of steel is close to the theoretical, Faradaic value of 9.1 kg A^{-1} $year^{-1}$. Consumption rates in excess of the theoretical value have been reported for steel in some waters.[1]

When buried, ferrous anodes tend to exhibit high resistance polarization because of the formation of a voluminous corrosion product. This can be alleviated by closely surrounding the anode with carbonaceous backfill; this of course increases the cost if the backfill is also not a locally available by-product. It is necessary to ensure compactness and homogeneity of backfill at all areas around the anode, as otherwise rapid loss of metal at poorly compacted areas can occur.

In recent years, deep-well groundbeds for the protection of clusters of oil or gas wells have been provided by using the steel casings of otherwise abandoned wells in the same area. In order to provide conductance to the active length of the casing, the wells have been filled with carbonaceous backfill, such as coke breeze. Commercial examples of such installations are known to be working well after the period of 28 years.[2] It is necessary to take considerable care to ensure the integrity of anode cable connections and to use multiple connections to ensure redundancy in the event of cable failure. Connections must be encapsulated to protect them from the environment.

4.20.2.2 Cast Iron

Cast iron may be used under similar circumstances to steel, but has inferior mechanical properties. It has been used, although not in recent times, for internal CP, of cooling water systems, where it has been demonstrated that the presence of ferrous ions in the cooling water is of benefit in reducing sulfide-induced attack on Cu alloy tube plate and tubes.[3] Ferrous sulfate dosing is now used as a more reliable means of achieving the same end.

4.20.2.3 Stainless Steel

Stainless steel has been tried as an inert anode, mainly under laboratory conditions and with only partial success. Even at low current densities, the majority of alloys pit rapidly in fresh water, although others show the ability to remain passive at a low current density.[4,5] However, at practical current densities, the presence of chloride ions, deposits on the anode, or crevice corrosion at the anode support leads to rapid failure,[6] but it may be possible that stainless steel could give useful service under certain conditions and with particular alloys.[7]

4.20.2.4 High-Silicon Irons (HSI)

4.20.2.4.1 Iron–silicon alloys

High-silicon iron (HSI) anodes are cast-iron alloys that contain 14–18% Si and were first developed in 1912,[8] although it was not until 1954 that they were first evaluated for use as impressed-current anode materials in CP.[1] Their major disadvantages are those of a hard brittle material unable to withstand thermal or mechanical shock. HSI has a long and successful history as a corrosion-resistant material in the chemical industry for such items as acid storage vessels and has been used in this application for more than 60 years. A typical analysis for HSI anodes is 14.5% Si, 0.75% Mn, 0.95% C, and remainder Fe. The anodes conform to either BS 1591:1975 or ASTM A518–80 Grade 2. The latter lists the permissible Si content range as between 14.20 and 14.75. As the material is not readily machined, it is cast into standard sizes to suit the general requirements of the CP industry. Anodes can be cast as solid rods, or centrifugally cast cylinders.

Used as an anode, HSI readily forms a protective film, which is reformed if removed mechanically. The film is gray–white in appearance and has a tendency to flake under the compressive stress produced at thickened areas. The film is 50% porous and contains 72–78% SiO_2.[8] It is a fairly good electron conductor, even though SiO_2 in its natural state is a dielectric. The mechanism whereby the SiO_2 becomes a conducting oxide has been reviewed in some detail by Shreir and Hayfield,[9] and is probably associated with doping of the SiO_2 with Fe ions.

HSI anodes are subject to severe pitting in the presence of halide ions, and this precludes their use in seawater or other environments in which these ions may be present. They are suitable for freshwater applications (below 200 ppm Cl^-), although not suitable for temperatures above 38 °C. The addition of Mo or Cr to the alloy can improve performance under these conditions, with an upper limit temperature of 56 °C,[10] which may be affected by the composition of the water and the operating conditions.

The consumption rate of HSI depends upon the current density and the environment in which the anode is used. HSI is superior to graphite in waters with resistivity greater than $10\,\Omega\,m$, but in waters of $0.5\,\Omega\,m$ and below, it is susceptible to pitting. Experience in fresh water in the pH range 3 to 10 indicates a nominal consumption rate of approximately $\sim 0.1\,kg\ A^{-1}\,year^{-1}$ at 20 °C. The precise value is dependent upon the solution composition and the temperature.[11] A number of reports on the performance of HSI anodes in different environments have been produced.[11–14]

The consumption rate of HSI anodes buried directly in soils will vary depending upon the soil composition and will be excessive in chloride-containing soils. In quicksand, consumption rates of $\sim 0.35\,kg\ A^{-1}\,year^{-1}$ have been reported,[11] while in other soils, consumption rates in the region of $1\,kg\ A^{-1}\,year^{-1}$ are possible. A consumption rate in the region of $0.1\text{–}0.25\,kg\ A^{-1}\,year^{-1}$ would be expected in a correctly installed carbonaceous backfill, when operating in a soil of insignificant chloride content and a surface current density of no more than $20\ A\,m^{-2}$. Higher consumption rates would result from high local current densities, often caused by inadequate backfill, partial submersion, or silting. A coke–breeze backfill can be installed around the anodes when buried in higher resistivity soil, so as to reduce the overall resistance to the earth and enabling the use of higher current groundbeds. There is a tendency for the surface resistance of a buried anode to increase, but not to an extent that it affects performance. The large resistance changes sometimes reported for carbonaceous beds are usually due to gaseous polarization (gas blocking) caused by poor venting or by inadequate compaction of backfill.

With any impressed current anode, an effective connection is vital. Loss of insulation at the connection point or penetration of water into the anode cable seal will bring about rapid failure. Hydrostatic pressure should be borne in mind when considering the seal required for any depth of water. End connections for solid rod anodes use compression, cast lead, or taper pin connections, sealed by a combination of epoxy filling and heat shrinkable sleeves. Cylindrical anodes have center connections with taper wedges or cast lead. The useful life of HSI anodes is usually considered at an end after a 33% reduction in diameter, but this depends upon the original diameter, the amount of pitting sustained, and the mechanical stresses to be withstood. Therefore, doubling the cross-sectional area may more than double the effective life of the anode.

4.20.2.4.2 *Silicon–molybdenum iron*

The addition of 1–3% Mo to HSI modifies the anodic oxide film resulting in improved performance in solutions containing above 200 ppm chloride or at temperatures of 38 °C or above. In seawater at 10 A m^{-2}, the addition of Mo reduced the consumption rate from 0.22 to 0.15 kg A^{-1} year^{-1} at ambient temperatures and from 0.63 to 0.21 kg A^{-1} year^{-1} at 51 °C.[15] However, a considerably higher rate of 0.9 kg A^{-1} year^{-1} at 10.8 A m^{-2} has been reported for molybdenum-containing silicon iron in chloride-containing waters.[11] Because the addition of Cr results in even greater improvements in performance, the molybdenum-enhanced alloy has been little used.

4.20.2.4.3 *High-silicon–chromium iron*

High-silicon chromium iron alloy (HSCI) came into commercial use by about 1959.[15] The addition of chromium, together with silicon, results in a film that has a high resistance to pitting in waters containing halide ions and these alloys can, therefore, be used with confidence in seawater- or chloride-containing soils. A typical analysis is 14.5% Si, 0.75% Mn, 1.0% C, 4.5% Cr, and remainder Fe. In the United Kingdom, this anode is manufactured to BS 1591:1975, which permits a variation in silicon content from 14.25% to 15.25% and of chromium from 4.0% to 5.0%, with a maximum carbon content of 1.40%. The equivalent US standard is ASTM A 518-64 Grade 2 with a silicon content of 14.2–14.75% and a chromium content of 3.25–5.00%. Neglecting possible mechanical damage and anode/cable joint failure, it is possible, in view of the very minor pitting sustained in free suspension, for the anode to continue operating until almost totally consumed. Note that HSCI anodes cannot be used in potable waters because of the possibility of chromium contamination.

Comparative tests of silicon iron and chromium-containing silicon iron in seawater at 93 °C and 10.8 A m^{-2} produced consumption rates of 8.4 kg A^{-1} year^{-1} and 0.43 kg A^{-1} year^{-1}, respectively.[16] These figures show that in seawater the consumption rate of HSI without the addition of chromium may approach that of steel, but because of the very deep pitting experienced in chlorides, and the fragility of HSI, it is effectively inferior to steel. However, in fresh waters, HSI has a far lower corrosion rate than steel. The consumption rate of chromium-containing variety, freely suspended in seawater, increased from 0.33 kg A^{-1} year^{-1} at 10.8 A m^{-2} to 0.48 kg A^{-1} year^{-1} at 53.8 A m^{-2}. Direct burial in seawater silt or mud also increases the consumption rate, with value of 0.7 kg A^{-1} year^{-1} at 8.5 A m^{-2} increasing to 0.94 kg A^{-1} year^{-1} at 23.4 A m^{-2}.[17] A recent evaluation of HSCI anodes in different soil conditions has been conducted by Jakobs and Hewes.[18] They report a consumption rate for different HSCI alloys between 0.32 and 0.87 kg A^{-1} year^{-1} in 3% NaCl, at a current density of 21.5 A m^{-2}, depending upon the alloy composition; while in soils containing 2% SO_4^{2-}, consumption rates varied between 0.29 and 0.53 kg A^{-1} year^{-1}, again depending upon the alloy composition.

Improvements in anode construction have been carried out to reduce the nonuniform material loss along the length of the HSCI anode, the so-called 'end effect' phenomenon. This involves incorporating a taper in the anode casting at the connection end, or the use of hollow, centrifugally cast anodes of uniform wall thickness with a centrally located interior electrical connection.[19] Similar configurations are now used for HSI anodes. Cable connections for solid rod anodes use compression, cast lead, or taper pin connections, sealed by a combination of epoxy filling and heat shrinkable sleeves. Cylindrical anodes have centre connections with taper wedges or cast lead. Care must be taken to ensure that the cable insulation and sheathing are adequate for use in an oxidizing environment, in which chlorine evolution occurs. Kynar and high molecular weight polyethylene are commonly used.

4.20.2.5 Magnetite Anodes

A compound, rather than an alloy, of iron, magnetite (Fe_3O_4) has been in use since the 1970s as a CP anode, although its use as an anode material had been known for some time previously.[20] As an oxide, and being very brittle, it cannot be formed into an anode by conventional means. Magnetite has a melting point of 1540 °C and can be cast using special techniques and with the addition of certain alloying elements.[21] The anodes are in the form of a cast alloyed magnetite shell, the centre of which is hollow. The internal surfaces of the magnetite shell are then lined with an electronic conductor so as to ensure a uniform distribution of current density over the external surface. This technique overcomes the longitudinal current attenuation that would occur because of the relatively high resistivity of magnetite (3.3 Ω m quoted by Linder[21] and 0.8 Ω m by Kofstad).[22] Magnetite anodes can be operated at elevated temperatures up to 90 °C, with the limitation in temperature being failure of the anode cable connection and not the magnetite itself.

In early magnetite anodes, the internal lining consisted of a thin copper layer, but the poor electrical contact between the copper layer and the magnetite, together with the fact that the cable-to-anode connection was made at the anode head, resulted in a nonuniform current density on the external magnetite surface, which contributed, in part, to the poor performance reported for some of the early anodes. Subsequently, the manufacturers perfected a method of electrodepositing a lead alloy lining onto the internal magnetite surface with spring-loaded cable-to-anode connection made at the mid-point of the anode. Special care and some ingenuity in design are required in insulating the connection.

Magnetite anodes exhibit a relatively low consumption rate and can be used in seawater, freshwater, and soils. This low consumption rate enables a light-weight anode construction to be utilized. For example, the anode described by Linder[21] is 800 mm in length, 60 mm in diameter, 10-mm wall thickness, and 6 kg in weight. Tests carried out in seawater over the current density range 30–190 $\mathrm{A\,m^{-2}}$ showed the consumption rate to be dependent upon current density, increasing from 1.4 to 4 $\mathrm{g\,A^{-1}\,year^{-1}}$ over the current density range studied (with the recommendation that to achieve the required life, the current density should not exceed 115 $\mathrm{A\,m^{-2}}$).[23] Later work by Jakobs and Hewes[18] indicated the consumption rate in seawater to be less than 1 $\mathrm{g\,A^{-1}\,year^{-1}}$ at 21.6 $\mathrm{A\,m^{-2}}$, while at 32.4 $\mathrm{A\,m^{-2}}$ a consumption rate of 12–41 $\mathrm{g\,A^{-1}\,year^{-1}}$ was observed. Higher consumption rates were reported for magnetite anodes in soils containing 2% SO_4^{2-}; namely 75 $\mathrm{g\,A^{-1}\,year^{-1}}$ at current densities of 21.6 and 32.4 $\mathrm{A\,m^{-2}}$. Jakobs[24] also conducted a survey of different anode systems in soils and found magnetite anodes after 2 years' exposure and operating at a current density of 43 $\mathrm{A\,m^{-2}}$ to be in good condition with little evidence of attack.

The main disadvantages of magnetite anodes are that they are brittle and susceptible to high-impact shocks, as is the case with silicon iron anodes, while some of the earlier anodes were subject to failure from thermal cycling.[9,21] Indeed, one evaluation of magnetite anodes reported a high incidence of failure,[24] and a more recent report[25] suggests an increased tendency to failure of magnetite anodes when compared with other, more conventional, anode materials. These failures were mainly associated with poor installation practice and operation at current densities in excess of the manufacturers' maximum recommended values (77 $\mathrm{A\,m^{-2}}$ for seawater and 30 $\mathrm{A\,m^{-2}}$ for soil). Improvements in design have now led to a more reliable anode with a decrease in the level of reported failures.[26]

Magnetite may also be used in combination with lead or electrodeposited onto a titanium substrate.[27] The latter anode system has been shown to exhibit good operating characteristics in seawater but at present it is only of academic interest showing no benefit over platinized and mixed metal oxide anodes.

4.20.2.6 Ferrite Anodes

Sintered and sprayed ceramic anodes have been developed for CP applications. The ceramic anodes are composed of a group of materials classified as ferrites with iron oxide as the principal component. The electrochemical properties of divalent metal oxide ferrites in the composition range around $0.1MO–0.9Fe_2O_3$, where M represents a divalent metal, for example, Mg, Zn, Mn, Co, or Ni, have been examined by Wakabayashi and Akoi.[28] They found that nickel ferrite exhibited the lowest consumption rate in 3% NaCl (of 1.56 $\mathrm{g\,A^{-1}\,year^{-1}}$ at 500 $\mathrm{A\,m^{-2}}$) and that an increase in the NiO content to 40 mol%, that is, $0.4NiO–0.6Fe_2O_3$ reduced the dissolution rate to 0.4 $\mathrm{g\,A^{-1}\,year^{-1}}$ at the expense of an increase in resistivity from 0.02 to 0.3 Ω cm.

Ceramic anodes may be cast or sintered around a central steel core which acts as the electrical conductor. However, anodes produced in this form are brittle and susceptible to mechanical shock. Ceramic anodes based on a plasma-sprayed ferrite coating on a titanium or niobium substrate have also been developed. These consist of plasma-sprayed lithium, nickel, or cobalt ferrite on a machined Ti or Nb button-shaped substrate fitted into a plastic electrode holder.[29] This method of anode construction is durable and not as prone to mechanical damage as the sintered ceramic anode, while the ceramic coating is abrasion resistant and has a long operational life. Kumar *et al.*[29] report a dissolution rate for a sprayed lithium ferrite of 1.7 g A^{-1} $year^{-1}$ at a current density of 2000 A m^{-2} in seawater. The anode exhibited good performance with no damage on the ceramic coating observed during a two-month trial. However, the normal restrictions on operating voltages for titanium electrodes (discussed below) were still found to apply, with pitting[30] of the titanium substrate reported at 9.66 V versus SCE.

4.20.3 Lead-Based Materials

4.20.3.1 Lead Alloys

Investigations into the use of lead and lead alloys for CP were carried out in the early 1950s[31–33] and a practical material had been developed by 1954. The general use of lead alloys in seawater had previously been established.[34,35] The anodic behavior of lead varies depending upon the electrolyte composition and the electrode potential and has been the subject of a number of reviews.[9,35,36] In NO_3^-, CH_3COO^-, and BF_4^{2-} solutions, lead will form highly soluble salts, while in Cl^- and SO_4^{2-} solutions, insoluble salts are formed.

The use of lead as an anode depends on the formation and maintenance of a hard layer of lead oxide, PbO_2. The PbO_2 acts as an inert anode, with the lead acting both as a source of PbO_2 and an electrical conductor. PbO_2 is relatively insoluble in seawater and its dissipation is more usually associated with mechanical wear and stress than electrochemical action. In alkaline solutions approaching pH 10, PbO_2 dissolves and for this reason lead anodes should be mounted clear of cathodic areas, where alkalinity will form. It should be noted that lead dioxide will discharge if electronically connected to a more base material, when in an unenergized state, with the consequent formation of lead chloride and corrosion of the anode.

Lead alloys have found considerable use as anodes in a wide variety of electrochemical applications, with studies dating back to 1924.[36–38] Pure lead has been tried as an anode in seawater and shown to be unsuitable, because of the formation of $PbCl_2$ beneath the PbO_2 which insulates the PbO_2 from the substrate. The anodic behavior of lead in Cl^- solutions depends upon Cl^- ion concentration, solution pH, and the presence of passivating anions such as CO_3^{2-}, HCO_3^-, and SO_4^{2-}. At low current densities and low Cl^- concentration, dissolution of Pb will occur and a $PbCl_2$ deposit will not be formed at the anode. In high Cl^- concentrations and at high current densities, the rate of formation of Pb^{2+} will be high enough for the solubility product for $PbCl_2$ to be exceeded and $PbCl_2$, not PbO_2, will be deposited at the anode. The formation of a PbO_2 coating on lead, when it is anodically polarized in Cl^-, is achieved more readily by alloying lead with silver or other metals or by incorporating inert conducting microelectrodes on the Pb surface.

Lead alloys have been investigated to determine their suitability as anodes for CP. Tests[39] were carried out on lead–silver alloys and found that Pb–1%Ag was suitable for use in seawater provided that the current density did not exceed 100–200 A m^{-2}, as at higher current densities an insulating film formed. Morgan[39,40] found that Pb–6Sb–1Ag alloy gave a lower consumption rate and exhibited a harder PbO_2 film than Pb–6Sb or Pb–1Ag. Pb–6Sb–2Ag alloys are slightly better, but ~50% more expensive. Other work[41] has also shown that additions of Mn to Pb–2Ag alloys may have a beneficial effect on anode performance in seawater. The Pb–6Sb–1Ag alloy is commonly used where lead–silver anodes are specified. The results of tests on Pb–6Sb–1Ag given in Table 1 are of interest in recognizing the scope for the use of lead alloys in waters of differing resistivity.

Additions of antimony, bismuth, and tin to the lead appear to be detrimental for anode applications. Dispersion-hardened lead alloys have been unsatisfactory, showing pronounced spalling in the direction of extrusion. There is an indication that the addition of 0.1% Ag is almost as effective as 1% and additions as low as 0.01% that have been utilized in practice. Pb–0.1Te–0.1Ag has been also used with apparent success.[42]

In electrolytes containing sulfate and chloride ions, the sulfate ion favors the formation of lead sulfate which is rapidly transformed to lead dioxide. The continuing satisfactory operation of the anode depends upon the initial conditions of polarization. In solutions containing higher sulfate concentrations, or when the water is agitated, the lead dioxide is of better quality and more adherent when formed below 108 A m^{-2}.[43]

It is important to realize that a minimum current density is necessary to ensure the passivation of lead–silver anodes and that anodes operating below this current density may experience rapid consumption rates. A minimum value of 32.3 A m^{-2} is quoted by Barnard *et al.*[34] The consumption rate of lead–silver is high in the initial stages of operation as can be seen from Table 1. However, the rate in seawater, over an extended period, is generally taken as 0.06 kg A^{-1} year^{-1}. If a lead alloy is used as a ship's hull anode, consideration should be given both to the make-up of the water in which the anode is initially passivated and that in which it will normally operate. The same consideration will apply for static structures in estuarine waters.

Experience with Pb–6Sb–1Ag (and Pb/Pt) anodes operating in seawater at depths greater than 25 m has revealed a marked increase in consumption rate compared with that found on the surface. Hollandsworth and Littauer[44] have calculated that on a fully formed anode at 400 A m^{-2}, only 6 × 10^{-5}% of the current is used to maintain the passive film, but at a depth of 180 m, this percentage increases to 2 × 10^{-3}% and results in a 30-fold increase in consumption rate. They propose that a combination of the mechanical forces acting on the PbO_2 at increased depths and the reduction in the evolution of chlorine are responsible for the increased consumption rate. It is, therefore, recommended that lead anodes are not used at depths below 25 m.

Table 1 Behaviour of Pb–6Sb–1Ag anodes

Resistivity of electrolyte at 35°C (Ωm)	*Average wastage rate at 108 Am^{-2} (kg A^{-1} year^{-1})*	*Length of trial (days)*	*Note*
0.163 (sea)	0.086	236	1
0.163 (NaCl)	1.99	1–75	2
0.5 (sea)	0.0145	234	1
0.5 (NaCl)	0.654	1–75	3
10 (sea)	23.80	5–75	4
10 (NaCl)	23.70	1–75	4
50 (sea)	0.10	236	5
50 (NaCl)	11.64	1–75	5

Notes:
1. Service indicates a practical consumption of between 0.057 and 0.114 kg A^{-1} year^{-1}. Under laboratory conditions, PbO_2 has been formed at current densities as low as 21.6 A m^{-2}. Typical operating current densities are 54–270 A m^{-2} at wastage rates of 0.045 to 0.082 kg A^{-1} year^{-1}.
2. Similar performance between 0.7 and 270 A m^{-2}: formation of this adherent film of PbO_2.
3. Similar performance between 2.7 and 160 A m^{-2}; thick nodules of PbO_2 in some areas; severe deterioration at 270 A m^{-2}.
4. Tests have indicated failure to form PbO_2; rapid deterioration, although at 100 A m^{-2} it shows down after several weeks. Increasing silver content results in some improvement. Anode passivated in 0.163 ohm m water continues to operate whilst PbO_2 is undamaged.
5. Above 22 A m^{-2}, deterioration rate may be low, but PbO_2 coating is poor and interspersed with $PbCl_2$.

4.20.3.2 Lead/Platinum Bielectrodes

The insertion of platinum microelectrodes into the surface of lead and some lead alloys has been found to promote the formation of lead dioxide in chloride solutions.[45,46] Experiments with silver and titanium microelectrodes have shown that these do not result in improvement.[42] Similar results to those when using platinum have been found with graphite and iridium, and although only a very small total surface area of microelectrodes is required to achieve benefit, the larger the ratio of platinum to lead surface, the faster the rate of formation of the oxide layer.[44] Platinized titanium microelectrodes have also been utilized.

Lead dioxide will readily form on lead with a platinum electrode as small as 0.076 mm in diameter.[44,45,47] It has been observed that the current density on the platinum is considerably less than that on the lead dioxide once polarization has been achieved, the proportion of current discharged from the platinum decreasing with increase in total current. A typical anode for practical use would be in the order of 25–48 mm in diameter, with hard platinum alloy pins of 0.50-mm diameter by 10-mm length, spaced every 150–300 mm and progressively positioned around the circumference.[48] The pins are a press fit into holes in the lead or lead alloy and lie flush with the surface. The lead is peened around the pins to improve mechanical and electrical contact.

The action of platinum microelectrodes has been extensively studied.[9,36] Trials carried out by Peplow[49] have shown that lead/platinum bielectrodes can be used in high velocity seawater at current densities up to 2000 A m^{-2} and that blister formation with corrosion under the blisters is decreased by the presence of platinum microelectrodes. The current density range in which the anode is normally operated is 200–750 A m^{-2} with the maximum working current density quoted as 1000 A m^{-2}. The consumption rate of these anodes ranged from 0.0014 to 0.002 kg A^{-1} year^{-1} at 500 A m^{-2}, but increased to 0.003 kg A^{-1} year^{-1} at 2000 A m^{-2}.[49] The results of work in this field[44,47,50,51] can be summarized as follows:

- Pt acts as a stable electrode for nucleation of PbO_2 and limits $PbCl_2$ formation.
- In the case of a lead anode (without a platinum microelectrode), the PbO_2 thickens during prolonged polarization with the consequent development of stresses in the film.
- The stresses result in microcracks in the PbO_2, thus, exposing the underlying lead, which corrodes with the formation of voluminous $PbCl_2$, resulting

in blisters; the resistance of the anode increases and high voltages are required to maintain the current (if the voltage is maintained constant the current falls to a low value).

- The platinum microelectrode appears to act as a potentiostat and maintains the potential of the lead–solution interface at any crack at a value that favors the reformation of PbO_2, rather than the continuous formation of $PbCl_2$, which would otherwise result in excessive corrosion.

It is known that an increase in the resistance of a lead electrode indicates that corrosion is taking place with the formation of an insulating film of a lead compound and this is confirmed in practice by observation of the anodes, which reveal localized areas coated with white corrosion products, although the PbO_2 remains intact at other areas. However, it is possible that an insulating film forms over the whole surface, thus, isolating the conducting PbO_2 from the lead. Wheeler[52] suggested that the sole function of the platinum is to provide a conducting bridge between the lead and the PbO_2. It has been demonstrated that, although initially the PbO_2 nucleates at the surface of the platinum, the initially formed $PbCl_2$ is rapidly converted into the PbO_2 that is in direct contact with the lead.[44]

The formation of PbO_2 is favored in the solutions containing passivating anions such as SO_4^{2-} and in the chloride solutions of intermediate concentrations; very high and very low concentrations of chloride inhibit the formation of PbO_2. The platinum/lead bielectrode performs best in seawater and is not recommended for use in waters of high resistivity.

4.20.3.3 Lead/Magnetite Composites

It has been demonstrated that the particles of magnetite in a lead matrix can produce results similar to those produced by platinum, acting as stable nucleation sites for PbO_2 formation.[53] Composite Pb/Fe_3O_4 anodes containing 10, 15, and 20% Fe_3O_4 were prepared by mixing powders of the constituents (Pb 30–60 mesh, Fe_3O_4 72 mesh) and compacting at a pressure of 300 MPa.[9,54] These anodes were found to operate successfully in both artificial seawater (resistivity 0.25 Ω m) and in the same water diluted with distilled water to give a higher resistivity of 10 Ω m.

In seawater, the anodes were found to operate best in the current density range 100–1000 $A\,m^{-2}$, a weight loss of 50 g A^{-1} $year^{-1}$ being recorded for a 20% composite anode at 300 $A\,m^{-2}$. No initial rise in voltage at a constant current density was observed, as is the case with Pb/Pt electrodes, where the potential increases because of the formation of $PbCl_2$. The steady-state potential of the anode was found to be dependent upon the Fe_3O_4 content. In freshwater solutions, the composite Pb–10% Fe_3O_4 anodes were also able to form a PbO_2 film, although an induction period was necessary before stabilization was complete. Hill reports that at current densities less than 150 $A\,m^{-2}$, the anodes were unable to stabilize. Consumption rates similar to those in artificial seawater were reported for the Pb–20% Fe_3O_4 composites, which were found to give the optimum performance. However, in tapwater with a high SO_4^{2-} and CO_3^{2-} concentration and low Cl^- concentration (36 ppm), a consumption rate of 100 g A^{-1} $year^{-1}$ was recorded.

4.20.3.4 Lead Dioxide on other Substrates

Lead dioxide on graphite or titanium substrates has been utilized as an anode in the production of chlorate and hypochlorites[55] and on nickel as an anode in lead–acid primary batteries.[56] Lead dioxide on a titanium substrate has also been tested for use in the CP of heat exchangers[11] and in seawater may be operated at current densities up to 1000 $A\,m^{-2}$.[57] However, this anode has not gained general acceptance as a CP anode for seawater applications, as platinized Ti anodes are more robust.

4.20.4 Carbonaceous Materials

4.20.4.1 Graphite

Graphite is the dense, crystalline, form of carbon. Graphite anodes are prepared by heating calcined petroleum coke particles with a coal tar pitch binder. The mix is then shaped as required and heated to ~2800 °C to convert the amorphous carbon to graphite.[58] Graphite is used in preference to amorphous carbon as it is a less porous and more reliable anode material, particularly in saline conditions. It is current practice to impregnate the graphite, traditionally with linseed oil, although synthetic resins are also successful. The concept behind impregnation is to reduce the porosity and hence inhibit subsurface gas evolution or carbon oxidation which would initiate spalling and early anode failure. Being a natural lubricant, the material can easily be machined. It has a negligible contact resistance and it is relatively simple to make a sound cable joint. It can be DC welded under high pressure argon. It is brittle but a little more shock resistant than silicon iron, in that it can absorb energy by localized damage, and it is a much lighter material to handle. Cable-to-anode joints need to be designed and made with the same care as those for high-silicon iron anodes.

The performance of graphite in seawater, where chlorine is the principal gas evolved, is considerably better than that in fresh water where oxygen is produced. Graphite is effectively immune to chlorine and has a long history in the chemical industry in this and similar applications.[59] In freshwater applications, considerable amounts of free oxygen are produced at the anode surface, which can attack both the carbon and any organic binders used to reduce porosity, resulting in a high consumption rate. The corrosion product is predominantly carbon dioxide. For this reason, graphite anodes for underground service are used in conjunction with a carbonaceous backfill.

If all the oxygen produced were to combine with the carbon, the maximum theoretical consumption rate would be of the order of 1 kg A^{-1} $year^{-1}$.[60] However, in practice, the rate is usually of the order of 0.2 kg A^{-1} $year^{-1}$ and in coke breeze may be as low as 0.05 kg A^{-1} $year^{-1}$. In seawater, where chlorine is the predominant gas produced, any oxygen formed will be quickly removed and the corrosion rate may be very low. Electrode reactions occur to a depth of 0.5 mm below the surface of the anode and the true current density can be shown to be only 1/400th of the value indicated by the superficial geometrical area.[61] Acidity has been found to increase the consumption rate,[62] as has the presence of sulfate ions.[63] Interestingly, when buried in soils containing 2% SO_4^{2-} Jakobs and Hewes[18] report the graphite consumption rates of 1.56 kg A^{-1} $year^{-1}$ at 21.6 A m^{-2}, which is considerably higher than the theoretical maximum consumption rate.

The anode is not recommended for use in water at above 50 °C, where the consumption rate increases rapidly and erratically. It is no longer the practice to use this material in cooling water plants where a secondary attack from contact with the relatively noble pieces of anode may occur, should pieces break off the anode.

Table 2 gives some results obtained with graphite under different conditions. Results obtained with one particular installation using a 100 mm diameter anode of 1 m length operating at 6.9 A m^{-2} indicate a predicted life of 20 years.[64]

Graphite anodes, when used in soils, are invariably placed in a carbonaceous backfill. This helps compensate for the lower electrical resistivity of graphite when compared with silicon iron. In such an environment, no build-up of a film of high resistance between the anode and backfill occurs, unlike silicon–iron anodes where the resistance can increase with time.[65]

Table 2 Performance of graphite anodes

Environment	*Wastage rate ($kg\ A^{-1}\ year^{-1}$)*	*Current density ($A\ m^{-2}$)*
Backfill	0.9	10.8
Hot water	0.9	
Seawater	***0.045***	***4.5–115***
Seawater	Little	10.8
Fresh water	0.45	3.5
Fresh water	0.45	2.7
Mud	0.91–1.36	71

Data reproduced from corresponding article in 3rd Edition of Shreir's Corrosion.

Failures of graphite anodes can occur by corrosion of the anode connection, high current densities at either end of the anode resulting in excessive consumption rates often referred to as 'end effect' corrosion, sealant failure, or surface contamination.

4.20.4.2 Carbonaceous Backfills

Carbonaceous backfill, either coke breeze, or, more recently, calcined petroleum coke, is used to surround a buried solid anode, or anodes, to produce an anode groundbed with an increased surface area, thus, significantly lowering the resistance to the surrounding environment. Groundbeds may be horizontal, vertical, or deep-well in form, depending on the soil resistivity in which they are installed. Such backfills have been used in conjunction with a number of different 'primary' anodes, including silicon iron, graphite, platinized titanium, and mixed metal oxide coated titanium. Canister anodes consist of a spirally wound galvanized steel outer casing containing a prepacked carbonaceous backfill which surrounds the primary anode element which may be graphite, silicon iron, platinized titanium, mixed metal oxide-coated titanium, or platinized niobium. Such anodes allow ease of installation and are often used as shallow vertical linear arrays.

By using carbonaceous backfill, the consumption of the primary anode is reduced, as the majority of the conduction from the anode to the backfill becomes electronic rather than electrolytic. The electrochemical and physical nature of the backfill results in the spread of the anode reaction (formation of CO_2 and O_2, or Cl_2)

over a large surface area, thereby reducing attack on the primary anode. The coke is slowly oxidized, primarily to carbon dioxide, which in a suitably vented groundbed will escape into the atmosphere together with any oxygen or chlorine formed. If all the oxygen reacted with the carbon, consumption would be 1.02 kg A^{-1} $year^{-1}$, but in practice the rate is of the order of 0.25 kg A^{-1} $year^{-1}$,[65] depending upon the environment.

Some typical properties of coke breeze and similar materials are shown in Tables 3–5. The densities given in Table 3 are for bulk material and are dependent upon grading. Flake graphite is not recommended for use in groundbeds as it tends to conglomerate and prevent gas emission.

Table 3 Densities of carbonaceous backfill

Backfill in bulk	*Density range ($kg\ m^{-3}$)*	*Typical density ($kg\ m^{-3}$)*
Coal coke breeze	650–800	690
Calcined petroleum coke granules	700–1100	720–850
Natural graphite granules	1100–1300	–
Man-made graphite, crushed	1100–1300	–

Data reproduced from corresponding article in 3rd Edition of Shreir's Corrosion.

Table 4 Typical coal coke specification for CP

To pass 16-mm screen	100%
To pass between 16-mm and 8-mm screen	8.9–9.8%
To pass between 8-mm and 1-mm screen	78–90%
To pass 1-mm screen	1–14%
Fixed carbon	82.7 min to 91% max
Volatile matter	0.1%
Ash	8.6%
Moisture	5% max, typically 4%
Sulfur	1.2% max, typically
Phosphorus	0.42–0.7%
Resistivity (uncompacted)	0.55 Ωm max, (typically 0.35 Ωm)
Specific gravity	1.4

Data reproduced from corresponding article in 3rd Edition of Shreir's Corrosion.

Table 5 Resistivities of carbonaceous backfills (Ω m)

Material	*Dry*	*Tamped*	*Wet*
Coal coke	0.55	0.45	0.15
Graphite granules	1.50	1.20	0.20

Data reproduced from corresponding article in 3rd Edition of Shreir's Corrosion.

The grading of the coke is of some importance in that too large a particle size offers large local contact resistance, leading to uneven consumption, while an excessively fine material leads to over-tight compaction and resultant gas blocking (gaseous polarization). Chemicals are sometimes added, for example, calcium hydroxide (5–10 wt%), to counteract the tendency to lose moisture by electroosmosis, as it is essential that an aqueous electrolyte is present to replace water consumed in the anodic reaction and conduct the current to the protected structure. The alkaline material also serves to neutralize anodically formed acid. Calcium sulfate is sometimes used in very dry conditions. A typical specification for coke suitable for CP groundbed use is given in Table 4.

The coke breeze is tamped down at a minimum pressure of 15 Pa. This ensures integrity of the groundbed while in operation and allows for the reduction in volume produced by chemical oxidation. A pressure of this magnitude will also reduce the initial bulk resistivity of the coke. In practice, resistivities between 0.08 and 0.29 Ω m have been recorded on coke samples used in typical groundbeds. The effect of pressure on the measured value for resistivity of different coke samples has also been reported elsewhere.[66] The resistivity of bulk metallurgical coke is given as 0.024 Ω m with a slightly lower value of 0.020 Ω m at a pressure of 0.43 Pa, while for calcined fluid petroleum coke at zero applied pressure the resistivity was 0.02 Ω m, which decreased to 0.002 Ω m when tested at an applied pressure of 1.31 MPa.

The backfill cross-section, in a typical horizontal groundbed, is normally ~300 × 300 mm. Deep-well groundbeds have a diameter of 150–300 mm. Bed length depends upon the required current output and the surrounding soil resistivity. In freshwater soil conditions, higher than average current density at the ends of the primary anodes can be prevented by not exceeding a primary anode spacing of twice its length. As the electrolyte resistance decreases, with a consequent increase in current density at the ends of the primary anodes, either a reduction in anode spacing or an increase in backfill cross-section should be considered.

Calcined petroleum coke breeze is often used in deep-well applications. The material has a low particle size and, with suitable additives, may be converted into a slurry and pumped into a borehole. The sulfur content of this material is high (1.4%), but moisture

(0.2%), ash (0.4%), and volatiles (0.4%) are low. The typical resistivity of this material is 0.15 Ωm. A petroleum coke with spherical grains is available, specifically for borehole CP applications.[67] The round grains ensure high bed porosity and enable gas to escape, allowing the coke to sink to the base of the borehole. The resistivity of this material is quoted as 0.1 Ω m.

4.20.4.3 Conductive Polymers

A continuous carbon loaded polymer anode system has been developed specifically for the CP of buried pipelines and tanks. The anode, marketed under the trade name AnodeFlex,[68] consists of a continuous stranded copper conductor (6AWG), which is encased in a thick jacket of carbon-loaded polymer, with overall diameter of 12.5 mm. To prevent unintentional short circuits an insulating braid is sometimes applied to the outer surface of the conductive polymer. The anode may be operated in the temperature range −18–65 °C and at currents up to 0.05 A per linear meter in soil and 0.01 A per linear meter in water, which corresponds to effective maximum surface current densities of 0.66 A m^{-2} in soil and 0.13 A m^{-2} in water. No precise details on the anode consumption rate have been provided by the manufacturer, but as the active component is carbon, the consumption rate would be expected to be of a similar order to that exhibited by graphite anodes. The anode may be installed in conventional groundbeds or laid in close proximity to the cathode, for example, parallel to a pipeline route. The anode may be buried either directly in soil or in carbonaceous backfill. The intended applications for this material are external tank base protection, internal vessel protection, mitigation of poor current distribution, and to supplement conventional CP systems by providing increased levels of CP in underprotected areas.

The disadvantage of this anode system for the CP of pipelines is that the anode length provided is by one single connection to the DC. Power source is limited by resistive losses along the copper conductors. Thus, the required current output per unit length and soil resistivity are limiting factors and a number of anode connections may be required to protect long lengths of pipeline. The anode has a poor chemical resistance to oils and should not be used in situations where oil spillage may occur.

A similar conductive polymer electrode has been designed specifically for the CP of steel reinforcing bars in concrete and has been marketed under the trade name Ferex.[69] The anode consists of a 16AWG stranded copper conductor surrounded by a carbon-loaded polymeric coating similar to that used on the AnodeFlex system[68] to provide a nominal anode diameter of 8 mm.[70] The manufacturer claims that at a maximum recommended current density of 0.08 A m^{-2} the anode life in concrete will be 32 years with a proportionately longer life at lower current densities. The anode is fixed to the concrete using nonmetallic fixings and may be supplied as a prefabricated mesh or more often as a continuous anode strand which is laid over the surface of the structure to be protected. The spacing between the anode strands may be adjusted to give the required current distribution and current density per unit area of concrete necessary to provide CP to a particular structure. A number of anode connections are made to the DC power source using proprietary splice kits (approximately one for every 60–80 m^2 of concrete to be protected). This will provide redundancy for anode failure and reduce resistive losses along the anode cable. Care must also be taken not to expose the copper conductor during installation or anode failure will take place. Once fitted to the concrete surface, a 15-mm thick cementitious overlay (gunite) is applied above the anode mesh, as recommended by the anode manufacturer, although thicknesses of up to 35–40 mm have been applied in some instances.

The major electrochemical reactions at the anode surface are oxygen and chlorine evolution coupled with oxidation of the active carbon to carbon dioxide. Eventually, all the carbon is removed from the anode coating and this allows perforation of the copper conductor leading to ultimate anode failure. Failures due to delamination of the concrete overlay coating have been reported in the United States, but have not been observed to any significant extent in Europe,[71] although some early failures of the anode system have been associated with high local current densities in areas of low concrete cover and high moisture or salt content.[72] The major application of this anode system is, therefore, on structures that are relatively dry with a uniform current requirement.

4.20.4.4 Conductive Overlay Systems

Early systems used for the protection of reinforced concrete bridge decks were on the basis of the use of a continuous layer of coke breeze/asphaltic cement (85%/15%) to ensure uniform current distribution.[73] Electrical connection was made using silicon iron anodes held in position using a nonconductive epoxy and covered with a conductive cement. Fromm[74] investigated the performance of different coke breeze/asphalt mixes and developed a mix containing only 45% coke breeze which had a resistivity of 0.03 Ω m and a void content of 5%. This was reported to give good results. The conductive mix was applied over the primary anodes, either silicon iron or graphite, to a total thickness of 50 mm and then given a protective top coat.

Schutt[75] reported that the coke breeze specification and conditions in which the mix is prepared are important factors in determining the optimum operation of such overlay systems, while further details on the coke breeze asphalt mix composition are given by Anderson.[76] Conductive concrete mixes with a polymer binder have also been developed as an anode system specifically for reinforced concrete CP systems.[77]

Conductive overlay systems are not practical propositions on vertical surfaces or surfaces where weight restrictions are important. However, they are proven CP systems and can be considered in conjunction with other reinforced concrete CP system anodes.

4.20.4.5 Conductive Paints

Carbon loaded conductive coatings may be used for the CP of steel reinforcing bars in concrete. They are always used in conjunction with a primary anode material, for example, a platinized-niobium or platinized-titanium wire or a conductive polymer rod. Brown and Fessler[78] have conducted a laboratory evaluation of conductive mastics that can be brushed or sprayed onto the concrete surface to achieve the necessary thickness. However, the most extensive study on conductive paints for CP purposes was undertaken by the US Federal Highway Authority.[77] Nine commercially available resins were evaluated in this work. It was shown that neither thermal cycling, freeze thawing nor the application of CP currents resulted in any deterioration of the most successful paint system, now referred to as DAC-85, a solvent-based acrylic mastic containing graphite. Minor failures with this system have been reported but only in localized areas with a high chloride contact. The anode system generally consists of platinized titanium or niobium wire laid in strips with the layers of carbon fiber interleaved between the strips. The paint is then mixed and applied on site. The paint consists of blends of resin and fine particles of coke. The performance of some paint systems is poor because of attempts to operate the anodes at currents in excess of 0.1 A m^{-2}.

The advantages of conductive paints are that they are easy to apply and a concrete overlay is not required. They can be applied to complex shapes and are not a problem where weight restrictions are imposed.

4.20.5 Platinum Anodes

4.20.5.1 Platinum

The properties of platinum as an inert electrode in a variety of electrolytic processes are well known, and in CP, it is utilized as a thin coating on a suitable substrate. In this way, a small mass of Pt can provide a very large surface area, and thus, anodes of this type can be operated at high current densities in certain electrolyte solutions, such as seawater, and can be economical to use. When platinum is made the anode in an aqueous solution, a protective electron-conducting oxide film is formed. Once this film has formed, current flow then occurs by oxygen evolution. In chloride-containing solutions, evolution of chlorine will also occur and is usually the predominant anodic reaction even at low chloride concentrations, for example, brackish waters. The relative proportions of oxygen and chlorine evolved will be dependent upon the chloride concentration, solution pH, anode potential, degree of agitation and nature of the electrode surface, with only a fraction of the current being used to maintain the passive platinum oxide film.[79] This results in a very low platinum consumption rate.

The dissolution rate of solid rods of high purity platinum over the current density range 1180–4600 A m^{-2} has been investigated. Values of 17.5–26.3 mg A^{-1} $year^{-1}$ were reported over the first year, but the rate decreased to a limiting value of 2.6–4.4 mg A^{-1} $year^{-1}$ over a 5-year period.[80] The high initial rate was attributed to preferential dissolution at grain boundaries and other high free energy sites. Tests carried out in the United Kingdom[81,82] on electrodeposited platinum on a titanium substrate indicate a consumption rate in seawater of 8.8 mg A^{-1} $year^{-1}$, although values of up to 15 mg A^{-1} $year^{-1}$ have been quoted elsewhere.[83]

4.20.5.2 Platinized Titanium

Titanium, which has been in commercial production since 1950,[84] is thermodynamically a very reactive metal, but has a strong tendency to passivate, that is, to form a highly stable oxide film which, although only a few atoms thick, is highly protective in most natural environments. When made anodic in a chloride-containing solution, this anodic film thickens with increase in voltage, remaining protective until a potential of ~8 V is reached, at which point localized film breakdown occurs with subsequent pitting. Until pitting occurs, the resistive nature of the oxide film prevents significant current, making titanium itself unsuitable for use as an anode material. However, this inertness makes titanium an eminently suitable substrate for platinum, which may be applied to the metal in the form of a thin coating. The presence of platinum allows electronic conduction across the oxide, with the resultant composite behaving in a similar manner to solid platinum. Any titanium exposed at discontinuities in the platinum layer remains protected by the anodically formed oxide film, provided surface potentials are maintained below ~8 V. Platinized titanium, therefore, provides an economical method of utilizing the inertness and electronic conductivity of platinum on a relatively inexpensive, yet inert substrate.

Titanium can be forged, bent, cut, stamped, rolled, extruded, and successfully welded under argon, making possible a large variety of electrode shapes, that is, rod, sheet, tube, wire, or mesh. It is a very light yet strong material with a high resistance to abrasion. Cotton[85,86] was the first to publish results on platinized titanium as an anode material and the first commercial installation utilizing platinum plated titanium anodes was completed in 1958 at Thameshaven for the protection of a large shipping jetty.

Platinized titanium anodes are usually produced by the electrodeposition of a thin coating of platinum from aqueous solutions[9] on to chemically etched titanium. Warne[87] states that electrodepositing coatings from aqueous plating solutions have the advantage that control of thickness is easily achieved, irregularly shaped substrates can be plated, and the electrodeposited coatings are hard and abrasion resistant, by virtue of interstitial hydrogen codeposited in the plating process. Titanium is a very difficult metal to electroplate because of the presence of the oxide film. Sophisticated pretreatments with acids are necessary to remove the oxide film and achieve good adhesion. Improvements in the level of adhesion can be obtained by heat treatment after plating.[88]

From aqueous solutions, platinum can only be applied as a relatively thin porous layer. Although the porosity decreases with increase in deposit thickness, so does the internal stress and if the platinum adhesion is poor, the coating may exfoliate. As a consequence, platinum thicknesses of 2.5–7.5 µm are normally used, although it is possible with care to apply coatings of 12.5 µm in one operation and still achieve good adhesion.[79] However, 7.5 µm is generally considered the maximum thickness from one plating operation. Thicker deposits may be obtained by deposition in a number of stages, with interstage anneals to expel codeposited hydrogen and relieve internal stresses.

Platinum electrodeposits may also be produced from molten salt electrolytes. The high temperature process has the advantage that the deposits are diffusion bonded to the titanium substrate and, thus, have good adhesion; if necessary, thick deposits can be produced. However, they have the disadvantages that, because of the complexity of the process, there is a limitation on the size and shape of the object to be plated, and the resultant deposits are softer and less wear resistant than those deposited from aqueous solutions.[89]

Metallurgically bonded platinized anodes have also been produced. These are achieved by wrapping a thin platinum sheet over a cylindrical billet of titanium, vacuum encapsulating within a copper can, which acts as a lubricant, and extruding it to the required shape.[9] When used in seawater systems, the resultant copper layer has the advantage that it prevents fouling of the anode prior to energizing. Low porosity, ductile platinum coatings can be produced, but only on rod or wire anode forms. A variant has been produced that consists of a titanium rod spirally wound with platinum wire spot welded to the surface of the rod.[90]

As indicated above, platinized titanium anodes have the disadvantage that the protective passive film on the titanium can break down and pit at high applied anodic voltages, leading ultimately to anode failure. The potential at which the breakdown of titanium occurs is dependent upon the solution composition. In seawater, the breakdown potential of titanium is often considered to be ~9.5 V versus SHE,[81] while values as low as 6 V in 5.8% NaCl have been reported.[91] The value of the breakdown potential for titanium is dependent upon the Cl^- concentration and in high purity waters may be relatively high.[92] The presence of certain anions for example SO_4^{2-}, favors passivation. At sulfate, when chloride ratios are above 4:1, the breakdown voltage increases from ~8 to 35 V.[93] The presence of bromides and iodides significantly reduce the pitting potential for titanium (down to as low as 2 V), while fluorides and sulfates will increase it to as much as

35 V.[93] Temperature also has a significant effect on the anodic breakdown voltage of titanium, with an increase in temperature decreasing the breakdown potential. A prudent maximum operating potential for platinized titanium in seawater is 8.0 V.

Platinized titanium anodes may be operated at current densities as high as 5400 A m^{-2} (94); however, at these current densities there is the possibility that the breakdown potential of titanium may be exceeded. The normal operating current density range in seawater is 250–750 A m^{-2},(79) while that in brackish waters is given as 100–300 A m^{-2} (95) with values within the range 100–150 A m^{-2} being favored.[9] The consumption rate for platinized titanium anodes in seawater over the current density range 300–5000 A m^{-2} has been found to be directly related to the charge passed, with values of 1–2 µg A^{-1} h^{-1} being generally used as the basis for system design. The consumption rate is also dependent upon solution composition, the rate increasing with decreasing chloride concentration and may reach a peak value of 435 mg A^{-1} $year^{-1}$ at a chloride concentration to be associated with the concurrent evolution of oxygen and chlorine, the rates of which are about equal in a neutral solution containing 2.5 g dm^{-3} NaCl.[81] In brackish waters, the platinum consumption rate may be as high as 20 µg A^{-1} h^{-1}, more than ten times the rate in seawater and increases with increase in current density. Baboian[96] reports consumption rates of ~13 mg A^{-1} $year^{-1}$ in seawater over the current density range 11.8–185 A m^{-2}, while those in 350 Ω cm water (brackish river water) he reports as 92.3 mg A^{-1} $year^{-1}$ at 11.8 A m^{-2}, increasing to 117.8 mg A^{-1} $year^{-1}$ at 185 A m^{-2}. The effect of temperature on the consumption rate of platinized titanium anodes has not been found to be significant over the ranges normally encountered in CP installations.

Failures of platinized titanium anodes have been found to occur for reasons other than consumption of platinum or attack on the titanium substrate caused by voltages incompatible with a particular electrolyte. The following are examples:

- Attack on the substrate when covered in mud or marine growth, prior to energizing, has been found to be a possible cause of failure, because of a buildup of acidity (reduction in pH) once the current is applied.[97,98] Some commercial guarantees require that the exposure period during which anodes remain unenergized must exceed 8 weeks.[99] If anodes are to be installed in seawater for extended periods prior to energizing, they should be coated with a copper antifouling paint or electrodeposit.[81] The copper coating will dissolve when the anode is energized and will not affect the anode's subsequent performance or operation.
- Attack on the substrate by contact with calcareous scale can also cause platinum loss to occur. Anodes located close to the cathode or operating at high current densities can lead to a rapid build up of calcareous deposit, the major constituents of which are $Mg(OH)_2$ and $Ca(OH)_2$.[100] The alkaline conditions so generated can lead to rapid dissolution of the platinum. The calcareous deposit can be removed by washing with dilute nitric acid.
- The formation of deposits on platinized anodes can cause anode degradation.[88,97] Thus, dissolved impurities present in water, which are liable to oxidation to insoluble oxides, for example Mn, Fe, Pb, and Sn, can have a detrimental effect on anode life. In the case of MnO_2 films, it has been observed that MnO_2 may alter the relative proportions of Cl_2 and O_2 produced and thereby, increase the Pt dissolution rate.[9] The oxides may be incorporated into the TiO_2 oxide film and decrease the breakdown potential[97] or form thick deposits. The latter may limit electrolyte access and lead to the development of localized acidity, at concentrations sufficient to attack the underlying substrate.[9]
- The superimposition of AC ripple on the DC output from a transformer rectifier can, under certain circumstances, lead to increased platinum consumption rates and has been the subject of considerable research.[97,101–103] Indeed, when platinized titanium anodes were first used, it was recommended that the AC component was limited to 5% of the DC voltage.[9]
- The frequency of the superimposed AC voltage signal has also been shown to affect the consumption rate of platinum, which increases with decrease in frequency. At 100–120 Hz (the frequency of the AC component signal from a full-wave single-phase transformer rectifier) and above, the AC signal has a negligible effect on consumption rate, provided that the AC component did not allow the electrode to become negative. If negative potential 'spikes' do occur in the output wave form, even at 100 Hz, a considerable increase in platinum dissolution can occur.[104] This could be the case with a thyristor-controlled transformer rectifier operating at a relatively low current

output. At low-frequency AC (2 Hz), an increase in platinum dissolution rate of two to three times has been reported, while negative current spikes of a few milliseconds duration at this frequency can cause dissolution rates of ~190 mg A^{-1} $year^{-1}$. It is, therefore, recommended that all spurious waveforms on the DC supply to platinized anodes be avoided.

- Organic impurities in the electrolyte have also been quoted as increasing the rate of platinum dissolution when the metal is used as an anode in electroplating.[97] Saccharose was observed to increase the anodic dissolution of platinum by a factor of ten in a 3% brine solution,[105] but did not affect the anodic breakdown voltage for titanium. Other organic compounds that may also have an effect are brightening agents for Ni plating solutions of the naphthalene trisulfonic acid type, detergents, or wetting agents.
- Fatigue failure of cantilever anodes in flowing electrolytes can occur as a result of vortex shedding.[106] However, with proper design and adequate safety factors, these failures can be avoided.[97,107]
- Attention must be paid to end effects, particularly on cantilever anodes, for example, on long anodes that extend away from the cathode surface. Under these circumstances, the anode surface close to the cathode may be operating at a considerably higher current density than the mean value, with the exact values dependent upon the system geometry. The life of the platinized anode in this region would then be reduced in inverse proportion to the current density.

In seawater and brackish waters, platinized–titanium installations have now been in use for 50 years for jetties, offshore installations, ships and submarines,[9,107] and for internal protection, particularly of cooling-water systems.[108] Anode forms include rod, tubular, mesh, and plate. For the protection of heat exchangers, an extruded wire of copper-cored titanium–platinum has shown a reduction in current requirement, together with improved longitudinal current spread, over cantilever anodes.[109,110] This 'continuous' or coaxial anode is usually fitted around the water box periphery a few centimeters away from the tube-plate.

Although not suitable for direct burial, platinized–titanium anodes may also be used in soils when surrounded by a carbonaceous backfill. Warne and Berkeley[111] have investigated the performance of platinized–titanium anodes in carbonaceous backfills and concluded that the anodes may be successfully operated in this way at current densities of up to 200 A m^{-2}. This also supplements the findings of Lewis,[112] who states that platinized–titanium anodes may be used in carbonaceous backfill without breakdown of the titanium oxide film. In a properly constructed groundbed, there will be little ionic conduction at the platinum surface, the primary conduction to the carbon being electron transfer.

Under some circumstances, platinized titanium can be used in open-hole groundbeds extending below the water table. However, the water chemistry within a borehole can be complex and may, in certain circumstances, contain contaminants which favor breakdown of the anodic film on titanium. In addition, the pH of the solution in a confined space will tend to decrease, and this will result in an increase in the corrosion rate of the platinum.

4.20.5.3 Platinized Niobium and Tantalum

Platinum electrodeposition onto tantalum had been carried out as early as 1913[113] and the use of platinized tantalum as an anode was suggested in 1922,[114] while platinum electrodeposition on to niobium was first successfully carried out in 1950.[115] These anodes are similar in principle to their titanium equivalent, differing only in the fact that they can tolerate much higher operating potentials and hence, they can operate at much higher current density. They are considerably more expensive than platinized titanium, especially when expressed in terms of price per unit volume.[88] As niobium is cheaper than tantalum, the use of the latter has become rare. The extra cost of Nb anodes may be offset in certain applications by their superior electrical conductivity and higher breakdown voltages. **Table 6** gives the comparative breakdown potentials of Ti, Nb, and Ta in various solutions under laboratory conditions.

Table 6 Comparison of breakdown potential

Solution	*Ti*	*Nb*	*Ta*
Seawater	9	120	120
Sulfate/Carbonate	60	255	280
Phosphate/Borate	80	250	280
Drinking water	37.5	250	280
Bromides	2–3		

Data reproduced from corresponding article in 3rd Edition of Shreir's Corrosion.

There have been instances reported in the literature where the breakdown potential for Nb and Ta in seawater has been found to be lower than the generally accepted value of 120 V, with reported values in extreme instances as low as 20–40 V.[116,117] This has been attributed to contamination of the niobium surface from machining operations, grit blasting, or traces of copper lubricant used in anode manufacture. These traces of impurities, by becoming incorporated in the oxide film, decrease its dielectric properties and, thus, account for the lower breakdown voltage. Careful control of surface contamination in the manufacture of platinized niobium is, therefore, essential to minimize the lowering of the breakdown potential of niobium.

Lower breakdown potentials, leading to unexpected premature failure, have also been observed on platinized niobium anodes which have become buried in seabed silt.

Platinized niobium anodes can be prepared by electrodepositing platinum onto grit-blasted niobium, metallurgical coprocessing (cladding) or by welding platinum or platinum/iridium wire to niobium rod.[116] They cannot be prepared by thermal deposition because niobium oxidizes at 350 °C and good adhesion cannot be obtained. Both materials may be welded under argon, utilizing butt or plasma welding techniques.

Platinized niobium and tantalum anodes have found use in applications where their high breakdown voltages and hence higher operational current densities can be utilized. These include ship and cooling system anodes, which may need to operate in estuarine waters and therefore, require higher driving voltages, offshore structures where high reliability in service is required, domestic water tanks,[118] and deep-well open-hole groundbeds.[119] Efird[104] found the consumption rate of platinized niobium in seawater over the range 5000–10 000 $\mathrm{A\,m^{-2}}$ to be similar to that of platinized titanium, that is, 1 $\mu\mathrm{g\,A^{-1}\,h^{-1}}$. However, at a current density of 30 000 $\mathrm{A\,m^{-2}}$, he observed an increase in the platinum consumption rate to 2 $\mu\mathrm{g\,A^{-1}\,h^{-1}}$ and concluded that this was the limiting current density for operating these anodes. Warne and Berkeley[111] report that the maximum current density for these anodes in seawater is 2000 $\mathrm{A\,m^{-2}}$, with a working current density of 500–1000 $\mathrm{A\,m^{-2}}$. The operating current density selected should, however, be commensurate with the desired anode life, platinum coating thickness, and platinum consumption rate in a given environment.

In open-hole deep-well groundbeds, platinized niobium anodes have been successfully operated at a current density of 215 $\mathrm{A\,m^{-2}}$ (120) and in the range 100–267 $\mathrm{A\,m^{-2}}$.[121] Toncre and Hayfield[95] have conducted work on the operating parameters of platinized niobium anodes in brackish waters and simulated groundbed environments. For an open-hole groundbed, they concluded that operational current densities of 400 $\mathrm{A\,m^{-2}}$ or higher were the most economical, as they led to a lower consumption rate in sulfate-containing groundwaters. The platinum consumption rate in a deep-well environment may well alter because of variations in the environmental conditions. On extruded platinized niobium anodes a consumption rate of 175 $\mathrm{mg\,A^{-1}\,year^{-1}}$ was considered for design purposes, while that for electroplated platinized niobium was taken as 87.6 $\mathrm{mg\,A^{-1}\,year^{-1}}$. In a backfilled deep-well groundbed, dissolution rates comparable with those for an open-hole environment were reported, that is, 87.6 $\mathrm{mg\,A^{-1}\,year^{-1}}$ at 200 $\mathrm{A\,m^{-2}}$. At lower current densities, it seems likely that the electrochemical processes would be limited to oxidation reactions involving coke alone and no electrochemical loss would occur on platinized niobium. Indeed, Baboian[122] reports negligible Pt consumption rates in carbonaceous backfill at current densities from 11.8 to 29 $\mathrm{A\,m^{-2}}$, increasing to 11.9 $\mathrm{mg\,A^{-1}}$ at 57.9 $\mathrm{A\,m^{-2}}$ and 13.5 $\mathrm{mg\,A^{-1}\,year^{-1}}$ at 185 $\mathrm{A\,m^{-2}}$. The wear rates at 57.9 and 185 $\mathrm{A\,m^{-2}}$ were comparable to those Baboian observed in seawater. The relative merits of platinized titanium and niobium in a deep-well environment, in comparison with those of other anode materials, have been discussed by Stephens.[123]

4.20.5.4 Mixed Metal Oxide Coated Titanium

Mixed metal oxide (MMO) anodes, as their name suggests, consist of a layer of precious metal oxide intermixed with titanium or tantalum oxide, on a titanium substrate. They were originally developed, by Beer,[124,125] for the production of chlorine and chlorates,[126,127] where they were used as a more corrosion resistant replacement for graphite at the very high current densities (10 000 $\mathrm{A\,m^{-2}}$) and extreme environmental conditions experienced in those applications. They are sometimes alternatively referred to as dimensionally stable anodes (DSA).

They have now gained wide acceptance as impressed current anodes for CP and have been in use for this purpose since 1971. The anode consists of a thin film of metal oxides deposited onto a chemically etched titanium substrate by thermal decomposition of a solution of metal salts, usually chlorides, in an organic solvent. The solution is applied by painting or spraying on to the titanium surface and then allowing the solvent to evaporate. The anode is heated in a controlled atmosphere to a temperature at which the metal salts decompose (between 350 and 600 °C)[128] and form the oxides. Multiple layers are applied and heated until the required deposit thickness, which is typically 2–12.5 μm, is obtained. Thicker deposits become brittle and poorly adherent,[129] although deposits up to 25-μm thick can be produced. Only titanium substrates can be coated in this way because at the temperatures required by the anode manufacturing process niobium oxidizes excessively.

MMO coatings are usually on the basis of the use of ruthenium or iridium oxides, in combination with titanium or tantalum oxides, although palladium has also been used for some applications and additions of tin oxide are also sometimes used. The composition of mixed metal oxide used is dependent on the environment in which the anode will operate and is adjusted to favor either oxygen or chlorine evolution by varying the relative proportions of iridium and ruthenium. For chlorine production, RuO_2-rich coatings are preferred, while for oxygen evolution IrO_2-rich coatings are utilised.[130] The former would be used in seawater, and the latter for buried or concrete CP application. The precise composition of the coating is generally considered proprietary information and is not divulged by the anode manufacturers.

MMO coated anodes have a significantly lower consumption rate than those using platinum metal. In seawater, with the anode evolving chlorine, the consumption rate is 0.5–1 mg A^{-1} $year^{-1}$, while in freshwaters and soils where oxygen evolution predominates the rate is 6 mg A^{-1} $year^{-1}$.(128) These are one fifth to one tenth of the platinized anode loss rate. The current densities normally used for design purposes are 600 A m^{-2} for seawater, and 100 A m^{-2} for fresh water, saline mud, and coke breeze backfill.[131] Higher current densities may be utilized in certain circumstances, but this reduces the anode life for a given coating thickness. MMO coatings are porous and, therefore, the limitations on operating voltage for platinized titanium anodes apply equally to MMO coated titanium electrodes. It has been reported that breakdown of mixed metal oxide anodes may occur at 50–60 V in low-chloride concentration water but at only 10 V in chloride-rich environments.[128]

MMO anodes, like platinized Ti, can be supplied in a number of different forms including rod, tube, plate, and wire. Their application is similar to that for platinized anodes, except that, with a suitable MMO formulation, they can be directly buried without the use of carbonaceous backfill. LIDA® anodes, consisting of tubular anodes distributed on a length of cable which passes through the tubes, which are then swaged to connectors at their center points, have been developed specifically for use in groundbeds, both deep-well and horizontal.

Another specific development has been the use of MMO coated titanium mesh for the CP of reinforcing steel in concrete structures.[132,133,134] The anode mesh is made from commercially pure titanium sheet ∼0.5–2-mm thick expanded to provide a very open, diamond-shaped, mesh. The mesh size selected is dictated by the required cathode current. The anode mesh is joined on site using spot welded connections to a titanium strip or by niobium crimps, while electrical connections to the DC power source are made at selected locations using suitably encapsulated or crimped connections. The mesh is fixed to the concrete using nonmetallic fixings. The MMO in this application is usually a combination of iridium and tantalum oxides. The material once installed is then covered with a concrete or mortar coating, the minimum thickness of cover above the anode mesh being 10 mm, while 15 mm is preferred. Alternative methods of application for concrete structures have included installation of anode strips in diamond cut slots and MMO coated titanium rods inserted in grouted holes. As well as being suitable for controlling reinforcement corrosion in existing structures by CP, all these anode variants can be installed in new structures to provide cathodic prevention, the advantage of the latter being that much lower current densities are required for 'prevention' rather than 'protection.'

4.20.6 Ceramic Anodes

An electrically conductive titanium oxide based ceramic material has been developed and is marketed under the trade name 'Ebonex.'®[135] This material consists principally of Ti_4O_7 but may also contain some higher oxides. It is black in color, has an electrical resistivity of less than $2 \times 10^{-4}\,\Omega\,m$ and can be operated at current densities up to 100 A m^{-2} in 10% NaCl; however, if coated with a precious metal, it can be operated at considerably higher current densities up to 400 A m^{-2}.(136) Consumption rates, even in concentrated sulfuric acid, are negligible. It is both porous and brittle, although it's mechanical strength can be improved and porosity reduced by resin impregnation, preferably with inorganic fillers. It has a high over-potential for oxygen evolution, is not affected by current reversal, and has no restriction on operating voltage, and the makers claim that it has an excellent resistance to both acid and alkali. It is, however, difficult and expensive to produce, requiring heating of pure compacted titanium oxide powder in hydrogen at ~1350 °C.

To date, the material has been used as an electrode in electrowinning, electrochlorination, batteries, and electrostatic precipitators. In tubular form, it has been used as a discrete anode on concrete CP and prevention. One feature restricting its more widespread application is the difficulty of making good, consistent electrical connection having sufficient reliability.

4.20.7 Applications of Impressed-Current Anodes

As will be clear from the discussions above, the types of anodes available for use in impressed-current CP have become more advanced with time, starting with steel, which is fully consumed with use and proceeding with increasing resistance to anodic dissolution, through silicon containing cast iron, graphite (and carbonaceous backfill), lead based alloys (including bielectrodes), platinized titanium to mixed metal oxide coated titanium. The current use of these materials in a number of CP applications is briefly outlined in the following sections. The final choice will be on the basis of a combination of operational factors (design life, environment, consumption rate, and ease of installation) and cost.

4.20.7.1 Offshore and Marine

The majority of offshore installations are protected from corrosion by the use of sacrificial-anode CP. A number of impressed current systems have been installed, but they have a number of disadvantages, most notably a need for continuing control and maintenance, and a tendency to mechanical failure. Where impressed-current protection has been used, it has been with platinized titanium or platinized niobium. MMO anodes have, on occasion, been used to retrofit protection to structures where life extension has been needed.

Impressed-current systems are more often used with marine structures such as jetties, where the possibility of automatic current control allows for the varying current demand because of tidal movements. Very early systems used scrap steel anodes. The use of lead–silver was common up to ~30 years ago, when platinized titanium became widely available. Most modern systems utilize MMO coated titanium in rod, tube, or plate form.

Systems for the protection of ship's hulls and, recently, floating production units used to use lead–silver anodes, but most installations today take advantage of the very low consumption rate of MMO materials.

4.20.7.2 Onshore

Most CP for onshore installations is provided using anode groundbeds backfilled with a carbonaceous material. The primary conductor anode is now commonly MMO coated titanium, which offers advantages in weight and ease of installation. However, silicon–iron is still in extensive use, while graphite and magnetite anodes are also available for these applications.

Canistered anodes utilize silicon–iron, platinized titanium or MMO anodes in carbonaceous backfill within a galvanized steel canister. Where ground conditions allow the use of open-hole deep-well groundbeds, silicon–iron or MMO anodes are usually used although again graphite and magnetite are also sometimes employed. Platinized niobium may be used where very high groundbed current output is required.

Under the bases of large diameter above-ground tanks, MMO coated titanium wire can be used to ensure good current distribution to the entire base surface. Conductive polymer coated wire is occasionally used for this application.

4.20.7.3 Internal

The earliest systems for the protection of the water boxes of seawater cooled condensers used steel or cast-iron anodes. The tendency now is to use platinized or MMO anodes, with occasional use of magnetite.

4.20.7.4 Concrete

Reinforced concrete structures that are fully immersed or buried in a corrosive environment may generally be protected using conventional cathodic protection groundbed design. However, for the CP of above-ground reinforced concrete structures, for example, bridge decks, jetties, tunnel parking garages, and concrete buildings, a number of specific anode systems have been developed.

Some of the earliest systems were for bridge decks and used conductive asphalts. Where the additional weight and thickness can be accommodated, modern systems use an MMO coated mesh attached to the surface and covered with a layer of sprayed concrete or mortar. If weight is an issue or the additional thickness of mortar cannot be accepted, conductive coating can be used, or, alternatively strip or rod anodes can be incorporated in the concrete by slot cutting or drilling, respectively. Titanium oxide ceramic has sometimes been used as an alternative to MMO coated rods.

References

1. Kimmel, A. L. *Corrosion* **1956**, *12*(1), 63.
2. Peabody, A. W. *Mater. Prot.* **1970**, *9*(5), 13–18.
3. Bengough, G. C.; May, R. *J. Inst. Met.* **1924**, *32*(2), 5.
4. Cotton, J. B. *Chem. Ind. Rev.* **1958**, *68*, 492.
5. Brand, J. W. L. F.; Tullock, D. S. 1965, CWE International Report, London.
6. Redden, J. C. *Mater. Prot.*, **1966**, *5*(2).
7. Applegate, L. M. *Cathodic Protection*; McGraw Hill: New York, 1960.
8. Bryan, W. T. *Mater. Prot. Perf.* **1970**, *9*(9), 25–29.
9. Shreir, L. L.; Hayfield, P. C. S. In *Impressed Current Anodes*; Conference on Cathodic Protection Theory and Practice – The Present Status, Coventry, 28–30 April, 1982.
10. Peabody, A. W. *Control of Pipeline Corrosion*; NACE: Houston, TX, 1967.
11. Tudor, S.; Miller, W. L.; Ticker, A.; Preiser, H. S. *Corrosion* **1958**, *14*(2), 93t–99t.
12. NACE T-2B Report. *Corrosion* **1960**, *16*(2), 65t–69t.
13. NACE T-2B Report. *Corrosion* **1957**, *13*(2), 103t–107t.
14. NACE T-2B Report. *Corrosion* **1955**, *10*(12), 62–66.
15. Doremus, G. L.; Davis, J. G. *Mater. Prot.* **1967**, *6*(1), 30–39.
16. Bryan, W. T. *Mater. Prot. Perfom.* **1970**, *9*(9), 25–29.
17. Durion Company, Dayton, OH, USA, Technical Data Bulletin DA/7c, 1984.
18. Jakobs, J. A.; Hewes, F. W. In Proceedings of Corrosion '81; NACE International: Houston, TX, 1981; Paper no. 222.
19. McKinney, J. W. *Mater. Perform.* **1979**, *18*(11), 34–39.
20. Allmand, A. J.; Ellingham, H. J. T. *Applied Electrochemistry*; Edward Arnold: London, 1931.
21. Linder, B. *Mater. Perform.* **1979**, *18*(8), 17–22.
22. Kofstad, P. *Nonstoichiometry, Diffusion and Electrical Conductivity in Binary Metal Oxides*; Wiley Interscience: New York, 1972.
23. Miller, J. Danish Corrosion Centre Report, May 1977.
24. Jakobs, J. A. *Mater. Perform.* **1981**, *20*(5), 17–23.
25. Matlock, G. L. In Proceedings of Corrosion 84; NACE International: Houston, TX, 1984; Paper no. 340.
26. Technical Data Sheet, Bergsoe Anti Corrosion.
27. Kubicki, J.; Trzepierczynska, J. *Ochr. Przed. Koroz.* **1980**, *11–12*, 301–303.
28. Wakabayshi, S.; Aoki, T. *J. Phys.* **1977**, *4*, pCl.
29. Kumar, A.; Segan, E. G.; Bukowski, J. *Mater. Perform.* **1984**, *23*(6), 24–28.
30. Tefsuo, F. *et al. Corros. Eng.* **1980**, *29*(4), 180–184.
31. Moller, G. E.; Patrick, J. T.; Caldwell, J. W. *Mater. Prot.* **1962**, *1*(2), 46–57.
32. Littauer, E. L.; Shreir, L. L. In Proceedings of the 1st International Congress on Metallic Corrosion, Butterworths, London, 1961; p 374.
33. Shreir, L. L. *Corrosion* **1961**, *17*, 188t.
34. Barnard, K. N.; Christie, G. L.; Gage, D. E. *Corrosion* **1959**, *15*(11), 501t–586t.
35. Von Fraunhoffer, J. A. *Anti Corrosion*, November 9–14 and December 4–7, 1986.
36. Kuhn, A. T. *The Electrochemistry of Lead*, Academic Press: London, 1979.
37. Fink, C. G.; Pan, L. C. *Trans. Electrochem. Soc.* **1924**, *46*(10), 349.
38. Fink, C. G.; Pan, L. C. *Trans. Electrochem. Soc.* **1926**, *48*(4), 85.
39. Morgan, J. H. *Cathodic Protection*; Leonard Hill: London, 1959.
40. Morgan, J. H. *Corros. Technol.* **1958**, *5*(11), 347.
41. Kubicki, J.; Bujonek, B. *Ochr. Przed. Koroz.* **1982**, *3*, 41–45.
42. Shreir, L. L. *Platinum Met. Rev.* **1968**, *12*(2), 42–45.
43. Private Report on Films on Lead-Silver-Antimony Electrodes, Fulmer Research Institute to CWE Ltd.
44. Hollandsworth, R. P.; Littauer, G. L. *J. Electrochem. Soc.* **1972**, *119*, 1521.
45. Shreir, L. L. *Corrosion* **1961**, *17*(3), 118t–124t.
46. Metal and Pipeline Endurance Ltd., U.K. Patent 870,277, 1961.
47. Fleischmann, M.; Liler, M. *Trans. Faraday Soc.* **1958**, *54*, 1370.
48. Shreir, L. L. *Platinum Met. Rev.* **1978**, *22*(1), 14–20.
49. Peplow, D. B. *Br. Power Eng.* **1960**, *1*, 31–33.
50. Shreir, L. L.; Weinraub, A. *Chem. Ind.* **1958**, *41*, 1326.
51. Shreir, L. L. *Platinum Met. Rev.* **1959**, *3*(2), 44–46.
52. Wheeler, W. C. E. *Chem. Ind.* **1959**, *75.*
53. Shreir, L. L.; Metal and Pipeline Endurance Ltd., U.K. Patent 19823/79; 1979.
54. Hill, N. D. S. *Mater. Perform.* **1984**, *23*(10), 35–38.
55. Barak, M. *Chem. Ind.* **1976**, *20*, 871–876.
56. Smith, J. F. *Trans. IMF* **1975**, *53*, 83.
57. Hamzah, H.; Kuhn, A. T. *Corros. J.*; **1980**, *15*(3).
58. Brady, G. D. *Mater. Perform.* **1971**, *10*(10), 20–23.
59. Heinks, H. *Ind. Eng. Chem.* **1955**, *47*, 684.
60. Palmquist, W. W. *Pet. Eng.* **1950**, *2*, D22–D24.
61. Bulygin, B. M. *Ind. Eng. Chem.* **1959**, *32*, 521.
62. Krishtalik, L. I.; Rotenberg, Z. A. *Russ. J. Phys. Chem.* **1965**, *39*, 168.
63. Ksenzhek, O. S.; Solovei, Z. V. *J. Appl. Chem.* **1960**, *33*, 279.
64. Oliver, J. P. Annual conference of the American Institute of Electrical Engineers, Paper 52–506; IEEE: New York, 1952.
65. Costanzo, F. E. *Mater. Prot.* **1970**, *9*(4), 26.
66. Espinolu, R. A.; Mourente P.; Salles, M. R.; Pinto, R. R. *Carbon*, *24*(3), 337–341
67. LORESCO™, Cathodic Engineering Equipment Co Inc., Missouri, USA.
68. AnodeFlex – Registered trade name, Raychem Ltd., USA.
69. Registered trade mark Raychem USA (manufacturing and marketing rights purchased by Eltech Corporation, 1989).
70. Ferex Technical Data Sheet.
71. Wyatt, B. S.; Lothian, A. In UK Corrosion 88; CEA: Brighton, 1988.

72. Wyatt, B. S. In *Cathodic Protection Theory and Practice*, 2nd International Conference, Stratford-upon-Avon, UK, June, 1989; Paper no. 23; Institute of Corrosion: UK.
73. Stratful, R. F. Experimental Cathodic Protection of Bridge Decks, Transportation Research Record, 500(1), 1974.
74. Fromm, H. J. In Proceedings of Corrosion '76; NACE International: Houston, TX, 1976; Paper no. 19.
75. Schutt, W. R. In Proceedings of Corrosion '78; NACE International: Houston, TX, 1978; Paper no. 74.
76. Anderson, G. Cathodic Protection of a Reinforced Concrete Bridge Deck, American Concrete Institute Convention, 1979.
77. Federal Highway Authority (USA). Cost Effective Concrete Construction and Rehabilitation in Adverse Environments, Project No. 4K, Annual Progress Report Sept., 1981.
78. Brown, R. P.; Fessler, H. J. In Corrosion 83, 1983; Paper no. 179.
79. Shreir, L. L. *Platinum Met. Rev.* **1977**, *21*(4), 110–121.
80. Warne, M. A.; Hayfield, P. C. S. *Mater. Perform.* **1776**, *15* (3), 39–42.
81. Hayfield, P. C. S.; Warne, M. A.; Jacob, W. R. In Proceedings of conference on UK Corrosion '81; Harrogate, Institute of Corrosion: UK, 1981.
82. Warne, M. A.; Hayfield, P. C. S. Durability Tests on Marine Impressed Current Anodes, IMI Marston/ Excelsion Ltd., 15 March, 1971.
83. Baboian, R. In Proceedings of Corrosion '76; NACE International: Houston, TX, 1976; Paper no. 183.
84. Lowe, R. A. *Mater. Prot.*; NACE: Houston, TX, 1966.
85. Cotton, J. B. *Chem. Ind. Rev.* **1958**, *68*, 68–69.
86. Cotton, J. B.; Williams, E. C.; Barber, A. H. UK Patent 877,901, 1958.
87. Warne, M. A. *Mater. Perform.* **1979**, *18*(8), 32–38.
88. Jacob, W. R. In Proceedings of Symposium on Cathodic Protection, London, May, 1975; Paper no. 5.
89. Baboian, R. In Proceedings of the 4th International Congress on Marine Corrosion and Fouling, Antibes, France, 1976.
90. U.S. Patent 3,443,055, 1966.
91. Baboian, R. *Mater. Perform.* **1977**, *16*(3), 20–22.
92. Segan, E. G. *et al.* Titanium Anodes in Cathodic Protection, Final Report, Army Construction Engineering Research Laboratory, Champaign, Illinois USA, Jan. 1982.
93. Dugdale, I.; Cotton, J. B. *Corros. Sci.* **1964**, *4*, 397–411.
94. Anderson, D. B.; Vines, R. F. In Extended extracts of the Second International Congress on Metallic Corrosion, March, 1963.
95. Toncre, A. C.; Hayfield, P. C. S. In Corrosion 83, 1983; Paper no. 148.
96. Baboian, R. In Corrosion 83, 1983; Paper no. 149.
97. Hayfield, P. C.; Warne, M. A. In Corrosion 82, 1982; Paper no. 38.
98. Warne, M. A.; Hayfield, P. C. *Br. Corros. J.* **1971**, *6*, 192–195.
99. Commercial Guarantee, Martson Excelsior, 1972.
100. Pathmanaban; Phull, B. Proc UK corrosion 82, Hammersmith, London, 1982.
101. Juchniewicz, R. *Platinum Met. Rev.* **1962**, *6*, 100.
102. Hoar, T. P. *Electrochim. Acta* **1964**, *9*, 599.
103. Juchniewicz, R.; Hayfield, P. C. S. In 3rd International Congress on Metallic Corrosion, Moscow, **1969**; Vol. 3, pp 73.
104. Efird, K. D. *Mater. Perform.* **1982**, *21*(6), 51–55.
105. Pompowski, J.; Juchniewicz, R.; Walaszkowski, E.; Strelcki, H.; Sadowska, J. In Marine Corrosion Conference; Technical University of Gdansk: Gdansk, 1967; p 87.
106. Love, T. J. Power USA, 80–81, Feb, 1981.
107. Dreyman, E. W. *Mater. Perform.* **1972**, *11*(9), 17–20.
108. Nekosa, G.; Hanck, J. *Laboratory and Field Testing of Platinised Titanium and Niobium Anodes for Power Plant Applications*; The Electrochemical Society Meeting, Pittsburgh, PA, October 1978.
109. Morgan, J. H. Proceedings of the Symposium on Recent Advances in Cathodic Protection; Marston Excelsior; Wilton, Birmingham, May, 1964.
110. Lowe, R. A.; Brand, J. W. L. F. *Mater. Prot. Perform.* **1970**, *9*(11), 45–47.
111. Warne, M. A.; Berkeley, K. E. In Corrosion 80, 1980; Paper no. 244.
112. Lewis, T. H. Corrosion 79, Atlanta, GA, USA, 1979; Paper no. 144.
113. Stevens, R. H. U.S. Patent 1,077,894; 1,007,920, November 1913.
114. Baum, E. U.S. Patent 1,477,000, August, 1922.
115. Rosenblatt, E. F.; Cohen, J. G. ULS Patent 2,719,797, October, 1955.
116. Hayfield, P. C. S. *Mater. Perform.* **1981**, *20*(11), 9–15.
117. Hayfield, P. C. S. In Corrosion 81, Toronto, Canada 1981; Paper no. 103.
118. Gleason, J. D. *Mater. Perform.* **1979**, *18*(1), 9–15.
119. Sly, P. M. *Platinum Met. Rev.* **1981**, *24*(2), 56–57.
120. Tatum, J. F. *Mater. Perform.* **1979**, *18*(7), 30–34.
121. Toncre, A. C. *Mater. Perform.* **1980**, *19*(3), 38–40.
122. Baboian, R. *Mater. Perform.* **1983**, *22*(12), 15–18.
123. Stephens, R. W. Corrosion 83, 1983; Paper no. 144.
124. Beer, H. B. UK Patent 1,147,442, 1965.
125. Beer, H. B. UK Patent 1,195,871, 1967.
126. Bianchi, G.; de Mora, V.; Gallone, P. US Patent 3,616, 445, 1967.
127. De Nora, V.; Kuhn von Burgsdorf, J. W. *Chem. Ing. Tech.* **1975**, *47*, 125–128.
128. Katowski, S. Chlorine. In Ullmans Encyclopedia of Industrial Chemistry; Wiley-VCH: New York, 1986; Chapter 7.
129. Schrieber, C. F.; Mussinelli, G. L. Paper 287, Corrosion 86, 1986.
130. Matusumoto, Y.; Tazawa, T.; Muroi, N.; Sato, E. *J. Electrochem. Soc.* **1986**, *133*(1), 2257–2262.
131. Reding, J. T. Paper 9, Corrosion 97, San Francisco, USA, 1987.
132. Tvarusku, A.; Bennett, J. E. In Proceedings of the 2nd International Conference on Deterioration and Repair of Reinforced Concrete in Arabian Gulf, Bahrain, 1987; pp 139–154.
133. Mudd, C. J.; Mussinelli, G. L.; Tettamanti, M.; Pedeferri, P. In Corrosion 88, St Louis, USA 1988; Paper no. 229.
134. Hayfield, P. C. *Platinum Met. Rev.* **1986**, *30*(4), 158–166.
135. Trade name of Ebonex Technologies Inc., California USA, (European Patent Application 0047595; US Patent 4,422,917).
136. Product Information Sheet, Ebonex Technologies Inc., 1988.

4.21 Practical Application of Cathodic Protection

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Glossary

Dolphin A harbor structure that extends above the water level and is not connected to shore; they are installed when it would be impractical to extend the shoreline (e.g., with a pier or wharf) to provide a dry access facility.

Abbreviations

AC Alternating current
DC Direct current
emf Electromotive force (V)
IR Voltage (ohmic) drop due to current flow (*I*) through a resistance (*R*)
In Natural logarithm
MMO Mixed metal oxide
PV Photovoltaic

Symbols

I Current
M Generic symbol for a metal
R Resistance
V Voltage
z Number of electrons transferred in electrochemical reaction
ρ Resistivity

4.21.1 Background and Introduction

The forms of corrosion that can be controlled by cathodic protection include all forms of general corrosion, pitting corrosion, graphitic corrosion, crevice corrosion, stress corrosion cracking, corrosion fatigue, cavitation corrosion, bacterial corrosion, etc. Cathodic protection can be applied to a wide range of metals and bimetallic couples of metals. Most applications are to steel, as this is the most common construction material, but cathodic protection, with revised protection criteria or limits, can be applied to stainless steels, copper, cupro nickel alloys, lead, aluminum alloys, and galvanized steel.

4.21.1.1 Structures that Are Cathodically Protected

There are many structures and installations that, in given circumstances, can benefit from the application of a cathodic protection system. For example, these include buried and submerged crude oil, fuel oil and gas tanks, and pipelines; offshore fixed oil and gas drilling and production platforms, buried and immersed water, fire protection, gas, and compressed air distribution schemes; metallic sewers and culverts; buried and immersed communication and power cables; deep-well casings for oil, gas, and water extraction; other buried tanks and the bases of tanks in contact with the ground; electrical transmission tower, aerial and wind-farm tower footings, sheet steel piling, tubular and ‘H’-piling associated with port and harbor facilities, and other infrastructure projects; immersed and buried steel tube tunnels; piers, wharfs, and other mooring facilities; cooling water systems including internals and externals of pipelines, intake screens, condenser water boxes pumps, etc.; gates, locks, and screens in irrigation and navigation canals; buried domestic oil distribution lines or buried pipelines for district central heating systems.

- Cathodic protection of internal surfaces is applied, in addition to the cooling water systems listed above, to surface and elevated water storage tanks (both potable and seawater, the latter often for firefighting purposes); condensers and heat exchangers; hot-water storage tanks, processing tanks, and vessels; hot and cold water domestic storage tanks; and process vessels in breweries and dairies (pasteurizers).
- Cathodic protection of floating structures is applied to the external hulls of most commercial and military vessels including vessels that are ‘laid up’ or ‘in mothballs’; to the ballast compartments of tankers; floating oil and gas drilling and production facilities; floating dry-docks; barges (interior and exterior); dredgers; caisson gates; steel mooring pontoons; and navigation aids, for example, buoys.
- Cathodic protection of steel in concrete is applied to buried and immersed steel, reinforced and prestressed concrete pipelines, generally for water distribution; steel reinforced concrete foundations, piles and caissons of buildings, and port and harbor facilities; steel-reinforced concrete offshore oil and gas drilling, production, and storage facilities; steel-reinforced atmospherically exposed highway structures (bridges, elevated road support structures, etc.) and bridge decks; buried and immersed tunnels; buried reinforcement concrete basements and car parks; multistory car parks; and buildings.

In many countries, the safety and environmental advantages of cathodic protection are sufficiently well acknowledged that there is legislation requiring effective cathodic protection of buried or immersed pipelines carrying products such as crude oil, refined product, and gas, and there are Insurance and Classification Society requirements for effective cathodic protection of offshore oils and gas drilling and production facilities and for ships.

4.21.1.2 Type of System

The use of an impressed-current system or galvanic anodes will provide satisfactory cathodic protection, but each has advantages and disadvantages with respect to the other (Table 1).

4.21.1.2.1 Reactions at anodes

Galvanic anodes and impressed-current anodes are discussed elsewhere, but further comment is relevant here in relation to the choice of a particular system for a specific environment. In this connection, it should be noted that the conductivity of the environment and the nature of the anode reactions are of fundamental importance. The main anodic reactions are electrochemical oxidation processes and may be summarized as follows:

For galvanic anodes:

Primary reaction: $M \Rightarrow M^{z+} + ze^-$ (i.e., metal dissolution)

Secondary reaction: $M^{z+} + zH_2O \Rightarrow M(OH)_z +$ zH^+ (i.e., precipitation of metal hydroxide)

where M represents the anode material and z the number of electrons transferred in the reaction (i.e., the electrochemical equivalent). For zinc and magnesium, $z = 2$ and for aluminum, $z = 3$.

For impressed-current anodes:

$3H_2O \Rightarrow 2H_2O^+ + 2e + \frac{1}{2}O_2$ (i.e., oxidation of water/evolution of oxygen) and/or

$2Cl^- \Rightarrow C_2 + 2e^-$ (i.e., evolution of chlorine)

or, in the case of graphite or graphite-filled polymer anodes

$C + O_2 \Rightarrow CO_2$ (i.e., oxidation of carbon to carbon dioxide)

It should be noted that when metals such as zinc and aluminum are used as galvanic anodes, the anode reaction will be predominantly as above although self corrosion may also occur to a greater or lesser extent. The emf between magnesium, the most active (negative) galvanic anode, and iron is ~0.7 V, the emf of power-impressed systems can range from 6 V to typically a maximum of 48 V (limited for personnel safety reasons), depending on the power source employed. Thus, galvanic anodes are normally restricted to environments having a relatively lower resistivity (e.g., $<50\,\Omega\,\mathrm{m}$), whereas there is no similar limitation in the use of impressed-current systems.

In the case of galvanic anodes, the electrons that are required to depress the potential of the structure to be protected are supplied by the primary reaction above and, providing the metal ions can diffuse away from the structure before they react with water to form insoluble hydroxides, the reaction will be unimpeded and will take place at a low overpotential. If, however, the metal hydroxide precipitates on the

Table 1 Comparison of galvanic anode and impressed current cathodic protection systems

Method	*Galvanic (sacrificial) anode cathodic protection*	*Impressed-current cathodic protection*
Characteristics	Protection by current from galvanic/sacrificial consumption of more electronegative metal anodes	Protection by current from DC power supply; typically a transformer rectifier passed through more inert anodes
Anode materials	Magnesium, aluminum, and zinc alloys. Occasionally iron for protection of copper and copper alloys	Mixed metal oxide (Pt, Ir, Ru)-coated titanium; platinum-plated titanium and niobium; cast silicon–iron and silicon with chrome; conductive ceramic (monolithic Ti_4O_7). Historically carbon; lead alloy, and lead alloy with Pt microelectrodes; scrap iron; conductive polymers
Power	Independent of power source	Requires electrical power supply
	Well established Ah kg^{-1} capacity figures for proven alloys	Can be connected incorrectly with polarity reversed and cause accelerated corrosion. (There are polarity reversal protection circuits available)
	Cannot be connected incorrectly with polarity reversed.	
Installation	Simple, but may require significant welding of anode steel cores to structure	Complex; requires significant cable routing between the power source, the anodes, and the cathode
Reliability	High, if properly designed and installed	High, if properly designed, installed, and maintained
	Entire cathodic protection system directly connected to the structure; only the galvanic (sacrificial) anode material is consumed by corrosion	Historically many offshore and port and harbor impressed-current systems have failed due to mechanically inadequate designs. Many marine systems have failed due to poor maintenance or simply being switched off
		The entire anode (+ve) circuit is at risk of forced corrosion if cables or anode/cable connections are improperly designed or are damaged. Positive cable damage and poor anode/cable design are significant risks to impressed current system performance
Design complexity	Simple, but requires competent anode and steel core design for anode current delivery through life and for certain applications may require rigorous structural assessment of welded connections between steel core and structure	Complex. Designs frequently ignore key elements of competent design such as optimum anode–cathode spacing calculations for optimum current distribution. Mechanical integrity of anodes, anode/cable connections, cable management systems, and monitoring systems often inadequate
Typical design life	5–50 years	10–100 years but electrical/electronic systems likely to require 100% replacement at *c.* 25 years
	High cost and weight for long-life systems	
Interaction or stray current	Due to normally low individual anode current outputs and large numbers of anodes, interaction effects to third-party structures are often negligible	Very likely
	High-current anode arrays can cause the same interaction effects as impressed-current systems of same current output	Interaction testing with third parties should be mandatory. Remedial action may be simple and low cost
	Interaction testing necessary in sensitive locations and with high-current designs	
Advantages	Simple. Reliable	Ability to easily increase or decrease current to meet changing demands or errors in design assessment
		Ability to remote-control and monitor via electronic devices
	'Self-control' current output to meet demand within a limited range if properly designed	Ability to measure 'instant OFF' potentials with minimum IR drop errors
		Ability to operate in high electrical resistivity electrolytes and provide high currents from relatively small installations

Continued

Table 1 Continued

Method	*Galvanic (sacrificial) anode cathodic protection*	*Impressed-current cathodic protection*
Limitations	Electrical resistivity of electrolyte Typically $<10\,\Omega\,\text{m}$ in saline water for aluminum anodes Typically $<20\,\Omega\,\text{m}$ in saline water and soils for zinc anodes (although Zn ribbon can be used effectively to say $50\,\Omega\,\text{m}$) Typically $<50\,\Omega\,\text{m}$ in waters and soils for Mg anodes (although ‘high voltage’ and ribbon anodes can extend this Typically, large numbers of anodes of considerable size are required for large current cathodic protection systems	May be uneconomical for small schemes due to high unit cost of electrical power supply and transformer rectifier or control system Can use photovoltaic and/wind generators for relatively small schemes All elements of the anodic (+ve) circuit must be electrically isolated from the structure. Thus risks of failure by short circuits (particularly relevant to reinforced concrete applications where anode/cathode spacings may be as low as 15 mm). Thus, hull penetrations are needed for ship and floating structure applications
	All anodes may not consume at the same rate if local current demands or resistivities vary Monitoring and control of galvanic anodes, although possible, is often limited	
Prime applications	Offshore oil and gas facilities due to high reliability	Offshore oil and gas facilities with weight limitations; very rigorous design process following multimillion £/$ failures
	Port and harbor piled installations; high reliability, low inspection/maintenance requirement and low interaction risk	Port and harbor applications wherein capital cost assessment has outweighed the risks. Some failures
	Lock gates, tidal and flood protection facilities	Large/long pipeline applications. High reliability due to established design practice and relatively benign environment
	Small onshore applications; short pipelines	Large buried tanks and tank bottoms of ‘on grade’ tanks
	Domestic water tanks	Cooling water applications where small anodes are essential
	Ships’ internal tanks	Reinforced concrete applications wherein the high resistivity of the concrete often dictates impressed current
	Offshore wind farm facilities	Ship’s hulls where the small size and low hydrodynamic profile is important
Inspection and maintenance	Limited simple testing to confirm performance and to monitor consumption of anodes. Typically annual. If design-adequate, maintenance limited to replacement of depleted/consumed anodes at end of design life	Significant regular inspection requirements. Typically monthly for function check and three-monthly for performance verification. Maintenance typically required to power supplies, anodes, and monitoring systems
Stray current or drainage bonds (DC)	–	Effectively impressed current systems deriving their current from DC traction or similar stray current DC source. Can be directly bonded, controlled to a limited extent with resistive and rectifier networks or supplemented with an additional DC power source
Stray current dissipation (DC and AC)	Effectively galvanic anode systems which might be used alone or to supplement an impressed-current system and used to provide a safe, low electrical resistance, connection to earth (soil or water typically) to allow DC or AC current to pass from the structure to earth without causing DC or AC corrosion to the structure Increasingly important on pipelines with very high electrical resistance coatings in the vicinity of AC electrical distribution networks	–

surface of the metal as a nonconducting passive film, the anode reaction will be stifled and this situation must be avoided if the anode is to operate satisfactorily. Much development work has been expended in developing galvanic anode alloys which are reliable in known electrolytes and which do not suffer from stifling by anode reaction products.

In the case of nonreactive impressed-current anodes, rapid transport of the reactants (H_2O and Cl^-) to and the reaction products (O_2 and Cl_2) away from the anode surface is essential if the anode reaction is to proceed at low overpotentials. This presents no problems in seawater, and for this reason the surface areas of the anodes are comparatively small and the anode current densities correspondingly high. Thus, in seawater, inert anodes such as mixed metal oxide-coated titanium (MMO/Ti) and platinized titanium can operate at up to 1000 $A\,m^{-2}$, since the anode reaction occurs with little overpotential, and there is rapid transport of Cl^- to and Cl_2 away from the anode surface. In this connection, it should be noted that even in a water of high chlorinity such as seawater, oxygen evolution should occur in preference to oxygen evolution on thermodynamic grounds. This follows from the fact that the equilibrium potential of the oxygen evolution reaction in neutral solutions is 0.84 V, whereas the corresponding value for the chlorine evolution is 1.34 V, that is, 0.5 V higher. However, the chlorine evolution reaction occurs with only a small overpotential, whereas very appreciable overpotentials are required for oxygen evolution, and this latter reaction will occur therefore only at high current densities. Even in waters of low salinity, chlorine evolution will therefore tend to occur in preference to oxygen evolution at low overpotentials.

In the case of MMO/Ti, the consumption rate of the coating will be at its lowest ($\sim$0.2 $\mu g\,(Ah)^{-1}$) when operated in open seawater, will increase in brackish water where a greater proportion of oxygen is evolved (to $\sim$0.45 $\mu g\,(Ah)^{-1}$), and will be maximum in saline mud ($\sim$1–1.5 $\mu g\,(Ah)^{-1}$).

In the protection of pipelines or other underground structures with buried anodes (often in 'groundbeds' or arrays of buried anodes), the anode reaction is dependent on diffusion of water to the anode surface and oxygen and CO_2 away from it. Since these processes do not occur with the same mobility as in water, it is necessary to use a very large surface area of anode and a corresponding low current density. For this reason and to further reduce the electrical resistance of the anode to earth, the actual anode is a carbonaceous backfill of considerably greater dimensions than the anodes laid within the backfill. Silicon–iron or MMO/Ti anodes are used primarily to make electrical contact between the cable and the backfill. It can also be seen from the oxygen evolution reaction above that the products of the oxidation of water are oxygen and hydrated hydrogen ions, which will migrate away from the anode surface under the influence of the field, thus removing two of the three water molecules that participate in the reaction, and this will tend to dehydrate the groundbed. In addition, the electric field between the anode and the cathode will cause electro-osmosis, which will further dehydrate the groundbed. These difficulties can be overcome, when feasible, by locating the groundbed below the water table.

4.21.1.2.2 Galvanic anode systems

Advantages: No external source of power is required; installation is relatively simple; the danger of cathodic protection interaction is minimized; it is more economical for small schemes; the danger of over protection is normally alleviated; uniform current distribution can be easily achieved by using small anode currents from many anodes; maintenance is not required apart from routine potential checks and replacement of anodes at the end of their useful life; it involves no running costs.

Disadvantages: Maximum anode output is delivered when first installed; this decreases with decreasing anode size with time when additional current may be required to overcome coating deterioration; current output in high-resistivity electrolytes might be too low and render anodes ineffective; large numbers of anodes may be required to protect large structures resulting in high anode installation and replacement costs; anodes may require replacement at frequent intervals when current output is high and/or maximum size is limited.

4.21.1.2.3 Impressed-current systems

Advantages: One installation can protect a large area of metal; systems can be designed with a reserve voltage and amperage to cater for increasing current requirement due to coating deterioration; current output can be easily varied to suit requirements; schemes can be designed for a life in excess of 25 years; current requirements can be readily monitored on the transformer-rectifier or other DC source; automatic control of current output or of the structure potential can be achieved.

Disadvantages: Possible interaction/stray current effects on other buried structures; their use is subject to the availability of a suitable AC supply source or other source of DC; regular electrical maintenance checks and inspection are required; running cost for

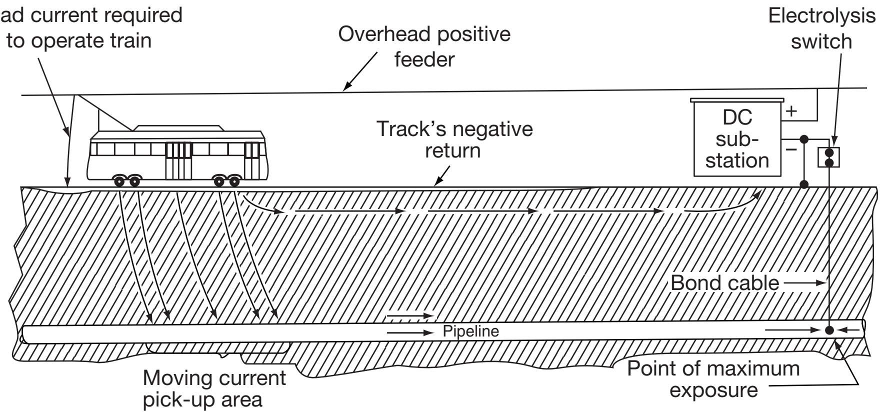


Figure 1 Bond between pipeline and DC substation.

electrical supply is usually not very high except in the case of bare marine structures and in power stations wherein structures are often bare and include bimetallic couples; it is subject to power shutdowns and failures.

4.21.1.2.4 Hybrid systems

Offshore structures are sometimes protected by hybrid systems using both galvanic and impressed-current anodes. These have the advantage that protection of the steel by the galvanic anodes will be effective as soon as the platform enters the sea, which is particularly advantageous since some time may elapse before the power generators required for the impressed-current system are operating.

4.21.1.2.5 Stray-current bonding or forced drainage

Stray-current schemes are once again increasing in occurrence in the United Kingdom, as more localities have widespread DC transport systems arising from new tram- or light rail-based mass transport systems in the major conurbations. Such systems are extensively used in overseas countries where DC transport systems are in widespread use, that is, most of mainland Europe, Australia, and South Africa, with large schemes having been introduced into North America.

Where stray-current bonding can be employed, it is normally the most economical method of applying cathodic protection since the power required is supplied gratis by the transport system.

In such systems, it is necessary to provide a metallic bond between the pipeline and the negative bus of the railway substation. By providing such a bond, the equivalent of a cathodic protection system is established whereby the current discharged from the traction-system rails is picked up by all portions of the pipeline and drained off via the bond. The bond must have sufficient carrying capacity to handle the maximum current drained without damage. In order to ensure that the direction of current flow in the bond does not reverse, it is normal to employ a reverse-current prevention device or 'electrolysis switch.' This may take the form of a relay-actuated contactor which opens automatically when the current reverses. Diodes are now more commonly used as blocking valves to accomplish the same purpose. They are wired into the circuit so as to ensure that the current can flow to the negative bus bar system only. Sufficiently rated diodes must be used in parallel to handle the maximum amount of current anticipated. Also, the inverse voltage rating (peak inverse voltage; PIV) of the diodes must be sufficient to resist the maximum reverse voltage between the negative bus bar and the pipeline (Figure 1).

Obviously the cathodic protection provided to the structure as a result of this system will be partial; it will not be provided when the traction system is not operational (many systems do not operate at night) or when the distribution of the traction units and substations is such that the current in the controlled bond is in the wrong direction and is blocked by the diodes or contactor. Some systems will include, separately or in the same installations, a potential-controlled transformer-rectifier, which will supplement the current from the traction bond and provide more continuous and better controlled cathodic protection.

4.21.2 Design of a Cathodic Protection System

4.21.2.1 Initial Design Process

The design of a cathodic protection scheme should follow the general process outlined below. (see also Table 2). The design of any cathodic protection

Table 2 Summary of the cathodic protection design process

<table>
<tr><th colspan="2">Common to both galvanic and impressed-current systems</th></tr>
<tr><td colspan="2">Determine electrolyte resistivity and corrosivity
Determine other factors that will affect corrosion rate and current density: Soil type, temperature, flow rate (in waters), chloride level in concrete, bacterial activity
Assess materials of construction and their impact on corrosion performance and cathodic protection current density and safe metal/electrolyte potential limits
Determine/agree structure design life with client and determine the optimum design life (and replacement strategy if required) for the cathodic protection system
Determine if cathodic protection is necessary to deliver design life of structure in the assessed environment with appropriate factors of safety
Determine appropriate metal/electrolyte protection potential (criteria) noting that bacterial activity will likely require a more negative metal/electrolyte protection criteria and that many metals and coatings will have a safe negative potential limit beyond which the metals may suffer hydrogen embrittlement (high-strength steels and cupronickel alloys) or corrosion (amphoteric metals such as aluminum) or the coatings may suffer disbondment
Determine coating quality (if any) and estimate initial, mean, and final coating breakdown %
Calculate metal surface area in the electrolyte; subdivide if conditions affecting current demand vary within structure/electrolyte
Determine/estimate initial, mean, and final current density figures taking account of the electrolyte/environment and coating performance as above. Where possible, consider past performance in same/similar electrolytes/environments/locations
Calculate initial, mean, and final current demand
Determine electrical continuity of structure and any requirements to establish necessary continuity
Consider necessity of electrical isolation of structure from other structures/elements in order to restrict cathodic protection current flow to other structures/elements OR estimate this current flow and make allowance for it.
Consider proximity of other structures/services and the impact of the new cathodic protection system on them (DC interference/stray current from the cathodic protection system to third-party structures). Make allowances for minimizing these impacts, testing, and remedial actions
Consider proximity of other structures/services and their impact on the new cathodic protection system (DC and AC interference/stray current to the structure receiving the new cathodic protection system from third-party structures). Make allowances for minimizing these impacts, testing, and remedial actions
Determine optimum cathodic protection solution: galvanic anode or impressed current, on basis of performance, cost, reliability, suitability to established client operational and maintenance capabilities, electrical power supply availability, and other relevant factors
Determine optimum performance monitoring provisions and procedures
Document all of the above</td></tr>
<tr><th>Galvanic anode systems</th><th>Impressed-current systems</th></tr>
<tr><td>Select optimum anode alloy for electrolyte and service (temperature, safety, potability)</td><td>Select optimum anode type for electrolyte and service</td></tr>
<tr><td>Determine realistic anode performance characteristics (capacity (Ah kg^{-1}) and closed-circuit operating potential) from the literature, and independent test data</td><td>Determine realistic anode performance characteristics (capacity (Ah kg^{-1} for silicon–iron and similar or wear rate for MMO/Ti, Pt/Ti and Pt/Nb)) and maximum safe operating voltage) from the literature, and independent test data</td></tr>
<tr><td>Calculate mass of alloy from capacity, mean current demand, design life, and utilization factor (the percentage of the total mass that can be utilized effectively in protection, typically 80–90% subject to steel core design, the remaining 10–20% of material may be too small to deliver end of life current or may be dislodged from the core). The core design is important in delivering high utilization factors</td><td>Determine optimum distribution of anodes and (if appropriate) the use of carbonaceous backfill to reduce resistance and increase anode life. Ensure anode/cable design and cable insulation/sheath materials are suitable for use in acidic, nascent chlorine, and oxygen-evolving environments so that the full capacity of the anode can be delivered</td></tr>
<tr><td>Select/design anode shape to deliver calculated mass and current output at all of initial, mean, and final conditions taking proper account of the reducing size of the anode and the impact of core design on end of life dimensions</td><td>Design anode shape/size (with groundbed backfill as appropriate) to deliver suitable anode/electrolyte resistance using classical electrode/earth resistance formulae. Allow for back emf (the potential between anode/electrolyte/cathode) and cable resistance in determining the required driving voltage from the DC power supply</td></tr>
</table>

Continued

Table 2 Continued

Galvanic anode systems	*Impressed-current systems*
This should be undertaken using the classical electrode/earth resistance formulae to determine anode/electrolyte resistance and the Ohms Law to calculate current output (using the driving voltage as the closed-circuit operating potential of the anode less the protection criteria potential selected earlier). For cable-connected galvanic anodes, include the cable resistance in these calculations	
Determine optimum anode–cathode and anode–anode spacings and then determine whether the calculated anode current outputs should be reduced because of anode/cathode or anode/anode mutual interference (anode and cathode tension hill) and that the attenuation of protection between anodes will deliver adequate protection at mid points	Determine optimum anode/cathode spacing to deliver uniform current distribution, to minimize interaction to third-party structures
	For buried applications, the locations should take account of the availability of electrical power supplies, the location of lower resistivity and wet soil conditions, and the avoidance of mechanical damage or future developments
	Calculate optimum anode–cathode spacing using the anode tension hill formulae. Simplistically: $V = \frac{I\rho}{2\pi r}$ where V is the local voltage shift in the electrolyte due to the voltage cone around the anode r meters from the anode and ρ is the soil resistivity in Ω m
	The spacing might be determined by interaction issues with a nearby third-party structure or by attenuation/distribution along a pipeline. The local voltage cone value will not affect pipe/soil potential remote from the anode, so the voltage cone value may need to be limited to, say, 0.5 V to avoid excessive pipe/soil potential at the nearest point to the groundbed
Confirm that the steel core design of the anode is structurally sufficient for the application	Determine (by classical attenuation formulae on pipelines, sometimes by mathematical modeling for more complex applications) the attenuation between the impressed current installation locations and the remote ends or mid-points between additional installations
–	Determine the optimum control for the impressed current system based on changes in electrolyte (e.g., sea/freshwater in estuaries or dry/wet ground conditions for buried applications, or flow/no flow in cooling water systems), in service (ships trading in different oceans, salinity, and temperature) or in structure/electrolyte immersion (tides): • Manual constant voltage (simple), optimum if all conditions stable • Manual constant current (simple closed loop) optimum if cathode current demand is stable but anode/electrolyte resistance changes • Potential control (more complex, relies on performance of steel/electrolyte potential measurement provisions of test connections and permanent reference electrodes being reliable) optimum if cathode current demand changes and will also accommodate anode/electrolyte resistance changes
–	Determine whether remote monitoring and/or remote control (typically via telephone or GSM modem) will deliver either or both greater security of performance and lower costs of performance verification and maintenance

Common to both galvanic and impressed-current systems
Where necessary these calculations may be iterative until a fully compliant solution is determined
Determine optimum performance verification monitoring and inspection procedures and facilities
Determine optimum inspection and testing requirements during installation and optimum precommissioning and commissioning procedures along with future operation and maintenance procedures
Undertake a design risk assessment to assess, document, and, wherever possible, minimize the risks involved in the implementation of the design
Document all of the above

scheme should be carried out by specialists who are suitably trained, experienced, and accredited as competent in the specific field of application.

Good practice in modern underground or underwater pipeline structures involves the use of good coatings in combination with cathodic protection. With a well coated structure, the cathodic protection system only protects the minute areas of steel exposed to the corrosive environment rather than the whole surface of an uncoated structure. The effect of coatings can be demonstrated by comparing the current density of a bare steel pipeline in average soil conditions, which could be up to $30\,\mathrm{mA\,m^{-2}}$, with that achieved on a well coated and inspected line where a current density of only $0.01\,\mathrm{mA\,m^{-2}}$ or even lower may be required to obtain satisfactory cathodic protection. In all cases, the current density for protection is based on the superficial area of the whole structure.

Caution should be exercised when considering the suitability of coatings for the long-term protection of structures either without or in conjunction with cathodic protection. It is important that the long-term adhesion of the coatings to the surface is secure and that the electrical properties of the coatings over the full life and their impact on matters such as ac corrosion, stray current, and monitoring are properly assessed. It may be that the superficially 'best performing' coating for, say, a pipeline may present long-term disbondment and corrosion risk below the outer sheath and/or high risk of significant AC or DC stray current effects plus difficult-to-interpret/irrelevant cathodic protection monitoring data due to the particular dielectric properties of the coatings.

Many offshore structures and piled port and harbor structures are of bare steel based on the economics that the application of a high-quality coating can actually cost more than the application of a simple cathodic protection system to these bare structures.

Cathodic protection to steel in concrete is almost always to bare steel in concrete; the performance of coated reinforcement in concrete has not delivered its early promise in preventing corrosion in chloride-contaminated concrete, and the application of cathodic protection to coated reinforcement is complicated by electrical continuity issues and may be less than optimally effective due to long-term disbondment of coatings.

4.21.2.2 Surface Area

In the case of underground pipelines, calculation of the superficial surface area can be obtained from the diameter and length of the line involved. The superficial surface area should include any off-takes and other metal structures in electrical contact with the main line.

For marine structures, the area should include all submerged steel work below the high-tide level for impressed-current systems, but for galvanic systems, surface areas at both the high-tide and mid-tide levels may be required for parallel calculations of peak current demand for anode shape calculations and mean current demand for anode weight calculations. The surface areas may need to be split into different levels, as the current density requirements will vary with flow rate, oxygen content, and temperature, all of which vary with depth. Particular attention may need to be given in the cathodic protection design to areas of geometric complexity such as riser frames and pile guides; these may need local anode provisions to ensure that there is sufficient current distribution into these complex areas.

In the case of plants such as power stations, details of the water boxes, number of passes on coolers, and detailed assessment drawings are required in order to determine the local current density requirements in what may be bimetallic couples and high flow rate locations of the systems. Some parts of the structures may be bare and others coated.

In the case of ships, details of the full underwater submerged area at full load are needed along with details of sea chests, thrusters, and other features of the vessel design that will affect the cathodic protection design, including whether the vessel is intended for ice service (which will affect both the anode design and the coating breakdown allowances).

For steel-reinforced concrete, the steel surface area and its local disposition (steel density) require to be calculated on a very local basis (typically in local areas of $\sim 1\,\mathrm{m^2}$) because most anode systems will be installed in the concrete only some 15–100 mm away from the reinforcement and current distribution will therefore be limited. It is therefore essential, for uniform protection levels and uniform anode consumption rates, that the local anode provision properly reflects the local steel current demand; thus the steel surface areas need to be calculated and presented in considerable detail.

4.21.2.3 Electrical Continuity

It is essential for any structure to be fully electrically continuous. In the case of pipelines, welded joints are obviously no problem, but mechanical joints require bonding. For marine structures, individual piles and fendering must be electrically connected by welding either via the reinforcing bars in the concrete deck slab or separately. In power stations and ships, rotating shafts must be bonded into the structure by means of brush gear or a suitable alternative. In the case of offshore mooring installations, it may be considered to install a bonding cable to bring dolphins, etc. into an impressed current system but it is more normal to protect isolated elements, such as dolphins without walkways, with their own galvanic anode systems even if the main cathodic protection system is impressed current.

For steel-reinforced concrete structures, normal steel-fixing good practice is generally adequate to present a steel matrix that is sufficiently electrically continuous to allow all individual bars to receive full cathodic protection. In cathodic protection to new reinforced concrete structures, electrical continuity testing will be undertaken during steel fixing, and limited provisions of welded continuity bars may be required to ensure that all bars are electrically continuous (it is normally taken that 1 Ω bar-to-bar resistance can be accepted as adequate within a matrix). In cathodic protection of existing reinforced concrete structures wherein corrosion has initiated, it is normal to test all bars exposed in concrete repair areas (at which the steel ties are likely to have corroded and corrosion products may have forced bars apart) and to undertake representative additional testing, following an assessment of the structure and its drawings, to prove the quality of general continuity within the reinforcement matrix. It is sometimes necessary to cut longitudinal and circumferential chases in the concrete to expose all bars and continuity-bond them.

4.21.2.4 Estimate of Current Required

The surface area of the structure is calculated, and the current density required for the particular environment is selected (Table 3). In the case of an existing structure, the condition of the coating may be unknown and the application of a temporary cathodic protection system may be necessary to determine the amount of current required for protection, as established by the potential. Such a test to determine the absolute amount of current required is known as a current drain test. Misleading information may, however, be obtained if the results from current drainage tests on bare or coated steel in seawater are extrapolated, because long-term polarization effects, together with the formation of a calcareous deposit on the structure, may considerably reduce eventual current requirements. On the other hand, in estuaries and polluted waters, special care must be taken to allow for seasonal and other variable factors that may require higher current densities.

4.21.2.5 Establishing Electrolyte Resistivity

To enable a satisfactory cathodic protection scheme to be designed, it is necessary to determine the resistivity of the electrolyte (soil, water, or concrete). This information is necessary to enable the current output of anodes to be determined together with their position and power source voltage, and it also provides an indication of the aggressiveness of the environment; in general the lower the resistivity, the more aggressive the environment.

4.21.2.6 Economics

After evaluating these variables, it must then be decided which type of system, that is, galvanic anode or impressed current, would be the most economical under the prevailing conditions. For instance, it would obviously be very expensive to install an impressed-current system on only 100 m of fire main. Similarly, it would be equally uneconomical to install a galvanic anode system on hundreds of miles of high-pressure, poorly coated gas main. Further, there is little benefit in providing a complex impressed-current system to an environment/location/client without resources to adequately monitor, adjust, and maintain the system. Therefore, each structure should be individually assessed taking note of all the factors involved in order to determine the optimum cathodic protection system (see Table 3).

4.21.3 Impressed-Current Systems

Cathodic protection schemes utilizing the impressed-current method fall into two basic groups, dictated by the anode material:

Group 1: These anode materials have relatively high consumption rates, and their dimensions generally change during consumption. They comprise silicon–iron (and historically graphite and scrap steel) anodes used for buried structures and landward faces of sheet steel piled jetties, wharves, etc.; conductive coatings containing graphite used in cathodic protection of steel in concrete; conductive polymers containing graphite used

Table 3 Typical current density figures for cathodic protection

Environment	*Estimated current density for cathodic protection based on superficial surface area* $\mathrm{mA\,m^{-2}}$
Bare steel	
Sterile, neutral soils	4–16
Well aerated neutral soil	20–35
Dry well aerated soil	5–16
Wet soil, moderate/severely corrosive	25–65
Highly acidic soil	50–165
Soil supporting active sulfate-reducing bacteria	400–500
Fresh water, no flow	50–60
Fresh water flow	50–70
Turbulent fresh water containing dissolved oxygen	50–170
Fresh water at 70 °C	50–170
Polluted estuarine water	500–1600
Seawater	
Tropical >20 °C	Initial: 120–180; mean: 40–90; final: 80–130
Subtropical 12–20 °C	Initial: 140–200; mean: 50–100; final: 90–150
Temperate 7–11 °C	Initial: 170–220; mean: 60–110; final: 110–170
Arctic <7 °C	Initial: 200–250; mean: 80–120; final: 130–170
Chemicals, acids or alkaline solutions in process tanks	30–300
Heat exchanger water boxes with nonferrous tube plates and tubes and no coatings	500–1500
Steel in concrete	
Note: These current densities are to protect steel in non-water-saturated concrete to the appropriate protection criteria for steel in concrete. For buried steel connected to steel in concrete (such as at valve pits or pump stations where isolation has not been provided), the allowance for current drained to the steel in concrete in order to protect steel in soil to its appropriate protection criteria should be increased by a factor of 3–5. The figure 'prior to corrosion initiation' is adequate for fully immersed concrete	
These figures are ALL with reference to steel surface area; some US designs are incongruously based on concrete surface area and presumably assume a uniform steel density per unit area of concrete; such an assumption is incorrect	
Following corrosion initiation temperate	Initial: 10–20; mean/final: 2–15
Prior to corrosion initiation	0.2–2
Coated steel pipelines <30 °C assuming 30-year life	
Coated with glass-reinforced coal tar or asphalt bitumen enamels, asphalt mastic, or butyl rubber tape assuming no massive failures	Initial: 0.040; mean 0.100; final 0.200
Fusion-bonded epoxy, liquid epoxy, coal tar epoxy assuming no massive failures	Initial: 0.010; mean 0.020; final 0.050
Three-layer polyethylene or polypropylene assuming no massive failure. Caution: failure can result in disbondment and shielding. Electrical characteristics can be so 'good' that the pipelines become vulnerable to AC and DC interaction and very difficult to monitor real pipe/soil potentials	Initial: 0.002; mean 0.005; final 0.010

Note: All of the above are general guidance figures only. Wherever possible, a design should be based on past performance or accurately determined current density figures for the metal in the electrolyte, at the temperature/flow/ambient conditions applicable to the structure, and should take into account long-term cathodic polarization and coating breakdown. These figures do not include any affects due to galvanic couples or stray currents.

historically in cathodic protection of steel in concrete, with many failures; and a similar conductive polymer wire anode used in buried applications.

Group 2: These anode materials have relatively low consumption (or wear) rates, and their dimensions generally do not change during consumption. They comprise MMO/Ti, platinized titanium, platinized niobium, and conductive ceramic (and historically lead alloy and lead alloy with platinum micro electrodes) anodes used for submerged structures, ships, and power stations. Backfilled in carbonaceous backfill, MMO/Ti are also used for buried applications. MMO/Ti and conductive ceramic are widely used in cathodic protection of steel in concrete.

4.21.3.1 Group 1 Anodes

4.21.3.1.1 Scrap steel

In some instances, a disused pipeline or other metal structure in close proximity to the project requiring cathodic protection may be used as the anode system. Reputedly, the first impressed-current jetty system in the United Kingdom used a keel of a scrap submarine as the anode. However, it is essential in cases of scrap steel or iron groundbeds to ensure that the steelwork is completely electrically continuous, and multiple cable connections to various parts of the groundbed must be used to ensure a sufficient life. Preferential corrosion can take place in the vicinity of cable connections, resulting in early electrical disconnection; hence the necessity for multiple connections. Scrap steel and iron are almost never used as anodes now.

4.21.3.1.2 Graphite

Graphite anodes are usually resin-impregnated and supplied in standard lengths, for example, 65-mm dia. 1.2-m long; and 75-mm dia. 1.5-m long, with a length of cable (called the anode tail) fixed in one end. Graphite anodes were particularly common in early cathodic protection systems. However, they have been almost completely replaced by silicon–iron, the main reasons being (1) graphite tends to spall in use, particularly in chloride environments; and (2) it has a relatively low operating current density (10–20 A m^{-2}, Table 4). Thus, graphite anodes are very seldom used now, having been replaced with more efficient and reliable silicon–iron and MMO/Ti anodes.

4.21.3.1.3 Silicon–iron

Silicon–iron anodes are generally supplied in standard sizes, for example, for solid castings 50 or 75 mm in dia. and 1.2 or 1.5 m in length and are complete with a cable tail. These anodes are made from cast iron with a high silicon content of 14–15%, together with small percentages of alloying elements such as chromium.

Anodes are available with enlarged heads within which the cable tails are terminated and encapsulated with resin and heat-shrink protective caps. They are available as 'single ended' or 'double ended' with, respectively, one cable connection at one end or one at each end. The 'double ended' anodes can be supplied in multiple anode strings with a single cable per string.

Centrifugally chill-cast tubular anodes are also available in diameters of 55–170 mm in lengths of 1.5 and 2.1 m with central connection of the cable. There are data that indicate the chill-cast anodes are more consistent in their performance, presumably due to their finer and more consistent grain structure and that the central connection of the cables results in a higher utilization factor for the anode mass, as the end effects do not result in early consumption of the cable connection end(s).

Silicon–iron with 4.5% chrome has become the most common silicon–iron alloy used for impressed current anodes, but it should be used only when the chloride content of the electrolyte is significant. In soils with low chloride content, the tenacious oxide film, which forms on the chrome alloy and provides its low consumption rate in seawater and other chloride environments, can become highly resistive and lead to anode/groundbed apparent failure.

The main disadvantages of silicon–iron anodes are their weight and extreme brittleness, resulting in high transport costs and possible breakages from the foundry to the cathodic protection site, especially if this is overseas. This anode continues to be widely used, as its performance is very well established and is resilient to variation in operating conditions.

4.21.3.2 Group 2 Anodes

This group includes mixed metal-oxide coated titanium, platinized titanium, platinized niobium and tantalum, and conductive ceramic (and historically lead alloy and lead alloy with platinum micro electrodes) anodes used for submerged structures, ships, and power stations. Backfilled in carbonaceous backfill MMO/Ti are also used for buried applications. MMO/Ti and conductive ceramic are widely used in cathodic protection of steel in concrete.

4.21.3.2.1 Platinized titanium

These anodes are usually in the form of a titanium rod, tube, or wire with an electroplated coating of platinum 2.5–5.0 μm thick. Diameters are generally in the range 3–25 mm. In order to reduce the voltage drop in very long anodes, a copper-cored variety is available. Platinized titanium anodes may also be used in mesh or plain sheet form and can be fabricated to suit particular applications. Co-extruded platinum on titanium (and niobium), with or without a copper core is also available.

4.21.3.2.2 Platinized niobium and tantalum

Niobium and tantalum can be used as substrate materials where environmental conditions dictate a higher driving voltage, for example, brackish water. Use is limited due to relatively high cost. Copper-cored materials are again available.

Table 4 Operating characteristics of impressed-current anodes

Anode material	*Maximum working current density (A m^{-2})*		*Nominal consumption (kg (Ay)$^{-1}$) except as stated in mg (Ay)$^{-1}$*	
	Soil	*Seawater*	*Soil*	*Seawater*
Scrap steel	5–6	5–6	8	10
Scrap cast iron	5–6	5–6	6	8
Silicon–iron	10–30	10–30	0.5	0.5–1.0
Silicon–iron in carbonaceous backfill	10–100	N/A	0.1	N/A
Silicon–iron 4.5% Cr	10–30	10–100	<0.1	<0.5
Silicon–iron 4.5% Cr in carbonaceous backfill	10–100 Do not use in soils with no chlorides; will become highly resistive	10–100	<0.1	N/A
Graphite	10	10–20	0.25–2.5	0.5–5
Lead–silver alloy	N/A	100–200	N/A	0.025–0.10
Lead–silver alloy/Pt microelectrodes	N/A	200–1000	N/A	0.002–0.10
Pt/Ti	50–100	500–3000	Negligible in carbonaceous backfill	1.2–10 mg (Ay)$^{-1}$
Pt/Nb	N/A	500–3000	N/A	1.2–10 mg (Ay)$^{-1}$
MMO/Ti	50–100	500–1000	6–7 mg (Ay)$^{-1}$ in soils 8–13 mg (Ay)$^{-1}$ in saline mud	1–2 mg (Ay)$^{-1}$ in seawater 2–4 mg (Ay)$^{-1}$ in brackish water
MMO/Ti in carbonaceous backfill	Negligible	500–1000	Negligible	N/A
Anode material	***Maximum working current density in concrete***		***Typical life in concrete***	
MMO/Ti mesh, strip, and ribbon surface-mounted and concrete-encased or cast into concrete	Short-term 220 mA m^{-2}		Subject to coating loading up to 100 years with a factor of safety (for nonuniform current density delivery) of 2.	
	Long-term 110 mA m^{-2}		Typical consumption for IrO$_2$/Ta$_2$O$_5$ coating 3.5–9 mg (Ay)$^{-1}$	
	Limited by acidification of concrete not anode parameters			
MMO/Ti tubular discrete anode drilled and mortared into concrete	800 mA m^{-2}		Subject to coating loading up to 100 years with a factor of safety (for nonuniform current density delivery) of 2. Typical consumption for IrO$_2$/Ta$_2$O$_5$ coating 3.5–9 mg (Ay)$^{-1}$	
Conductive ceramic of monolithic Ti$_4$O$_7$ tubular discrete anode drilled and mortared into concrete	800 mA m^{-2}		Up to 100 years	
Conductive organic coating with carbon filler to concrete surface	20 mA m^{-2}		<15 years	
Arc- or flame-sprayed Zn to concrete surface	20 mA m^{-2}		<25 years	
MMO/Ti rod anodes in carbonaceous backfill drilled into concrete	800 mA m^{-2} to carbonaceous backfill		<50 years subject to performance of carbonaceous backfill	
Ni-plated carbon fibers incorporated into a cementitious overlay	20 mA m^{-2}		<25 years	

Note: The above data are indicative only and based on a variety of sometimes conflicting data from numerous sources. Actual performance may vary due to particular electrolyte conditions.

4.21.3.2.3 *Lead silver alloy with or without platinum microelectrodes*

The alloy is lead, together with 1–2% silver in rod or extruded section form with platinum microelectrodes inserted every 150 mm. The purpose of these microelectrodes, which take the form of pins, is to stabilize the formation of lead peroxide on the anode surface. These anodes have seen extended service as ship hull anodes and were favored by some designers for seawater cooling systems in power stations. They have been largely replaced with MMO/Ti anodes.

4.21.3.2.4 *Mixed metal oxide-coated titanium (MMO/Ti)*

This anode material has become very widely used in seawater, in soils (generally backfilled in carbonaceous backfill), in saline muds (directly buried), and in concrete. The MMO compositions are held by some manufacturers to be proprietary as are the coating loading onto the titanium substrate. Some manufacturers declare their coatings to be IrO_2/Ta_2O_5 mixtures and declare coating loadings and consumption rates. Others do not declare these critical parameters and the designer must rely on accelerated testing of samples from production batches to be secure in the design life.

Anodes for immersed and buried applications are available in tubular, rod, wire, and sheet forms, with tubular anodes having center-connected cables being widely used in strings as single anodes. Perforated and expanded Ti mesh and ribbon coated after perforation and expansion is widely used in carbonaceous backfill for the anode systems placed beneath tank bottoms during construction and in horizontal groundbeds. In deep-well groundbeds, tubular anodes are widely used in carbonaceous backfill.

MMO/Ti mesh, ribbon, strip, and tubular discrete anodes are widely used in cathodic protection of steel in concrete. The mesh and ribbon anodes are used surface-mounted within sprayed concrete overlays, or the ribbon and strip anodes have been used installed into cut slots in the concrete surface. Tubular anodes used as discrete point sources of current delivery are grouted into drilled holes in the concrete. Ribbon, in particular, is widely used in the application of cathodic protection to new construction reinforced concrete structures, in extreme environments or where its service is particularly critical, and the design life is beyond that which can be securely delivered by durable concrete design.

4.21.3.3 Other Anodes for Reinforced Concrete Applications

Much cathodic protection of reinforced concrete is undertaken on existing structures, which have suffered corrosion due to chloride contamination, as part of concrete repair and strengthening works. Many of these systems require anodes to be installed on atmospherically exposed (above ground) concrete surfaces with the minimum of impact to the structure. Thus a whole range of anode systems has been developed for these applications since the mid-1970s in the United States and the late 1980s in Europe and elsewhere.

Some of these anode systems have been used briefly and either failed or not delivered their promised economic advantages to their developers. The former category includes a conductive polymer wire that proved to have failed approximately one-fifth of that claimed by its manufacturer and many conductive coatings and mastics that did not perform as claimed. In the latter category is an early bridge deck cathodic protection system from Ontario in Canada, which utilized cast silicon–iron ‘pancake anodes’ in a conductive overlay of coke breeze and mastic. Many of these systems performed very well, but they were not proprietary; they were heavy, and the physical properties of the coke-filled mastic were not ideal; they have fallen out of use.

Systems still in use include a limited number of good, well proven conductive coatings; a small range of products using proprietary nickel-coated carbon fibers in a carbonaceous mortar that can be low pressure-sprayed onto concrete as thick coating or a thin overlay; a proprietary MMO wire discrete anode in a carbon backfill; and conductive ceramic tubes of monolithic Ti_4O_7 (registered name Ebonex).

Flame- and arc-sprayed zinc has been quite widely and successfully used in North America as an impressed-current anode in the colder northern regions and as a galvanic anode in the warmer regions such as Florida. A thermally sprayed Al–Zn–In alloy is a proprietary product with claimed advantages over zinc.

Galvanic anodes of cast zinc are available in a small range of proprietary forms precast into a high-pH lithium-dosed mortar, which is claimed to enhance the corrosion activity of the zinc. These systems were originally designed to be fitted into concrete repair areas to provide partial cathodic protection and principally to overcome the incipient corrosion cell between steel in new chloride-free repair mortar and the surrounding chloride-rich original concrete; they fulfilled this function quite well. These systems, and developments from them, are now being promoted for cathodic protection of entire structures; it is uncertain whether they can deliver sufficient current to achieve the established protection criteria for steel in concrete, and it is almost impossible to monitor them effectively due to their direct connection to the reinforcement.

4.21.4 Cathodic Protection of Buried Structures

4.21.4.1 Soil or Water Resistivity

Soil resistivity measurements are carried out by the Wenner technique using commercially available instruments. Resistivity data are not only required to determine the anode resistance and size but also to indicate the probable corrosivity of the soil or water. In the case of a pipeline route, variations in soil resistivity may stimulate localized corrosion and can cause long line currents; the area in the soil of lower resistivity is usually anodic (more negative) compared to that in the soil of higher resistivity. It is therefore impossible to give any precise ruling as to the rate at which corrosion will occur under any particular soil conditions, and the results of any survey must be taken as giving only a general indication of the probability of corrosion. More rigorous corrosion assessment surveys determine the soil types, the dissolved salts, and the presence of bacteria and critical species such as free sulfur or carbonaceous material, and produce a corrosivity index.

Chemical and other forms of industrial contamination of the soil can significantly influence soil resistivities and corrosion characteristics and it is essential to investigate these in detail where such contamination may have occurred (e.g., in the proximity of chemical plants, etc.).

A typical soil resistivity survey is shown in Figure 2. Soil resistivities will normally indicate whether a cathodic protection system is advisable in

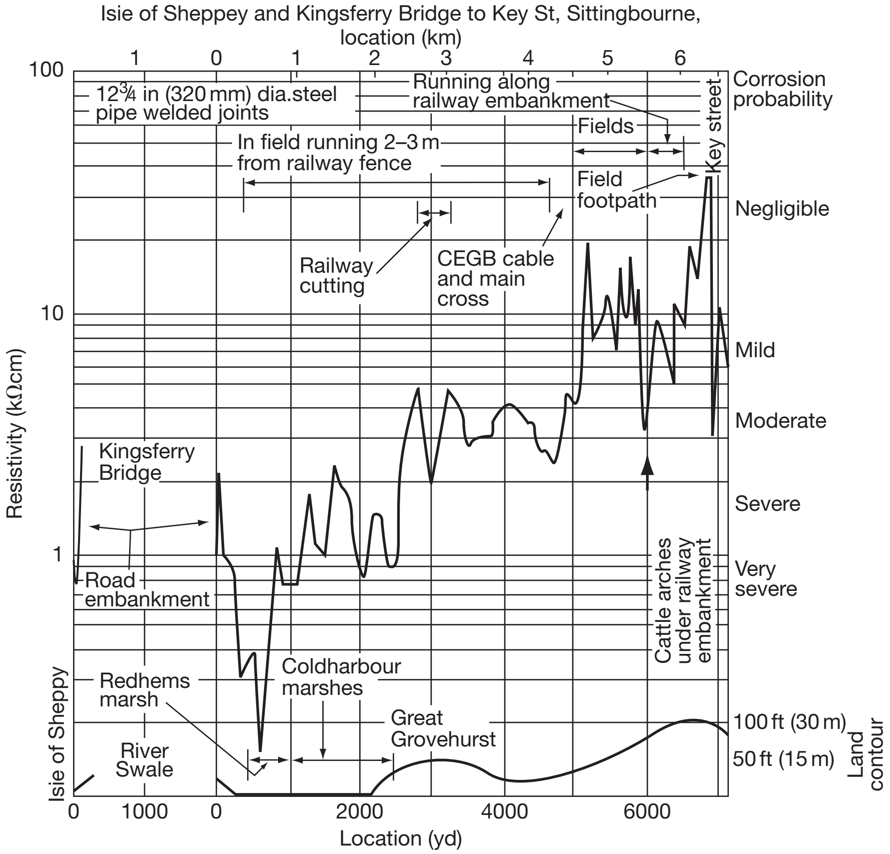


Figure 2 Typical soil resistivity survey.

principle and whether impressed-current or galvanic anode schemes in particular are preferable. It may, as a result of the survey, be considered desirable to apply protection to the whole line or to limit protection to certain areas of low soil resistivity or 'hot spots.'

The cost of cathodic protection to uncoated buried pipeline structures is relatively high and expense may prohibit complete protection, in which case the galvanic anodes may be installed in the lowest resistivity areas only – on the basis that these are likely to be the most corrosive. This was a situation regularly encountered by cathodic engineers in the 1950s and early 1960s in the United Kingdom and the United States when extending the life of old oil and water pipelines in particular. In the case of high-pressure gas and oil lines, it is normal practice (it is mandatory in many countries) to apply cathodic protection irrespective of the soil resistivity in view of the low cost when associated with modern pipeline coatings and the potential hazards that could occur should even a minute pinhole perforate the pipe. In such cases, a soil resistivity survey is required only in the probable areas of groundbeds in order to enable the size of the groundbed, rectifier voltage, etc. to be determined. The soil resistivity also determines the current output of magnesium or zinc anodes should this type of system be preferred.

The soil resistivity, measured using the Wenner technique, determines the average soil resistivity in a hemisphere to a depth equivalent to the distance between the pin spacings, and it must therefore be recognized that the design figure for groundbed design in a particular location may not be highly precise. At least 10% error in the calculated resistance may be expected.

Soil resistivity surveys are often impractical in built-up areas, but in such areas impressed-current cathodic protection is often avoided on account of the danger of interaction. Under such conditions, adequate protection can be achieved by installing magnesium anodes in the pipe trench should the soil resistivity measurements made when the trench is opened indicate that this is necessary.

4.21.4.2 Impressed-Current Design

Designs can be prepared once soil resistivities and groundbed locations have been determined. Figure 3 illustrates typical installations. Design steps have been summarized in Table 3 and are summarized below for a simple pipeline.

1. Select the current density to be applied from the results of cathodic protection tests and from any available data. On pipeline structures, attenuation is always a factor and the average current density is determined from the attenuation curves, or the total current to give protection at the points most distant from the drainage point may be computed.
2. Compute the total current requirement to achieve the required current density (total current = current density × superficial surface area). Undertake this for initial, mean, and final estimated coating conditions.
3. Determine the optimum spacing between groundbeds based on availability of electrical power supplies and the classical attenuation formulae.
4. Based on the most negative permitted pipe/soil potential near the installation and the necessary potential change for the attenuation formula, determine the maximum permitted impact of the anode tension hill and thus calculate the distance between groundbed and pipeline.
5. Design the groundbed system in accordance with classical electrode-to-remote-earth resistance formulae for the selected anode groundbed type (continuous horizontal, deep well, multiple shallow boreholes).
6. Design the DC wiring system for the most economical cable size in accordance with standard electrical practices and then calculate the total IR (ohmic) drop in the circuit.
7. Select transformer rectifier voltage and current outputs.
8. Design the electrical circuits, fittings, and switchgear in accordance with standard electrical practice.
9. Select the location of cathodic protection test stations.
10. Prepare project drawings and specifications.

The total circuit resistance of a groundbed installation includes cable resistance, resistance of the anode to the carbonaceous backfill, and resistance to earth of the backfill column itself. In the case of seawater installations, the anode resistance is between the seawater and the anode surface only. The back emf between the anode and cathode should be included in the calculations to determine the transformer rectifier output voltage. It is normal for personnel and animal safety to limit the output voltage of transformer rectifiers to 48 V (lower if possible), and it is good practice in areas of third-party pipelines and structures to limit the individual installations to a low output current in the range 5–25A.

4.21.4.3 Anode Backfill

The carbonaceous backfill surrounding an anode is essential and serves a number of functions, as given below for example:

1. Being of low resistivity, it has the effect of increasing the anode size with resulting reduction in resistance to earth.
2. Most of the current is transmitted to the backfill from the anode by direct contact, so that the greater part of material consumption is on the outer edges of the backfill column, enabling the anodes themselves to have an increased life.

The backfill composition may be of several types, varying from coke breeze to manmade graphite particles. A coke-breeze backfill consists of high temperature-fired coke breeze or calcined petroleum coke with not less than 95% dry weight of carbon with a maximum resistivity of 50 Ω cm when lightly tamped, dry, and prior to the addition of lime. A typical specification requires that 100% will pass through a 16-mm aperture, 90% will pass through an 8-mm aperture, and not more than 15% will pass through a 1-mm aperture, and that the coke breeze should be thoroughly mixed with 5% by weight of slaked lime.

4.21.4.4 Resistance of Groundbeds

The resistance of groundbeds for protection of pipelines or anodes for protection of jetties or other seawater structures is usually calculated in accordance with the formulae originally developed by Dwight. However, the following abridged formulae are normally used and are sufficient for all practical purposes.

Resistance of a single horizontal rod anode:

$$R_{\mathrm{H}} = \frac{\rho}{2\pi L}\left\{\ln\frac{4L}{d} - 1\right\}$$

Resistance of a single vertical rod anode:

$$R_{\mathrm{v}} = \frac{\rho}{2\pi L}\left\{\ln\frac{8L}{d} - 1\right\}$$

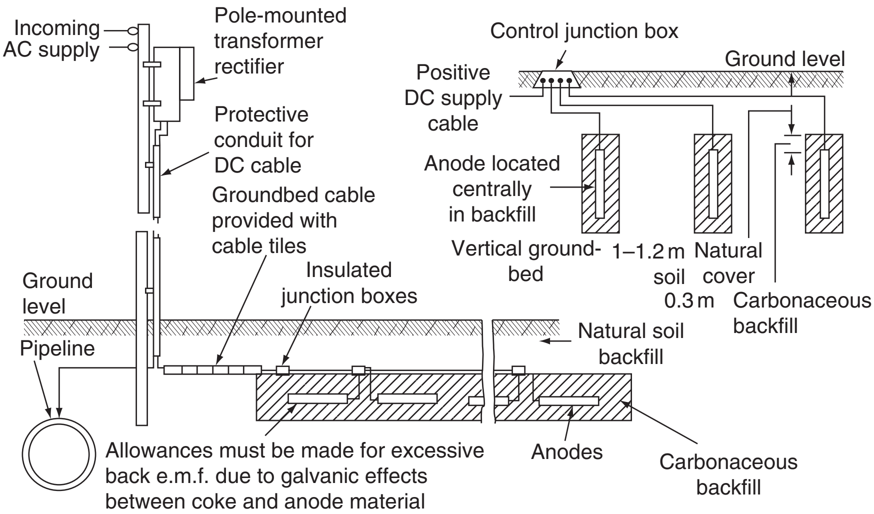
where R_{H} is the resistance of a single horizontal anode (Ω), R_{V} is the resistance of a single vertical anode (Ω), ρ is the resistivity (Ω cm) of soil or backfill, L is the length of the rod (cm), and d is the diameter of the rod (cm).

Where anodes are installed in special backfill, two series resistances are present – anode to backfill and backfill to soil. In practice, and with coke breeze backfill, a single calculation based upon the dimensions of the backfill column and soil resistivity is satisfactory.

Resistances of several anodes in parallel can be calculated by the formula

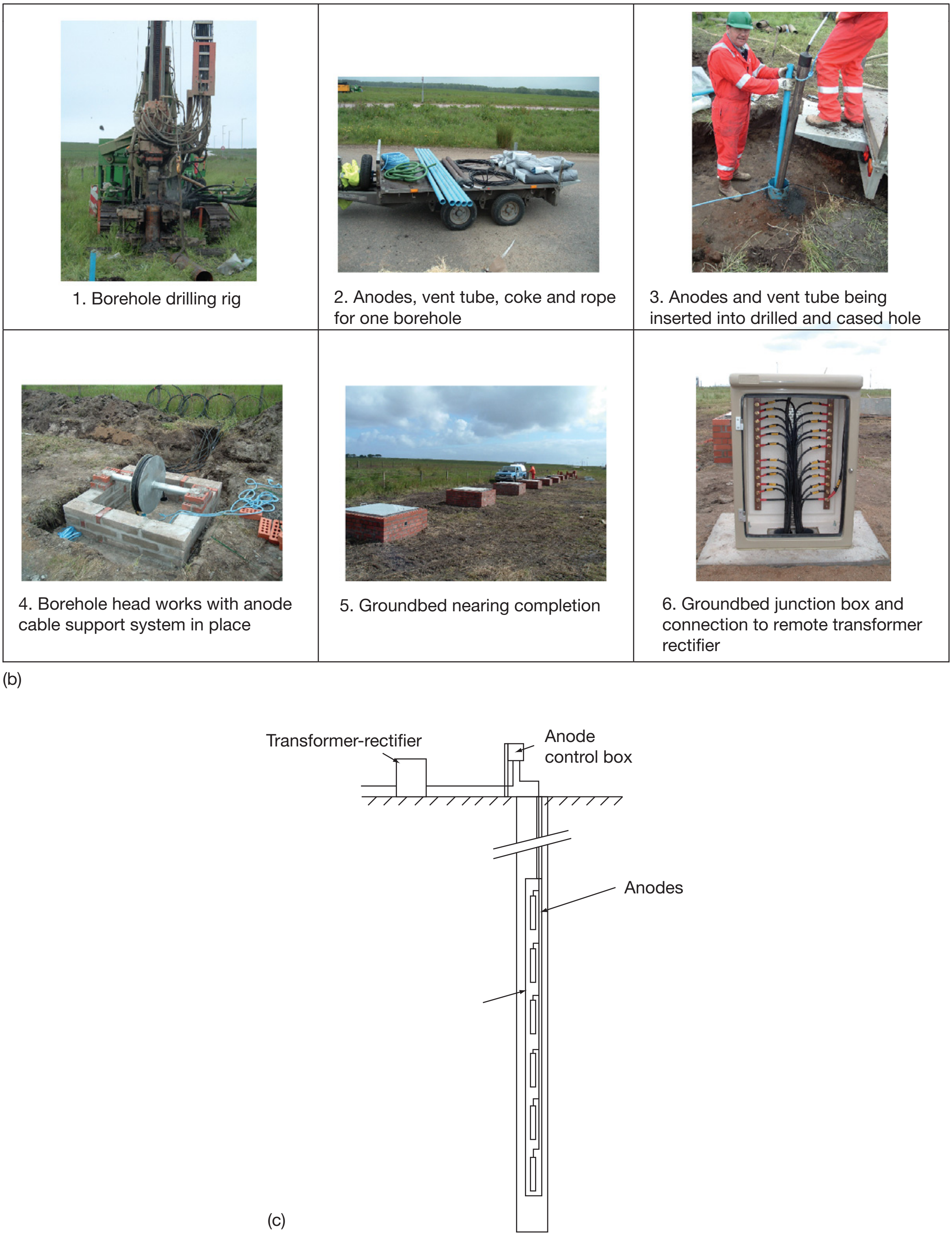
$$R = \frac{\rho}{2\pi NL}\left\{\ln\frac{8L}{d} - 1 + \frac{2L}{S}\ln 0.656N\right\}$$

where R is the resistance to earth (Ω) of the vertical anodes in parallel, r is the soil resistivity (Ω cm), N is the number of anodes in parallel, L is length of the anode (cm), d is the diameter of the anode (cm), and S is the anode spacing (cm).



(a) Horizontal ground bed

Figure 3



1. Borehole drilling rig

2. Anodes, vent tube, coke and rope for one borehole

3. Anodes and vent tube being inserted into drilled and cased hole

4. Borehole head works with anode cable support system in place

5. Groundbed nearing completion

6. Groundbed junction box and connection to remote transformer rectifier

Figure 3 Continued. Deep-well installation. (a) Groundbeds for buried pipes using impressed current. (b) Groundbed installation using multiple shallow boreholes (above a rock substrata) utilizing silicon–iron anodes with Kynar-insulated polyethylene-sheathed cable (note the large-diameter cable support system) and calcined petroleum coke. The boreholes were sacrificial steel lined except for the top 5 m, which was plastic pipe lined. Courtesy of R & R Corrosion Ltd and Corrosion Control Affiliates Ltd. (c) Deep-well installation.

4.21.4.4.1 Deep-well groundbeds

This type of groundbed is illustrated in Figure 3 and is normally employed where the surface soil resistivities are very high, for example, in desert areas. They have the advantage of taking up little surface area and can be installed, in the case of a pipeline project, in the existing pipeline wayleave. They have the further advantage of minimizing interaction on foreign structures. Abandoned oil or water wells can sometimes be used for this purpose. The type of groundbed can be of the design illustrated, or alternatively can be assembled on the surface in a steel case and lowered down a suitably drilled hole.

4.21.4.4.2 Determining rectifier voltage

In determining the rectifier voltage, the following must be taken into consideration:

1. The groundbed resistance, as previously explained; this will generally be the major resistance in the calculation.
2. Back voltage polarization between groundbed and pipeline. In the case of graphite, MMO/Ti and silicon–iron anodes in carbonaceous backfill, an allowance of 2 V is normally used. This back voltage is that which exists between the anodes and the structure in opposition to the applied voltage.
3. Resistance to earth of the pipeline at the groundbed location. This resistance to earth depends on the quality of the pipeline coating. The better the coating, the higher the resistance; generally the pipeline resistance will be a lower order than the groundbed resistance.
4. Resistance of the cable from the pipeline to the power source and from the power source to and along the anodes comprising the groundbed. This cable resistance must be determined from the standard tables supplied by the cable manufacturer.

Once the total circuit resistance and the required current output are known, applying Ohm's law will allow the transformer rectifier or power source voltage to be calculated.

4.21.4.5 Attenuation

When cathodic protection is applied to an underground metal structure, the greatest effect on the pipe-to-soil potential is at the drainage point. This effect decreases, or attenuates, as the distance from the drainage point increases.

Complex structures such as tank farms, tank bottoms, and marine installations have complicated attenuation patterns and it is not feasible to use complex equations to determine the effect. This must be determined by a current drain test, by practical experience, or by mathematical modeling. For pipelines, the attenuation depends on the linear resistance of the pipe, coating resistance, and to some extent the resistivity of the soil. Connections to foreign structures and the method of termination of the line also affect the attenuation. There are relatively simple classical attenuation formulae for pipelines.

4.21.4.5.1 Field measurements

In order to obtain the actual field attenuation characteristics, a pipeline can be placed under temporary cathodic protection and measurements made under different cathodic protection current conditions. A 'natural' pipe-to-soil potential survey should be made over the length of the line to which cathodic protection is to be applied. These static measurements supply a reference level on which to base the subsequent readings. After the natural survey is completed, measurements are made at the same test points with the temporary cathodic protection system installed. The pipe-to-soil potential should be read twice, once with the test current ON and once with the current Instant OFF (potential measured ideally between 0.2 and 1s after switch OFF). The data are then plotted as shown in Figure 4.

The horizontal scale is the distance along the pipeline from the drainage point 0, and the vertical scale is the pipe-to-soil potential. The polarization potential and the driving voltage may then be plotted on semilogarithmic paper using the same horizontal scale (Figure 5). Attenuation is more rapid in low-resistivity soils or with less good coatings than in high-resistivity soils or with good coatings. If nonuniform conditions prevail, the curves will not be

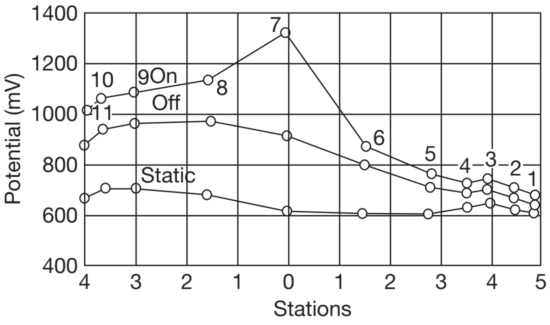


Figure 4 Longitudinal distribution potential on pipeline. Note: 'Stations' refer to points at which the potential is measured.

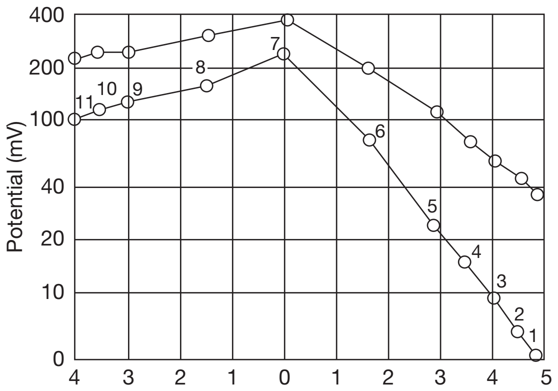


Figure 5 Attenuation curve on pipeline shown in Figure 4. Upper curve shows the ON-static values (which include IR drop errors) and the lower curve shows the instant OFF-static values.

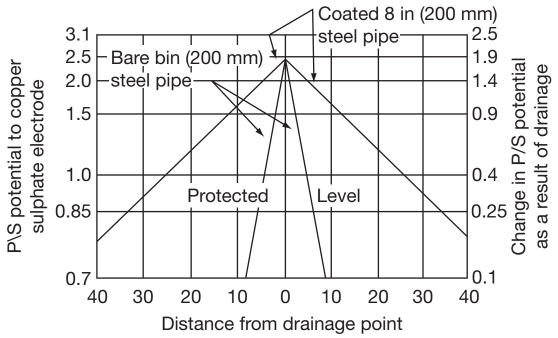


Figure 6 Attenuation curves for bare pipe and poorly coated pipe in similar soils. Note P/S (pipe/soil) potentials are negative.

straight lines as shown in Figure 5, in which the lines in the left of the figure are typically curved as a result of low resistance.

4.21.4.5.2 Measurement between drainage points

Figure 6 shows typical curves for a bare pipe and a poorly coated pipe in similar soils, and it can be seen that the former has a much steeper attenuation curve than the latter. Figure 7 shows how the desired protection level of potential has been attained between widely spaced drainage points, in which the dotted curves show the attenuation curves for the individual drainage points.

4.21.4.5.3 Coating resistance

The electrical resistance of a coating on a pipeline will depend upon the effectiveness of its initial application to the metal and on its condition at the time of testing; absorption of moisture may decrease the resistance by as little as 10% during the initial few years. The leakage resistance of a given section of pipeline may be determined as follows:

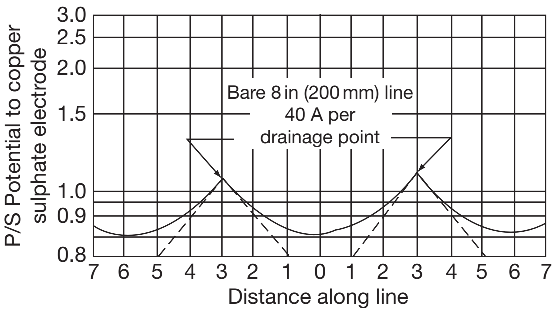


Figure 7 Attenuation curves for multiple drainage points of moderate size.

1. Applying temporary cathodic protection to the pipeline and measuring the pipe-to-soil potential for a given driving voltage of various test points spaced along the pipeline from the drainage point. The drainage current should also be measured.
2. Calculating the attenuation constant.
3. Measuring or calculating the longitudinal resistance of the pipeline. The resistance can be calculated from

$$R = \frac{2\rho l}{dt}$$

where ρ is the specific resistivity, l is the length of the pipeline, d is the diameter, and t is the thickness in appropriate and consistent units.

4.21.4.5.4 Types of cable for anode installations

Cables used for anode groundbeds must be well insulated and suited to operational conditions. Mechanical damage from sharp coke particles and chemical attack from generated gases (e.g., chlorine) may be prevented by the use of polytetrafluroethylene (PTFE) sleeving or a similar material. Alternatively, chemically resistant cable insulation such as cross-linked polyvinylidene fluoride (Kynar) may be used along with high molecular weight polyethylene (HMWPE) protective sheath. This type of cable is essential for deep-well groundbeds where nascent chlorine generation and highly acidic conditions may have to be tolerated. However, caution should be exercised when using Kynar-insulated cable, as the Kynar is brittle at low temperatures and may crack particularly if bent through a small radius.

For less severe applications, cross-linked polyethylene (XLPE) insulated and XLPE-sheathed cables may be sufficiently resistive to the anode reaction products.

4.21.4.6 Power Sources for Cathodic Protection

Where AC supplies exist, transformer rectifiers are the most economical source of DC for cathodic protection systems. A typical output for a well coated cross-country pipeline in the United Kingdom would be 5 A, 48 V. In the case of seawater jetties, where the voltage required is usually low because of the lower seawater resistivity, a typical rectifier size for a major installation would be 500 A, 18 V. For oil or gas terminals, offshore structures, and loading platforms where an incendiary sparking hazard exists, it is usual to locate the transformer rectifiers remote from hazardous areas or to employ certified flameproof or intrinsically safe rectifiers to overcome any possibility of explosion hazard during operation of the equipment.

Where ac supplies do not exist, other sources of power can be used such as DC generators, either diesel or gas driven. Alternatively, thermoelectric generators may be considered if the power requirement is relatively low, as they are only available in relatively small outputs. They may have the advantage of being able to be completely self-contained since they can be powered by taking off some of the gas that passes through the pipeline. Photovoltaic (PV) cells or wind-driven generators and battery systems have been successfully used for the protection of well coated pipelines and for reinforced concrete systems. However, as they tend to be used in remote locations which are short of distributed electrical power, there is a history of them being stolen.

4.21.5 Seawater-Cooled Circulating Water Systems

4.21.5.1 Galvanic Anodes

The use of galvanic anodes in circulating water systems is limited to the application of cathodic protection to stop gates, coarse screens, and other plants that are readily accessible so that the anodes can be replaced when they are consumed. Such anodes are not normally used in condensers, pumps, and auxiliary coolers for the following reasons:

1. Frequent replacement is required with consequent shutdown of the plant concerned.
2. Anodes are required to be very large to provide the current density necessary with a reasonable life. Anodes can interfere with the water flow.
3. Corrosion products or dislodged anode particles from anodes can cause tube blockage and subsequent failure.

4.21.5.2 Impressed-Current Anodes

Anodes for the internal protection of the plant are normally of MMO/Ti (historically platinized titanium or lead alloy).

4.21.5.2.1 Continuous anodes

They consist of considerable lengths of relatively flexible copper-cored material which can be contoured to suit restricted spaces or to distribute current in a localized fashion. Typically, they may be used in water boxes at a nonferrous tube-plate/ferrous water box junction. Anode terminations pass through the water box via insulating entry points, and the anodes are supported on insulators within the box. Anode–cathode distance must be such as to prevent the anode becoming engulfed in calcareous deposit that forms on the cathode.

4.21.5.2.2 Rod anodes

These consist of solid or copper-cored titanium rod, portions of which can be platinized. They range from 6 to 25 mm in diameter and are normally supplied preassembled in a steel or polymer mount ready for screwing into prepared bosses on the plant under protection. Electrical connections are made via cables in the usual way. The anodes are spaced to give even current distribution. Anodes are typically designed to have sufficient mechanical strength to withstand being used as foot and hand holds, particularly in water boxes.

4.21.5.2.3 Tubular anodes

Tubular anodes are supplied in diameters between 12.5 and 32 mm and have been designed for installations where water conditions on the plant under protection are known to be turbulent. The tubular anode has a number of holes drilled in the active portion of the anode, and the nonactive portion is filled with sand to act as a damping agent. As in the case of rod anodes, they are supplied complete with mounts ready for installation in the prepared bosses on the plant under protection. They are particularly suitable for the internal protection of pump casings and the internal protection of pipelines carrying salt water or other low-resistivity liquids.

More recently, other methods have been used to assess anodes for their ability to withstand the fatigue loadings from eddy shedding which can occur in relatively high electrolyte flow rates.

4.21.5.3 Impressed-Current Systems

Impressed-current systems for power stations are somewhat more sophisticated than those required for pipelines or marine structures inasmuch that a large number of items of the plant, with a wide range of current requirements, are often protected by one multichannel transformer rectifier. Each section of every water box requires one or more anodes in order to provide even current distribution. In the case of a large circulating water pump, as many as 30 anodes may be required to provide the necessary current distribution. Three types of system should be considered as follows:

1. Manually controlled.
2. Automatically thyristor-controlled.
3. Automatically controlled modular.

4.21.5.3.1 Manually controlled system

A manually controlled system comprises one or more transformer-rectifiers each with its associated control panels which supply the DC to the various anodes installed in the water box spaces. Each transformer rectifier is provided with its own control panel, wherein each anode is provided with a fuse, shunt, and variable resistor. These enable the current to each anode to be adjusted as required. Reference electrodes and test connections should be provided in order to monitor the steel/electrolyte potential values achieved by the cathodic protection system. In the case of a major power station, one transformer rectifier and associated control panel might be provided for separate protection of screens, circulating water pumps, and for each main condenser and associated equipment.

When coolers or condensers are shut down but remain full of water, the amount of current required to maintain satisfactory cathodic protection is considerably reduced. If the current is not reduced, overprotection occurs and excessive amounts of chlorine can be generated which would tend to accumulate in the upper section of the water boxes causing considerable corrosion, not only to the water boxes but also possibly to the tubes. To ensure against this, a standby condition should be included on the control panel which effectively reduces the current required under shutdown conditions. This control is effected by a limit switch fitted to the outlet valve of the condenser or cooler concerned. It is impossible to determine the exact requirements for the protection of circulating water systems in advance, and it is normal to adjust the current to provide protection during commissioning.

These simple resistor-controlled systems have lost favor as the costs of more sophisticated electronic control systems have dropped and have become more available. However, the principle of simple transformer rectifiers and resistive-controlled individual anode outputs is occasionally used in other applications.

4.21.5.3.2 Automatic potential controlled system

This method is basically the same as the manual system. However, the current output of the transformer rectifier is automatically maintained at a level to ensure satisfactory cathodic protection under all operating conditions. This is achieved by means of sensing reference electrodes located in the main item of the plant, for example, main condenser, which feeds back steel/electrolyte/reference electrode potential data to an automatic control device within the transformer rectifier. The control device is preset at the required potential, and any incoming signals are compared with this preset potential and the level of current either raised or lowered until the incoming signal agrees with that of the preset potential in the automatic device.

It is also usual to fit additional (monitoring) reference electrodes and test connections as an independent check on the performance of sensing (controlling) electrodes.

4.21.5.3.3 Automatically controlled modular system

This method employs one large, manually controlled transformer rectifier used in conjunction with a number of modular controlled outputs either within the main cabinet or in smaller cabinets located adjacent to each item of the plant requiring protection. The main transformer rectifier feeds DC to each of the module units, and the modular unit provides the exact amount of current required by the item of the plant in question.

4.21.6 Marine Structures

The method of applying cathodic protection to immersed structures will depend on several factors including the following:

1. Size of the project.
2. Availability of power supply.
3. Possibility of problems from interaction.
4. Necessity for safety from spark hazard.
5. Expected economic life of the system.

Figures 8(a) and 8(b) give an indication of the relative numbers of anodes that may be involved for galvanic anode and impressed-current systems.

However, the offshore experience in severe environments such as the North Sea is clear. A significant number of impressed-current systems designed in the 1970s and early 1980s failed due to inadequate design, insufficient mechanical integrity of the anode and monitoring system supports, and even gross errors in surface area calculations. These included systems with anodes as inferred in Figure 8(c), which were

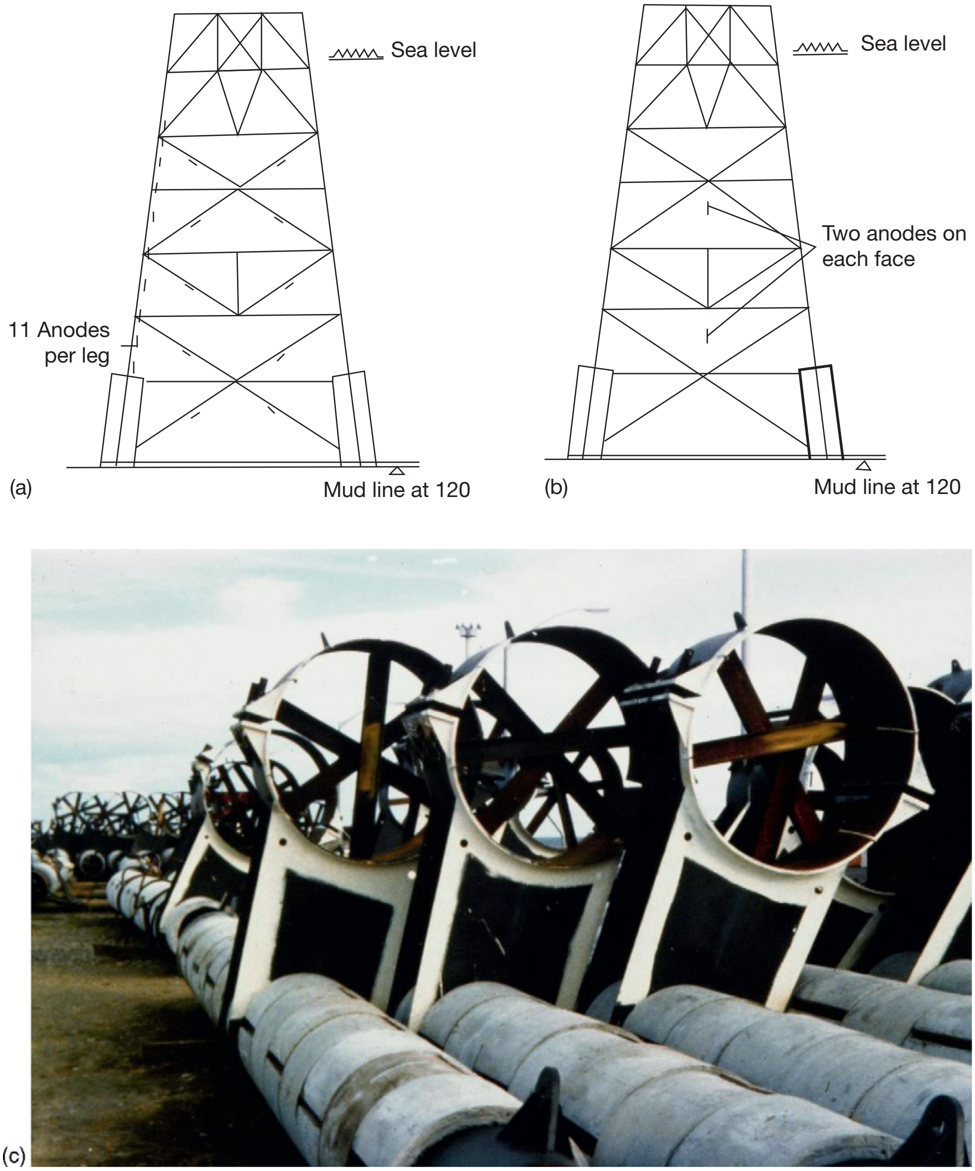


Figure 8 Protection of offshore oil drilling/production platform. (a) With galvanic aluminum anodes and (b) with impressed current using MMO/Ti, platinized titanium, or platinized niobium anodes. (Compare the large number of anodes used in (a) with the small number used in (b)). (c) Galvanic anode arrays as part of a 100% galvanic anode retrofit to replace a failed impressed current system of the type represented in Figure 8(b). Courtesy of Impalloy Ltd and B S Wyatt.

installed using small-diameter anode riser tubes to carry the anode and its cable to the positions as shown. Many such systems were the subject of major retrofits with galvanic anodes. Some notable impressed-current systems were designed in the 1980s and later have been made reliable, but the costs of the design and implementation of such reliable systems are high (Figure 9).

Current-density requirements depend on the environment, galvanic effects, velocities, and other factors influencing polarization. In the absence of galvanic influences or other secondary effects, 60 mA m^{-2} may be sufficient in seawater to maintain adequate polarization for protection once it has been achieved; it is, however, normally necessary to apply 120–250 mA m^{-2} to achieve initial polarization within a reasonable period, and if rapid protection is required, current densities as high as 300 mA m^{-2} may be applied.

(a)

(b)

Figure 9 (a) A late 1980s design of North Sea impressed-current anode design incorporating Pt clad Nb anodes, duplicated for redundancy, with the cables run within the main structure legs to the platform decks above. Courtesy of Impalloy Ltd and B S Wyatt. (b) A dual silver/silver chloride/seawater reference electrode and Zn/seawater reference electrode similar to those used on the above project. Courtesy of Global Cathodic Protection Ltd and B S Wyatt.

Anodes placed on the seabed remote from the structure can be considered, but these installations may have problems due to damage to the connecting cable by ships' anchors, etc., and, more importantly, there have been serious interaction problems in the North Sea from such seabed remote anodes to the incoming production and outgoing export pipelines/risers which are normally electrically isolated from the jacket due to different cathodic protection performance characteristics.

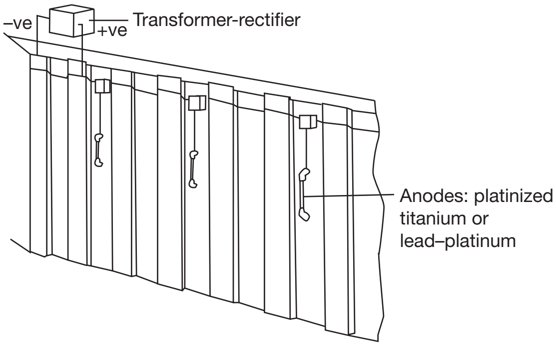
The calculation of rectifier voltage/anode resistance is exactly as described for impressed-current pipeline installations except that the voltage required is very small because of the low resistance of the electrolyte: normally 25–35 Ω cm for typical seawater. In the assessment of seawater resistivity, it should be remembered that the resistivity increases significantly with decreasing temperature.

For cathodic protection of sheet steel piling, the impressed-current or galvanic anodes are normally mounted within the re-entrants of the piles to prevent mechanical damage by berthing ships, dredging, etc. (Figure 10).

As in the case of power stations, where there is known to be considerable variation in operating conditions due to tidal changes, or variations in salinity of estuary waters, automatic control of impressed-current systems is generally desirable. For such systems, the current output of the transformer rectifier is controlled by the use of thyristor-controlled rectifiers. Sensing electrodes are permanently installed on selected piles, which transmit the steel/seawater/electrode potential back to the controlling device. This type of system enables the most appropriate current to be provided under all operating conditions in order to deliver uniform levels of protection.

4.21.7 Ships

Cathodic protection is effectively supplied to ships' external hulls and also to the tanks of oil tankers and other vessels wherein seawater is used for ballast or other purposes. For internal protection, galvanic anodes of the zinc or aluminum are normally employed; magnesium and impressed-current anodes are not used in tanks, which can contain explosive gases due the incendiary spark hazards. Impressed current can also generate chlorine inside closed water spaces; both magnesium and impressed current can also generate hydrogen gas, so both should only be used with extreme caution and appropriate



(a) Sheet steel piling installation

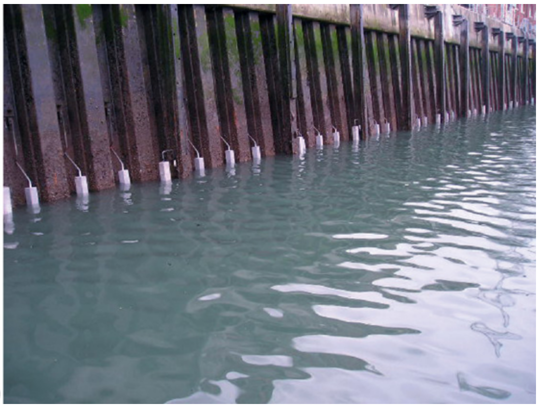


Figure 10 (a) Sheet steel piling impressed-current installation. More modern installations would utilize MMO/Ti anodes and their mounting system would include a dielectric shield that would, subject to anode current rating, extend the full width of the in pan and extend above and below the anode. (b) Galvanic anode (Al–Zn–In) system to sheet steel piled wall and associated fenders at extreme low tide. Note that anodes to piles are within the in-pans and all anodes are behind the fender line. The coated piles were the subject of accelerated low water corrosion (ALWC), a form of microbial corrosion common in ports and harbors, which is able to cause local section loss at *c.* 2 mm/side per year. The anodes are normally fully immersed; the extended anode cores allow critical structural support welds to be made above the water for lower cost and more secure quality. Courtesy of B. S. Wyatt Corrosion Control.

precautions in confined spaces. External hulls can be protected either by galvanic or impressed-current methods, although impressed current is now preferred at least for larger vessels (Figure 11). Anodes of MMO/Ti, platinized titanium, or lead–silver alloy with platinum bielectrodes, are mounted on the hull below the water line and can be designed to have current outputs of up to 200 A. In vessels such as tankers, where there may be access problems, the anodes are located at both the stern and the forward end of the ship. All cable or other entries through the hull plate must be carefully designed using a special cofferdam, and the complete system has to be submitted to the ship approval authorities prior to installation. Because of the rapid variation in electrolyte conditions during passage of the vessels and the need to both maintain uniform protection levels and prevent overprotection and damage to the specialist marine coatings, all schemes for ships are automatically potentially controlled.

The transformer rectifiers typically contain thyristor-controlled rectifiers and operate in a manner similar to that described for power stations.

4.21.8 Water Storage Tanks

Galvanic anodes are of limited application because of accumulation of anode corrosion products and also, in many cases, of high water resistivity.

Impressed-current systems are normally based upon anodes of MMO/Ti, platinized titanium, or platinized niobium. The method of anode installation is usually by suspension. The anode configuration and number must be such as to ensure uniform current distribution. Considerable use is made of wire-type platinized titanium and niobium anodes, which offer minimal weight and relative ease of mounting/suspension.

Coatings are normally employed for water storage tanks, which result in relatively low total current requirements in association with the current densities given in Table 4.

4.21.9 Internal Protection of Pipelines

The current spread from an internally immersed anode is directly related to pipe size and the resistivity and temperature of the water; with seawater having a resistivity of ∼30 Ω cm, anodes are normally required within a 250-mm-diameter pipe at ∼1-m centers and in the case of a 760-mm-diameter pipe at ∼3-m centers (Figure 12). Small bore, high resistivities, and high electrolyte velocities further reduce the anode spacing.

Cathodic protection is therefore normally practicable only in large-bore pipes carrying salt water or relatively low-resistivity river water used for cooling inland power stations or chemical plants. Under special circumstances, however, it has been found necessary to use cathodic protection in relatively high-resistivity

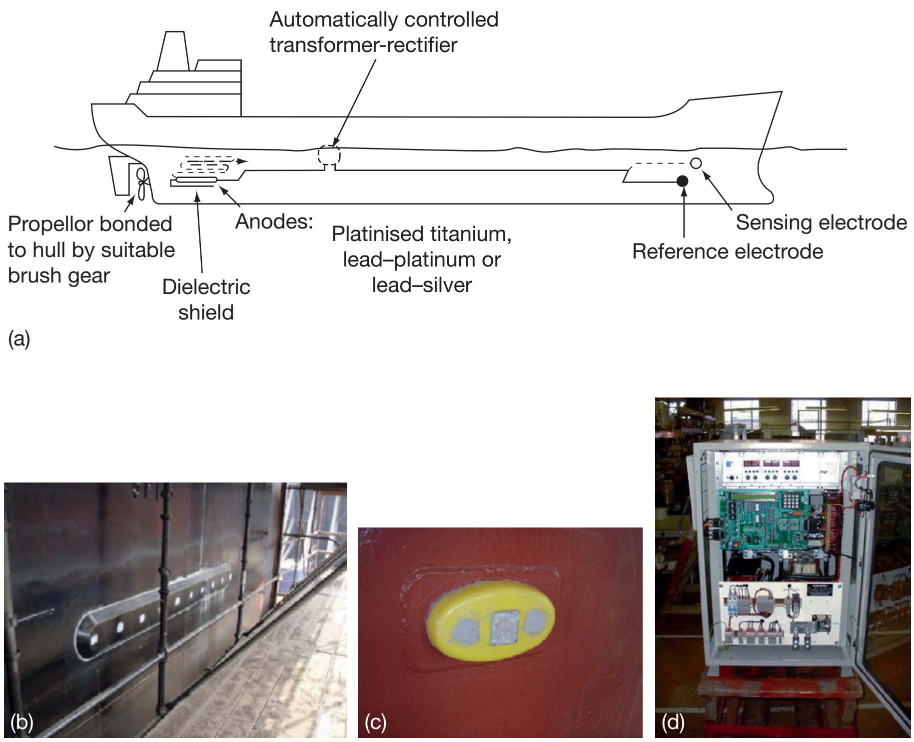


Figure 11 (a) Impressed-current cathodic protection system for ships. Larger vessels would also have bow-mounted anodes which would normally be smaller, recessed, and round to prevent damage to them. Anodes of MMO/Ti are now often used. The dielectric shields around the anodes are generally high-build epoxy coatings selected for their very good cathodic disbondment resistance and high (electrical) dielectric (insulating) properties. (b) Ship's impressed-current anode installed on the hull (anode elements masked during coating). Courtesy of Corrpro Companies Europe Ltd. (c) Ship's reference electrode. Courtesy of Corrpro Companies Europe Ltd. (d) Ship's impressed current transformer rectifier. Courtesy of Corrpro Companies Europe Ltd.

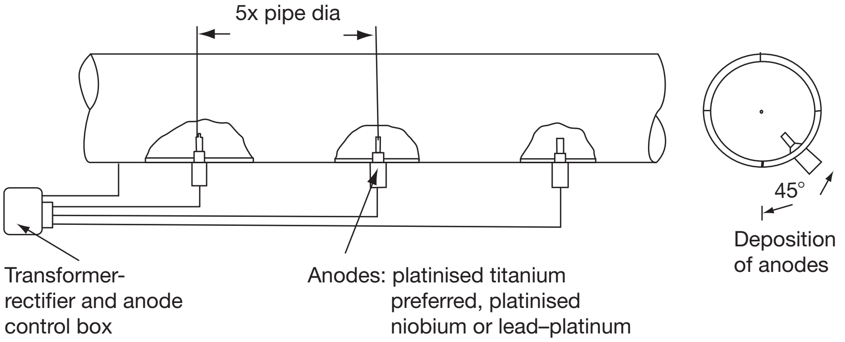


Figure 12 Internal protection of pipeline. Typical current density (seawater) = 200 mA m^{-2} to bare steel at low flow rates: significantly greater for polarization at higher flow rates.

fresh water, particularly where microbial corrosion has been present; in these instances, anodes have been run longitudinally down the entire length of the pipe. In such applications, particular attention is required to avoid fatigue failures of the anode supports due to eddy shedding within the water flow.

4.21.10 Cathodic Protection of Steel in Concrete

Cathodic protection of steel in concrete has developed from limited applications to buried reinforced and prestressed concrete pipelines in the 1950s, through small-scale trials on bridge structure in the 1960s, to a major industry in the twenty-first century. Cathodic protection is applied to both new construction (prior to corrosion initiation) and to existing structures that have suffered corrosion initiation and often have suffered considerable corrosion damage to the steel and cracking and spalling of the cover concrete.

Due to the nature of reinforced concrete structures, their cathodic protection systems are significantly different from other applications. The anode–cathode spacings are typically in the range 15–100 mm in concrete compared with 5–250 m between anodes/groundbeds to pipelines in soil or 300 mm or more between anodes and steel in seawater. Further, the concrete electrolyte (actually the cement paste gel that binds the sand and stone aggregate into an effective structural composite) has an electrical resistivity that is high compared with most soils, typically in the range 20 000–200 000 Ω cm. This results in very considerable IR voltage drop errors in concrete, greater even than those in buried-pipeline applications.

In addition, whereas most steel in soil or waters cathodic protection applications the electrolyte is near neutral, in concrete the pH is typically greater than 10.5. Thus, the protection criteria for steel in concrete differ considerably from those for steel in soils or waters. The absolute protection criterion is accepted as −720 mV with respect to Ag/AgCl/0.5 M KCl (equivalent to −720 mV with respect to Ag/AgCl/seawater) compared with −800 mV for steel in aerobic soils or waters with respect to Ag/AgCl/seawater (or −850 mV with respect to Cu/$CuSO_4$ saturated) or −900 mV with respect to Ag/AgCl/seawater in the presence of active microbial corrosion. Potential shift, more normally, due to time-dependent changes in depolarized potentials; potential decay values of 100 mV over 24 h or 150 mV total decay over longer periods are the normally used criteria for atmospherically exposed concrete. These may be compared with the 300 mV potential shift criterion favored by some North American pipeliners.

Current densities for actively corroding steel in concrete are typically in the range 2–20 mA m^{-2} (of steel in temperate climates), and for preinitiation (where the purpose of the cathodic polarization is to maintain the passivity of the steel in the concrete even at high chloride concentrations), they are typically in the range 0.2–2 mA m^{-2}. Typical applications of cathodic protection to steel in concrete are shown in Figure 13.

Anodes used in cathodic protection of steel in concrete are summarized in Table 4. Power supplies are typically quite complex multichannel transformer rectifiers, typically with individual channel outputs <10 A and <18 V (for complex projects, some individual channels may be only 0.5 A, 12 V, whereas for larger more uniform zones on the same project, they may be 5 or 10 A, 12 V) and due to the complex nature of such structures, with their varying steel densities and varying exposure to chlorides, each channel may be associated with several monitoring channels of test connections associated with both permanently installed reference electrodes and pseudo (reference) electrodes or potential decay probes.

Owing to the complexity of these systems, the large number of dc power channels, the even greater number of monitoring channels, and the need to collect potential decay data over periods often in excess of 72 h, it is normal for cathodic protection of reinforcement systems to be fitted with data logging and remote monitoring systems using telephone landline or GSM modems.

4.21.11 Economics

Cathodic protection design involves achieving an economic balance between installation costs, maintenance costs, initial cost of power units, and power consumption. Because both the cost of the rectifier and the cost of the electric power consumed are contingent on the operating voltage of the system, it is desirable to keep the operating voltage as low as possible; for this reason, a low-resistance anode system is desirable when it is economically feasible. Further, there are higher risks to personnel and animals at higher voltages. Simulated cost curves plotted on a cost versus the number of anodes in a groundbed for an assumed set of conditions are shown in **Figures 14** and **15**. Figure 14 is based on installed capital costs only, whereas Figure 15 is the minimum annual cost.

4.21.12 Recent Developments

4.21.12.1 Galvanic Anode Systems

As the general standard of protective coatings has improved (materials, application, and construction standards), the use of galvanic anodes has extended to soil of *c.* 10 000 Ω cm or more for well-coated buried pipelines. By using anodes in extruded or continuously cast and hot rolled 'ribbon' form and placing them in the pipeline trench, they can be effective in soils of high resistivity.

The use of high-strength steels and alloys in offshore oil and gas developments and in submarines occasionally results in structures, pipelines, or vessels that are subject to hydrogen embrittlement and which cannot be subject to the more normal range of protection criteria of −800 mV (or −900 mV in the presence of microbial corrosion) to −1050 mV with respect to a silver/silver chloride/seawater. Some high-yield materials, when subjected to significant stress levels, may have safe cathodic protection potential limits as positive as −780 mV; other materials may be safe at potentials in the range −800 to −900 mV. In order to achieve safe protection of such materials, two different approaches have emerged. One that has been quite widely used on offshore oil and gas facilities is the use of carefully selected Schottky barrier rectifiers (SBRs), which are inserted between the normal Al–Zn–In anode and the high-strength steel or alloy structure and which limit the polarized metal/electrolyte potential level to a predetermined safe limit. The other is an Al–Zn–Ga anode alloy that operates at a closed circuit potential which is safe for some grades of high-yield steel; this is less extensively used than the SBR approach, but has the benefit of simplicity if reliable for long-term use.

With the developments in very high dielectric strength coatings, in particular the three-layer polyethylene or polypropylene (a thin fusion-bonded epoxy coating followed by an adhesive followed by

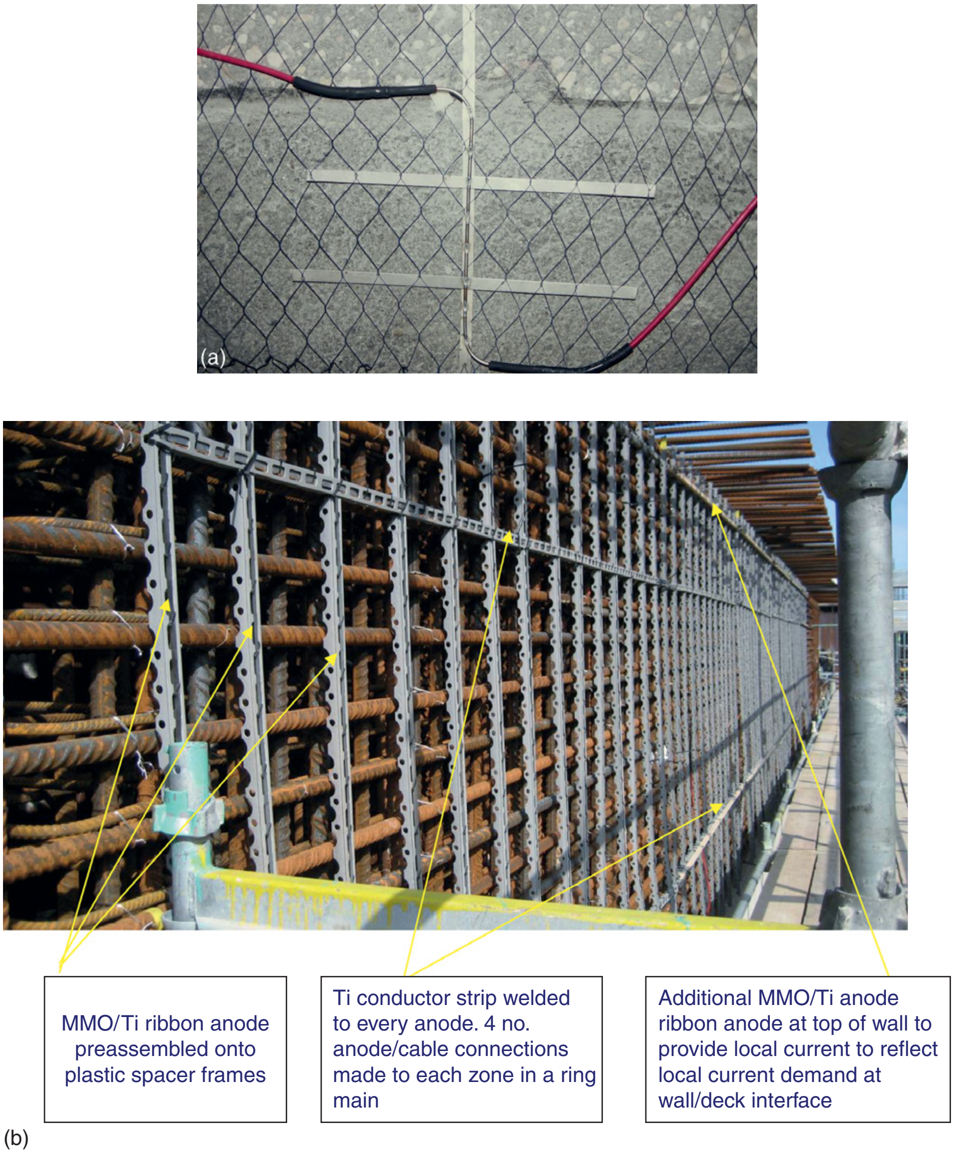
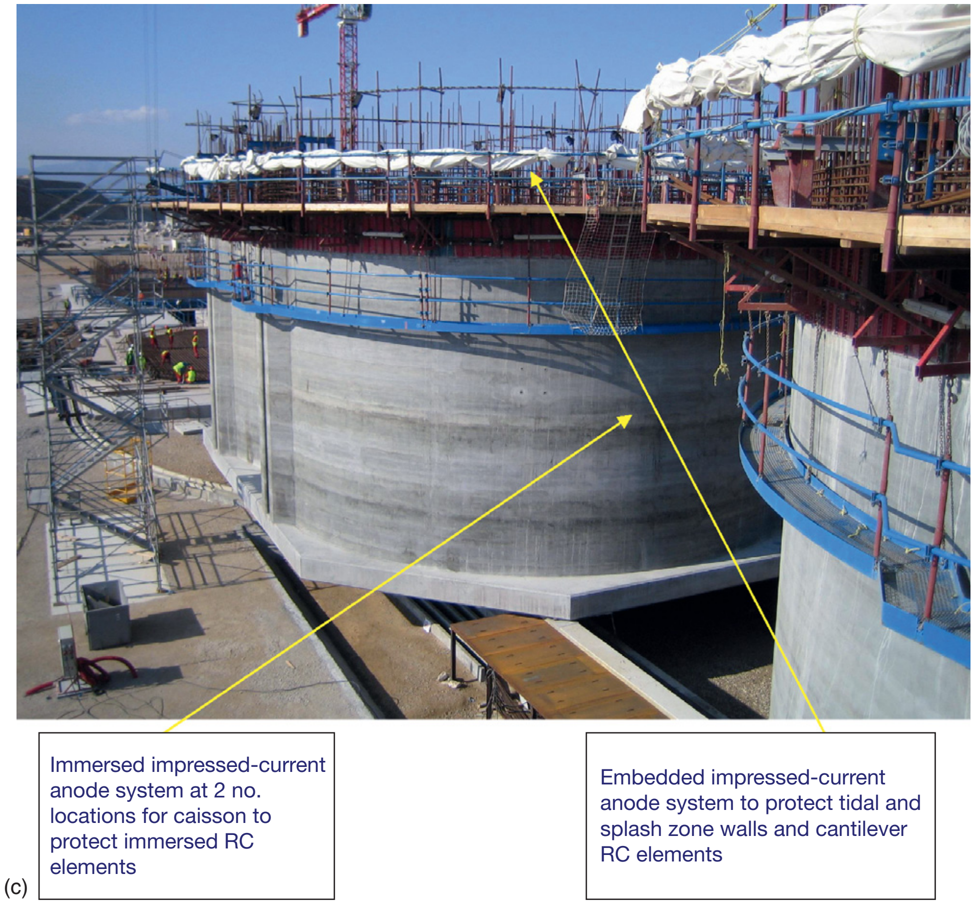


Figure 13 Continued



Immersed impressed-current anode system at 2 no. locations for caisson to protect immersed RC elements

Embedded impressed-current anode system to protect tidal and splash zone walls and cantilever RC elements

Figure 13 (a) Sprayed concrete repair to severely corrosion-damaged marine concrete beam with MMO/Ti anode and cable/anode connection shown fitted awaiting sprayed concrete overlay. Courtesy of Tarmac Global and B. S. Wyatt. (b) MMO/Ti ribbon preassembled onto plastic rail cages to limit installation cost and risk of short circuits. New construction of floating reinforced concrete pontoon. Courtesy of Corrosion Control Affiliates Ltd. (c) New port caisson construction with cathodic protection with MMO/Ti ribbon anodes cast into slip formed caisson walls and *in situ* cast cantilever decks in the tidal and splash zones and immersed anodes in seawater for the immersed zones. Courtesy of B. S. Wyatt Corrosion Control.

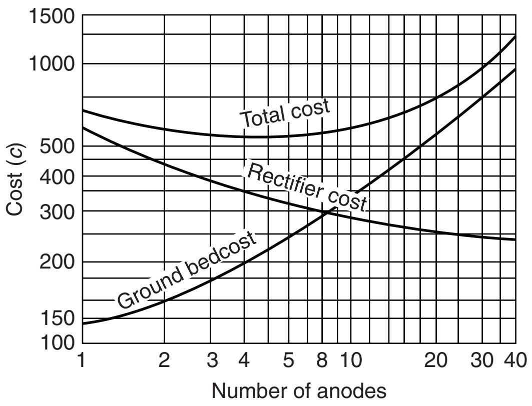


Figure 14 Total cost in relation to number of anodes installed.

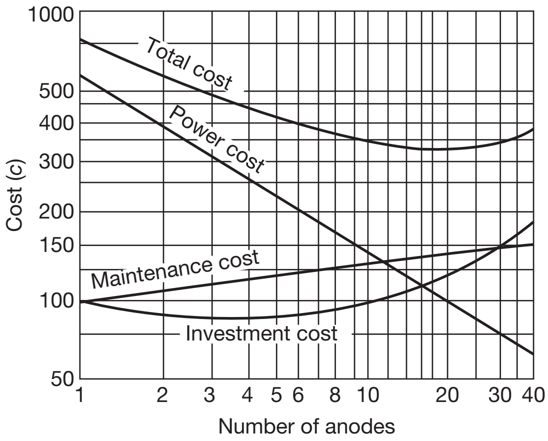


Figure 15 Variation of minimum annual cost with number of anodes installed.

an extruded thick-wall tube or coating over the pipe), small coating defects on pipelines are vulnerable to very rapid corrosion due to ac current discharge/pickup at the coating defects. There have been significant and unexpected gas and oil pipeline failures/major section loss by pitting due to ac corrosion. Many such pipelines, while nominally protected with impressed current (at extremely low current densities, which present their own control and monitoring difficulties), are being fitted with extensive networks of zinc or magnesium ribbon anodes primarily for electrical earthing purposes. The AC currents are collected/discharged preferentially via these galvanic anode systems.

The development of large-scale galvanic anode retrofit anode systems for extending the design life of offshore jackets or pipelines has resulted in very large bracelet anode and anode arrays on tubes and sleds being designed. Most of these systems have been in Al–Zn–In anodes, but some very successful systems with design lives (that have been delivered in practice) have used magnesium anodes on pipe arrays and sleds, remote from the structure being protected, with the design of the anode resistance, the connecting cable resistance, and the distance between the anode and the structure being carefully balanced to prevent exceeding the normal $-1050\,\mathrm{mV}$ steel/seawater potential limit with respect to silver/silver chloride even when using anode material with a closed circuit potential of $-1500\,\mathrm{mV}$.

There have been major changes in the production/supply chain for magnesium anodes (most Mg was produced from seawater using the Dow process and Dow Chemical Corporation in the United States were the major international producers of Mg anodes until the 1990s). Since the 1990s, there has been the development of many small-scale producers, mainly in China, using a smelting route of production that has led to alloys, which, although are clearly within accepted chemical composition limits, perform below their anticipated efficiency or $\mathrm{Ah\,kg^{-1}}$ capacity. It is now a good practice to test each batch of magnesium anodes for its capacity before purchase/sale. This does not mean that the alloys or anodes are of deliberate or accidental poor quality; it means that either metallurgical or trace element issues which are not presently well understood and were previously uniform are now variable and can significantly affect anode performance.

4.21.12.2 Impressed-Current Anodes

Anodes of scrap steel, graphite, and lead alloys have virtually ceased to be used. Silicon–iron is still widely used due its robust and secure performance. MMO/Ti anodes have developed immensely in the late 1990s and into the twenty-first century; their use in cathodic protection of steel in concrete is extensive, but they have also replaced other anode materials in many applications in soils and waters.

Specific anodes for cathodic protection of steel in atmospherically exposed (above ground) concrete have been developed; some have failed to deliver their early claimed promise. Pt/Ti and Pt/Nb anodes are still used but are becoming specialist items as MMO/Ti anodes take more market share due to near-equivalent performance (better in some respects) and lower cost.

4.21.12.3 Power Sources for Cathodic Protection

The most commonly used cathodic protection power supplies, that is, transformer rectifiers, for the traditional applications of cathodic protection of steel in soils and waters have not changed significantly in the period 1990–2009 except more have been supplemented with elements of remote monitoring and/or remote control. Units manufactured in Europe are now almost exclusively thyristor-controlled silicon diode rectifiers with improved efficiencies and service life expectancies than the old selenium rectifiers and transductor, rotary transformer or tap changed transformer controls that were used in the 1960s through the 1980s.

Switch-mode power supplies offer possible advantages of small size and lower cost. Some remain concerned by their apparent fragility in response to the typical surge and spike conditions that cathodic protection power supplies often are subject to.

Microelectronics has allowed the design and reliable manufacture of distributed power supplies of the type that were pioneered for power station cooling water cathodic protection in the early 1970s. However, there have been many examples of small suppliers dedicated to small-volume cathodic protection applications producing ‘clever’ integrated cathodic protection power supplies and data logging/remote monitoring systems, which have been unreliable and incapable of maintenance once the producing company ceased to trade or even the individual designer left the company. There is great merit in the use of industry-standard monitoring and control hardware and software that can be purchased from many sources and is produced in such volume as to reasonably assure adequate development, testing, and ongoing upgrades and software support.

Reinforced concrete cathodic protection has forced the pace in development of multichannel, heavily monitored power supplies with integrated monitoring and control.

4.21.12.3.1 Solar and wind power

With improved technology and production methods, considerable use is being made of solar power in remote locations. The output of PV arrays is used to maintain conventional storage batteries in a state of charge. The cathodic protection system is in turn energized from the batteries. It is usual to incorporate sufficient battery storage to accommodate a number of 'no-sun' days. Quite large capacity schemes have been effectively used in north and east Africa. Theft is a problem.

Wind power has been used to a small extent but it is likely, as domestic wind 'microgeneration' becomes more popular for environmental reasons, that such systems will fall in cost and increase in efficiency. Combined PV and wind systems may be optimum solutions in some locations.

4.21.12.3.2 Other power supply systems

Thermoelectric generators using catalytic converters and direct dc electrical generation with no moving parts, small gas turbine generators, turbines powered by water, oil, or gas flow across a flow constricting valve with a bypass loop, as well as gas and oil fuelled generators have all been used for cathodic protection in remote locations. They remain small scale due to the cost and efficiency advantages of AC power distribution and transformer rectifiers.

4.21.13 Conclusion

Although the principles of cathodic protection are essentially simple and were in fact first outlined by Sir Humphrey Davy in 1824, the application of the method to practical problems was described as more of an art than a science by the authors of the earlier edition of this chapter. In the years that have passed since that edition, the science and calculation procedures have been developed and proven that have, in the view of this author, taken the element of art out of the science and technology of cathodic protection. A properly designed cathodic protection system will be economic and effective and will deliver reliability for its design life. Regrettably, such systems can only be delivered by designers, suppliers, and contractors with sufficient expertise and experience to warrant certification of competence; there continue to be some cathodic protection systems that do not deliver economic, effective, or reliable solutions to owners or operators who sadly find themselves served by less competent people claiming to be specialists. These schemes can be inefficient and uneconomical and, under certain circumstances, may accelerate corrosion instead of controlling it.

Bibliography

1. Von Baeckmann, W.; Schwenk, W.; Prinz, W. Eds.; Handbook of Cathodic Corrosion Protection, 3rd ed.; Gulf Publishing Co: Houston, TX, 1997, ISBN 0–88415–056–9.
2. Ashworth, V.; Booker, C. J. L. Eds.; Cathodic Protection Theory and Practice; Institute of Corrosion and Ellis Horwood: Chichester, 1986, ISBN 0–85312–510–0.
3. Ashworth, V.; Googan, C. Eds.; Cathodic Protection Theory and Practice; Institute of Corrosion and Ellis Horwood: Chichester, 1993, ISBN 0–13–150038–4.
4. *Design and Operational Guidance on Cathodic Protection of Offshore Structures, Sub-Sea Installations and Pipelines*; The Marine Technology Directorate Ltd: London, 1990, ISBN 1–870553–04–7.
5. BS 7361: Part 1: 1991, Cathodic Protection Part 1: Code of Practice for Land and Marine Applications. BSI London 1991.
6. Wyatt, B. S. *Anti-Corros. Methods Mater.* **1985**, *32*(6), 4–14; *32*(7),8–10; 32(8), 7–11, Sawell, London.
7. Wyatt, B. S. In NACE Corrosion'79, 1979, Houston Paper 252.
8. Wyatt, B. S. In Corrosion 2007, Australasian Corrosion Association, Sydney, 2007.
9. Martin, B. A., Brodribb, R. Corrosion 2007, Australasian Corrosion Association, Sydney, 2007.
10. BS EN 12954: 2001 Cathodic Protection of Buried or Immersed Metallic Structures – General Principles and Application for Pipelines CEN Brussels, BSI London 2001.
11. BS EN 12473: 2000 General Principles of Cathodic Protection in Sea Water, CEN Brussels, BSI London, 2000.
12. BS EN 12495: 2000 Cathodic Protection for Fixed Steel Offshore Structures, CEN Brussels, BSI London 2000.
13. BS EN 12696: 2000 Cathodic Protection of Steel in Concrete, CEN Brussels, BSI London, 2000.
14. BS EN 13174: 2001 Cathodic Protection for Harbour Installations, CEN Brussels, BSI London, 2000.
15. BS EN 15257: 2006 Cathodic Protection – Competence Levels and Certification of Cathodic Protection Personnel, CEN Brussels, BSI London, 2006.
16. Recommended Practice: Cathodic Protection Design: (*Of Galvanic Anodes for Fixed Offshore Structures)* DNV-RP-B401, Det Norske Veritas, Hovik, 2005.
17. ISO 15589–1: 2003 Petroleum and Natural Gas Industries – Cathodic Protection of Pipeline Transportation Systems – Part 1: On – Land Pipelines, ISO, Geneva, 2003.
18. ISO 15589–2: 2004 Petroleum and Natural Gas Industries – Cathodic Protection of Pipeline Transportation Systems – Part 2: Offshore Pipelines, ISO, Geneva, 2004.

4.22 Interaction and Stray-current Corrosion

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Abbreviations

AC Alternating current
CP Cathodic protection

Symbols

ρ Soil resistivity (Ω m)
U_{ac} Alternating current voltage (V)
J_{ac} Alternating current density (A m^{-2})

4.22.1 The Phenomenon of AC Corrosion

The primary factor in alternating current electrolysis is current density.[1] This statement was made in *The Engineering Journal*, the journal of the Engineering Institute of Canada, and was made in 1927.

A long time has passed since then and AC effects have been experienced and investigated in depth.

More recently, since 1986, some instances of corrosion on gas pipelines due to alternating current (16.6 and 50 Hz) have been reported in Europe and elsewhere.[2–4] In all these cases, the cathodic protection (CP) values, measured with conventional techniques and instruments, satisfied the conventional criteria. It is also most probable that some previous corrosion failures have not been recognized as being caused by alternating current, because CP personnel have not been made aware of the AC corrosion risk.

Very often in the past, AC corrosion was not correctly diagnosed, because usually, CP instrumentation rejects industrial AC frequencies and the knowledge of the AC corrosion phenomenon itself is still growing every day.

In the last decade, quite a number of corrosion instances have been clearly attributed to AC corrosion.

AC corrosion is a concern for owners operating long structures (mostly pipelines) running parallel or close to overhead high-voltage transmission power lines (typically 15 kV and higher) or AC traction systems. The problem also exists in municipal areas (structures buried near AC power distribution systems), in reinforced concrete structures (e.g., road bridges also carrying electricity power lines), and inside tunnels for AC electrified railways.

It is not uncommon to measure AC voltages in the range of 15–100 V_{rms} on coated pipelines exposed to AC influence. This may cause safety hazards to people, malfunction of the pipeline equipment, and corrosion problems.

In the last two decades, a better knowledge of the AC corrosion phenomenon has been gained, thanks to the many studies that mainly gas operators have sponsored or directly performed.[4–6]

These studies started in the 1980s and are still in progress. Since this period, high-quality/high-resistance coatings have been used for buried pipelines, thus increasing the effects of AC interference.

4.22.2 Sources of AC Interference

The AC influence is referred to as ‘inductive,’ ‘resistive,’ or ‘capacitive’ interference in technical literature.

The most common long-term AC interfering sources on buried metallic pipelines are

- AC overhead or underground electricity power lines;
- AC traction systems fed by a parallel high-voltage feeding line (50 or 16.6 Hz).

Long-term AC interference on a buried pipeline may cause corrosion because of an exchange of AC current between the exposed metal of the pipeline and the surrounding electrolyte at the coating holidays.

This exchange of current depends on the AC voltage, whose amplitude is related to various parameters such as

- the configuration of AC power line phase conductors and shielding wires;
- the distance and the length of parallel path between the AC power line/traction system and the pipeline;
- the current flowing in the AC power line/traction system phase conductors;
- the average insulating resistance of the pipeline;
- the thickness of the coating; and
- the soil resistivity.

4.22.3 Interference Effects

When an AC voltage is present on a cathodically protected pipeline and defects in the coating are present, an AC current will flow across the metal–soil interface. This current depends on the impedance of the system.

During the negative half-wave, the combined AC and DC current will result in the reduction of any reducible species that is in contact with the metal, for example, the formation of hydrogen and hydroxyl ions according to eqn [3]. During the positive half-wave, the current may cause the charging of the double layer capacitance, possible oxidation of hydrogen, and reduced corrosion products due to the CP, and oxidation, that is, corrosion, of the pipeline steel. Since this current leaving the metal surface can be consumed by several noncorrosive processes, generally, voltages higher than 10 V are required to result in a significant corrosion attack to the pipeline steel. Various additional parameters influence this process; among others, the most important ones are the leakage or earth resistance of the defect, the level of CP and the chemical composition of the soil.

- The leakage or earth resistance R_L is generally due to the geometry of a defect that is in contact with the soil of resistivity (ρ). Considering a circular defect with diameter d, the following formula yields

$$R_L = \rho/2d \qquad [1]$$

Equation [1] is useful for a rough estimation of R_L; however, it should be considered that the soil resistivity may vary significantly in the vicinity of a coating defect, and both the soil resistance in the defect (considered within the thickness s of the coating) and the polarization resistance have been neglected.

- CP generally creates electrochemical reducing conditions at the steel surface and results in the formation of hydroxyl-ions according to

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \qquad [2]$$

and/or

$$2H_2O + 2e^- \rightarrow 2OH^- + H_2 \qquad [3]$$

This is combined with an increasing alkalinity (up to pH 11–12 and even more) and a significant decreasing of the resistivity of the soil close to the steel surface.

- From soils containing calcium (Ca^{2+} or other alkali earth ions), it is known that insoluble calcareous layers ($CaCO_3$) are formed on the cathodically protected steel surface. This is due to the highly alkaline conditions and reactions with CO_2 in the soil. The result is an increasing leakage or earth resistance of the defect. In alkali ion (Na^+, K^+)-rich soils, however, similar reactions produce soluble bicarbonates (e.g., $NaHCO_3$), thus resulting in a decreasing leakage resistance.[7]

The processes thought to be taking place have been summarized as follows:[8]

During the positive half-wave, the bare metal surface is oxidized, resulting in the formation of a passive film. This is due to the current that leaves the metal surface. During the negative half-wave, when both AC and DC current enter the metal surface, this passive film may be reduced to iron hydroxide. In the following anodic cycle, a new passive film grows. Upon reduction of the passive film, the amount of iron hydroxide is increased. Hence, every AC cycle results in some oxidation of the metal. In the long term, this can result in a significant metal loss.

4.22.4 Calculation of AC-Induced Voltage

An AC voltage that may cause corrosion can result from resistive or inductive interference from high-voltage power lines and/or electrified railways; induction is the most frequent interference mode. The AC voltage U_{ac} should be calculated in accordance with CIGRE Technical Brochure No. 95 published in 1995 "*Guide on the Influence of High Voltage AC Power Systems on Metallic Pipelines*."[9]

The evaluation of U_{ac} is generally based on the calculation of the induced longitudinal field strength E for a segment of the pipeline.

The field strength E depends on

- the value and the frequency of the inducing current;
- the mutual inductance – related to the unit length – between the conductor(s) of the high-voltage line and the pipeline, that is, a function of their clearance and of the soil resistivity;
- the reduction factor, allowing for the protective effect of adjacent earthed conductors.

For simplified conditions (e.g., parallel routing between high-voltage line and pipeline, uniform coating resistivity of the pipeline, constant soil resistivity, and both ends of the pipeline being terminated by a low resistance to earth), an analytical solution for U_{ac} as a function of pipeline length may be evaluated.[9] In practice, however, calculations are generally carried out by using computers, taking into account the relevant parameters of the high-voltage line and the pipeline.

These calculations are, among others, based on the following information and documentation:

- drawings showing the right way of the high-voltage lines and the pipeline together with the location of power stations, substations, transformer stations, overhead line towers, and pipeline CP stations;
- the rated voltage and the type of earthing of the high-voltage system;
- nominal or operating and peak (inducing) current of the high-voltage line;
- the configuration of the towers and the conductors;
- the diameter and insulation resistance of the pipeline;
- the location of isolating joints and leakage resistance of any structure that provides grounding of the pipeline; and
- the reduction factor of the high-voltage line and the case being of other reducing conductors.

U_{ac} as a function of pipeline length, l, is then obtained from the vectorial sum of the induced voltage from each considered individual pipeline segment.

As an example, Figure 4 shows the results of calculated U_{ac} for a pipeline, DN 500, laid in 1999. Isolating joints are installed at km 0 and km 62. The pipeline is inductively interfered by four 50 Hz high-voltage lines (110 kV/220 kV); the level of operating currents is between 520 and 960 A. The coating insulation resistance is 1 and 100 kΩ m^{-2} according to results from CP measurements. By installing two grounding electrodes, U_{ac} may be kept below the safety threshold for people, even though, to avoid AC corrosion, further measures are still to be adopted.

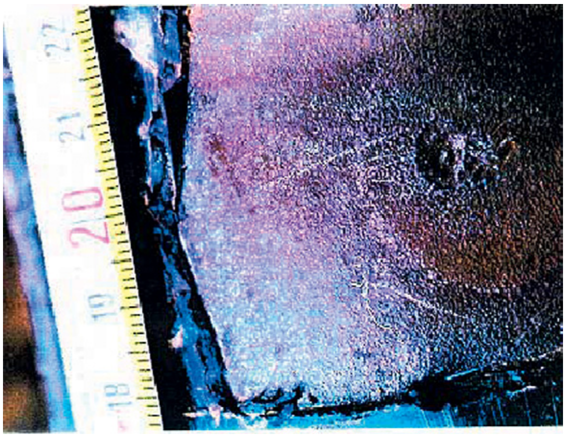

Figure 1 Typical AC corrosion on a PE-coated pipeline. Reproduced from Corrosion due to AC on metallic buried pipelines: Background and perspectives L. Di Biase APCE, 2nd National Conference, Rome, Nov. 1996; pp 21–22.

Figure 2 Typical AC corrosion on a bituminous-coated pipeline. Reproduced from Corrosion due to AC on metallic buried pipelines: Background and perspectives L. Di Biase APCE, 2nd National Conference, Rome, Nov. 1996; pp 21–22.

Figure 3 Typical AC corrosion on an fusion bound epoxy-coated pipeline. Reproduced from AC Induced Corrosion on Onshore Pipelines, A Case History, Roger Ellis Shell UK, Stanlow, 2001. Pipeline Manager UKOPA (United Kingdom Onshore Pipeline Operators' Association).

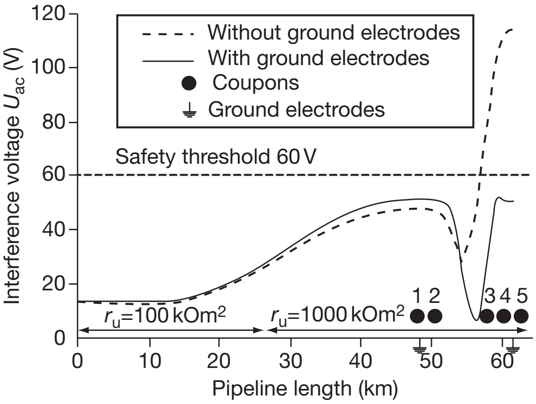

Figure 4 U_{ac} along a pipeline, DN 500, built in 1999.

4.22.5 Evaluation of the AC Interference Effects

On pipelines suffering from AC interference, pipe-to-soil protection potentials satisfying the requirements of the relevant standards do not guarantee efficient protection against corrosion. A specific approach to assess the likelihood of AC corrosion should be adopted.

The AC voltage induced on a pipeline is considered as the most important parameter to be taken into account when evaluating the adverse influences of an AC system.

The factors which mainly influence the AC corrosion phenomena are

- the induced AC voltage;
- the AC current density on the exposed metal;
- DC polarization;
- the size of coating defects;
- the local soil resistivity; and
- the local soil chemical composition.

In order to assess the actual risk of AC corrosion on a pipeline interfered by a high-voltage power line, the following methods can be used:

- Indirect assessment by installing coupons along the right of way of the pipeline where the corrosion risk is expected to be highest. Appropriate locations may be found at pipeline sections where the AC voltage reaches the highest values (see **Figure 4**).

These coupons (typically having a bare steel area of 1 cm^2) are bonded with cables to the pipeline, thus allowing to measure the voltage and the current density (DC, AC).

According to EN TS 15280 issued in March, 2006,[6] the following limits apply:

> The pipeline is considered protected from AC corrosion if the rms AC current density (J_{ac}) on the coupon is less than 30 A m^{-2}.

In practice, the evaluation of AC corrosion likelihood on a broader base can be made as follows:

- J_{ac} lower than 30 A m^{-2}: no or low likelihood;
- J_{ac} between 30 A m^{-2} and 100 A m^{-2}: medium likelihood;
- J_{ac} higher than 100 A m^{-2}: very high likelihood.

If electrical resistance (ER) coupons are used, the corrosion rate can be measured instantly. The coupon sensitivity should be carefully chosen in such a way that corrosion rates in the order of 0.01 mm $year^{-1}$ can be measured with sufficient accuracy over a period of some months.

- Indirect assessment by measuring the AC voltage along the pipeline and correlating the results with the actual operating conditions of the interfering high-voltage system.

According to EN TS 15280 issued in March, 2006,[6] the following limits apply:

To reduce the AC corrosion likelihood on a buried pipeline, the pipeline AC voltage, measured at selected test points, should not exceed at any time:

- 10 V at which the local soil resistivity is greater than 25 Ω m^{-1},
- 4 V at which the local soil resistivity is less than 25 Ω m^{-1}.

These values should be considered as threshold limits, which significantly reduce the AC corrosion likelihood; they are based on a long-term practical experience of many European pipeline operators.

- Direct assessment by performing potential gradient measurements along the pipeline, followed by excavation of sites where results indicate small defects in the coating. In case of pipelines that can be inspected with an intelligent pig and after a sufficient duration of the interference (e.g., 2 or more years), the loss of wall thickness may also be detected by ultrasonic or magnetic flux leakage intelligent pigs.

4.22.6 Mitigation of AC Interference Effects

In order to reduce the AC corrosion risk of an existing pipeline, generally, the AC voltage between pipeline and soil and the level of the CP system can be modified and adjusted by the operator.

The AC current density in a defect of the pipeline coating is directly proportional to the AC voltage, thus any reduction of the voltage reduces the likelihood of AC corrosion.

The following **Table 1** summarizes some possible mitigating measures and shows advantages and the associated, possible drawbacks:

- The level of the CP should also be considered. Some laboratory tests have shown[8] that excessive DC current densities (e.g., exceeding 5 A m^{-2}, measured on bare coupons) may increase the AC corrosion rate, due to the accumulation of hydroxyl-ions close to the metal–soil interface. The subsequent reduction of the leakage resistance at the defect may lead to increasing AC and DC current densities and an increased likelihood to reduce the passive film that is formed during the anodic half-wave of the AC current.[10,11]

According to the aforementioned reactions, in order to further reduce the likelihood of AC corrosion, besides the reduction of the AC voltage on a pipeline, its On-potentials (which are the driving force for the CP current) should not be much more negative than the ones needed to satisfy the CP Off-potential criterion of the pipeline.[11]

However, in case of DC-interfered pipelines with high-quality coatings (which are more prone to AC corrosion), it is difficult to practically cope with the reduction of the On-potential and the simultaneous control of the DC corrosion risk.

4.22.7 Major Evidence from Field Studies and Laboratory Tests

1. AC corrosion is more likely to happen on buried pipelines coated with high-resistance coatings (e.g., three-layer polyethylene) than on pipelines with older bituminous coating types (even though some case histories have been reported where AC corrosion also happened on pipelines coated with bituminous coatings).
2. AC corrosion usually appears in the area along the pipeline that is highest interfered.
3. AC corrosion likelihood could further be reduced by carefully adjusting the On-potential of pipelines to values no more negative than the ones needed to satisfy CP Off-potential criteria

Table 1 Summary of measures to reduce the AC voltage on interfered pipelines

Mitigation measure	*Advantages*	*Possible drawbacks*
Increasing the distance between pipe and high-voltage line/electrified railway	–	• Very efficient solution but only possible for new designed pipes or interfering systems • Not possible for existing systems
Arrangement of phase and earth wires of high-voltage line	–	• Only possible for new designed high voltage power lines • The solution only depends on the electricity company
Earthing of pipeline through AC discharge devices	• Generally good technical solution and cost efficient	• Problems may occur in high resistivity soil due to high resistance of groundings
Compensation of AC voltage	–	• Difficult to settle • High cost of installation and operation
Installation of isolating joints	• Good possibility to vary an optimum configuration by calculation and design	• Installation of joints involves direct interference with pipeline operation
Earthing of pipeline by using earthing wires	–	• High cost and poor efficiency

(e.g., EN 12954).[12] Nevertheless, this mitigation measure is to be considered quite difficult in its practical application and sometimes (e.g., presence of DC interference) not possible.

References

1. Shipley, J. W. *Eng. Y. Can*. **1927**.
2. Stalder, F.; Bindschedler, D. Wechselstromkorrosion – Einfluss der Bodenzusammensetzung; CEOCOR, Jahrestreffen: Lugano, 1992.
3. Corrosion due to AC on metallic buried pipelines: Background and perspectives L. Di Biase APCE, 2nd National Conference, Rome, Nov. 1996; pp 21–22.
4. AC Induced Corrosion on Onshore Pipelines, A Case History, Roger Ellis Shell UK, Stanlow, 2001. Pipeline Manager UKOPA (United Kingdom Onshore Pipeline Operators' Association).
5. Nielsen, L. V.; Baumgarten, B.; Cohen, P. On-site measurements of AC induced corrosion: effect of AC and DC parameters – a report from the Danish Activities-CEOCOR Dresden – Sector A – Germany, Paper N. 03, 2004.
6. CEN/TS 15280 – Evaluation of AC corrosion likelihood of buried pipelines – Application to cathodically protected pipelines, March 2006.
7. Detection of AC corrosion A. Ph. Pourbaix, Carpentiers (CEBELCOR, Brussels); Gregoor, R. (DISTRIGAZ, Brussels), CEOCOR Conference, BIARRITZ/FRANCE Oct. 2001.
8. A new electrochemical method for the detection of AC corrosion CEOCOR Dresden-Sector A, Paper N.07, 2004. Büchler M.; Stalder F.; Schöeneich H.G.; SGK, Swiss Company for corrosion protection Technoparkstr. 1, CH-8005, ZÜrich, Switzerland; Ruhrgas AG, Essen, Germany.
9. CIGRE Report: Guide on the influence of High Voltage AC Power Systems on Metallic Pipelines, 1995.
10. Nielsen, L. V. Role of alkalization in AC induced corrosion of pipelines and consequences hereof in relation to CP requirements; NACE 2005, paper #05188.
11. Büchler, M.; Voûte, C.-H.; Schöeneich, H.-G. Evaluation of the effect of cathodic protection levels on the AC corrosion on pipelines EUROCOR- 2007, Freiburg, Germany.
12. EN 12954 Cathodic protection of buried or immersed metallic structures – General principles and application for pipelines, January 2001.

Further Reading

CCITT: Directives concerning the protection of telecommunication lines against harmful effects from electric power and electrified railway lines. vol III, Capacitive, inductive and conductive coupling: physical theory and calculation methods, ITU Geneva 1989.

IGU (International Gas Union) Milan – Fault Location on Pipeline Coatings, 1994.

CeoCor (Comité d'etude de la Corrosion et de la Protection des Canalisation), AC Corrosion on Cathodically Protected Pipelines – Guidelines for risk assessment and mitigation measures, 2001.

Nielsen, L. V.; Nielsen, K. V.; Baumgarten, B.; Breuning-Madsen, H.; Cohn, P.; Rosemberg, H. AC induced corrosion in pipelines: Detection, characterisation and mitigation; NACE Corrosion, 2004.

Yunovich, M.; Thompson, N. G. AC corrosion: Corrosion rate and mitigation requirements; NACE Corrosion, 2004.

4.23 Cathodic Protection Instrumentation

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Abbreviations

AC Alternating current
ALWC Accelerated low water corrosion
BS British Standard
CIPS Close interval potential survey
DC Direct current
DCVG Direct current voltage gradient
DMM Digital multimeter
emf Electromotive force
EN European Norm
GPS Global positioning system
SHE Standard hydrogen electrode
SRB Sulfate reducing bacteria

Symbols

I Current
R Resistance
V Voltage

4.23.1 Introduction and Historical Background

4.23.1.1 Voltage, Current, and Resistance Measurement

This chapter is essentially a review of former methods for electrical measurement. Although a description of these older instruments and methods is now of historical interest, it presents a valuable understanding of the principles of measurement, which are obscured when considered in conjunction with modern digital instruments.

Historically, nearly all DC electrical measuring instruments were of the moving-coil permanent-magnet type, which gave a coil deflection (and thus pointer deflection) proportional to the current in the coil. The damping of the movement to prevent over swing or the oscillation of the needle is provided by the eddy currents induced in the metal former on which the coil is wound, and further damping (i.e., critical damping) can be obtained by placing a low resistance across the coil. The main advantages of this type of instrument are uniformity of scale, high torque–weight ratio, and low power consumption. By the insertion of suitable shunts and/or resistances, it is possible to use one instrument to measure both current and voltage over a wide range.

It is often not appreciated that modern digital multimeters (DMMs) function in exactly the same way as traditional instruments except that the moving coil meter is replaced by an electronic operational amplifier and that the display is digital rather than analog. The main measurement advantage of a DMM is their considerably higher input impedance as voltmeters. They also have a number of obvious technical advantages, such as robustness, ease of use, etc.

4.23.1.2 Voltmeters and Potentiometers

The current flowing through any potential-measurement circuit must be as small as possible to avoid errors due to polarization of the voltage source. Moreover, if the current flow is too large, errors will be introduced owing to the voltage drop caused by the contact resistance between the reference electrode and the electrolyte. It is thus clear that the prime requirement of an accurate potential measurement circuit is high resistance. For direct-reading instruments, the input impedances were typically as low as $50\,000\,\Omega\,V^{-1}$, and instruments were commercially available with input impedances of $\sim 1\,M\Omega\,V^{-1}$. Direct-reading meters were usually made to show several ranges, which are obtained by the use of suitable resistances placed in series with the indicating instrument (Figure 1).

For digital instruments, the input impedance is dependant upon the characteristics of the input amplifier used; instruments are available in three bands of performance: 10–20 MΩ for inexpensive, robust devices; 1 GΩ for more specialist equipment; and $>10^{14}\,\Omega$ for electrometer type instruments. This avoids significant polarization of reference electrodes and measurements of accurate steel/electrolyte/electrode potentials in high resistivity electrolytes in soils and concretes. However, it is still important to understand the principles involved.

To measure structure/electrolyte/electrode potentials in electrolyte resistivities in excess of 20 Ω m, bridge 'backing off' potentiometer instruments as shown in Figure 2 or potentiometric voltmeters as

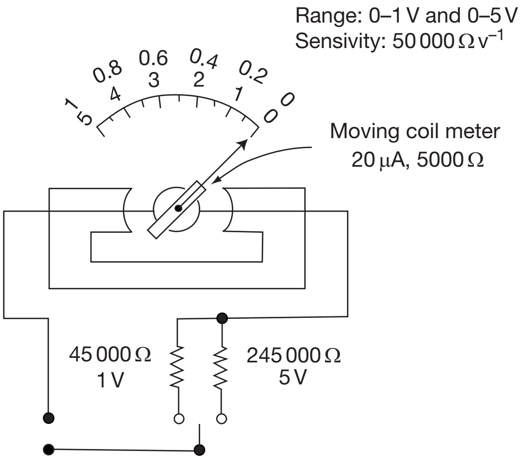


Figure 1 Direct reading voltmeter.

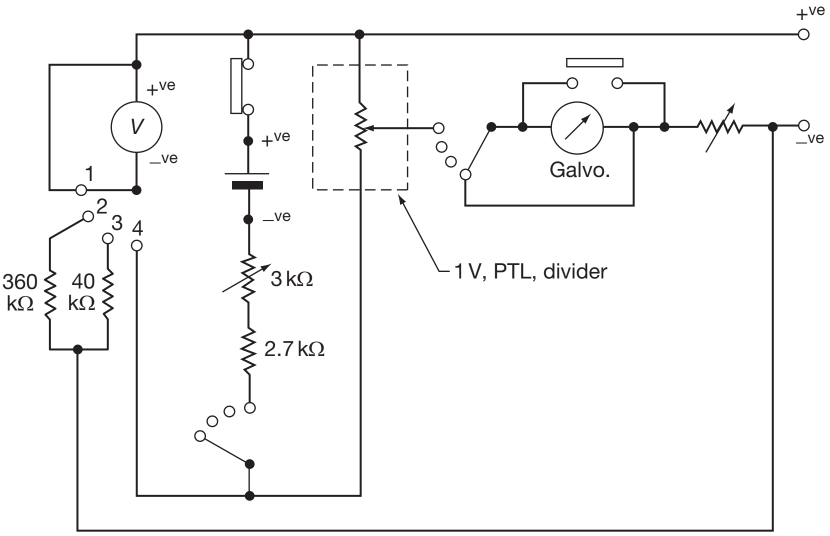


Figure 2 Potentiometer voltmeter (courtesy of The Post Office).

illustrated in Figure 3 were traditionally used until the advent of high-impedance digital technology.

In both types of instrument, the voltage to be measured is balanced against an external applied voltage (usually from batteries within the instrument). At balance, no current flows through the external circuit and thus errors due to contact resistance and source impedance are eliminated.

The potentiometer requires to be calibrated against a standard cell, while with the potentiometric voltmeter, the voltage to be measured is balanced against a battery emf, using uncalibrated resistors and the voltmeter as a galvanometer. At balance, the voltage is transferred to the voltmeter and read directly. The magnitude of voltage that can be measured by both instruments is limited by the maximum voltage of the (usually) dry cell they contain. It is, however, possible to extend the range by using a potential divider or volt box. For normal field work, the potentiometric voltmeter was the more popular instrument, being usually of lighter construction and not requiring calibration against a standard cell. Where extremely small potentials (usually potential shifts) of the order of 1 mV were to be measured, however, the potentiometer was more suitable and accurate.

The technique adopted in measuring structure/electrolyte potential is illustrated in Figure 4. It should be noted that the position of the reference electrode in relation to the structure is important. Theoretically the half-cell should be placed as near to the structure as possible (i.e., within a few millimeters) to avoid *IR* (ohmic) drop in the electrolyte. This is often not possible in practice as, for example, with a buried pipeline. In such a case, the cell should be placed in the soil directly over the structure, and it is accepted good practice, historically, to allow a 'safety factor' of say 50 mV over and above the minimum protective potential to compensate for IR drop.

These IR drop errors are now (and have been since the 1950s in continental Europe) minimized by the measurement of Instant OFF potentials, typically within a period of 0.1–1 s after interrupting the cathodic protection current. There remains (in 2009) a debate in the US pipeline industry regarding the need for such 'sophistication' in measurement and whether there is a need to increase the level of polarization to pipelines to accommodate the previously unknown IR drop errors, in particular for pipelines where existing levels of polarization have historically controlled corrosion to adequate levels. The key issue appears to be that the magnitude of the IR error will vary with soil resistivity, coating quality/defect size, the quality of polarization films on the steel surface and may be as much as several hundreds of millivolts; without the 'sophistication' of Instant OFF potential measurements, there can be no reliance on the accuracy of potential measurements. This concept is well accepted in most of the world.

4.23.1.3 Current-Measuring Instruments (Ammeters)

These may be classified generally according to whether they are used to measure current delivered or drained by a structure receiving cathodic protection or to measure current flowing within the structure itself.

By the use of suitable shunts, the basic moving-coil movement (and the DMM) can be adapted to measure an almost unlimited range of currents. Figure 5 illustrates a direct-indicating instrument with shunt to

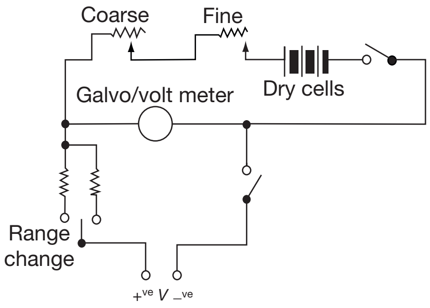


Figure 3 Basic circuit potentiometer voltmeter.

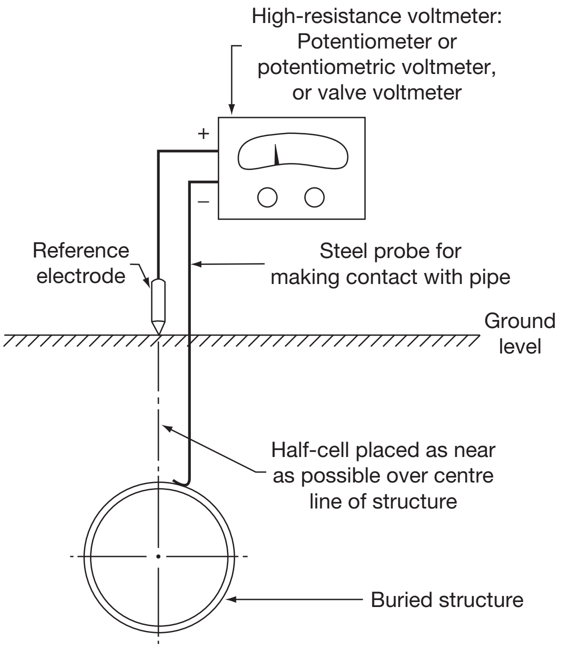


Figure 4 Measurement of structure/electrolyte potential.

measure current up to 5 A DC. To ensure that the resistance of the circuit is not materially altered by the insertion of an ammeter, it is usual to install either a shunt or the meter itself (usually a moving-coil meter with internal shunt) permanently in the circuit. Ammeter shunts are normally of the four-terminal type to avoid contact resistance errors, that is, two current terminals and two potential terminals.

Importantly, in making measurements of current flowing within a structure, it is extremely important that additional resistance, for example, an ammeter shunt, is not introduced into the circuit, as otherwise erroneous results will be obtained. One method is to use a tong test meter. Such instruments are, however, not particularly accurate, especially at low currents, and are obviously impracticable in the case of, say, a 750-mm diameter pipeline. A far more accurate method and one that can be applied to all structures is the zero-resistance ammeter or, as it is sometimes called, the zero-current ammeter method. The basic circuit of such an instrument is shown in Figure 6.

From Figure 6, it will be seen that if I_b is adjusted until there is zero voltage on the voltmeter, then $I_s = I_b$. When this type of instrument is used to measure current in, say, a bond between one structure and another, if simultaneous measurements are made at locations on the structure (i.e., interference testing) inaccurate results will be obtained, because at balance there is no current in the structure at the measurement point, and this could materially alter the current distribution to the structure.

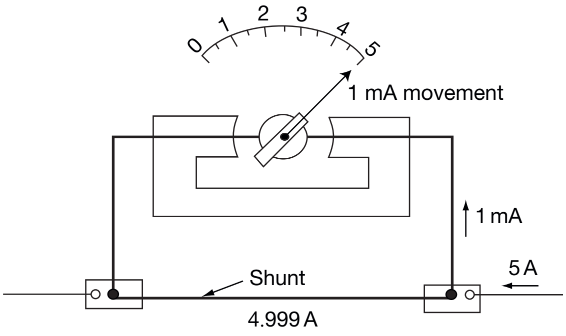


Figure 5 Direct-indicating current measuring instrument (ammeter).

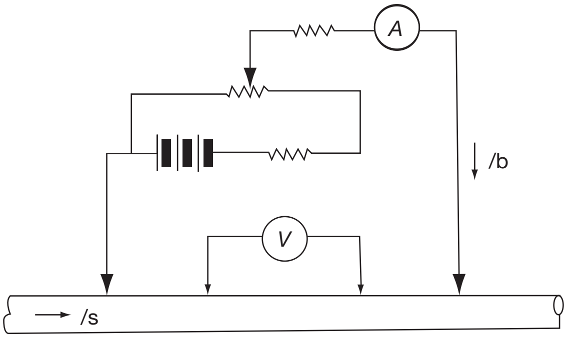


Figure 6 Zero-resistance ammeter.

The zero-resistance ammeter is seldom employed for routine testing; however, the above circuit can be used utilizing modern digital instruments and a current source to 'back off' the current flowing in the structure and measure this current in the external ammeter/shunt. As already noted, a DMM measures current in precisely the same manner as a moving coil instrument. Thus, the modern use of a DMM does not negate an understanding of how current shunts function in practice.

4.23.1.4 Measurement of Resistivity/Conductivity

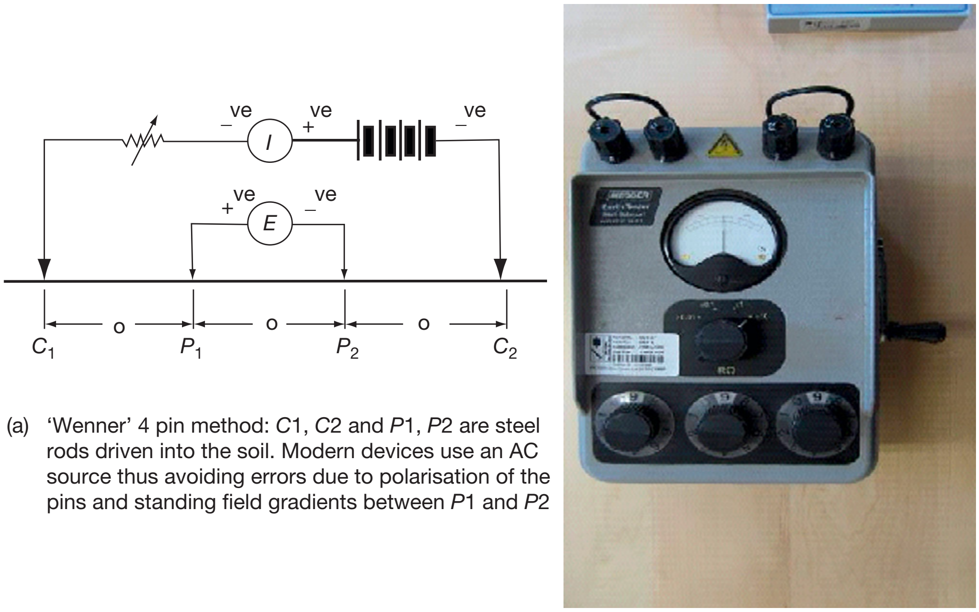
The most usual method of measuring soil resistivity is by the four-electrode 'Wenner' method. Figure 7 indicates the basic circuit. The mean resistivity R_m is given by

$$R_m = 2a(E/I)$$

where I is the current applied between the current electrodes C_1 and C_2 and E is the potential developed between the potential electrodes P_1 and P_2 by the current I^*. The value given by this method is the average resistivity of the soil to a depth equal to the spacing of the electrodes. The average is weighted to the surface material as the 'sampled' volume is actually a hemisphere below the two center pins P_1 and P_2 in Figure 8. There is a simple calculation technique whereby measurements taken at the same general location but at different pin spacings/depths can be expressed as the resistivity of the individual layers from the surface to the maximum depth measured. This analysis is extremely useful in assessing the likely corrosivity at pipeline depth and is essential as a precursor to the design calculation of groundbed resistance/optimum dimensions.

It is most important to note that for accurate and consistent results, the electrodes must be equidistant from one another and placed in a straight line. The relatively simple setup, illustrated in Figure 7, suffers from inaccuracies arising from the polarization of the potential electrodes and effects of possible stray currents in the soil.

To avoid the errors of polarization and stray currents, four-pin earth resistivity meters are employed.



(a) ‘Wenner’ 4 pin method: $C1$, $C2$ and $P1$, $P2$ are steel rods driven into the soil. Modern devices use an AC source thus avoiding errors due to polarisation of the pins and standing field gradients between $P1$ and $P2$

(b) 4 Pin Earth Resistivity Meter using a hand cranked AC generator. More modern devices use battery/electronic AC circuits but this device remains one of the most sensitive

Figure 7 ‘Wenner’ 4 pin earth resistivity determination.

These use an alternating current produced from battery-powered electronic, or in older equipment, a hand-generated current passed through the current coil of an ohmmeter and then through a current reverser so that an alternating current is delivered. The effective resistance is measured by a modified Wheatstone bridge with balance indicated by a galvanometer, Figure 8.

The resistivity of an electrolyte can also be measured by passing a known current through a known length and cross section of the electrolyte and measuring accurately the voltage drop across the length. It is normal to use alternating current in order to avoid polarization effects. Special cells also exist for use with resistivity meters, which are so constructed and calibrated that resistivity can either be read directly from the instrument or simply calculated from the product of the measured resistance and known cell constant. Measurements of resistivity on samples will give accurate results only on liquid electrolytes and are also used commonly for the measurement of selected soil or saline mud samples, but caution should be exercised as the value of resistivity measured will vary with the degree of compaction of the soil. The measurement of electrolyte conductivity, the reciprocal of the resistivity, is calculated from the resistivity as measured by some of the methods described earlier.

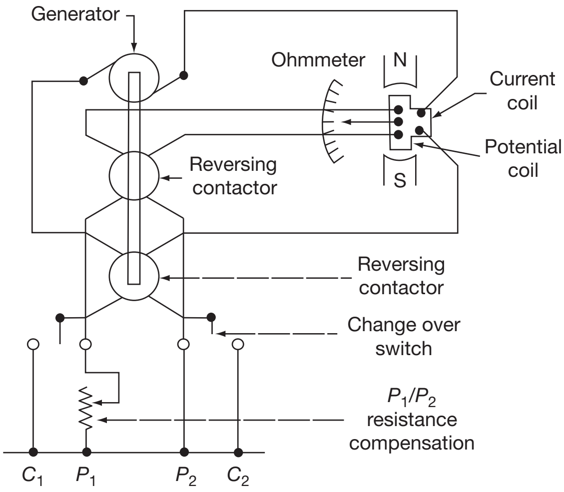


Figure 8 ‘Megger’ earth resistivity meter (courtesy Evershed and Vignoles).

Often it is necessary in designing a cathodic-protection system to know the conductivity of a protective coating (coating conductance) on a structure. This measurement may be carried out in an approximate manner by finding the resistance between an electrode of known area placed in contact with the coating and the structure itself. The electrode placed on the structure can be either of thin metal foil or, preferably, of material such as flannel soaked in weak acidic solution. The resistance between the pad and the metal is measured by means of a resistivity meter, as previously described. More accurate data on coating conductance can be calculated, postconstruction and after commissioning the cathodic protection system, using the classic attenuation formulae and measured pipe/soil potential shifts along the pipeline. In some pipeline construction contracts, such measurements are used as a quality management tool and failure to comply with a maximum coating conductance will result in remedial works being required.

4.23.1.5 Measurement of Resistance/Conductance

As previously mentioned, four-pin earth resistivity meters can be used to measure resistances. Modern DMMs are also able to measure resistance. The measurement of resistance to the remote earth of a metallic structure is normally carried out with a four-electrode instrument. The connections are shown in Figure 9. A current is passed between the structure and a remote electrode and the potential difference measured between the structure and a second remote electrode. In this way, the ohmmeter records the resistance of the structure to earth, that is, V/I. The spacing of the electrode from the structure is important and must be such that the remote potential electrode lies on the horizontal part of the resistance–distance curve, as shown in Figure 9. Generally speaking, a minimum distance of 15 m from the structure is necessary for the potential electrode to lie on the flat part of the curve, with the current electrode usually at least twice the distance of the potential electrode.

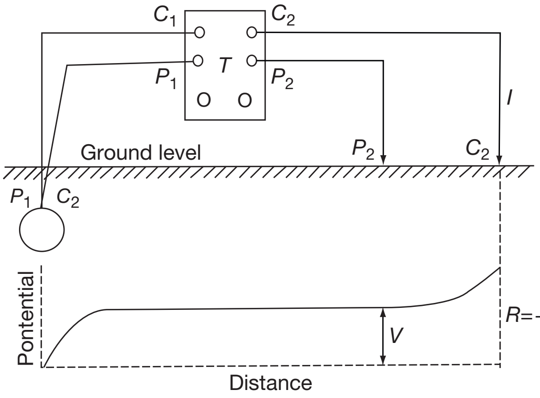


Figure 9 Measurement of resistance of structure to remote earth.

4.23.2 Basic Requirements for Routine Testing Instruments

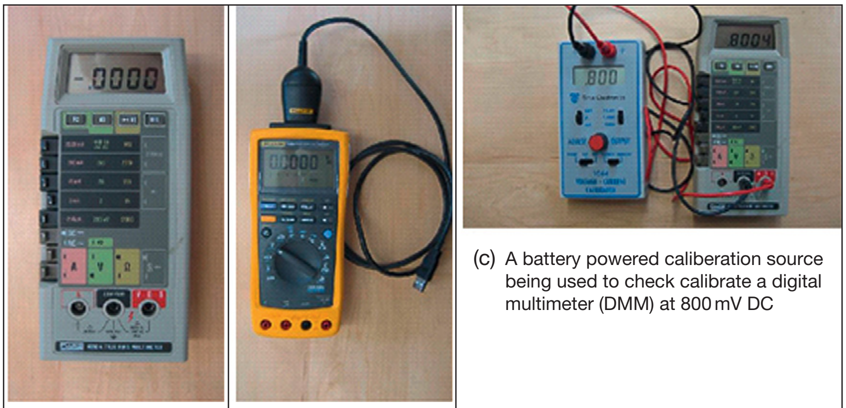
4.23.2.1 Digital Instrumentation

All instruments used in cathodic protection work must be sufficiently rugged for field use with appropriate ranges, resolution, and accuracy. They should be externally, formally, calibrated and calibration records and copies of the certificates should be available to the engineers or technicians using them so that they can be certain that the instruments they use are within calibration.

Most cathodic protection measurements comprise DC voltage/potential values, along with resistance and DC currents, either low current directly via shunts within the meter or using external high-current shunts, plus a range of AC measurements (subject to appropriate training and certification of personnel to work on mains voltage equipment). Thus, a wide range of conventional electrical test multimeters are extensively used. For general field applications, suitable instruments are available that are water resistant to BS EN 60529 IP 64 dust-tight and splash resistant or IP 67 dust-tight and resistant to immersion; explosion hazard certificated equipment is available for use in hazardous areas. Some typical high-quality digital instruments are shown in Figure 10 and will have characteristics generally similar to those listed in Table 1.

These devices comprise a microcomputer, a data acquisition device, and an analog-to-digital converter along with a digital display, selector switches, fuses, shunts, battery, and terminals. The instruments include self-test and internal calibration checks; DC voltage measurements take typically 0.5–1 s to complete and replenish on the display, whereas AC voltage measurements may take considerably longer and resistance measurements generally take longer than DC measurements and less than AC measurements.

For the important DC voltage measurements used in performance assessment of cathodic protection systems, the input impedance is important, particularly for measurements in high-resistivity soils and concretes. Typical input impedance values for the normal 2 V DC range will be 10 or 20 MΩ, which



(a) This DMM can be switched between 10 MΩ and >10 000 MΩ input impedance on 200 mV and 2 V DC ranges

(b) This DMM can log (record) data and transfer to a computer via the USB connector

(c) A battery powered caliberation source being used to check calibrate a digital multimeter (DMM) at 800 mV DC

Figure 10 Typical digital multimeters (DMMs) used in cathodic protection measurements.

Table 1 Typical characteristics of a DMM

Voltage range		*Resolution*		*Accuracy, ±% of reading + no. of digits*	
DC	AC	DC	AC	DC	AC: 45–1000 Hz
200 mV	200 mV	0.01 mV	0.01 mV	0.04% + 2	0.2% + 10
2 V	2 V	0.1 mV	0.1 mV	0.04% + 2	0.5% + 10
20 V	20 V	1 mV	1 mV	0.05% + 2	0.5% + 10
200 V	200 V	10 mV	10 mV	0.05% + 2	0.5% + 10
1000 V	750 V	100 mV	100 mV	0.05% + 2	1% + 10
Current range		*Resolution*		*Accuracy, ±% of reading + no. of digits*	
DC	AC	DC	AC	DC	AC: 45–1000 Hz
200 µA	200 µV	0.01 µV	0.01 µV	0.02% + 2	0.75% + 10
2 mA	2 mV	0.1 µV	0.1 µV	0.02% + 2	0.75% + 10
20 mA	20 mV	1 µV	1 µV	0.03% + 2	0.75% + 10
200 mA	200 mV	10 µV	10 µV	0.03% + 2	0.75% + 10
2 A	2 A	100 µV	100 µV	0.03% + 2	1% + 10
Resistance range		*Resolution*		*Accuracy, ±% of reading + no. of digits*	
DC	AC	DC	AC	DC	AC: 45–1000 Hz
200 Ω	200 Ω	0.01 Ω	0.01 Ω	0.07% + 4	0.07% + 2
2 kΩ	2 kΩ	0.1 Ω	0.1 Ω	0.07% + 2	0.07% + 2
20 kΩ	20 kΩ	1 Ω	1 Ω	0.07% + 2	0.07% + 2
200 kΩ		10 Ω		0.07% + 2	
2 kΩ		100 Ω		0.15% + 2	
2 MΩ		10 kΩ		0.2% + 2	
20–100 MΩ		100 kΩ		1% + 3	
100–300 MΩ		1 MΩ		2% + 3	

will be insufficient for accurate measurements with normal reference electrodes in soils and concretes of $\sim > 500\,\Omega$ m. Very few instruments are available with a switchable input impedance; one favored for use in reinforced concrete applications is switchable between 10 and > 10 000 M Ω.

Noise rejection, the avoidance of error in the DC measurement due to AC, which may be superimposed on the structure being measured (typically but not exclusively a pipeline) or may be collected (typically by induction) into the test cables used in the measurements, is also important in measurements of cathodic protection DC voltage, particularly with high-impedance instruments where very low currents flow in the measurement circuits. Good quality instruments will have high levels of noise rejection with typical good values being > 60 dB at 50–60 Hz normal mode noise rejection and > 120 dB common mode noise rejection at DC and > 90 dB at 50–60 Hz.

With the ability to deploy to site such extremely versatile and accurate multifunction digital test equipment, cathodic protection personnel should also use, some on a daily basis or at the start and end of a 'campaign' of measurements, a portable calibration device or a second instrument such that the accuracy of the instrument used for measurements in the field can be confirmed.

4.23.2.2 Measurement Errors

It is all too easy to be 'fooled' by an instrument into assuming that the number presented on its display, or recorded for later analysis, is somehow 'accurate.' This is completely untrue. The terms sensitivity, accuracy, and precision have precise definitions and it is important for operators to understand what they mean.

Sensitivity is the smallest possible signal that an instrument can measure, accuracy is the degree to which the measurement is close to the actual (true) measurement, while precision is the degree to which further measurements will show the same or similar results (also called reproducibility).

A single measurement or a series of measurements may be accurate (but not precise), precise (but not accurate), both of these, or neither. These differences essentially relate to errors in measurement, which may be random or systematic. Random error relates to unquantifiable differences in how a measurement is undertaken; systematic error is an always-present offset from the true value. This difference is illustrated in Figure 11.

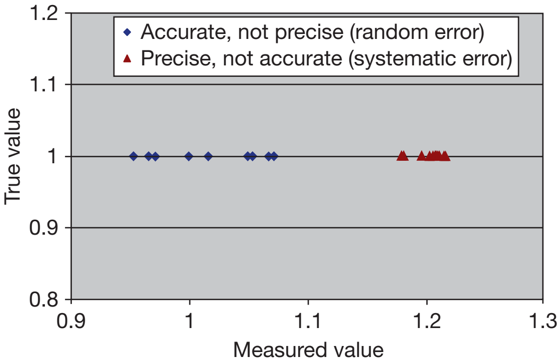


Figure 11 Random and systematic errors.

4.23.3 Reference Electrodes

The generally accepted criteria for the effectiveness of a cathodic protection system are all related to the structure/electrolyte potential. The protection criteria for carbon (mild) steel in various electrolytes are summarized in Table 2.

Note: Aluminum alloys have protection criteria similar to those for steel. Higher strength steels, aluminum, high-strength copper–nickel alloys, and coated steels have negative potential limits to avoid hydrogen embrittlement and coating disbondment or, in the case of aluminum, amphoteric corrosion. Elevated temperatures require more negative protection criteria. Stainless steels have less negative protection criteria and duplex stainless steels may be subject to hydrogen embrittlement. Steel in concrete has a potential limit of −1100 mV for reinforcing steel and −900 mV for prestressing steel both referred to Ag/AgCl/0.5 M KCl.

In order to measure the metal/electrolyte potential, it is necessary to make a metallic contact to the metallic structure itself and an electrolytic contact with the electrolyte (soil, water, or concrete). The problem of connection to the structure normally presents no significant difficulties except in respect of access; for example, in the case of concrete, the steel needs to be exposed for connection and the electrical continuity between the bars needs to be established. However, contact with the electrolyte must be made with a reference electrode that presents a stable interface or half-cell potential with the electrolyte under all conditions. (If e.g., an ordinary steel probe were used as a reference electrode, then inaccuracies would result for two main reasons: first, electrochemical action between the probe and the soil, and second, polarization of the probe owing to current flow

Table 2 Cathodic protection criteria for carbon steel in various environments

Electrolyte	*Prime criteria*	*Alternative criteria*	*Alternative criteria for consideration*	*Prime standards*
Aerobic soils, insignificant microbial activity (notably sulfate reducing bacteria SRBs)	More negative than −850 mV referred to $Cu/CuSO_4$ (sat.) polarized potentials (instant OFF)	100 mV decay or polarization (measured instant OFF)	More negative than: −750 mV for $100 < \rho < 1000$– 650 mV for $\rho < 1000\,\Omega\,m$	ISO 15589–1: As revised for BS EN 14919–1. BS EN 12954 (not 100 mV decay/shift)
Anaerobic soils with significant microbial activity (notably sulfate reducing bacteria SRBs)	More negative than −950 mV referred to $Cu/CuSO_4$ (sat.) polarized potentials (instant OFF)	N/A	N/A	ISO 15589–1 As revised for BS EN 14919–1. BS EN 12954
Aerobic Waters, insignificant microbial activity (notably SRBs)	More negative than −800 mV referred to Ag/AgCl/sea water (equivalent to −850 mV referred to $Cu/CuSO_4$ (sat.) Polarized potentials Instant OFF)	N/A	N/A	BS EN 12473
Anaerobic waters (e.g., under decaying marine growth as in accelerated low water corrosion (ALWC) with significant microbial activity (notably SRBs)	More negative than −900 mV referred to Ag/AgCl/sea water (equivalent to −950 mV referred to $Cu/CuSO_4$ (sat.) polarized potentials instant OFF)	N/A	N/A	BS EN 12473 CIRIA C 634 management of ALWC in steel marine structures
Concrete	Potential decay from instant OFF of: At least 100 mV during 24 h Or At least 150 mV during a period > 24 h	More negative than −720 mV referred to Ag/AgCl/0.5 M KCl (equivalent to −720 mV referred to Ag/AgCl/sea water) (instant OFF)	Fully depolarized or unprotected steel in concrete less negative than −150 mV referred to Ag/AgCl/0.5 M KCl (passive within protective concrete)	BS EN 12696

through the measuring circuit.) Reference electrodes are metal electrodes immersed in a solution of one of its salts; in the simplest form the copper/copper sulfate (saturated) reference electrode, $Cu/CuSO_4$ (sat.), comprises a pure copper electrode immersed in a saturated solution of $CuSO_4$.

The silver/silver chloride electrode range is of a second type where the metal electrode is coated with a salt of that metal and then immersed in a solution of the salt. Thus, there are many types of silver/silver chloride electrodes, with a range of electrode potentials; calling an electrode a silver/silver chloride electrode or Ag/AgCl is an incomplete description and can lead to confusion. Two types of these electrodes are commonly used in cathodic protection. These are the Ag/AgCl/sea water electrode the potential of which is ONLY stable in sea water of 3.5 wt% salinity. The potential changes with salinity and thus these electrodes should only be used in open sea water. The second is the Ag/AgCl/KCl electrode where the concentration of the potassium chloride will determine the electrode potential. For convenience, the Ag/AgCl/0.5 M KCl, which has an electrode potential within a few millivolts of the Ag/AgCl/sea water (in 3.5 wt% salinity), is widely used but other concentrations are also available. These electrodes are widely used in steel in concrete applications, both as portable survey electrodes and as electrodes permanently cast into concrete, but they should also be used in estuarine waters and can be used as permanent buried electrodes in saline soils. The KCl concentration is maintained in a fixed, stable, condition as is necessary for long-term electrode potential stability by using a very impermeable porous plug and a gel agent in the solution. The Ag/AgCl/KCl electrode is probably the best reference electrode for measuring potentials of waters at elevated temperatures.

All reference electrodes are subject to small variations in potential due to temperature. For example, the $Cu/CuSO_4$ (sat.) electrode potential changes at ~0.9 mV/°C so that a pipe/soil potential measurement recording −900 mV. $Cu/CuSO_4$ (sat.) on a hot day (30 °C) will, at 5 °C, be measured as −878 mV. $Cu/CuSO_4$ (sat.). Electrode potential changes also occur when the Cu electrode/electrolyte interface is exposed to sunlight; although these effects are reportedly measured to be as much as 50 mV more negative in sunlight, they appear to reduce with repeated exposure and are generally accepted to be limited to 10 mV. It is good practice to cover the transparent housing of these electrodes when used outdoors. To avoid errors due to polarization effects, it is necessary to restrict the current density on the copper rod to a value not exceeding $20\,\text{mA cm}^{-2}$; this is not an issue with modern digital instrumentation.

The $Cu/CuSO_4$ (sat.) electrode is vulnerable to electrode potential changes due to chloride contamination; it should not be used in chloride-rich environments such as sea water, estuarine muds, and similar. These electrodes have been unfortunately used in the portable surveys of steel/concrete potential in reinforced concrete structures such as highway bridges, largely because the ASTM Test Method (C876) unwisely specified its use. If, as is the case with most $Cu/CuSO_4$ (sat.) electrodes, there is contamination of the wooden or ceramic porous plug with copper sulfate, there is a likelihood that there will be significant errors in measurements that may reach 120 mV. This is due to a concentration gradient effect known as 'streaming potentials' as the concrete is contaminated with copper sulfate. As this error cannot be detected or quantified, it is poor practice to use $Cu/CuSO_4$ (sat.) electrodes in surveys of steel in concrete.

Another electrode used in sea water and often wrongly called a reference electrode is the zinc electrode. Commonly, both 99.99% pure zinc and the US Mil Spec 18001 anode grade (~99.3% pure with small additions of Cd and Al to avoid passivation) are used as electrodes for potential measurement. Neither is accurate and surface condition can result in significant changes in electrode potential; they are however rugged and reliable if inaccurate. If these electrodes are used for permanent installation (they are not normally used for survey purposes except for approximate potential measurements in oil-contaminated ballast water tanks where the electrode can be introduced through a 'crust' of oil and still operate with reasonable accuracy), it is good practice to draw a small current from the electrodes during nonmeasurement periods or if used for potential sensing and control, so that the consumption of the zinc will keep the surface clean and active.

All reference electrode potentials are related to each other. Thus, if the potential of the structure is found to be + 200 mV versus Zn, it will be −900 mV versus $Cu/CuSO_4$ (sat.), and −850 mV versus Ag/AgCl/(sat.) KCl. Approximate values of the these reference electrodes on the standard hydrogen scale (SHE) are as follows: $Cu/CuSO_4$ (sat.) = 0.30–0.32 V; Ag/AgCl (sat.) KCl = 0.020 V (0.025 V in sea-water); Zn/sea-water = −0.75 V; this is shown in Table 3. A historic (Admiralty pattern) electrode is shown schematically in Figure 12, while examples of current reference electrodes are illustrated in Figure 13.

4.23.4 Other Equipment

4.23.4.1 Recording Instruments

Miniaturization of electronic components has enabled the construction of compact, portable, battery-operated recording voltmeters. The principal use of these instruments is to measure pipe/soil potential fluctuations over a period of time, in particular for monitoring the effects of stray traction currents on pipelines. The instruments can be utilized with shunts to measure current variations.

Modern units are now sufficiently small such that they may be mounted into conventional pipeline pipe/soil potential measurement test posts. They can communicate via satellite or global positioning system (GPS) networks and can operate for many months without battery change, for example, as shown in Figure 14. Such units are now becoming of sufficiently low cost to enable operators to consider using them to replace routine pipe/soil potential measurements by technician staff.

4.23.4.2 Ancillary Instruments

Apart from the instruments described in previous paragraphs, there are others that, while not directly connected with cathodic protection as such, are extremely useful tools to a corrosion engineer. They include pH meters, Redox probes, protective-coating test instruments, and buried-metal-location instruments.

Table 3 Approximate comparison of potentials (*V*) using Zn/seawater electrodes, Cu/$CuSO_4$ (sat.), and Ag/AgCl, saturated KCl reference electrodes

Silver/silver chloride/ saturated potassium chloride	−1.3	−1.2	−1.0	−0.8	−0.6	−0.4	−0.2	0
Silver/silver chloride/ seawater	−1.4	−1.2	−1.0	−0.8	−0.6	−0.4	−0.2	0
Copper/copper sulphate	−1.4	−1.2	−1.0	−0.8	−0.6	−0.4	−0.2	0
Zinc/seawater	−0.4	−0.2	0	+0.2	+0.4	+0.6	+0.8	+1.0
Calomel/saturated potassium chloride	−1.4	−1.2	−1.0	−0.8	−0.6	−0.4	−0.2	0

Structure/electrolyte potential (V)

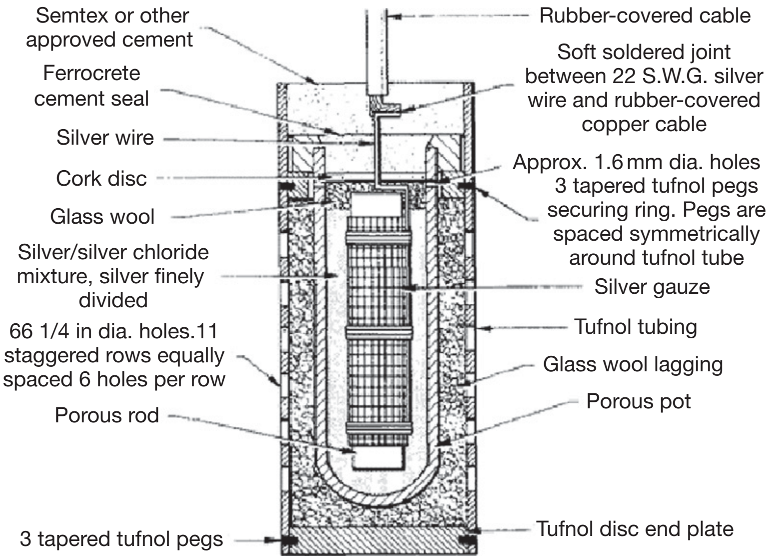
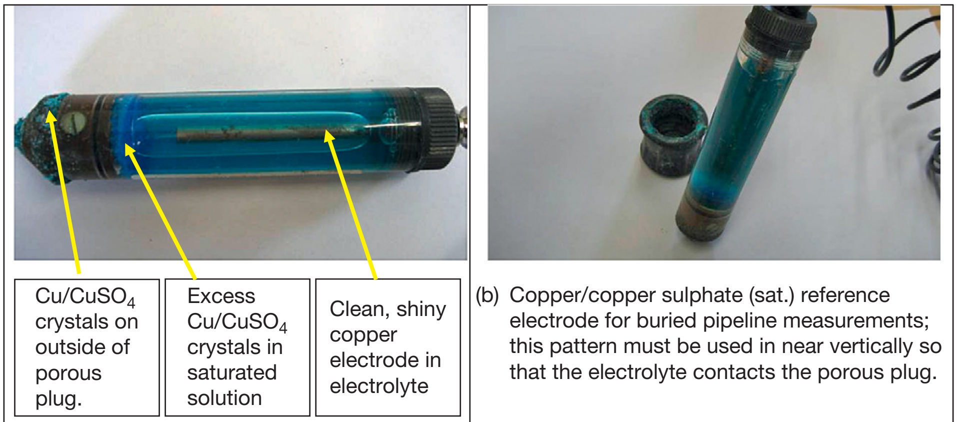
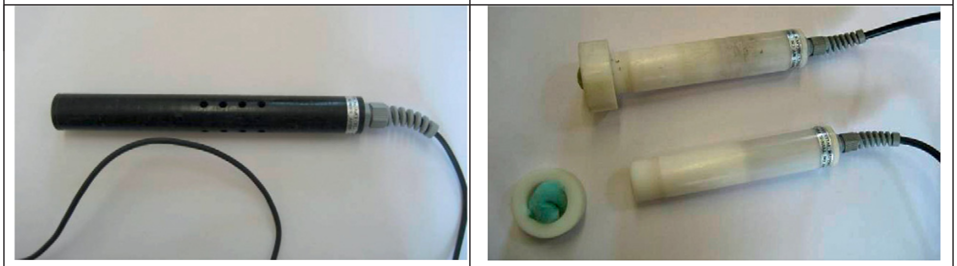


Figure 12 Historical silver/silver chloride half-cell (admiralty pattern). The electrode is immersed in a chloride-containing solution, which diffuses through the porous pot and thus comes into contact with the Ag/AgCl mixture.



(a) Copper/copper sulphate (sat.) reference electrode for buried pipeline measurements.

(b) Copper/copper sulphate (sat.) reference electrode for buried pipeline measurements; this pattern must be used in near vertically so that the electrolyte contacts the porous plug.



(c) Silver/silver chloride/sea water reference electrode as used for measurements in open seawater. It is weighted to be deployed vertically within still water.

(d) Silver/silver chloride/0.5 M potassium chloride reference electrodes as used for measurements of steel/concrete/electrode potentials using the wet sponge to interface between the porous plug and the concrete. Also used in open sea water, estuarine water, fresh water and saline soils. Electrode potential within a few millivolts of Ag/AgCl/seawater electrodes.

Figure 13 Typical reference electrodes used in cathodic protection surveys.

4.23.4.2.1 High-voltage coating-testing equipment

When cathodic protection is applied to a structure that has a protective coating, the current required is proportional to the bare metal area on the structure. Thus, whenever a protective coating is applied, it should be of good quality, with very few failures or pin holes in it, so that the cathodic protection system may be economical.

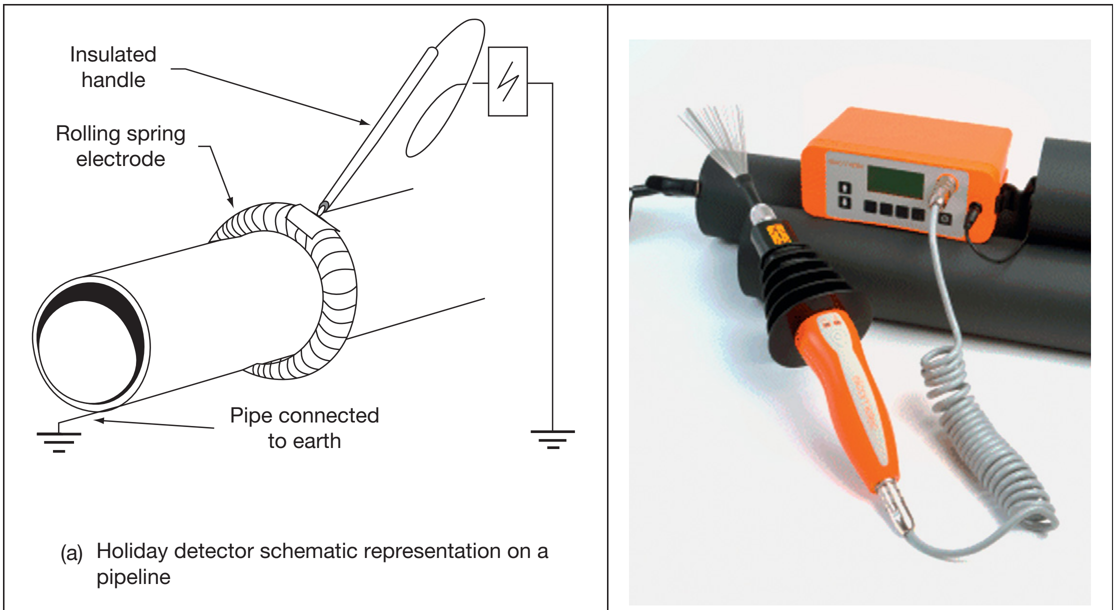
It is standard practice, particularly in the case of pipelines, to carry out an inspection of the protective coating (after application) with a high-voltage tester, known as a holiday detector. Basically, a high voltage is applied between an electrode placed on the coating and the structure. At any ‘holidays’ (flaws) in the coating, a ‘spark-over’ occurs and is usually accompanied by a visual or audible alarm. For pipelines, the electrode often takes the form of a rolling spring clipped round the pipe. Other electrodes are in the form of wire brushes. The high voltage is obtained from batteries and electronic circuitry with a high-tension coil. Such an instrument is illustrated in Figure 15.

For the examination of paint films or special coatings, for example, pipe linings, low-voltage holiday detectors with wet sponge electrodes are available. The choice of voltage for use with a holiday detector depends on the thickness and type of coating applied to the structure. As a guide, in the case of pipelines, a voltage equivalent to $\sim 5\,\text{kV mm}^{-1}$ thickness is used in testing a thick-film enamel coating.

(a) Test post monitor unit which can measure pipe/soil potentials daily for 5years and transmit the data via GSM/SMS network (courtesy Abriox Ltd.)

(b) Multichannel DC or AC voltage or DC current measurement data logger for field deployment (courtesy abi CP-log)

Figure 14 Recording devices for cathodic protection field deployment.



(a) Holiday detector schematic representation on a pipeline

(b) Modern DC holiday detector which can be used for a variety of coatings/thicknesses with test voltage in the range 0.5–30 kV (Courtesy of Elcometer Ltd.)

Figure 15 Holiday detector.

4.23.4.2.2 Buried metal locating and attenuation measuring instruments

Instruments in this category are used to locate buried metallic structures, to detect possible electrical discontinuities in buried structures, to locate possible junctions or points of contact between one structure and another, and to indicate the condition of a protective coating applied to a buried structure. A signal of a given frequency is either injected or induced into the structure and traced with a search coil and earphones. Most instruments use a high-frequency signal of 1 kHz or higher, although one or two use a simple interrupter.

Buried pipeline coating survey instruments are available, which, by measurement of the electromagnetic field radiating from a pipeline created by an applied AC signal, are able to compute the attenuation of the signal in dB/km and hence provide an assessment of pipeline coating quality. The signal generator typically operates at a frequency of ~1 kHz for thick coatings being selected to minimize interference from commonly occurring frequencies while maximizing the distance the signal will travel, some 5–10 km on a reasonably well-coated pipeline. For thin-film coatings, such as a fusion-bonded epoxy, a frequency of 200 Hz has been found more appropriate.

4.23.5 Field Data Loggers and Survey Equipment

4.23.5.1 Monitoring and Surveys

It is necessary to understand the difference between monitoring cathodic protection performance and surveying cathodic protection performance. Monitoring is undertaken routinely at fixed points.

For example, on a pipeline, monitoring will be of cathodic protection current and voltage at impressed current transformer rectifiers or at galvanic (sacrificial) anodes and at test points at some 1–2 km spacing along the pipeline at which there will be connections to the pipeline and where there may be buried permanent reference electrodes and or coupons. Coupons may comprise steel elements, possibly of different dimensions (5–25 cm^2 are typical), that are normally connected to the pipeline and are used to measure instant OFF potentials without interrupting the cathodic protection current to the pipeline and which are increasingly used to monitor AC current collection/discharge from the pipeline. At these test points, portable $Cu/CuSO_4$ (sat.) reference electrodes will be used in conjunction with the other facilities to measure pipe/soil/electrode potentials at these fixed locations. These data may be plotted to assess time-dependent changes.

Cathodic protection monitoring on an offshore oil/gas drilling/production jacket with a galvanic anode cathodic protection system will typically comprise permanent Ag/AgCl/seawater reference electrodes, sometimes paired with Zn/seawater electrodes, at representative locations at different depths. The measured steel/seawater/electrode potentials may be carried back to measurement and data logging facilities in hard-wired cabling provisions or by acoustic transponders. These facilities enable time-dependent changes in the cathodic protection performance to be assessed, in particular during periods of storm conditions when divers and remotely operated vehicles cannot be deployed to collect survey data.

Cathodic protection monitoring on impressed current cathodic protection systems for steel in concrete will typically incorporate remote data logging of all individual cathodic protection zone transformer rectifier current and voltage outputs and steel/concrete/reference electrode and potential decay probe or pseudo reference electrode ON and instant OFF potential data and potential decay data collected over periods of typically 24 h and often > 72 h from multiple permanent monitoring facilities embedded in the structure. These data will typically be collected every 3 months and plotted/trend analyzed to produce performance verification reports and system review reports.

For all of these applications (but less commonly on steel in concrete applications, as they are typically provided with many fixed monitoring points and surveying of long-term potential decay data can be difficult), in addition to these fixed point monitoring data sets regular steel/electrolyte/electrode potential surveys are undertaken to measure the adequacy of the cathodic protection performance over all or selected parts of the structure between the fixed monitoring locations.

It is the combination of fixed point monitoring and variable/moveable/portable point surveys that enables a cathodic protection system’s performance to be properly assessed. Data from fixed points alone may be insufficient to demonstrate adequate performance.

4.23.5.2 Fixed-Point Data Monitoring Devices

Potential measurement instruments have been incorporated into what are best described as ‘data recording and management devices,' which enable relatively untrained staff to collect, typically pipe/soil potential data, from fixed test points to a predetermined schedule. These units will prompt the operator to collect data from particular locations; some will display historical data from that location for immediate comparison in the field and will store the new data for later retrieval and processing. The units incorporate high-impedance digital voltmeters with an integral microprocessor for data and code entries into a solid-state memory. Data and codes are inputted by the use of an α-numeric keyboard, although auxiliary data may also be inputted via a barcode reader. Barcodes may be used, for example, at test points to store identification data. The units contain real-time clocks and automatically store electronically entered data and time.

4.23.5.3 Pipeline Cathodic Protection Survey Devices

More important has been the development of pipe/soil potential data loggers to undertake close interval pipeline surveys. These surveys are now accepted as the key performance verification tool for cathodic protection of pipelines and enable the measurement of pipe/soil/reference electrode potential at intervals typically of as little as 1 m. Measurements are recorded at each point of both the pipe/soil potential with the cathodic protection system 'ON,' together with the instantaneous OFF potential some 100–300 ms after the cathodic protection current is interrupted (switched 'OFF' at the DC side). This 'instantaneous OFF' potential significantly reduces the IR drop component present in the 'ON' potential measurement, although some element of IR error can remain due to equalizing currents flowing in, on, and off the pipeline.

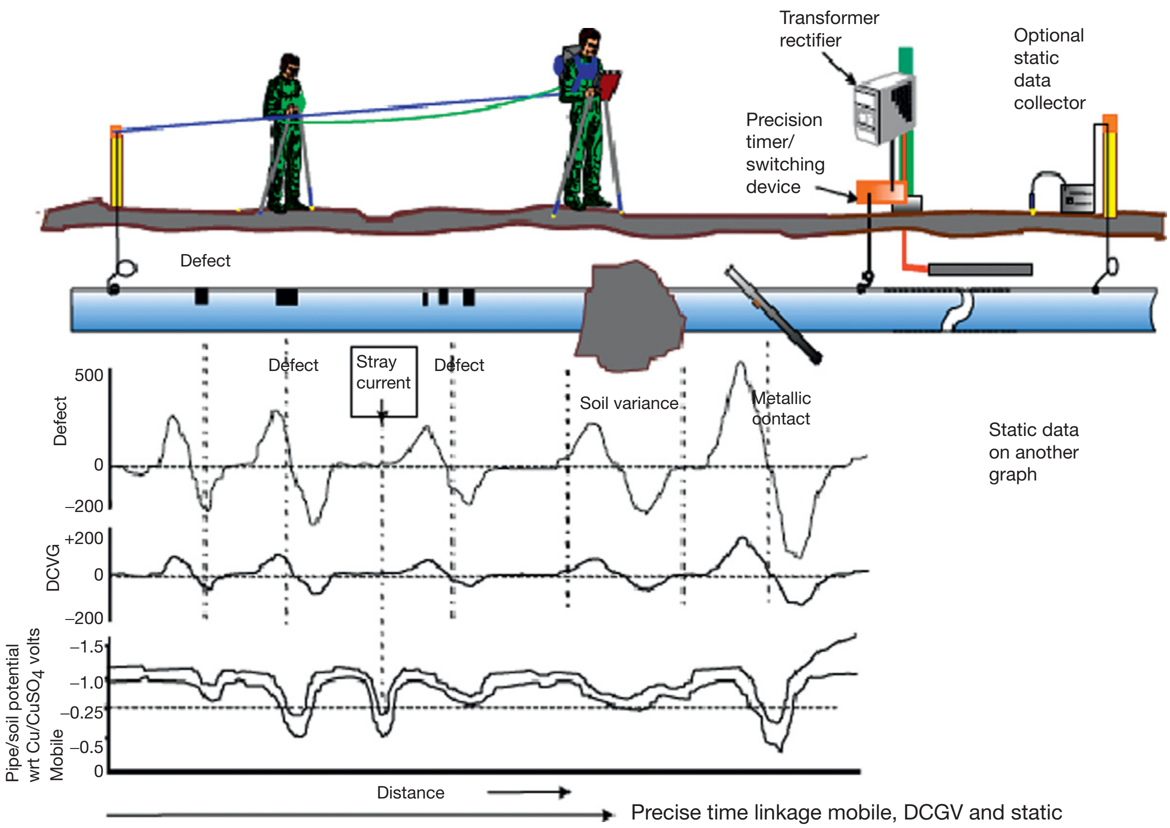
Best practice systems measure ON and instant OFF potentials and simultaneous ON and instant OFF voltage gradients in what is known as combined digital close interval potential surveys (CIPS) and direct current voltage gradient (DCVG) surveys. These surveys enable not only an accurate measurement of pipe/soil potential at close intervals over the pipeline but also the location and an estimation of the size of coating defects. The data can also be used to calculate fully IR free pipe/soil potentials.

Typical combined CIPS and DCVG data loggers are based on the integration of multichannel high-impedance voltmeters with an electronic solid-state battery-backed memory. Measurements are taken with reference to one of the two parallel connected 'ski-stick' $Cu/CuSO_4$ (sat.) electrodes for each channel, and utilize a cable connection to a test point facility on the pipeline, Figures 16 and 17. The combined CIPS and DCVG surveys may collect the DC voltage gradient longitudinally over the pipeline at a distance of some 3–10 m or transversely to one or both sides of the pipeline. Mobile data logging units are provided with long lengths of light gauge insulated wire to provide the contact between the data logger and the test point and to provide a calibrated distance measurement, with an accuracy normally better than ± 0.1%. The data loggers are capable of time synchronization with additional units, which can be used either for static potential measurements at chosen locations or for 'switching' the impressed-current power sources in the 'ON'/'OFF' mode. The synchronization may be initially established by hard wire between the devices, or increasingly common is the use of the GPS satellite network, which allows accurate and repeat time synchronization and GPS location of the mobile survey position. It is possible to provide an accuracy of synchronization between all units of ± 10 ms over a 12-h period. Thus, overall, the mobile data logger combines ON and instant OFF pipe/soil potential measurement, ON and instant OFF voltage gradient measurement, with some systems a repeat ON and instant OFF pipe/soil potential measurement for quality audit purposes along with distance, sometimes GPS location, synchronized time together with any codes added to record geographic, topographic, or pipeline/cathodic protection features such as crossing points with other services and test points.

4.23.5.4 Offshore Monitoring and Surveying

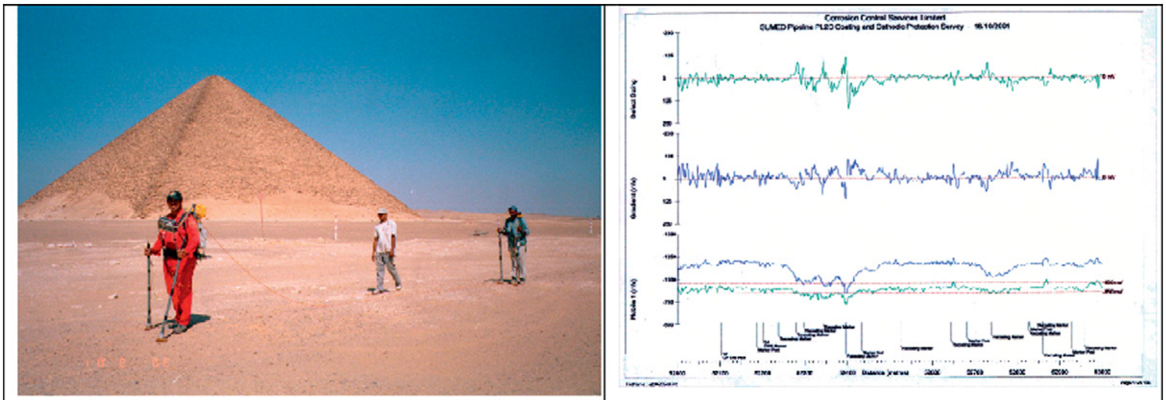
For the potential monitoring of offshore oil/gas fixed and mobile jackets and rigs, it is necessary to emplace numerous reference electrodes at all levels on the structure. The hard-wire connections from these electrodes together with, for example, similar connections from specially monitored sacrificial anodes are best terminated and displayed at the surface on 'mimic' display and recording/monitoring panels, Figure 18.

Monitoring steel/seawater/electrode potentials can be undertaken on offshore platforms and pipelines by the use of combined reference electrodes and acoustic transponders, thus minimizing the need to rely on vulnerable cabling. The installations comprise remote monitoring units, which may be interrogated by a surface unit. The monitoring units are typically each provided with an Ag/AgCl/



Combined enhanced CIPS and recorded DCVG to indicate defect size

Figure 16 Principles of combined CIPS and DCVG surveys.

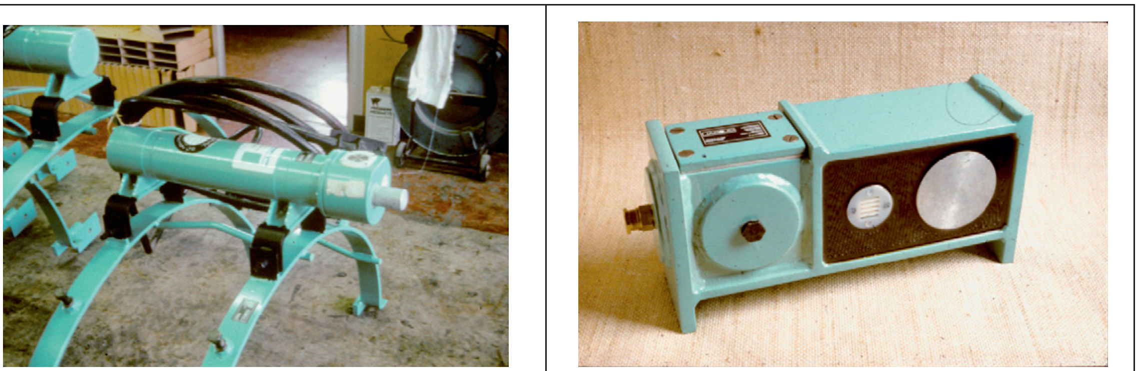


(a) Combined CIPS and DCVG survey (courtesy Corrosion Control Services Ltd.)

(b) Combined CIPS and DCVG survey data (courtesy Corrosion Control Services Ltd.)

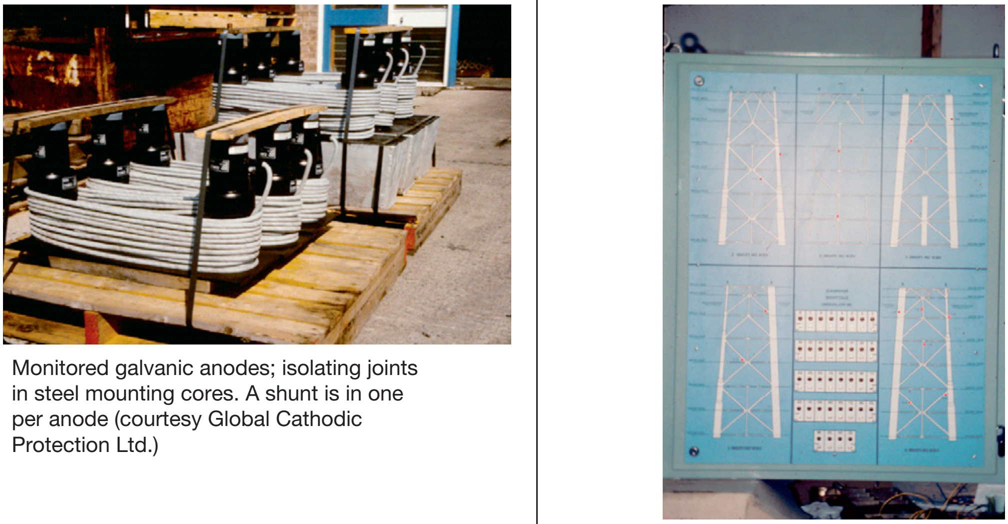
Figure 17 Buried pipeline combined CIPS and DCVG surveys.

seawater reference electrode and a Zn/seawater electrode both connected to an electronic circuit, comprising two comparators, an encoder and a battery powered transponder, capable of emitting coded acoustic pulses into the surrounding seawater over an ~10–25-year service-life. The structure connection is made through the watertight housing of the unit, which becomes electrically common to the



(a) Acoustic linked offshore monitoring system; dual electrode (courtesy Global Cathodic Protection Ltd.)

(b) Hard-wired offshore monitoring system; dual electrode (courtesy Global Cathodic Protection Ltd.)



(c) Monitored galvanic anodes; isolating joints in steel mounting cores. A shunt is in one per anode (courtesy Global Cathodic Protection Ltd.)

(d) Mimic panel for offshore CP monitoring system (courtesy Global Cathodic Protection Ltd.)

Figure 18 Offshore structure monitoring equipment.

structure on installation. The surface unit, which may be located on the platform or a vessel, is used in conjunction with a surface transponder immersed in the sea to activate the data collecting/reference electrode units to transmit their data to the monitoring unit. The structure/seawater/electrode potential information is decoded for presentation on a digital display.

It is normally necessary to locate multiple reference electrodes/data collecting units on a structure. Thus, each unit will only transmit its information on receiving coded instructions. Surface units can commonly accommodate up to 80 different codes. The ability to interrogate and receive over any distance is dependent upon the acoustic operation frequency. Relatively high frequencies are preferable, as they avoid problems of pulse reverberations and echoes from structural members. Typically, data can be transferred over a distance of 2 km. This type of acoustic unit gives accuracies in potential measurement of ±10 mV.

To supplement the fixed point monitoring data, it is normal for fixed and mobile offshore platform jackets and rigs to be surveyed every 1–3 years using divers or, more commonly, remote-operated vehicles (ROVs). These deploy one or more reference electrodes and should have the facility to either/both connect to the structure being surveyed topside (above the water by means of a cable connection) and to make local ('stab') connections to particular components of the facility that may not be in electrical connection with the main structure (risers, piles, riser clamps, etc.). These surveys, which need to be deployed offshore from diving or survey vessels, are extraordinarily expensive but are surprisingly often poorly specified, do not properly calibrate their electrodes or measuring devices, may even not properly confirm proper connection to the structure, and have even been known to simply measure remote potential data of the survey vessel and not the structure.

For offshore pipelines, continuous potential profile surveys have employed reference electrodes mounted on a 'tow-fish' designed for streamlined towing from a boat traveling along the line of the pipeline. Connection to the pipeline at the originating platform or the shore is maintained by means of a light gauge insulated coated copper or stainless steel wire, and a continuous measurement is recorded of pipe/seawater or seabed/electrode potential along with the position coordinates. Moving at a velocity of 3–4 $\mathrm{m\,s^{-1}}$, the tow-fish carries the reference electrode at a supposed uniform depth and proximity to the pipeline. Typically, in practice however, the reference cell is maintained between 5 and 30 m from the pipe. Thus, the accuracy of the recorded potential is affected by the increasing IR drop as the electrode is remote from the pipe (presenting data that imply better levels of protection than are real) and this technique can only be taken as being an approximate indication of cathodic protection performance.

More accurate pipeline surveys are delivered by using ROVs to accurately place the reference electrodes at known distance from the pipeline. The ROVs carry cameras and magnetometers to detect the pipeline location. Some ROVs have the capability to also 'stab' the pipeline or a galvanic anode fitted to the pipeline, such that local potentials can be measured either to confirm the pipe/sea/electrode potential measurement with the long wire connection to the pipeline (with the IR drop error within the pipe wall which may be significant) or to allow measurements with respect to a remote electrode to be 'calibrated' so that pipe/sea potentials can be estimated without contact to the pipeline.

4.23.5.5 Current Density Devices

The measurement of current densities in the vicinity of a cathodically protected structure has been the subject of standards in continental Europe for many years in respect of buried pipelines (DCVG as already discussed and the German Ruhrgas/DIN standard for 'intensive surveys') and has been widely used offshore. These measurements are undertaken by twin electrode devices either installed for stationary use or moved about the structure by diver or remote-controlled vehicle.

The voltage drop required to be measured in seawater to provide current density levels will inevitably be small, and therefore, the difference between the two reference electrodes should also be as small and as constant as possible. A current density sensor designed to overcome this possible source of error utilized two zinc electrodes fixed to a rotating shaft. The zinc electrodes are shielded from water flow by porous material in order to reduce the tendency toward fluctuations in the potentials of the electrodes. The sensor assembly provides two signals that are separated by a filter: a sine signal produced by the cell rotation and the signal due to the difference between the potentials of the two cells. Both these signals are amplified and recorded at the surface. Competing systems utilize more accurate Ag/AgCl/0.5 M KCl reference electrodes in a defined array. These data are equivalent to the DCVG data measured between two reference electrodes in buried pipeline surveys as already detailed. With computerized mathematical modeling using finite element analysis, calculated estimates may be made in respect of galvanic anode current outputs, predicted anode life, and the presence of defects in the structure coating.

Further Reading

Morgan, J. H. *Cathodic Protection*, 2nd ed.; NACE: Houston, 1987, ISBN 0–915567–28–8.

Peabody, A. W. *Peabody's Control of Pipeline Corrosion*, 2nd ed.; Bianchetti, R. L., Ed.; NACE: Houston, 2001, ISBN 1–57590–092–0.

BS EN 13509 *Cathodic Protection Measurement Techniques*; CEN Brussels: BSI London, 2003.

DIN 50 925. *Verification of the Effectiveness of the Cathodic Protection of Buried Structures*; DIN: Berlin, 1992.

Ansuini, F. J.; Dimond, J. R. *Factors Affecting the Accuracy of Reference Electrodes, Materials Performance*; NACE: Houston, 1994; Vol. 33, Chapter 11, pp 14–17.

Wyatt, B. S. Advanced Systems of Overline Assessment of Coatings and Cathodic Protection, UMIST Cathodic Protection Conference, UMIST, Manchester, 2003.

Design and Operational Guidance on Cathodic Protection of Offshore Structures, Sub-Sea Installations and Pipelines; The Marine Technology Directorate Ltd.: London, 1990, ISBN 1–870553–04–7.

Taylor, J. R. *An Introduction to Error Analysis: The Study of Uncertainties in Physical Measurements*; University Science Books: Mill Valley, CA, 1999.

4.24 Anodic Protection

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Glossary

Activation energy Characterizes the slope of temperature dependence of the reaction rate (expressed by, e.g., current density i) in the coordinates of $\log i - 1/T$ according to the Arrhenius equation.

Anodic protection Means an electrochemical protection (corrosion protection achieved by electrical control of corrosion potential) by increasing the potential to the stable passivity range.

Breakdown potential Means a potential, above which the passive metal dissolves by pitting.

Free corrosion potential Means a corrosion potential in the absence of external electrical current flowing to or from the metal surface.

Passivation current density Means a current density at the passivation potential.

Passive current density Means a current density within the passive range.

Passivation potential Means the lower limit of the passive range separating the active potential range from the passive one.

Passive range Means a potential range where passivity prevails.

Protection potential Means a potential value, at which the corrosion rate becomes acceptable.

Transpassivation potential Means a potential, above which a passive metal gets uniformly activated and dissolves as ions in a higher oxidation state.

Abbreviations

AP Anodic protection
b.p. boiling point
FeCr18Ni10(Mo) Stainless steel with 18 wt% Cr, 10 wt% Ni alloyed with Mo
m.p. melting point
SCC Stress corrosion cracking
SHE Standard hydrogen electrode

Symbols

E_{corr} Free corrosion potential (V(SHE))
E_{prot} Protection potential (V(SHE))
E_a Activation energy (kJ mol^{-1})
E_b Breakdown potential (V(SHE))
E_p Passivation potential (V(SHE))
E_t Transpassivation potential (V(SHE))
i_{cc} Passivation current density (A m^{-2})
i_p Passive current density (A m^{-2})
W Concentration (wt%)
ΔE Passive range (mV)
γ Specific conductivity (S m^{-1})

4.24.1 Introduction

The first practical use of anodic polarization for corrosion protection was demonstrated by an English author, Edeleanu,[1] in 1954. However, the principle of anodic protection (AP) had been mentioned in USA patents[2] already in 1945. Along with Edeleanu's work, another study on AP was published by Russian authors, Novakovsky and Levin.[3] The passivation by current was also proposed in the dissertation of Cernova (1954), published later with Tomasov[4] in 1955. The first commercial application of the industrial AP is alleged to have taken place in the USA in 1958.

More than 50 years after the first rational experiments to use anodic polarization for the deceleration of corrosion rate of passivable metals, due to the change in corrosion potential, the use of AP in industrial applications was established for corrosion systems such as carbon steel in sulfuric acid and alkaline environment, and stainless steel in sulfuric acid. This means that in cases where AP stood up to the competition of other corrosion protection methods despite its relative operation complexity and a certain degree of risk. Considering the perspective of an industrial user, AP possesses, besides indisputable advantages, a general disadvantage of the necessity to continuously monitor a due operation of the system, since any failure of the regulating circuits can lead to an extremely fast damage of the protected equipment. It is because the corrosion rate of many corrosion systems, for which the AP is very effective in laboratory or semioperating conditions, is absolutely unacceptable outside the passive range, even for a short while. Such corrosion systems failed in long-term practical applications.

The essential difference between anodic and cathodic protection is in the degree of risk. The failure of cathodic protection is tolerable for a longer period of time and does not lead to a sudden damage of the protected equipment. Similar to the AP, the protective effect of cathodic protection is also frequently given by the formation of a passive layer. As for the cathodic protection, it is caused by composition changes in the superficial electrolyte during cathodic polarization of steel in neutral environment, where cathodic passivation occurs due to alkalization induced by the limited environment convection. Another difference between both types of corrosion protection lies in the aggressiveness of the corrosion environment. Cathodic protection is mostly used in relatively benign environments, frequently as a complementary protection method to coatings, whereas the AP is applied in a strongly aggressive environment as a fundamental protective measure. If we compare current needs per metallic surface unit that is in contact with the electrolyte, there is no substantial difference between the two types of electrochemical protection.

The AP is usually understood as a method consisting in the use of polarization to shift the protected metal from active to passive state, which is usually connected with high current demands to exceed the passivation potential. However, this understanding does not apply to corrosion systems with successful operation applications. Long-term success is typical for applications where a metal tends to passivate spontaneously in a given environment or where spontaneous passivation occurs under low temperatures and where anodic polarization in the passive range further increases the corrosion resistance of the metal. In such cases, there is no longer any need to use high currents for passivation, and many problems relating to the throwing power of AP and the danger of damages to shadowed spaces and attached equipment are thus eliminated. Another great advantage is that an accidental failure of the proper operation of the regulating circuits does not lead to a fast catastrophic increase of metal corrosion.

There are approximately 400 literature references dealing directly with AP, but most frequently, they only describe results from experimental laboratory experiments – long-term operation experience is rather rare in the literature. Although the AP has become a standard part of technological sets, there are only few details available, because it is a part of business know-how.

The overview of industrial applications of AP was published by a German author Gräfen[5] in 1971. Monographs on AP summarizing most of the specialized literature were published in the 1970s and early 1980s. Rather extensive Russian chapter by Makarov[6] from 1974 refers to publications back to 1973 and the American monograph by Riggs and Locke[7] from 1981 has a bibliography dating back to 1790. The Russian work of Kuzub[8] from 1984 contains references back to 1981 and Novák's Czech monograph[9] from 1987 refers back to 1983. The overview of later Russian information can be found in summarizing articles by Agafonova and Makarov[10] of 1989 and Kuzub[12] of 1991. German experience with 30 years of industrial application of AP is summarized by the work of Gräfen *et al.*[11] dated 1991, Czech operation experience with 25 years of industrial application of AP is briefed upon in the study of Novak and Mokra[13] dated 2006.

Literature data from the past 25 years are rare and the number of relevant references is estimated in tens. There have been no breakthrough suggestions that would expand substantially the application area of AP. Another big problem of specialized literature is that the inclusion of many literature references under the entry of 'anodic protection' is unjustified. Many literature references under this entry fail to comply with the definition under the ISO 8044 terminology standard – "Anodic protection is electrochemical protection (corrosion protection achieved by electrical control of corrosion potential) by increasing the potential to a value corresponding to the stable passive state" – and deal generally with the use of passivation to protect metals or, for example, sacrificial anodes, and recently, also conductive polymers, the function of which is assumed to be similar to that of cathodic alloying elements or AP by protectors.

The main purpose of AP use is to ensure sufficient resistance of passivable metal against uniform and localized corrosion. The effectiveness of AP cannot be simply expressed by comparing corrosion rates of protected and unprotected materials, since the particular material cannot be used without AP under given conditions. The effectiveness must be assessed in light of the comparison of various corrosion protection alternatives that ensure technically acceptable resistance in the required construction arrangement.

Prolongation of a service life of anodically protected equipment does not have to be the biggest benefit, though the corrosion resistance is the basic qualification. The same applies to, for example, the requirement for high purity of a manufactured or stored product. The necessity of a pure environment is the reason why AP is applied to storage tanks for sulfuric acid.

Limitations of production technology caused by low corrosion resistance of the production equipment can be mitigated by AP application. Intensification of the sulfuric acid production by increasing the operating temperature could serve as a good example.

Very slow corrosion rate under AP enables better and long-term use of metallic materials, and sometimes it is possible to ensure sufficient service life of less costly materials, which limits the use of precious metallic and nonmetallic structure materials.

Thanks to AP, it is possible to construct devices with better parameters representing new ways of technological solutions, such as an effective consumption of heat energy, which, without AP, is wasted in the cooling process during the sulfuric acid production.[14,33] Coolers of concentrated sulfuric acid are nowadays the most effective application.

Secure and reliable operation of anodically protected equipment consists not only in minimum corrosion, but also in, for example, the prevention of undesirable evolution of hydrogen during the acid storage.

AP can be also used in nonaqueous environments, when their electrolytic conductivity is high, for example, in glass melts where heating electrodes can be thus protected from corrosion.

AP can also be applied in areas that are not related to corrosion, for example, in the prevention of undesirable deposition of nickel on the device walls during the electroless nickel plating process. In addition to the enhancement of work productivity, this application increases material savings.

4.24.2 Passivity of Metallic Materials

The corrosion rate of most metals grows with the increasing environment oxidizing power (Figure 1(a)). Once the oxidizing power reaches a given threshold, a steep drop of the chemical reactivity of various metals can be observed. This phenomenon was first described more than two centuries ago, but the mankind had been encountering it in practice since the beginning of the use of nonnoble metals. This process is called passivity, and in the corrosion perspective, it is a totally positive process, which substantially slows down the course of electrochemical metal dissolution.

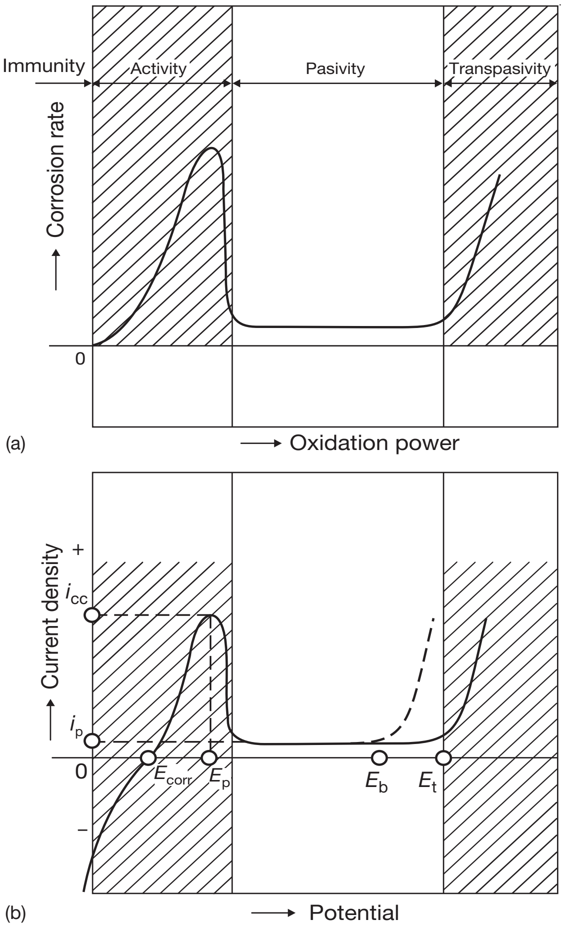

Figure 1 (a) Dependence of passivable metal corrosion rate on the electrolyte oxidation power. (b) Polarization curve potential–current density (E_{corr} – free corrosion potential, E_p – passivation potential, E_b – breakdown potential, E_t – transpasivity potential, i_{cc} – passivation current density, i_p – passive current density).

Passivability means the rate of difficultness of transforming a metal in a given environment from active to passive state. It is characterized by the values of passivation potential (E_p) and passivation current density (i_{cc}) (Figure 1(b)). Corrosion resistance in a passive state and the stability of the passive state are given by the values of passive current density and the width of a passive range (ΔE), that is, the potential difference between the potential of full passivity (is a bit more positive than the passivation potential) and the transpassivation (E_t) or breakdown potential (E_b). Factors affecting the passivability (E_p, i_{cc}) and the stability of passivity (ΔE, i_p) are almost identical though their influences can apply in different ways. Properties of a metal that apply to such case include composition, structure, internal stress, and superficial state. When it comes to the properties of environment, factors that matter are, particularly, composition, concentration, temperature, and flow. Construction, time of exposure, and polarization are other factors that apply.

Passive metals that we encounter the most enter the solution usually in the form of Fe^{3+}, Ni^{2+}, Cr^{3+}, and Ti^{4+} ions. According to the Faraday's law, it is possible to make the calculation of corrosion rate from the passive current values, on condition that the only reaction participating in the measured current is the anodic dissolution of the passive metal. In a gross estimate, the value of current density in ampere per square meter corresponds approximately to the corrosion rate in millimeter per year.

Considering the mechanisms, the processes leading to passivation of metal can be divided into three basic groups: passivation by influencing cathodic process, passivation by influencing anodic process, and passivation by changing an electrode potential by polarization from an external current source.

Passivation by influencing cathodic process can be achieved either by the addition of substances that get easily reduced at potentials in a passive range of the metal, or by the facilitation of the reduction of the environment elements by connecting the protected passivable metal to or alloying it with metals that have only small overvoltage of cathodic reaction and greater current density of such reaction. Even an extension of the area of the connected cathodic material can lead to passivation of passivable metal in an environment with sufficient oxidizing power. The oxidizing power of the environment is characterized by the oxidation–reduction potential on the one hand, and by the value of exchange or limiting current density on the other hand.

Passivation by influencing anodic process can be achieved by alloying with metals that shift the passivation potential in the negative direction or with metals that reduce anodic dissolution in active state, passivation current density. The passivation is also facilitated by the addition of substances (in the corrosion environment) that decelerate the anodic dissolution of the metal, or by the removal of corrosion stimulators from the solution.

The change of electrode potential by polarization from an external current source is a procedure enforcing a potential lying in an area of low corrosion rate to the metal, without any influence on the anodic or cathodic dependence. If this is achieved by cathodic polarization (shifting the corrosion potential in a negative direction), we talk about cathodic protection; if it is achieved by anodic polarization (shifting the potential in a positive direction) into the passive range, we talk about AP.

Intervention in a corrosion system frequently affects both cathodic and anodic processes. Both procedures are exploitable to facilitate passivability in AP.

Several types of potential–current curves (Figure 2(a)–(d)) can be the result of oxidizing effect of the environment on the passivable metal:

Type-I – the oxidizing ability of the environment is low to passivate metal and retains it in the activity range. AP can be used for passivation (Figure 2(a)).

Type-II – the oxidizing ability of environment suffices to retain the metal in the passivity range, but is insufficient to passivate an active metal. The passive state is unstable. The AP can be used for passivation (Figure 2(b)).

Type-III – the oxidizing ability of the environment suffices for spontaneous passivation and the passive state is stable, if there is no occurrence of localized forms of corrosion. In case of threatening localized corrosion, AP can be used for positive potential shift to the range of stable passivity (Figure 2(c)).

Type-IV – the oxidizing ability of the environment is high; corrosion and pitting corrosion occur in the area of transpassivity or beyond the breakdown potential, respectively. Cathodic protection can be used for polarization into a stable passive range (Figure 2(d)).

Transition between particular types of dependencies in a specific corrosion system can be caused by temperature or a presence of small amounts of specific substances in the basic corrosion system.

As for the practical applications of AP, carbon steel, stainless steel, and titanium are the most important metallic materials. Passivability of iron alloys is influenced the most by chromium, which significantly facilitates passivation if the addition exceeds 12%. The mechanism of chromium effect can be explained by the shift of the passivation potential in the negative direction and the decrease of a passivation current density. Iron alloys containing chromium in excess of 12% (stainless steels) are resistant against corrosion in many environments just because of simple passivability. Nickel applies to iron–chromium alloys where it reduces passivation current

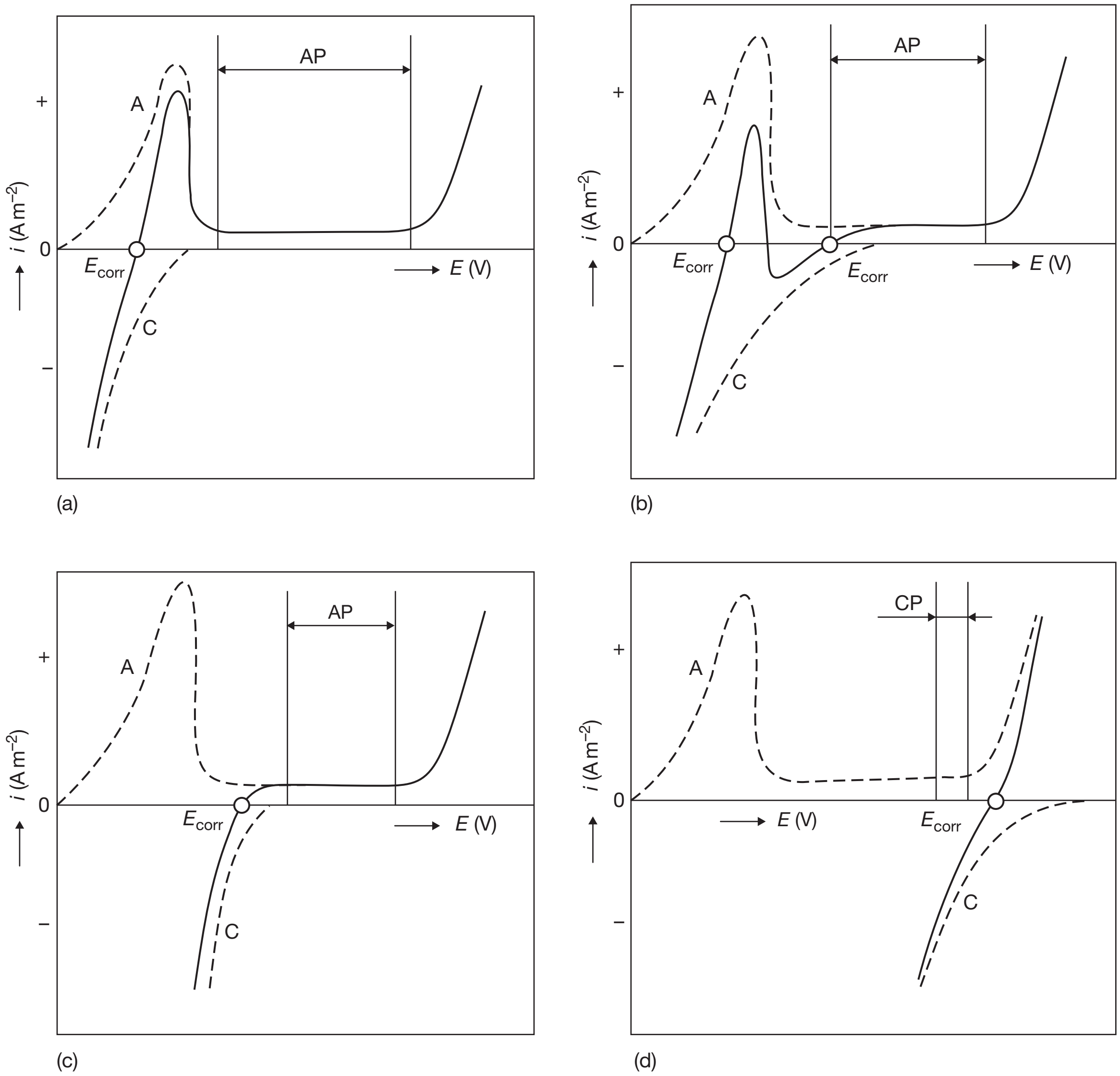

Figure 2 Different types of potential–current cumulative curves as a result of electrolyte oxidizing effect on the passivable metal. (a) Type-I – the oxidizing ability of environment is low to passivate metal and retain it in the activity range. AP can be used for passivation. (b) Type-II – the oxidizing ability of environment suffices to retain the metal in the passivity range, but is insufficient to passivate an active metal. The passive state is unstable. The AP can be used for passivation. (c) Type-III – the oxidizing ability of environment suffices for spontaneous passivation and the passive state is stable if there is no occurrence of SCC. In case of threatening SCC, AP can be used for a positive potential shift to the range of stable passivity. (d) Type-IV – the oxidizing ability of environment is high; corrosion and pitting corrosion occur in the range of transpassivity or beyond the breakdown potential, respectively. Cathodic protection can be used for polarization into a stable passive range.

and corrosion in an active state. The addition of molybdenum increases the stability of a passive layer on stainless steels against crevice and pitting corrosion, in particular.

Titanium is also alloyed (by Al, Cr, Mo, Fe, V, Mn, Sn, Zr), but we can say that none of these elements substantially improves passivation properties of titanium. But alloying with cathodic alloying elements such as platinum, palladium, etc., has the greatest influence on passivability of titanium and its alloys. These metals reduce the overvoltage of cathodic reaction. In commercial production, titanium is made with 0.2% of palladium. Cathodic alloying leads to autopassivability of metal and applies to stainless steels too (Cu in FeCrNiMo alloys). An autopasivable metal shows polarization curves of the Type-III (see **Figure 2(c)**) and can be used for AP to eliminate crevice corrosion.

In addition to the composition, the structure of metal is another important factor. The structure can be influenced by both composition and heat or mechanical treatment of the material. The impact of structure applies the most to different chemical composition of structural phases, which causes great differences in passivability. The origination of structural inhomogeneity of metal leads to the reduction of a passive range and to the increase of characteristic currents. This usually results in the occurrence of localized forms of corrosion attack, such as intergranular or pitting corrosion. Materials with homogeneous structure are easier to passivate and show better resistance in a passive state.

Weld seams usually belong to the most critical parts of a majority of metallic equipment. Passivability of a weld seam or heat-affected areas is given, again, by the homogeneity of chemical composition. An inhomogeneous weld seam or chemical composition that fails to ensure sufficient passivability can lead to localized forms of corrosion or cause earlier corrosion of the weld seam material. However, for good passivability and resistance in the passive range, it is not necessary to have an identical chemical composition of the weld and the basic metal. The only prerequisite is to keep the corrosion or protection potential within the overlaps of passive ranges of all metals concerned.

The galvanic connection of passivable metal and a noble material that spontaneously achieves a potential in a passive range and at the surface of which reduction proceeds with lower overvoltage leads to passivation. Depending on the area of the cathodic material surface, the connection results either in spontaneous passivation (**Figure 2(c)**, curve type-III), or more frequently, in a curve of the type-II (**Figure 2(b)**), at which there are two corrosion potentials in both active and passive state. The corrosion rate accelerates in the activity. Noble metals, such as platinum, palladium, copper, silver, and in some environments, other metals, graphite, and also some electrically conductive metallic oxides can be used as a cathodic material.

4.24.3 AP and Localized Forms of Corrosion

4.24.3.1 Pitting Corrosion

Pitting corrosion is, under the conditions of anodic polarization by an external source of current, noted for several peculiarities compared with the corrosion in a redox system at identical potential. Migration of aggressive ions to the places of intensive anodic dissolution is much more significant, because the polarization current concentrates on the top of the pit. Therefore, the pitting attack can be more frequent and more intensive on an anodically polarized surface than on the nonpolarized surface.

The fact that pitting corrosion is bound to the existence of a passive layer on the metal surface and that it is accelerated by anodic polarization represents a serious problem for AP in the presence of aggressive anions. The anions that cause damage to the passive layer, which subsequently leads to the pitting corrosion, are predominantly chlorides.

Growing concentration of an aggressive ion makes the breakdown potential shift in a negative direction, increases the passivation current, and narrows the stable passive range. In addition to the damage of the passive layer above the breakdown potential, aggressive anions cause the growth of current in the stable passivity, which somewhat decreases the protection effectiveness. Even the passivation of active surfaces is aggravated in such environments as a result of higher passivation current density. The proportion between activities of the basic nonaggressive anion and the aggressive anion that causes pitting significantly affects the width of a stable passive range. The growth of concentration of anions with weaker passivation effect (OH^-, SO_4^{2-}, PO_4^{3-}) makes the breakdown potential shift in the positive direction. Laboratory data on limitations of AP given by its application in environments with aggressive ions are available predominantly for stainless steels in sulfuric acid solutions containing chlorides. Besides aggressive anions, corrosion environment can contain anions with inhibiting (passivating) effects as nitrates. In such a case, the stable passive range can exist at potentials more positive than the breakdown potential, and the AP can thus be used for protection against pitting corrosion. This phenomenon enables the AP to effectively prevent pitting corrosion of stainless steels in nitrate environments in the presence of chlorides.

4.24.3.2 Intergranular Corrosion

The reason for intergranular corrosion is a structural and chemical inhomogeneity of metal at a grain boundary. Preferential dissolution of less-resistant metal and phases at the grain boundary leads to the intergranular propagation of corrosion. This type of localized corrosion proves to be the most significant for heat-treated and welded stainless steels.

Considering the AP utilization in equipment made of stainless steels after sensitization-inducing heat treatment (e.g., after welding), it is essential to choose a protection potential within the range where active–passive or transpassive–passive type of intergranular corrosion is avoided. The reduction of the usable passive range from the side of activity is given by the degree of the grain boundary depletion; from the side of transpassivity, it is given by the number of phases in the structure that show low corrosion resistance at high oxidizing potentials. The optimal protection potential constraining intergranular corrosion of austenitic stainless steels, such as FeCr18Ni10 in sulfuric acid, ranges from 0.5 to 0.8 V(SHE). It was experimentally proved that sensitized samples, which are highly susceptible to strong intergranular corrosion, remain unattacked if protected by AP. Nevertheless, these findings are based on relatively short laboratory experiments, during which the passive–passive type of intergranular corrosion had no chance to show up more significantly. Therefore, it is necessary to ensure a sufficient resistance to intergranular corrosion not only by a due choice of the protection potential, but also by the appropriate metal composition and structure that weaken the susceptibility to passive–passive intergranular corrosion. The best solution is to use pure materials, that is, steels with a very low content of carbon, ensuring resistance against common types of intergranular corrosion. Practical experience shows that the AP can prevent intergranular corrosion, which occurs for example, in the vicinity of weld joints.

4.24.3.3 Stress Corrosion Cracking

The finding that stress corrosion cracking (SCC) is bound to the existence of a passive layer on the metal surface and that it is accelerated by anodic polarization led to a misleading generalization that the AP creates conditions for this type of localized corrosion attack.

Even the authors of first AP works were aware of the danger of SCC and observed experimentally the effect of the passive-range directed polarization on the susceptibility of mechanically stressed samples to SCC. This research was especially noted for demonstrating that the AP is a recommendable way to eliminate corrosion in environments where SCC occurs without polarization. It relates particularly to carbon, or low-alloyed steel in sodium or potassium hydroxide or ammonium nitrate, in Kraft liquor, and stainless steel in sulfuric acid with a low content of chloride ions. For AP, it is important to know that SCC is bound to the potential range of instability of a passive layer, that is, to the bordering area between the active and passive state and to the range of a damaged passive layer at higher potentials.

It is possible to apply AP to prevent hydrogen embrittlement of iron alloys in the acrylonitrile synthesis environment, and the negative effect of hydrogen on carbon steel in the concentrated sulfuric acid environment can also be eliminated by the use of AP. Generally, anodic polarization can eliminate all kinds of negative effect of hydrogen, which evolves in electrolytes on metallic surfaces.

4.24.3.4 Erosion–Corrosion

Erosion–corrosion is a process accelerating corrosion by mechanic damage of metallic surface in an aggressive environment. Erosion can be caused by the presence of solid particles in a corrosion environment or by a turbulent flow of liquid. Erosion can be also caused by gas bubbles. Erosion of metallic superficial layer is typical for materials, the corrosion resistance of which is given by the effect of their passive layer. This fact implies other limitations of the use of AP in erosive environments. The biggest problem with corrosion–erosion attack is the level of an acceptable erosive effect of a liquid stream on the anodically protected surface, at which the corrosion rate would be technically acceptable.

Mechanical resistance and solubility of the forming passive layer are important features. If the layer is formed predominantly by salts, the drop of protective effect can be observed even in the area of the laminar liquid flow. It applies particularly to anodically protected carbon steel in concentrated sulfuric acid where corrosion is 2–10 times faster even at low liquid speeds. The flow occurring in the laminar area was detected to have no effect on the corrosion resistance of passive surface of materials, the protective layer of which consists of oxides (e.g., stainless steels).

The stability of the stainless steel passive state in flowing 93–99% acid strongly depends on a weak contamination of the acid by iron ions. The iron content and acid temperatures are the decisive factors of the potential–current type of dependency. (Figure 2) To achieve effective AP, the minimum concentration of iron ions in flowing sulfuric acid (98.5%) at 100 °C must be 7 ppm (solubility of ferric sulfate). The stability of the passive sulfate layer during acid flow is conditioned by the origination of trivalent iron compounds, whose solubility in concentrated acid is approximately by two orders lower than that of bivalent iron compounds. Spontaneous passivation results in the formation of Fe^{2+} sulfate passive layer, while anodic polarization above 0.85 V(SHE) leads to the formation of Fe^{3+} sulfates. This is the reason why cooling systems with AP do not need any significant limitations of acid flow rate and why erosion–corrosion does not occur in them, in contrast to systems without AP.

The erosion effect of a corrosion environment can be caused by solid particles in the corrosion environment, penetrating the equipment as impurities or given by the technology (e.g., ore leaching), or formed during the production process (e.g., crystallization of salts). Besides the mechanical and chemical resistance of the passive layer is important repassivation rate, the decisive factors comprise the rate and the angle, at which the particles strike the surface, their hardness, weight, concentration, and shape. Erosion effect of solid particles in a liquid can preclude the application of AP even where allowed by the composition of the basic solution.

The reaction mixture prepared during fabrication of formic acid where crystalline ammonium sulfate is formed can serve as an example. Under model conditions corresponding to the operational mixing of the reaction mixture, the passive current density increases by three orders of magnitude compared with the state without mixing. In consequence, the corrosion rate grows to a technically unacceptable value.

4.24.4 Anodically Protected Objects

4.24.4.1 The Basic Requirements for Protected Equipments

Metallic parts of an object suitable for the AP must be made of passivable metal showing an acceptable corrosion rate in a passive state (usually <0.1 mm year^{-1}) under the operation conditions. This applies also to all other metallic parts that are conductively connected to the protected equipment and are placed in the same corrosion environment. The best thing would be that the whole equipment is made of a single material. If possible, the equipment should be free of any shadowed spaces that may cause difficulties, namely narrow crevices. Therefore, it is necessary that the equipment is welded rather than put together with joints where crevices may appear, for example, under sealing. For the same reason, it is not advisable to anodically protect coated surfaces. Weld seams must be perfect, with no pores or cracks.

The inlet and outlet pipes, closing elements, and attached devices must be, if essential for the environment, protected against an undesirable side effect of AP. AP of functional shadowed spaces (e.g., inside the pipes, spaces between desks) is possible, if the throwing power is respected.

The construction of the equipment must allow installation of one or more reference cathodes in places that are suitable for reliable regulation of protection potential throughout the entire equipment.

Since AP is effective only below the electrolyte level, it is desirable to keep the protected surface completely immersed. Therefore, it is highly recommended to have completely filled, continuously working equipment where no spaces filled with gas could occur. Most equipment fails to live up to this requirement, and still, it is possible to have them effectively protected. However, it is necessary to take into consideration that the surface emerging above the electrolyte level is left unprotected. Therefore, it must be made sure that the stability of a passive state in the electrolyte film above the level was sufficient. If the level is stable for a longer period of time, its negative effect can be eliminated by construction adaptation.

If the level varies, it is advisable that a minimum level of liquid remains in the equipment so that electrolytic connection between the protected object, cathode, and reference electrode is ensured. If the equipment must be completely drained from time to time, the arrangement of operation technology must enable easy passivation when refilling the equipment. It is difficult to ensure reliable AP in equipment where a part of the metallic surface is in contact with the electrolyte film only. Moreover, the equipment construction should eliminate the erosive effect of a flowing environment as much as possible.

4.24.4.2 Types of Protected Objects

Heat exchangers and storage vessels are the most frequently anodically protected objects, which we have long-term operation experience with. These objects are in continuous operation. However, discontinuously operating objects can be anodically protected as well, even those that are completely drained, for example, digesters, stripers, measuring vessels, and various reactors. Most of the equipment, except for storage and transportation vessels, operates under elevated temperatures, usually above 100 °C, sometimes even more. AP in melts is feasible even at much higher temperatures.

The equipment, such as autoclaves or kraft digesters, operates under elevated pressure. In many objects, there is a rather small motion of liquid, but in heat exchangers, the flowing rate can reach units of meters per second.

The volume of protected objects ranges from units to 10 000 m^3 and the protected area from units to thousands square meter.

The remarkable thing about AP is that it proved useful even for very complicated equipment and it was used to protect the inner surface of pipes. The level of complexity of protected equipment is given particularly by conductivity and by the aggressiveness of the corrosion environment.

4.24.4.3 Throwing Power of AP

If a metallic surface is polarized by an external source of current, the potential drops as a consequence of the current passage through electrolyte. This drop is especially significant with the polarization of active metal in shadowed areas, such as crevices filled with electrolyte or at pipe inlets to the protected equipment.

The protected surface is polarized to the protection potential in a passive range, and as getting deeper into the interior of the shadowed area, the potential drops from this value to more negative values. If the distance is long enough, it can reach the value of a free corrosion potential in active state. The potential interval between protection potential and free corrosion potential (in active state) comprises the potential, at which the corrosion rate of the metal equals the passivation current density, which substantially exceeds the corrosion rate at the free corrosion potential. This problem has been addressed by a number of authors.[15,16]

The current distribution within anodically protected equipment is described by mathematical relations referred to in literature.[17–23]

To express quantitatively the said dependencies, it is necessary to know the shape of the polarization curve, potential dependence of the corrosion rate, geometry of the shadowed area, and the conductivity of the electrolyte.

Relations were derived not only for the throwing power and formation of crevice corrosion under the conditions of anodic polarization, but also for the anodic passivation at the liquid level, for the passivation of continuously filled vessels and to calculate the parameters of measures to be taken to eliminate the undesirable effects of AP, resulting from the limited throwing power.

Generally, the throwing power of AP applied to completely passivated surfaces (which is the prerequisite of proper operation) is extraordinarily high compared with the throwing power of cathodic protection applied to the same geometry.

Considering the throwing power of AP of complicated constructions containing shadowed areas of critical dimensions, it is more advisable to apply a permanent potentiostatic polarization that secures safer operation and enables protection of more complicated equipment with a minimum number of cathodes.

If the length of the piping connected to the protected equipment exceeds critical dimensions and cannot thus be passivated by current from the cathode placed in the protected equipment, it is important to take measures eliminating undesirable corrosion of the attached device. If it is feasible to ensure reliable electric insulation of the protected equipment from grounded parts, the attached devices will be preserved from the negative effect of AP. However, most objects are grounded, and thus, conductively interconnected. There are a number of compatible procedures that can reduce the negative effect of AP, such as the passivation by auxiliary cathodes, passivation in an environment with better oxidizing power, passivation in a less aggressive environment (concentration, temperature, and composition), passivation at high positive potentials, and the use of an insulation section and a section with an intentionally induced potential drop.[24]

To prevent crevice corrosion under the conditions of anodic polarization, it is essential to avoid the formation of crevices by a suitable construction of the equipment, widen the crevice where necessary, or use self-passivating materials in places where crevices are unavoidable, or materials that show a low passivation current density and a narrow activity range in the given environment.

4.24.4.4 Influence of the Level on the AP Effectiveness

The effect of AP is limited to the surface below the electrolyte level and practically ends at the electrolyte–atmosphere interface. Similar to crevices, the AP cannot ensure passivation of the metal by a thin layer of electrolyte (a film of electrolyte on walls) due to the ohmic drop during the passage of passivation current. If the surface below the level is passivated and the environment aggressiveness does not lead to a spontaneous activation, the undesirable effect of the level does not show up. Nevertheless, if the passive state stability above the level is low or lowered by the effect of atmosphere (humidity, gases with activating effect), corrosion may grow similar to the shadowed areas.

The problem with the liquid level is even more significant if the surface coming through the level transfers heat. That is the case of heating coils, desks, and incompletely filled heat exchangers. The most effective measure is to prevent the level to get in contact with the protected surface, which can be achieved by the complete filling of the equipment, the removal of spaces filled with gas, or by placing the entire protected surface below the liquid level. The negative effect of the liquid level is caused not only by the film of electrolyte on the walls, but also by accumulated deposits. This happens if the liquid level is in the same position for a long period of time, the electrolyte is not changed or mixed, and the corrosion products have low solubility in the environment. In practice, however, the liquid level fluctuates and is mixed regularly, and the electrolyte gets changed.

Relations derived for the continuous passivation of an active surface above the liquid level is noted in particular for the start-up modes.[25,26]

When the anodically protected equipment with activated surface above the liquid level is filled continuously, current is predominantly given by the ratios in the film of a corrosion environment above the level, where the potential gradually changes from the free corrosion potential in activity to the protection potential in passivity. The current is essentially independent of the mass of the electrolyte in the equipment (the size of immersed surface), which indicates that the main portion of the passivation current passes in the film of the corrosion environment closely below the liquid level in the active section that forms, similar to the shadowed spaces, as a consequence of the ohmic drop in the electrolyte level. Changing the electrolyte level in operating conditions, where metallic surface below the liquid level activates spontaneously, is mostly unacceptable for the use of AP.

4.24.4.5 AP at Heat Transfer

At present, sulfuric acid coolers and other types of heat-transferring devices are the most widespread anodically protected objects. The principle of most of such objects is that the protected surface has different temperatures in different places. Since temperature substantially affects the passivation properties and the passive state stability, the nonisothermal surface represents a serious heterogeneity, considering AP. It complicates, in particular, the estimate of currents for AP of the equipment on the grounds of laboratory tests.

Model tests showed that the stability of a passive state on a nonisothermal surface is given by the warmest part, which tends to activate the most. Even the current demands for the protection of the warmest parts are higher than for the colder ones. It must be taken into account when constructing cathodes that they should be placed preferentially in the vicinity of the warmest places. Current demands in colder places of the surface are lower.

Heat-transferring devices should not be anodically protected in conditions where the corrosion environment is boiling. Boiling may constrain the electrolytic connection between the protected surface and the corrosion environment, which may cause a situation in which the surface is not protected by current for some time. Emerging bubbles may induce the formation of crevices and undesirable spaces filled with gas. The boiling of the film may result in a complete loss of the electrolytic connection. The surface can thus get excessively overheated and activated, and the corrosion rate in passivity can grow tremendously. Overheating of the surface above the liquid level induces activation and excessive corrosion close above the liquid level. Generally said, neither the heat transfer nor the formation of nonisothermal conditions on the immersed surface reduces the effectiveness of the AP, but boiling is undesirable for the protected surface.

4.24.5 Modes of AP

Anodically protected objects can be operated in three basic modes. The passivation takes place in a start-up mode, in which the protected surface potential shifts from the free corrosion potential to the protection potential in the passive range and current or the frequency of current switching is stabilized. The AP itself is applied under the conditions of an operation mode when the potential of the object is maintained at the required level in the passive range. Security, even during the main power supply and potential controller failure, is ensured by an emergency mode that temporarily prevents the potential from shifting to the active range.

4.24.5.1 Start-Up Modes

The metallic surface of new unfilled devices is mostly covered with an oxide layer formed in air. Although this layer exerts certain protective effects, it depends on the aggressiveness of the operation electrolyte, if it resists after the first filling. The resistance of this layer is usually insufficient and fits only for low-aggressive environments.

To passivate an initially active surface, a minimum value of direct current is needed, which is expressed by the value of passivation current density. The order of magnitude i_{cc} for common corrosion systems ranges from 10 to 1000 $\mathrm{A\,m^{-2}}$. It is thus obvious that it is usually impossible to passivate the entire protected surface by current under the operation conditions, because it would require very strong current sources. That is why it is necessary to apply the following procedures, which decrease the passivation currents to acceptable values (up to 100 A per object): passivation with continuous filling of the object, passivation in a less aggressive solution, passivation after the prior chemical passivation of the surface.

Passivation with continuous filling is a common procedure used in the start-up mode. Problems relating to the passivation with continuous filling deal with the placing of a cathode, because AP can work properly only if at least partly immersed, which happens, for example, in vertical cylindrical vessels, only after the entire bottom is covered; high currents are needed then for passivation. The solution is based on the modification of the vessel's bottom to a conical one or a spherical one with a pit where the end of the electrode encroaches.

Continuous filling is often combined with the reduction of the operation environment aggressiveness. The reduction of aggressiveness can be achieved by a drop of temperature, change of concentration of the aggressive element, change of hydrodynamic conditions, or addition of passivating substances. Environment parameters (temperature, concentration, flowing rate) are continuously modified during the start-up mode to correspond to the values of operation without draining the equipment content.

The reduction of temperature is important, particularly for equipment operating under elevated temperatures. This procedure is very effective, since the dependence between passivation current and temperature is exponential. Temperature reduction can eventually result in self-passivability of the metallic material.

In the start-up mode, metallic surface can be passivated by direct current without any automatic regulation of potential. The reference electrode then has a controlling function only. The power supply is controlled manually according to the potential of the passivated device.

It is not advisable to apply automatically controlled start-up mode for equipment operating continuously. It only makes sense with discontinuous productions with periodical passivation cycles.

To reduce the needs for passivation current, it is also advisable to place the cathode asymmetrically in the vicinity of the protected surface. The nearest place to the cathode passivates at first, and the rest of the surface follows. If required by conditions, auxiliary cathodes must be used, for example, for passivation of a storage vessel bottom, since the current needs to identify the minimum surface of the cathode.

Time of the start-up mode depends on the corrosion environment aggressiveness against the specific metallic material and on the source power used for the operation mode, which the protected equipment will be migrated to. The start-up mode takes hours, at the maximum, tens of hours.

The time of the actual passivation is relatively short, but the stabilization of the passive current is slow. It is necessary to wait until the current on the filled equipment drops, under the operation conditions, below the maximum output values of the automatically regulated source. During the start-up mode of AP of complicated equipment, requirements given by the protection throwing power must be taken into consideration, and the appropriate start-up mode procedure must be selected accordingly.

4.24.5.2 Operation Modes

Once the start-up mode, which usually consists in a one-off action, is over, the protected object is reconnected to regulating circuits that ensure permanent protection process. The methods of polarization that might be used to ensure operation modes of AP can be divided into types continuous, discontinuous, and combined.

4.24.5.2.1 Potentiostatic polarization

Polarization is referred to as potentiostatic if the potential of the protected surface is maintained on the specific value by direct current. This type of polarization uses a three-electrode connection (protected object, cathode, reference electrode) where the potential difference between the protected surface and the reference electrode is permanently compared to the voltage corresponding to the required value of protection potential, and the differences are compensated by the current passing between the protected surface and the cathode. A regulator that ensures this joint regulation of the protected surface potential is called a potentiostat.

The protected object must be connected to the regulator by two wires (measuring and power), because the voltage, which is added to the value of the actual potential of the equipment, drops in the protected object power supply during the current passage. In operation, the regulating and power parts of the potentiostat are sometimes divided in two devices and the power part is usually placed close to the protected object.

For potentiostatic polarization, potential is the optional quantity and protection current is the depending quantity.

4.24.5.2.2 Polarization under constant terminal voltage

Polarization under constant voltage used to be common for cathodic protection, but for AP, it is useful only if the corrosion systems lack transpassivity. This procedure can be used in practice for the AP of titanium in the sulfuric acid environment. The anodic polarization from a DC source was also proposed as a method of reduction of carbon steel corrosion in liquid fertilizer containing ammonium nitrate in Lawrence's and Eagle's patents[2] from 1945, which is the first documented proposal of the AP. In addition to the AP of titanium, at present, the polarization under constant terminal voltage is important, especially for starting and emergency modes.

4.24.5.2.3 Periodic polarization

Periodic polarization by direct current is a method that brings certain simplifications to the AP. Similarly, to the potentiostatic polarization, the connection is effected through three electrodes (four wires). It applies the principle that the potential of an anodically protected metal, once the polarization current is switched off, shifts automatically to the negative direction. As soon as the lower potential threshold is reached, the current is switched on again in the preset value. It passes through the circuit as long as the protected surface potential achieves the upper threshold of the required potential interval. The periodical switching of the current in the cathode-protected surface circuit is ensured by the regulator controlled by the potential balance between the reference electrode and the protected surface.

Periodical polarization offers a lot of advantages, because it does not require the construction of power potentiostats and the source powers can be easily changed according to the size of the protected object. The periodical polarization has been used since the beginning of a wider industrial application of AP; nevertheless, nowadays it is being left for potentiostatic polarization.

4.24.5.3 Emergency Modes, Failures, and Maintenance of AP System

The AP requires a reliable regulation of the protected surface potential within a given potential interval, outside of which very intensive corrosion occurs. To avoid such corrosion under both threshold operation conditions and the main regulating circuit outage, it is essential to establish an emergency mode, regular controlling, and maintenance of the entire anodically protected device. To properly select the emergency mode, which includes not only the polarization method but also all restoration measures, we have to consider all causes of the emergency.

To make the emergency mode ensure proper protection against the consequences of failures, it must be complemented with regular preventive checkups and have the protected equipment maintained by qualified personnel. Reference electrodes (testing by an independent electrode), the resistance of conductors, operation of regulators, sources, signalization, and the state of corrosion attack of critical places of the protected object should be subjected to regular checkups as well.

Maintenance should consist in timely replacement of those AP system parts that show signs of lower reliability, for example, the reference electrode when the potential oscillates outside the permitted interval. It is also essential to renew those parts that get worn by the operation, for example, electrodes and joints in the circuit.

The basic requirement for a reliable operation of AP is a timely signalization that alerts the personnel that the conditions of the operation mode are no longer complied with. The signalization can be complemented with an automatic action that decreases the aggressiveness of the corrosion environment (e.g., temperature reduction). The signalization should mean that the equipment operates in an emergency mode or that the emergency mode is needed. Failures that do not directly jeopardize the reliability of the operation and are thus not a reason for transition to the emergency mode should not be connected to this signalization; they should be removed by regular maintenance.

The emergency mode should ensure the operation of the AP system for a period of time necessary to remove the failure or to finish the production operation so as to avoid any production losses. After transition to the emergency mode, the personnel must distinguish the level of urgency, since some states may mean that even the emergency mode cannot prevent vast corrosion – in such a case, the equipment must be immediately shut down. Usually the operation can continue for several, even, tens of hours in the emergency mode. However, it is not advisable to opt for emergency modes that ensure long-term operation, because the personnel is thus not forced to promptly remove the failure that caused the transition from the operation mode to the emergency mode.

Since the AP-suitable corrosion systems' time to spontaneous activation must be at least 10–15 min (1 h is better), short-time source outage should not matter.

To enhance operation safety, back-up elements of the AP system are usually installed on the protected equipment. It concerns especially the reference electrodes that are installed in the minimum number of three – the operating one and the other two as back-up or controlling ones. The difference (higher than permitted) between the operating and back-up electrode usually causes the transition to the emergency mode. The installation of more reference electrodes also enables simple identification of the defective electrode and the exchange of the operating electrode. The back-up regulating circuit is also available, which consists of an independent regulator (or a source) and a back-up reference electrode. Therefore, it is possible to connect two potentiostats in parallel (Figure 3), and a periodic regulator in parallel to a potentiostat.

The transition from the operation mode to the emergency mode should be automatic.

Operation guidelines must be provided to each AP installation. It should solve specific problems of the equipment and give unambiguous directions for the personnel regarding controlling and maintenance as well as the identification of failures.

At present, AP systems are computerized. The computer records the operation parameters of the protected equipment. It enables the personnel to

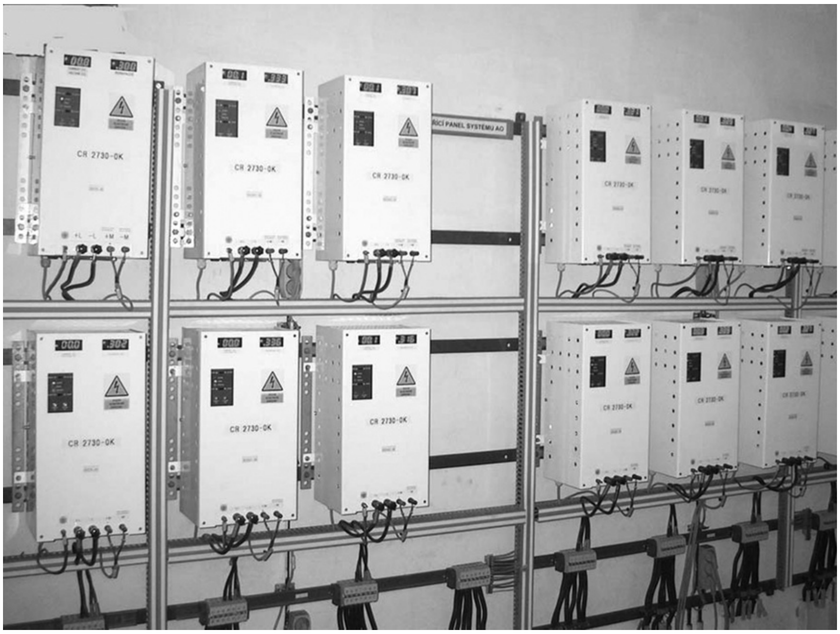

Figure 3 Main and back-up sources (potentiostats) for six anodically protected objects.

identify the cause of a failure and define the process of restoration to the normal state.

4.24.5.4 AP by Protectors

The source of current maintaining the potential of the protected surface in a passive range can be, in principle, formed directly in the protected equipment, if connected with a cathodic material (protector) in which reduction reactions proceed spontaneously. The AP by protectors is based on the principle of passivation by connection to cathodic materials. These requirements can be complied with by materials that can be divided into sacrificed and inert ones.

The sacrificed materials include oxide protectors composed of metal oxides that release electrons when dissolved in a corrosion environment, in particular, oxides of iron (Fe_2O_3) and manganese (MnO_2). Oxide protectors can be considered analogous to sacrificed anodes of cathodic protection, since they provide the necessary current by its dissolution, but of the opposite polarity.

Most of other materials that could be used as protectors provide the essential current by a reduction reaction of the solution components. It is given by the fact that cathodic reactions proceed on the surface of the protector (Pt, graphite) with lower overvoltage than on a passive metal.

Titanium is the best material for AP by protector, because it usually has a low passive current density and the passivation potential is substantially negative.

Protectors are not used in practice, since oxide protectors are consumed by spontaneous dissolution and must be thus frequently replaced or supplemented. Moreover, we cannot be satisfied with the existing fixation of protectors, because they have insufficient contact with the inside of the protected equipment. Inert protectors lose their activity continuously and their surface must be retreated by anodic polarization.

4.24.6 Elements of the AP System

The AP system consists of a protected object, cathodes, reference electrodes, and electric equipment (a regulated source of direct current and connection cables) (Figure 4).

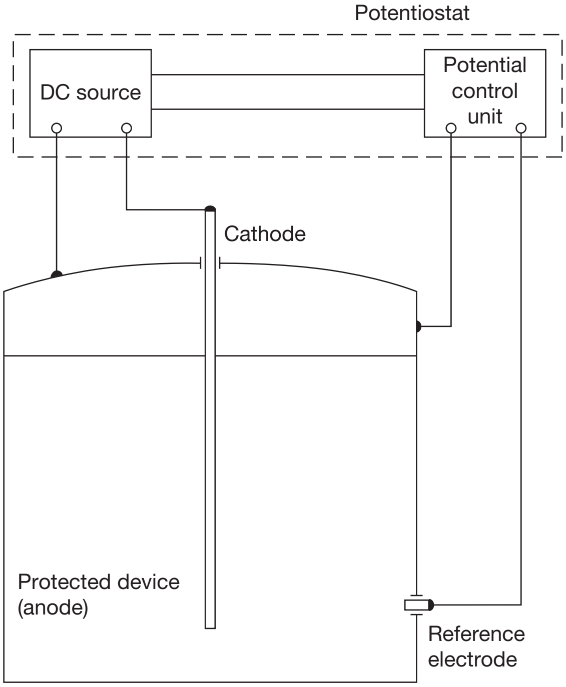

Figure 4 Diagram of anodically protected apparatus.

4.24.6.1 Cathodes

The passage of current polarizing an anodically protected metallic surface is ensured by an auxiliary electrode connected to a negative pole of the direct current source. During the passage of direct current, a reduction reaction of environment components proceeds at the cathode and the cathode partly corrodes. The distribution of the current on the protected surface must be ensured by a suitable construction of the cathode, and corrosion resistance of the cathode must be ensured by selecting a suitable material, protection mode, and the construction as well. The cathode material must have a sufficient service life. It must be recognized for its suitable mechanical properties, good electric conductivity, low cathodic reaction overvoltage, and an acceptable price. During the cathode polarization, it is theoretically possible to achieve a state of immunity where no corrosion occurs. This, however, requires very high current density, which, considering the uniform distribution of the protection current, is undesirable. High current densities can cause problems with the formation of nonconductive deposits or hydrogen entry in a metal. It is thus much more common to use the cathode under conditions of suppressed anodic dissolution, along with the continuous polarization. The cathode construction depends, in particular, on the construction of the protected equipment. The requirement to have cathodes usable for both passivation by current in the start-up mode and the operation mode is unrealistic in many cases, because it depends on the specific corrosion system (passivation currents, environment conductivity) and on the technology regime applied within the protected equipment (batch, continuous, liquid-level fluctuation). The necessity to construct cathodes for operation modes, while considering the throwing power, is overrated, given high conductivity of electrolytes applied successfully for AP. The throwing power of AP is very high on passive equipment. Given that the conductivity of corrosion environments suitable for AP often exceeds 10 S m^{-1} and the current densities do not achieve 0.1 A m^{-2}, there is no essential difference, for example, for sulfuric acid coolers, between polarization of surface in the distance of 1 mm and meters from the cathode. The main ohmic resistance in the system is exerted by the passive layer. The smallest distance between the cathode and the protected surface is given by the risk of a galvanic contact at operation vibrations of the protected equipment, and the greatest distance is given by the acceptable deviation from the protection potential, which can rise in many cases up to 100 mV.

Different types of stainless steels, nickel alloys, nickel, carbon steel, silicon casts iron, graphite, lead, copper, platinum, platinum plated metals, tungsten, and others are materials used for cathodes, depending on the corrosion environment.

In case of the most frequent applications of AP on sulfuric acid coolers, cathodes are usually placed in parallel to the exchanger axis. Even the cathodes placed transversally through an unbound bundle of pipes proved to be very successful (Figure 5). The advantage of this solution is that short weld-free cathodes can be used. The length of cathodes equals the exchanger's outside diameter plus the allowance for sealing and electric contact.

Another advantage of the transversal arrangement is that it is necessary to seal only the opening for a cathode at the outside shell. With this arrangement, it is possible to refit the sealing during operation without any risk of acid leakage to the cooling water in case of sealing failure. This construction solution also eliminates intensified corrosion of cathodes going through baffle plates. Practical experience shows that the service life of cathodes made of common austenitic steel at temperatures of acid up to 90 °C is ~3 years and they are simply replaceable. Cathodes made of nickel alloys are recommendable for higher temperatures and lower concentrations of acid.

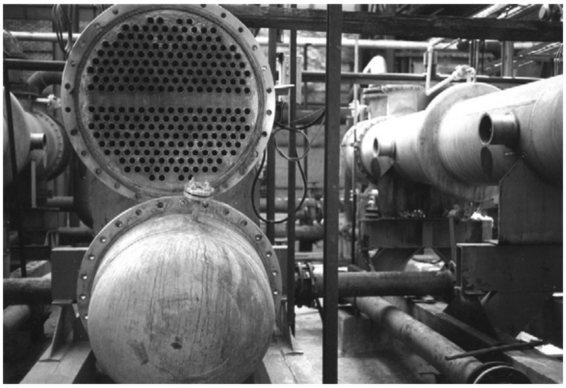

Figure 5 Horizontal shell and tube coolers with spacing of tube bank. Rod stainless steel cathodes are placed transversally through an unbound bundle of pipes.

In vertical storage vessels, it is advisable to use cathodes in the vessel axis so as to avoid galvanic contact with the bottom, however, to secure operation even with the minimum volume of liquid in the vessel.

The size, number, and location of cathodes are individual according to the type of the protected object. The potential distribution over the protected surface is approximately calculated according to mathematical relations derived for different regimes.[17–23] Nevertheless, it must be taken into consideration that, in case of the industrial AP applications that stood up the competition of other anticorrosion measures, the protected surface predominantly passivates spontaneously and the conditions of current distribution at passivation thus do not have to be addressed.

4.24.6.2 Reference Electrodes

To make the AP system work well, it is necessary to keep the potential of the entire protected surface within the potential passivity range where corrosion rate is technically acceptable. The reference electrode, which is contained as a permanent part in all existing AP systems, acts as a potential measurement sensor. Bad function of a reference electrode can cause critical damage to the protected equipment, that is why reliable types of electrodes are used and more electrodes are placed in an ingle piece of protected equipment. Electrodes act as sensors, which the direct current source is attached to as well as sensors for back-up and controlling systems. The reference electrodes must prove to be stable enough under operation, and to have a minimum service life of 1 year. Bad function of a reference electrode may cause that a potential of the protected equipment lies outside the required passive range. Any shift to both positive and negative directions may lead to the growth of corrosion rate – in some cases, by several orders of magnitude, the consequence of which is damage of the equipment.

Any electrode that is difficult to polarize and the potential of which does not significantly change in time or in environment may serve as a reference electrode to measure potential in an electrolytically conductive environment. The requirement of the operating reference electrode potential oscillation by ±30 mV suffices for most anodically protected equipments.

In practice, reference electrodes are loaded with current that corresponds to the input resistance of a potential controller and the potential difference between the reference electrode and protected equipment. Polarizability of a reference electrode can be decreased by increasing its electrochemically active surface. Change of the electrode potential in time is given by the fluctuation of temperature and composition of the electrolyte solution. Temperature dependence of the potential of most reference electrodes can be disregarded to the extent of minor fluctuation of operation temperatures.

Electrodes that can be used as reference electrodes are generally distinguished to electrodes of the first and the second kind. On electrodes of the first kind, the reaction of charge transfer proceeds directly between the electrolyte components or between the electrode and an electrolyte component. Electrodes of the second kind exchange the charge through an insoluble salt or oxide.

The existence of equilibrium is supposed for the said kinds of electrodes, but the electrochemical protection may work even with reference electrodes that are in a stationary state in which mixed potential is established. These are electrodes upon which corrosion or metal deposition proceeds spontaneously, or electrodes to which the potential is enforced by a passage of direct current.

The majority of reference electrodes used or usable for AP belong to electrodes of the second kind, such as calomel electrode, silver chloride electrode, and mercury sulfate electrode for sulfuric acid environments, and mercury oxide electrode for alkaline environments (Figure 6).

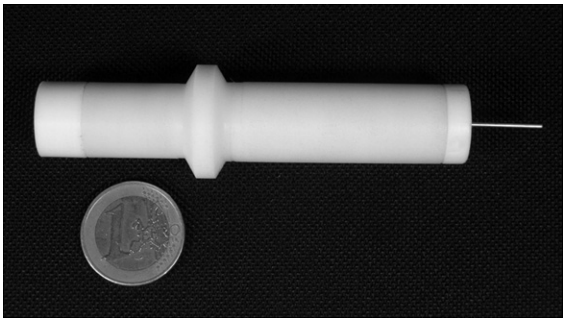

Figure 6 Reference electrodes filled with working medium are used for sulfuric acid and sodium hydroxide applications.

The equilibrium on oxide electrodes of all kinds is affected by the concentration of OH^- or H^+ ions, that is, by the pH of the solution. The advantage of these electrodes is that they can be used (except for the mercury oxide electrode) directly in the corrosion environment without the necessity to separate electrolyte. The disadvantage is that they have a lower potential reproducibility, which is given by the effect of other oxidation–reduction reactions of the corrosion environment components. A number of oxidized metals were tested for AP in terms of their use as a reference electrode. Pt, Au, Rh, Ir, Hg, Sb, and Mo oxide electrodes are used preferentially.

A nickel electrode in the environment of electroless nickel bath is one of the nonequilibrium electrodes upon which a stationary reaction proceeds and which can be used as a reference electrode. The electrodes that maintain their potential as a consequence of a corrosion reaction include, for example, bismuth in liquid fertilizers containing ammonium nitrate, carbon steel, and lead in the solution of ammonium hydrogencarbonate, and silicon cast iron in hot concentrated sulfuric acid. Also, other metals can be used in the environment where the acceptable corrosion rate below 1 mm $year^{-1}$ secures sufficient potential stability along with the acceptable service life of the electrode. This type of electrode can be used only if there is no risk that the electrode suddenly turns from the active to the passive state and vice versa. Metal depositions must be regularly removed from the surface of nonequilibrium electrodes and corroding electrodes must be replaced with new ones. The overview of reference electrodes used in operation is given in Table 1.

Construction solution of the reference electrode or the whole potential sensor is applied according to the specific type of equipment and conditions given by the corrosion environment. With the potential sensor, we understand not only the electrode itself, comprising the filling and the electrode casing, but

Table 1 Reference electrodes for industrial anodic protection

Electrode	*Environment*
Calomel (Hg/Hg_2Cl_2)	Sulfuric acid Ammonium nitrate–urea Alkaline solutions Universal
Mercurosulfate (Hg/Hg_2SO_4)	Sulfuric acid Hydroxylammoniumsulfate
Silver chloride (Ag/AgCl)	Sulfuric acid Ammonium nitrate–urea Universal
Silver sulfide (Ag/Ag_2S)	Kraft liquor
Platinum Pt/PtO_2	Sulfuric acid Phosphoric acid Mixed fertilizers
Gold (Au/Au_2O)	Sulfuric acid Phosphoric acid
Molybdenum (Mo/MoO_3)	Sodium hydroxide Sulfuric acid Phosphoric acid
Bismuth (Bi)	Ammonia environment
Nickel (Ni)	Electroless nickeling Sodium hydroxide Mixed fertilizers
Silicon (Si)	Mixed fertilizers
Chromium (Cr)	Mixed fertilizers
Passive austenitic steel	Ammonium nitrate
FeCr18Ni10	Sodium hydroxide
Silicon iron	Sulfuric acid
Mercuroxide (Hg/HgO)	Sodium hydroxide
Mercurophosphate (Hg/Hg_3PO_4)	Phosphoric acid
Wolfram (W/WO_3)	Sulfuric acid
Graphite	Ammonia environment Ammonium nitrate–urea

also fittings for the electrode installation and connection to the regulating circuit.

Reference electrodes are distinguished to immersing, level, pressure, and external electrodes according to how they are attached to the equipment. Pressure electrodes are most frequently used in completely filled equipment and below the liquid level in pressure-free equipment. The advantage is that the electrode–circuit connection and the shielded wires are located outside the aggressive environment. On the other hand, the necessity to have reliable pressure plugs and the impossibility to replace electrodes without the equipment shut-down are disadvantageous. These electrodes should be able to operate in all positions.

A reference electrode is located in a place with a permanent electrolytical connection with the protected surface close to that surface. The best thing is to place the operating reference electrode close to the surface that is the least accessible for current from the cathode, or in places with critical temperatures or concentrations.

4.24.6.3 Electric Equipment

Direct current sources that are connected with conductors to the AP system components and the protected equipment are used in AP to polarize the protected surface to the potential within the passivity range. Other complementary electric devices are connected to control the operation and enhance reliability. The connection and the function of the AP electric devices vary according to the selected modes. Considering the technological development, many connections publicized in literature can be assumed as outdated.

A power-supplied rectifier is usually the source of direct current for AP. For AP, the final rectified voltage does not have to show low oscillation, since it was detected that filtration has no effect on the protection effectiveness. Automatically controlled sources operating in the mode of potentiostatic polarization are used the most frequently for AP (Figure 3).

The installed output per one AP unit mostly does not exceed 5 kW. The energetic needs of the AP system are negligible, the operational requirements for current are below $0.1\,\mathrm{A\,m^{-2}}$ (mostly $<10\,\mathrm{A}$), when the supply voltage is lower than 10 V. The price of the regulation device does not depend on the size of the protected object.

The automatic compensation of ohmic drop is desirable under operation conditions only in environments with low specific conductivity approximating $1\,\mathrm{S\,m^{-1}}$. If the reference electrode is placed in the vicinity of the protected surface, the ohmic drop is mostly not remarkable.

Some operation electric devices used for AP of objects with fluctuating liquid level have additional circuits that switch off the AP system automatically after emersion of the operating reference electrode, or cathode.

Cabling, with which the protected equipment, cathodes, and reference electrodes are interconnected with the source, regulator, and controlling devices, can be distinguished to power and measuring. Power cabling supplies the protection current to the protected equipment–source–cathode circuit and it must be rated to the values required by AP of the specific object.

The perspective development of electric devices used for AP is seen in the field of digital technologies. Controlling and operation will be secured by a computer or a microprocessor. Operation data of both the AP system and the protected equipment are continuously recorded and make it thus possible to identify the causes of potential deviations from the operation mode of the AP system.

4.24.7 Environments Suitable for AP

AP is used with passivable metals in electrolyte, having a sufficient width of a stable passive range (minimum 300 mV) and a low corrosion rate (usually <0.1 mm year^{-1}), where localized forms of corrosion do not occur at the protection potential. The minimum environmental erosion incidence and stable chemical composition are other important factors. Moreover, the environment must not be decomposed at the protection potential. The time to activation, after the polarization current is switched off, must be also sufficiently long (minimum 15–30 min).

Most literature data on metal passivation in aggressive environments are based on the results of laboratory experiments performed under conditions very difficult to be compared. This chapter summarizes, in general, the literature data in order to identify, considering significant corrosion systems, important parameters of optimal protection, and location of iso-corrosion lines (curves connecting conditions under which the rate of uniform corrosion achieves a given level) in the concentration–corrosion environment temperature graphs. The objective assessment is complicated by different testing times, different levels of corrosion environment pollution, and the dependence of the optimal protection potential on concentration and temperature of the corrosion environment.

Corrosion diagrams shown in this Chapter must be treated as orientation diagrams displaying zones with corrosion rate below 0.1 mm year^{-1} with or without AP. Zones with corrosion rate below 0.1 mm year^{-1} under AP are distinguished in two parts. In the first part, there is a high probability that the corrosion rate will dwell below this threshold, in the other so-called indefinite zone, the probability is ~50%.

In addition to corrosion rates, potential and current levels, another parameter vital for the AP is the corrosion environment conductivity. The conductivity acts as the decisive factor of the AP feasibility, it affects the throwing power, essential voltage of a direct current source, construction of a cathode, and the location of a reference electrode.

The conductivity of electrolytes changes within wide thresholds, depending on the composition, concentration, and temperature. Specific conductivity γ (S m^{-1}), that is, the reciprocal value of resistivity ρ (Ω m), is very important for AP. The concentration dependence of specific conductivity (γ) for some strong electrolytes at 25 °C is shown in Figure 7.

If the specific conductivity exceeds 10 S m^{-1}, no special measures are essential to be taken to ensure uniform distribution of current on the protected passivated surface, except for cases when the surface is shadowed (e.g., in crevices or in narrow pipes).

With specific conductivity ranging from 1 to 10 S m^{-1}, the AP is feasible, if more cathodes are used and their surface is located in approximately the same distance from all parts of the protected surface.

With specific conductivity below 1 S m^{-1}, the electrolyte resistance in a usual construction arrangement is comparable with the resistance exerted by the passive layer during the current passage. Even the voltage of a source relates, in particular, to the resistance of electrolyte between a cathode and an anode and rises up to tens of volts. After that, it is impossible to ensure a uniform distribution of protective current. The need for power supply grows and the safe source voltage is exceeded. Therefore, AP is not recommendable for specific conductivity below 1 S m^{-1}. Specific conductivity of electrolytes grows along with the temperature by 2% to 1 K.

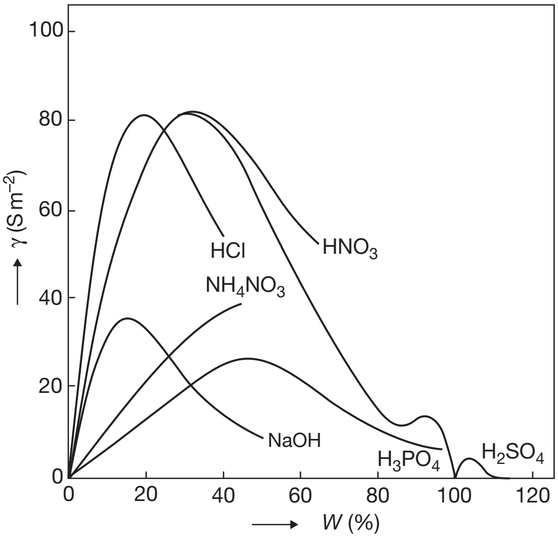

Figure 7 Concentration dependence of specific conductivity (γ) on various strong electrolytes at 25 °C.

4.24.7.1 Sulfuric Acid

A good deal of literature references deal with this environment, because it belongs among the most widespread in industrial conditions. Specific conductivity of sulfuric acid solutions with concentration of 2–96% exceeds $10\ \mathrm{S\,m^{-1}}$ under normal temperature. For concentrations above 96%, the specific conductivity decreases and hits the minimum at the concentration of 99.75% ($0.8\ \mathrm{S\,m^{-1}}$). Then it grows again and the oleum under normal temperature can reach a specific conductivity of $5\ \mathrm{S\,m^{-1}}$.

4.24.7.1.1 Carbon steel and cast iron

Technically acceptable corrosion rate of unprotected carbon steel can be allowed for only in an acid with a concentration over 70% at temperatures not exceeding 20–25 °C. Moreover, the corrosion resistance of steel remarkably drops with the motion of the corrosion environment. Carbon steel behavior in sulfuric acid during anodic polarization was observed under laboratory conditions by many authors within the entire concentration interval and also at elevated temperatures.

The potential–current polarization curves for carbon steels in sulfuric acid solutions can be divided into three types, characterizing a specific concentration interval. For low concentrations to those of 60 or 65%, the polarization curve of carbon steel in the sulfuric acid environment has a shape characterized by curve 1 in Figure 8. On the curve above the corrosion potential, there is a very wide range of activity with high currents. Passivation can be observed within a wide range of potentials where the current considerably oscillates. The passive range is limited by a transpassivation potential at which oxygen starts to evolve. Curve 2 in Figure 8 is characteristic of steel in acid with a concentration of 65–77%. The activity starts to be less significant and a second maximum appears in the passive range, and is followed by a range of low passive currents as far as the transpassivation potential, at which oxygen starts to evolve (similar to the previous case). Both curve 1 and curve 2 are the curves of the type-I in Figure 2(a). The third type of a curve is typical for steel in acid with concentration beyond 78%, including oleum. The initial progress is analogous to curve 2, that is, insignificant or no activity (curves of type-II or III in Figure 2(b) and 2(c)), the passive range is not limited by the transpassivation potential (up to 4 V(SHE)).

Sulfuric acid with a concentration up to 60% is noted for extremely high passivation current densities i_{cc} (asi $10^3\ \mathrm{A\ m^{-2}}$) (Figure 9) and high current densities in a passive range i_p (Figure 10) even at normal temperatures. The time to activation is usually very short, once the polarization is switched off.

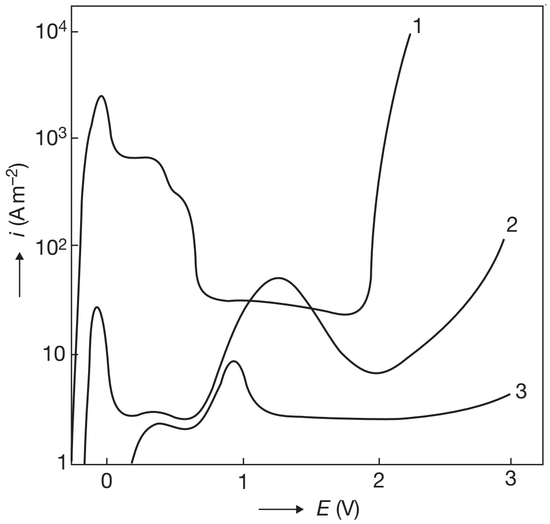

Figure 8 Potentiodynamic curves of mild steel in sulfuric acid at 25 °C. 1–25%, 2–70%, 3–90%.

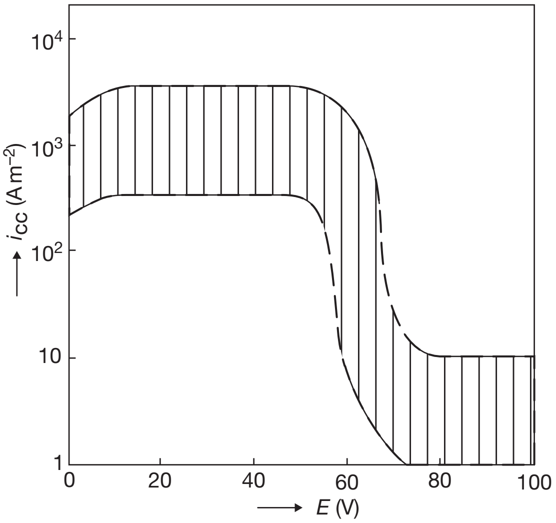

Figure 9 Dependence of mild steel passivation current density (i_{cc}) on the sulfuric acid concentration (wt%) at ambient temperature.

The use of AP is feasible only for concentrations over 70% where active range practically vanishes, since the steel shows a better tendency to spontaneous passivation. i_{cc} values drop exponentially with time to $1–10\ \mathrm{A\,m^{-2}}$ and even the passive current densities reduce significantly (below $0.1\ \mathrm{A\,m^{-2}}$).

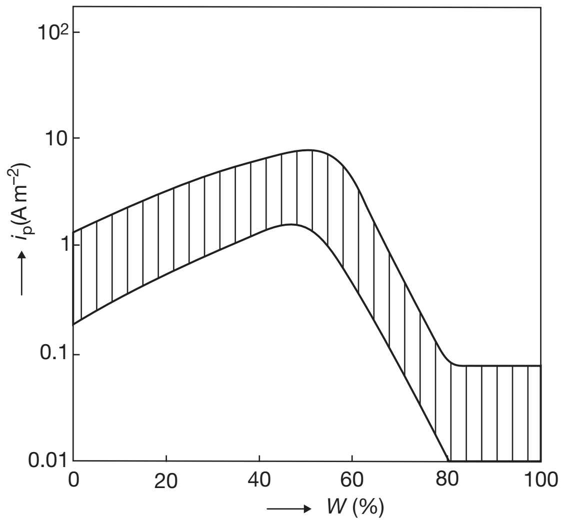

Figure 10 Dependence of mild steel passive current density (i_p) on the sulfuric acid concentration (wt%) at ambient temperature.

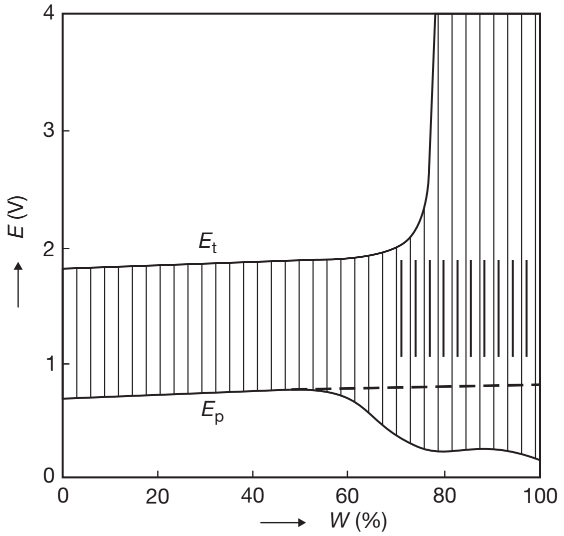

Figure 11 Dependence of mild steel passive range on the sulfuric acid concentration (wt%) at ambient temperature (close hatching – potential range suitable for AP).

Carbon steel behavior, depending on the acid concentrations, markedly changes according to the composition and higher stability of the forming passive layer. Within the range of potentials from 0 to 0.7 V, the steel resistance is based only on the layers composed of iron compounds in the oxidation state II; the stability of these layer is rather small in acid with concentrations up to 70%. At higher concentrations, the solubility of ferrous sulfate in acid diminishes. At higher potentials (over 0.7 V(SHE)), we can observe oxidization of compounds in the oxidation state II and formation of an oxide layer with iron in the oxidation state III, which is relatively resistant within the whole interval of acid concentrations. Beside the oxide layer, it is the ferric sulfate layer that applies at higher acid concentrations (over 70–80%).

The oxidization of Fe^{2+} to Fe^{3+} in compounds forming the protective layer leads to the send maximum on potentiodynamically obtained potential–current curves (curves 2 and 3 in Figure 8). The steel is passive practically from the potential of 0.2 V(SHE) and the second maximum has nothing to do with activity of the steel. It also explains the great influence of flow on the corrosion of anodically protected steel. The flow aggravates the passivation process within the whole concentration interval by eroding the primary salt layer that precedes the formation of the oxide layer.

Concentration dependencies of characteristic current densities i_{cc}, i_p and the potential E_p, E_t are depicted in Figures 9–11. The scattering of current values in Figures 9 and 10 is caused by different methodology and different hydrodynamic testing conditions.

Passivation current density (i_{cc}) values (Figure 9) lying within a concentration range over 70% depend, a lot, on time and are low, since the salt layer of ferrous sulfate forms spontaneously on the surface, and so it is disputable whether the notion ‘passivation current density’ is used correctly.

The dependence of a passive current density i_p on concentration is more complicated. Even the optimal protection potential within the sulfate layer (Fe^{2+}) depends on the acid concentration, and therefore, there are big discrepancies in the results presented by different authors. The relatively highest i_p and thus the corrosion rate values range within the interval of 75–100% for 95% H_2SO_4, minimum i_p and corrosion values can be observed at 80–90% and at 98–99%. The flow of acid can easily increase both the passive current and corrosion two to five times, and in the stability range of the sulfate layer (Fe^{2+}), even ten times.

At concentrations up to 60%, the passive range (Figure 11) is limited by potentials of 0.7 and 1.9 V; with the increase of acid concentration, it expands to both the negative side (the range of salt passivity of ferrous sulfate) and the positive side, because the overvoltage of oxygen evolution reaction is growing. With concentrations above 78%, oxygen does not evolve even at 4 V(SHE). Hatching of the range of potentials suitable for AP is more dense and lies within 1.0 and 1.8 V(SHE). At higher concentrations (∼96%), the best resistance is achieved within the potential range of 0.9–1.2 V(SHE).

Corrosion resistance data of the anodically protected carbon steel are generalized in a corrosion graph (Figure 12). The graph makes it obvious that if we need to have the corrosion rate below 0.1 mm year^{-1}, we can use carbon steel only at high concentrations of sulfuric acid and up to temperatures of ∼40–50 °C. The zone of probability defines the aggressiveness maximum within the exploitable concentration interval (at 95% concentration).

Since the unprotected steel, due to its low price, can be used to a limited extent even at temperatures when AP is effective, it makes sense to compare corrosion rates with and without protection. This proportion depends very much on concentration, temperature, and probably, also the flow. Mostly it varies between 10 and 100.

Results of tests of carbon steel AP were applied in operation conditions of storage of both pure concentrated sulfuric acid and oleum.

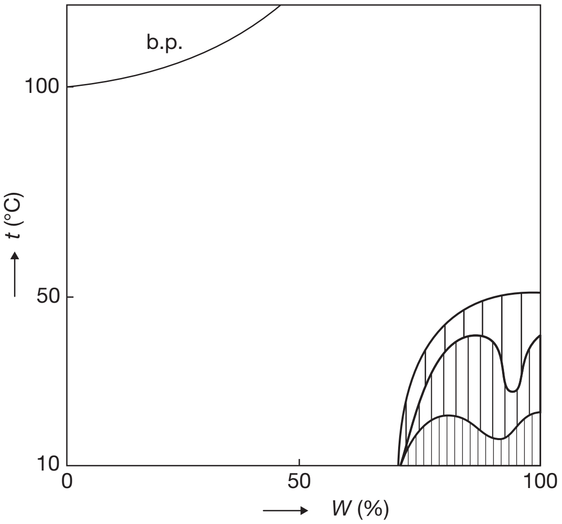

Figure 12 Range of corrosion rates below 0.1 mm year^{-1} for mild steel in sulfuric acid (closest hatching –without AP, thin hatching – with AP).

4.24.7.1.2 *Stainless steels and alloys*

Stainless steels and alloys on iron, chromium, and nickel basis are the fundamental construction material for heavily aggressive environments where AP can be applied. The properties of stainless steels can be modified by alloying, which gave rise to a number of types of stainless steels. The FeCr18Ni10(Mo) austenitic steels are of the greatest importance. Highly alloyed steels and alloys used for the construction of chemical plants are usually materials with sufficient resistance to corrosion, and mostly, it is not necessary to protect them anodically. AP allows their replacement by less costly chromium–nickel stainless steels.

Unprotected FeCr18Ni10 steels in sulfuric acid solutions have corrosion rate below 0.1 mm year^{-1} at normal temperature with concentration intervals below 10% and over 78%; FeCr18Ni10Mo steels below 20% and over 75%. The resistance drops with increasing temperature and at 50 °C, the FeCr18Ni10 unprotected steels can only be used at concentrations below 2%; the FeCr18Ni10Mo steel below 10% and over 90%. At temperatures over 70 °C, unprotected steels of this type are inapplicable in sulfuric acid up to 99% (Figure 13).

Corrosion resistance of chrome–nickel stainless steels largely depends on the content of oxidizing substances (e.g., oxygen, ferric ions) and the presence of activating substances (e.g., chloride ions) in the solution. Localized forms of corrosion (e.g., pitting, intergranular, corrosion cracking) can occur, depending on the composition and structure of the metal as well as on the presence of other substances in the sulfuric acid solution and its temperature.

The potential–current polarization curves for chromium–nickel austenitic steels have a typical shape at concentrations up to 80% (Type-I in Figure 2(a)), where significant activity is followed by a passive range limited by the transpassivation potential, above which the metal dissolves and oxygen evolves.

At a concentration over 80%, the activity range is gradually suppressed, the passive range is interrupted with a significant maximum at ∼1.7 V, beyond which there is a range of low currents. For concentrations exceeding 93%, the drop of current is permanent (to 4 V(SHE)), for concentrations from 80% to 93%, it grows again in the range above 2.3 V(SHE).

Although the passive layer is formed exclusively by oxides in the range of concentrations up to 80%, the sulfate layer applies even at higher concentrations and mitigates the oxygen evolution and anodic dissolution.

The passive range is determined by the passivation and transpassivation potential, see Figure 14. In fact, the passive range at higher potentials (over 1.5 V(SHE)) has no importance for AP. The potential range of the stable passivity is almost independent of the temperature; with the growth of acid concentration, the passivation and transpassivation potential slightly shifts to more positive values. The optimum

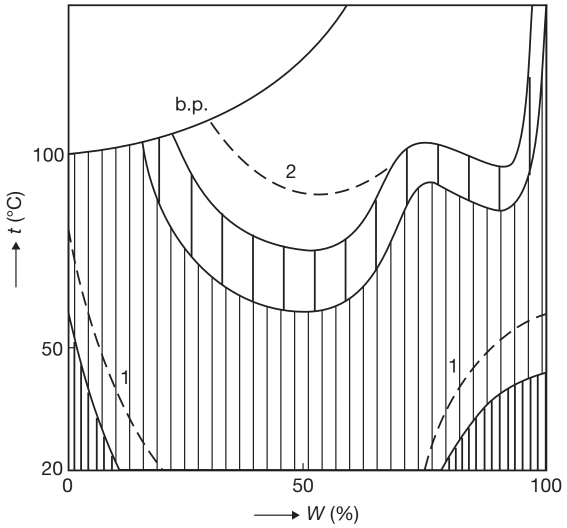

Figure 13 Range of corrosion rates below 0.1 mm $year^{-1}$ for stainless steel FeCr18Ni10(Ti) in sulfuric acid (closest hatching – without AP, thin hatching – with AP). 1 – isoline 0.1 mm $year^{-1}$ for FeCr18Ni10Mo without AP, 2 – isoline 0.1 mm $year^{-1}$ for FeCr18Ni10Mo with AP.

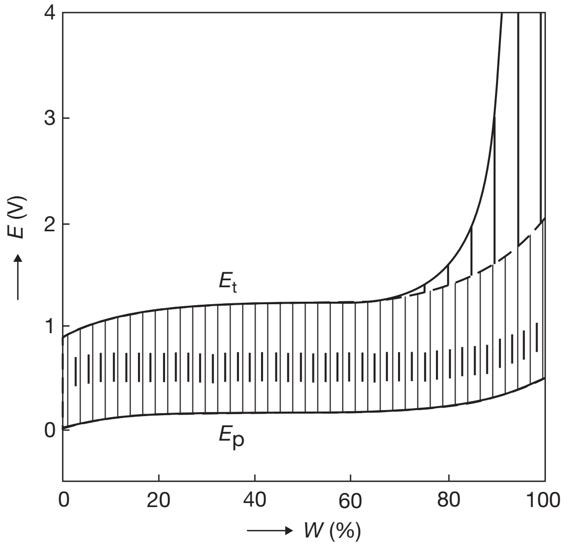

Figure 14 Dependence of stainless steel (FeCr18Ni10(Mo)) passive range on the sulfuric acid concentration (w (wt%)) at ambient temperature (closest hatching – potential range suitable for AP).

protection potential lies within 0.55 and 0.75 V(SHE) for concentrations up to 80%. At higher concentrations, the optimum potential shifts in a positive direction up to ~1 V(SHE) for 98% acid.

The values of passivation current density are concentration and temperature wise strongly dependent (Figure 15). The scattering of values in Figure 15

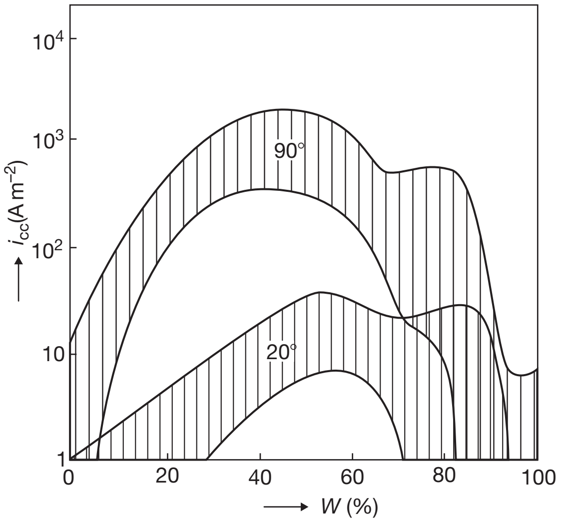

Figure 15 Dependence of passivation current density (i_{cc}) of stainless steel FeCr18Ni10(Mo) on the sulfuric acid concentration (wt%) at 20 and 90 °C.

is given, on the one hand, by the fact that the graph summarizes data for austenitic steels of various types, and on the other hand, by various experimental conditions. The growth of passivation current values i_{cc} along with the acid concentration is reported to be steep up to ~50%, which is followed by a drop, and steels in acid with concentrations higher than 70% at 20 °C or 85% at 90 °C are, according to other conditions, self-passivable. Spontaneous passivation also occurs at low concentrations of sulfuric acid.

Passive current densities grow more substantially with the concentration growth up to 20%. A steep drop follows after a flat maximum at 50–60%.

At 20 °C, the values i_p are stable within the whole concentration interval below 0.02 A m^{-2}; at 50 °C, below 0.1 A m^{-2}. The sulfuric acid concentration–temperature diagram with isolines of corrosion rate of 0.1 mm $year^{-1}$ is shown in Figure 13 for stainless steels of the FeCr18Ni10(Mo) type.

According to these data, AP extends the range of use of stainless steels of the FeCr18Ni10 type to the whole concentration interval of sulfuric acid solutions up to the temperature of 60 °C (for steels of the FeCr18Ni10Mo type up to 75 °C).

Corrosion rate with AP is technically acceptable up to 100 °C for concentrations lower than 20% and higher than 95%. For high concentrations, the maximum at corrosion rate isolines is achieved at ~78% and the growth after the minimum at 93% is steep; at concentrations of ~98%, sufficient resistance can be allowed for even at temperatures substantially exceeding 100 °C, if there is a minimum content of iron. The resistance of steels containing molybdenum is higher within the range of concentrations below 75%.

At concentrations below 80%, the potential–current polarization curves for chromium–nickel austenitic steels have a shape corresponding to the type-I (**Figure 2(a)**). The range of significant activity is followed by a passive range limited by the transpassivation potential, above which the metal dissolves and oxygen evolves.

At concentrations over 80%, the curve has a shape of either Type–I, II, or III according to the temperature and iron content (**Figure 2(a)–(c)**). The range of activity is gradually suppressed, the passive range is interrupted with a significant maximum at ~1.7 V, beyond which there is a range of low currents. For concentrations exceeding 93%, the drop of current is permanent (to 4 V(SHE)); for concentrations from 80 to 93%, it grows again in the range above 2.3 V(SHE). Although the passive layer is formed exclusively by oxides in the range of concentrations up to 80%, the sulfate layer applies even at higher concentrations and mitigates the oxygen evolution and anodic dissolution.

To achieve effective AP, the minimum concentration of iron ions in flowing sulfuric acid at 100 °C must be 7 ppm (solubility of ferric sulfate). The stability of the passive sulfate layer during acid flow is conditioned by the origination of trivalent iron compounds whose solubility in concentrated acid is, by approximately two orders, lower than that of bivalent iron compounds. Spontaneous passivation results in the formation of Fe^{2+} sulfate passive layer, while anodic polarization above 0.85 V(SHE) leads to the formation of Fe^{3+} sulfates. This is the reason why cooling systems with AP do not need any significant limitations of acid flow rate and why erosion corrosion does not occur in them, in contrast to systems without AP.

Austenitic stainless steel in hot concentrated acid has a curve with the shape of type-I (free corrosion potential in activity only) (**Figure 2(a)**) merely in pure acid, while in acid with increasing iron content, the shape is of a type-II (two free corrosion potentials) (**Figure 2(b)**), exceeding 7 ppm Fe type-III (free corrosion potential in passivity only) (**Figure 2(c)**).

In hot concentrated sulfuric acid, we can observe a spontaneous oscillation of free corrosion potential between the active and passive state. The oscillations are caused by reversible changes in the exchange current relating to the cathodic reduction of sulfuric acid, depending on the presence or absence of nickel sulfide on the steel surface.

Moreover, AP increases corrosion resistance of chromium and high-alloyed steels. Their curve of concentration dependencies of characteristic current densities i_{cc}, i_p is identical, in terms of quality, with that of chromium–nickel steels. Values of optimal protection potentials are also approximately the same. Temperature dependence of currents typical for stainless steels can be predominantly expressed by the value of activation energy 60–80 kJ mol^{-1}.

Laminar flow of sulfuric acid solutions facilitates the passivation of stainless steel and does not affect corrosion in a passive range. Turbulent flow can have an adverse effect in the interval of acid high concentrations. The time to spontaneous activation gets shortened by the flow of concentrated acid.

Stainless steels can be anodically protected even in environments where sulfuric acid is mixed with organic substances, for example, in the production process of acrylamide, isobutylene, sulfonic acid, nitrobenzene, and others. AP is also possible in the presence of small amounts of chloride and fluoride ions. Their addition, however, gives rise to i_{cc} and i_p values and narrows the passive range.

4.24.7.1.3 Titanium

The corrosion resistance of unprotected titanium in sulfuric acid is limited to concentrations below 10%. At 70 °C, however, the corrosion rate exceeds the threshold of 0.1 mm year^{-1} even at low concentrations. Titanium is resistant at the boil only in solutions with concentration below 0.1% (**Figure 16**). Concentration dependence of unprotected titanium corrosion rate shows two maxima, the first at 40% and the other at 80%.

The anodic polarization of titanium in sulfuric acid solutions leads to passivation after the passage through the active range. Further polarization to high positive potentials (over 2 V(SHE)) makes the current grow gradually, but the passive layer remains stable up to very high values, even over 80 V. The growth of current in this range is not interrelated with the growth of corrosion rate, it is rather given by the oxygen evolution rate that is limited by high overvoltage resulting from low electron conductivity of the passive layer.

Current–time potentiostatic dependencies show that current drops at high positive potentials with time to relatively low values; the proportion of corrosion reaction on such current amounts from tenths to percentage points at maximum. Currents

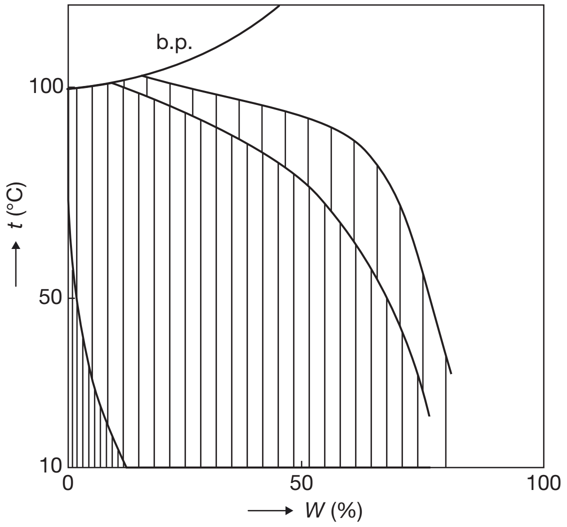

Figure 16 Range of corrosion rates below 0.1 mm year^{-1} for titanium in sulfuric acid (closest hatching – without AP, thin hatching – with AP).

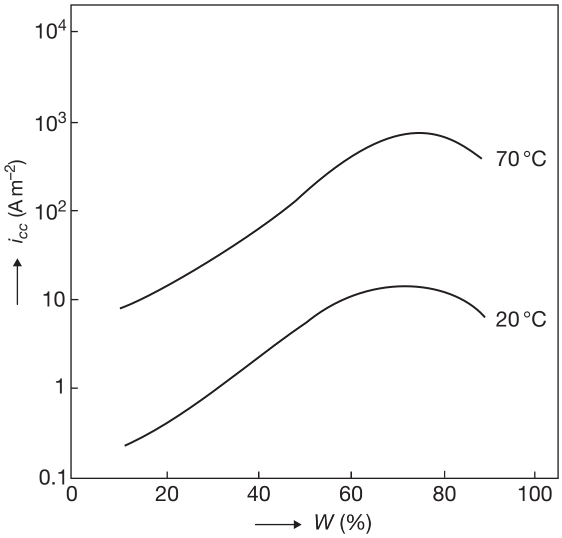

Figure 17 Dependence of passivation current density (i_{cc}) of titanium on the sulfuric acid concentration (wt%).

exceeding the potential of 2 V(SHE) are always higher than those within the interval from 0.5 to 2 V (SHE).

The use of protection potential over 0.6 V(SHE) provides sufficient protection under all conditions where AP of titanium in sulfuric acid is effective. Optimal values of protection potential, in terms of both corrosion and consumption of protection current, range from 0.6 to 1.5 V(SHE). If it is necessary to increase the throwing power of the protection, high potential values, such as 12–15 V, can be used for polarization. Corrosion is not tremendously accelerated, and thereby, only the consumption of protection current is higher.

The critical passivation current density also depends on the acid concentration and grows within the exploitable concentration interval (Figure 17). Temperature dependence of i_{cc} and i_p currents is expressed by the activation energy from 60 to 75 kJ mol^{-1}.

The corrosion graph in coordinates of sulfuric acid concentration–temperature is depicted in Figure 16. It is apparent from the graph that AP substantially widens the range of titanium corrosion resistance in sulfuric acid. Another important feature is the resistance of anodically protected titanium within the range of concentrations from 30 to 60% at elevated temperatures, when even the use of AP cannot guarantee sufficient resistance of stainless steels.

Another significant advantage of AP of titanium in sulfuric acid is its efficiency even at the presence of substances aggravating the passivity of stainless steels (chloride ions, sulfides). Chlorine bubbling has an oxidizing effect on titanium in sulfuric acid, which can be used for protection above the electrolyte level. The stability of a passive layer on titanium is considerably high, and when the polarization current source is switched off, it gets activated no sooner than after several hours. AP of titanium is not applicable if even small amount of fluorides is present in the solution.

Laboratory experiments as well as operation installations proved the efficiency of AP of titanium on sulfuric acid solutions in the presence of sodium sulfate, zinc sulfate, sulfane (hydrogen sulfide), and carbon sulfide. AP can be also used for titanium alloys, but we definitely cannot expect better results than those with pure titanium. Alloys with molybdenum have the passive range limited by the transpassivation potential of 0.75 V(SHE) and alloys with chromium by the transpassivation potential of 1.2 V(SHE).

Low passivation currents facilitate the passivation of titanium compared with stainless steels. Because of the passive range unlimited by transpassivity, it is possible to provide protection by polarization under constant terminal voltage.

4.24.7.2 Other Inorganic Acids

The aggressiveness of phosphoric acid depends on its purity, which is indicated by the production method. Technical phosphoric acid contains sulfates, fluorides, chlorides, and other anions. Carbon steel is attacked by both pure and technical phosphoric acid within the entire concentration interval. The resistance of stainless chromium–nickel steels in phosphoric acid is good. Up to 50% concentration, all of their types resist even at a temperature of 100 °C; at higher concentrations, it is especially the composition of austenitic stainless steel that applies. Steels alloyed with molybdenum show sufficient resistance at all concentrations up to 90 °C.

Technical phosphoric acid is more aggressive to stainless steels, particularly in terms of the content of chlorides and fluorides (fluorosilicates). The corrosion rate then exceeds the acceptable thresholds even at low concentrations of these anions. Pitting corrosion occurs in 75% phosphoric acid containing chlorides in the amount within 15–20 mg l^{-1}. Titanium shows much worse resistance against phosphoric acid than do stainless steels.

Carbon steel can be passivated in concentrated solutions of phosphoric acid and the passive range in 75% acid at normal temperature lies within 0.6 and 1.75 V, but currents in the passive range are high and the corrosion rate substantially exceeds 0.1 mm $year^{-1}$. Slightly better results can be achieved with AP of carbon steel in mixtures of phosphoric and sulfuric acids. In general, we cannot expect that AP of carbon steel in phosphoric acid will be used more widely.

The passivity of stainless steels in pure concentrated phosphoric acid ranges in the interval of potentials from 0.3 to 1.2 V(SHE). Currents in the passive range are, by orders of magnitude, lower than those of carbon steel, and the AP can thus be considered even for higher temperatures.

It is shown in the corrosion graph (Figure 18) that was set up for pure phosphoric acid. What is probably more important than AP of stainless steels at high temperatures in pure acid is the possibility to reduce high corrosion aggressiveness of phosphoric acid contaminated with chlorides and fluorides.

Although the application of AP to titanium in phosphoric acid substantially widens the range of temperatures and concentrations at which the titanium corrosion resistance is below 0.1 mm $year^{-1}$, there is a number of cheaper metallic materials that, even unprotected, are much more resistant (e.g., stainless steels and lead). AP of titanium could be considered effective in phosphoric acid solutions containing higher amount of chlorides, with no fluorides though.

With hydrochloric acid, it is only possible to consider the AP of titanium. The corrosion resistance of unprotected titanium in hydrochloric acid is limited to low concentrations only, according to the presence of oxygen and other oxidizing elements.

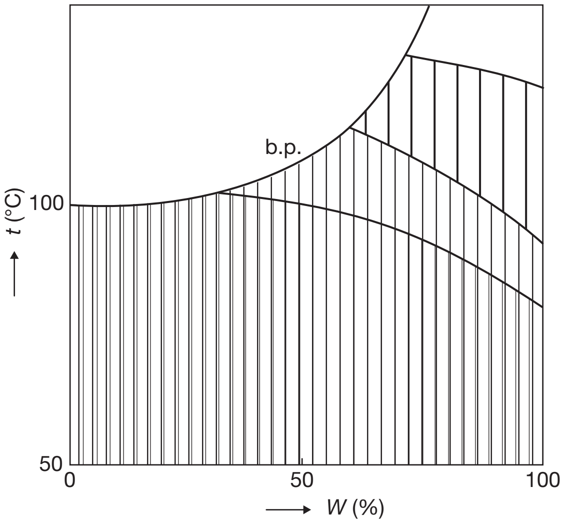

Figure 18 Range of corrosion rates below 0.1 mm $year^{-1}$ for stainless steel FeCr18Ni10(Mo) in phosphoric acid (closest hatching – without AP, thin hatching – with AP).

The titanium passivation potential shifts with the growth of hydrochloric acid concentration to positive values and the protection potential above 0.4 V(SHE) guarantees effective protection at all concentrations and temperatures suitable for the AP of titanium (Figure 19). The optimal interval of protection potentials ranges from 0.5 to 1.5 V(SHE). At potentials over 5 V(SHE), the passive layer is broken through and titanium is attacked by pitting corrosion.

The corrosion graph with coordinates of hydrochloric acid concentration–temperature (Figure 20) clearly shows that AP widens the corrosion resistance of titanium from 20 to 50 °C to the entire concentration interval.

AP of stainless steel can be effective also in nitric acid containing chlorides, where nitrate anions substantially inhibit formation of pitting corrosion.

4.24.7.3 Organic Acids

The anodic passivation of metals is also possible in aqueous solutions of organic acids, though the specific conductivity of their pure solutions is usually less than 1 S m^{-1} at normal temperature (save for the oxalic acid, the conductivity of which exceeds 1 S m^{-1} already from 1%).

There are just seldom literature references regarding the AP of titanium, carbon steel, stainless steels,

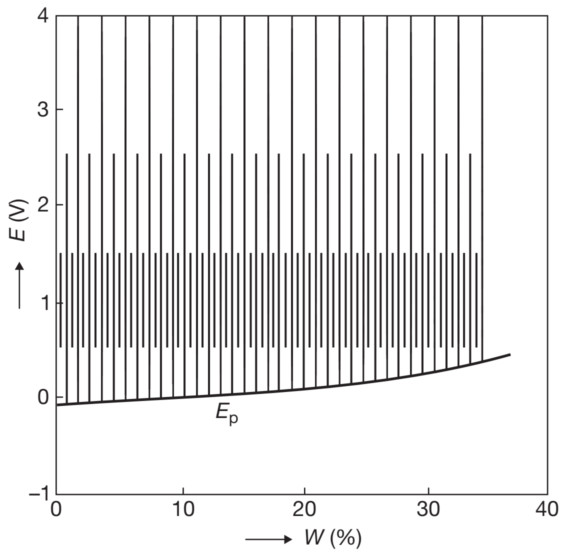

Figure 19 Dependence of titanium passive range on the hydrochloric acid concentration (*W*) (close hatching – potential range suitable for AP).

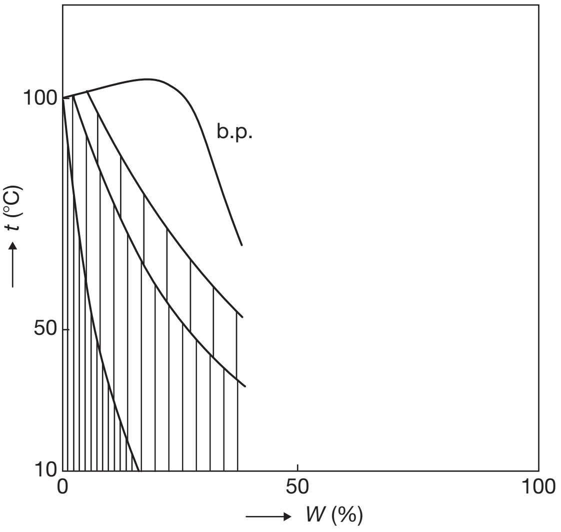

Figure 20 Range of corrosion rates below 0.1 mm year^{-1} for titanium in hydrochloric acid (closest hatching – without AP, thin hatching – with AP).

nickel, and its alloys in formic, acetic, oxalic, lactic, citric, and sulfane acids.

4.24.7.4 Inorganic Salts

4.24.7.4.1 Ammonium nitrate

Ammonium nitrate is widely used as a part of liquid nitrogen fertilizers, and very often, is the most aggressive part of such solutions. With increasing concentrations of ammonium nitrate from 10 to 60%, the carbon steel corrosion rate grows up to the maximum at 40% concentration. Stainless steels are resistant in the ammonium nitrate environment.

Besides free ammonia, nitrogen fertilizers also contain urea, which acts there as a solvent. The addition of urea slightly reduces the corrosion aggressiveness of ammonium nitrate, still the corrosion rate is technically unacceptable. A substantial reduction of corrosion aggressiveness of the $NH_4NO_3–CO(NH_2)_2–H_2O$ system can be achieved by addition of ammonia up to 3%. The possibility to anodically protect carbon steel in ammonium nitrate solutions with $pH = 4.5–11$ is addressed already by the first studies on AP. Another type of liquid fertilizers containing high amount of ammonium nitrate, where AP of carbon steels can be used, are solutions containing ammonium carbonate. Corrosion resistance of carbon steel in ammonium nitrate solution containing calcium carbonate can be increased by anodic passivation.

The most widespread type of an ammonium nitrate-based liquid fertilizer is the solution containing 40–45% of ammonium nitrate, 25–30% of urea, and 20–30% of water, (UAN): carbon steel can be placed in the liquid fertilizer UAN in both active and passive state within the whole range of pH values (5–9). At $pH < 7$, the originally passive surface spontaneously activates and the passive state can be restored only by AP. However, the increase of pH values over 7.5 after the steel activation does not induce spontaneous passivation, but accelerates the corrosion rate. At $pH > 7.5$, the passivated surface (oxidized in air) does not activate and the AP is not essential.

4.24.7.4.2 Sulfates, phosphates, chlorides, thiocyanates

Neutral sulfate solutions do not cause any major problems due to their corrosion aggressiveness to metallic materials. Corrosion is affected, in particular, by the solution pH and by the content of substances influencing the oxidation–reduction potential of a metal. Corrosion aggressiveness grows with the drop of the pH value of the solutions.

The applicability of AP to stainless steels was verified for solutions of zinc sulfate, manganese sulfate, aluminum sulfate, alums, hydroxylammonium-sulfate, and ammonium sulfate.

Ammonium sulfate is present in extremely acidic solutions where AP of stainless steel can be applied, similar to the production of formic acid.

High aggressiveness of sulfate against carbon steel can be mitigated by AP. It is advantageous in solutions containing ammonium nitrate, which suppresses the activating effect of sulfates on steel. Solutions of hydroxylammoniumsulfate (NH_3OHSO_4) used in the ε-caprolactam production process are very aggressive because of their hydrolyzing effect and the content of free 10% sulfuric acid. Unprotected stainless steels in active state corrode in this solution at elevated temperatures. The behavior of the solution is analogous to that of the sulfuric acid solution and the salt itself does not participate significantly in its corrosion aggressiveness. Similarly, to sulfuric acid, AP of stainless steel ensures high corrosion resistance in this environment.

Mixtures of phosphates and sulfates make the fundament of combined fertilizers. Parameters of stainless steel AP were verified just for the conditions in reactors for the production of such fertilizers. The conditions of producing fertilizers by the decomposition of apatite by sulfuric and nitric acid, after ammoniation and addition of potassium chloride solution, give rise to the formation of a solution inducing pitting corrosion of stainless steel. This can be eliminated by AP over the inhibition potential, which exists at polarization curves, depending on the steel composition, temperature, and the content of chlorides and nitrates in the solution.

Stainless steel in active state can corrode in thiocyanate solutions (SCN^-). Its passivation can be achieved by anodic polarization, but the passive range is limited by potential, above which thiocyanate oxidizes. With AP, it is possible to mitigate the corrosion of FeCr18Ni10MoTi steel at temperatures between 90 and 120 °C in concentrated sodium thiocyanate solutions, and thus, reduce the iron content in the solution. Iron ions enter the solution due to the equipment corrosion and thus slow down the polymerization in the production process of polyacrylonitrile fiber.

4.24.7.5 Aqueous Solution of Ammonia

Aqueous solutions of ammonia are not very aggressive toward carbon steel (the corrosion rate is below 0.1 mm year^{-1}), though the corrosion rate may reach the values of 0.5 mm year^{-1}, if the solution contains a small amount of other substances. The corrosion rate of carbon steel depends not only on the content of these substances (CO_2, Cl^-, NO_3^-, CH_3COO^-), but also on the content of oxygen, the pH of the solution, and ammonia concentration (pH of the solution does not depend only on the ammonia concentration but also on the content of other substances). Up to 5% of ammonia, carbon steel passivates spontaneously. At higher concentrations and $pH < 12$, passive steel spontaneously activates. At $pH > 12$, the activation depends on the oxygen content in the solution, the superficial state, and other factors. The corrosion rate of active specimens grows with the access of oxygen, whereas, in case of passive specimens, the effect of oxygen is positive.

The specific conductivity of pure ammonia solutions is very low, but in operation conditions, achieves values up to 10 S m^{-1} due to contamination.

The curves of potential–current polarization dependencies for carbon steel in pure aqueous ammonia solutions with concentration exceeding 25% have a shape analogous to Type-III in Figure 2(b). The corrosion rate within the passive range is negligible, thousandths to hundredths of mm year^{-1} in the order of magnitude. The content of oxygen positively affects the effectiveness of AP, and thus, it is advisable to ensure oxygen access to the metallic surface by stirring the solution.

4.24.7.6 Hydroxides of Alkaline Metals

Nonalloyed steels have, in sodium hydroxide solutions up to 60 °C, a very low corrosion rate of 0.1 mm year^{-1} for all concentrations (Figure 21). In 15% solution of sodium hydroxide, they show sufficient resistance even at the boil. However, the occurrence of corrosion cracking is more important than the uniform corrosion rate. The range of possible occurrence of corrosion cracking is defined in the sodium hydroxide concentration–temperature graph (Figure 21) by curve 2. Its position shows that it is this dependence that is decisive for the use of nonalloyed steels in the sodium hydroxide solutions rather than the isoline of corrosion rate 0.1 mm year^{-1}.

The specific conductivity of solutions of alkaline metal hydroxides exceeds 10 S m^{-1} at normal temperature within the almost entire concentration interval.

AP in sodium hydroxide solutions is important particularly for nonalloyed and low-alloyed steels. At higher temperatures and pressures, or at higher concentrations of sodium hydroxide, AP of austenitic stainless steels can be considered.

The anodic polarization of nonalloyed and low-alloyed steels in the sodium hydroxide solution leads to passivation, and the shape of the curves strongly depends on the presence of oxidizing agents and other substances. The range of potentiodynamic

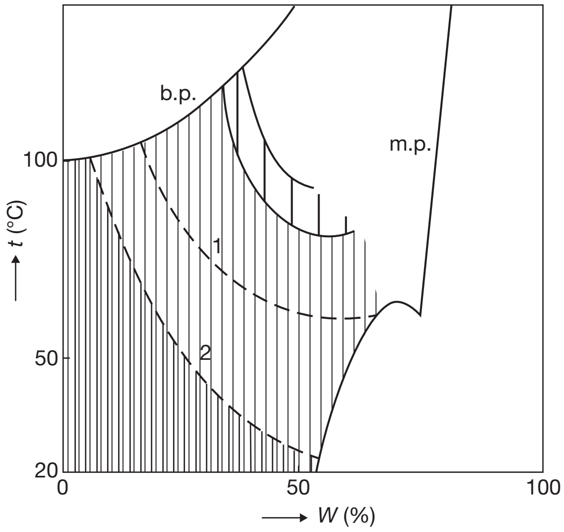

Figure 21 Range of corrosion rates below 0.1 mm year^{-1} for mild steel in sodium hydroxide. 1 – corrosion rate 0.1 mm year^{-1} without AP, 2 – limit of possible SCC occurrence without AP (closest hatching – without AP, thin hatching – with AP).

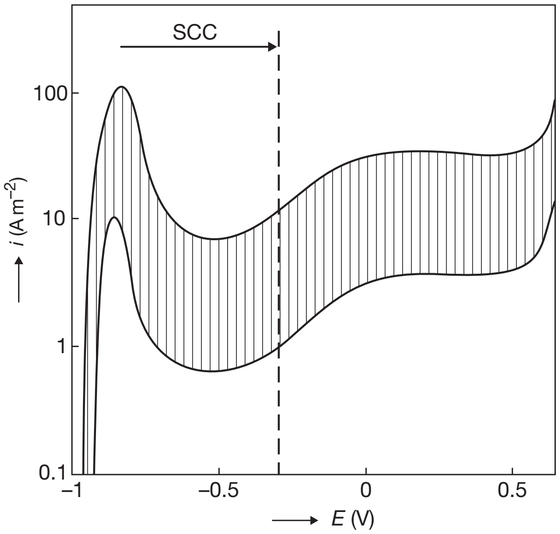

Figure 22 Courses range of potentiodynamic curves of carbon steel in 35% sodium hydroxide at boiling point (SCC – potential range of SCC).

dependencies in 35% solution of sodium hydroxide at the boil is depicted in Figure 22.

The passive range relating to sodium hydroxide concentrations from 5 to 50% lies within the potential interval from −0.7 to 0.5 V(SHE). However, only the part where corrosion cracking does not occur is exploitable. Having summarized the data of various authors, we can claim that the safe range for AP lies above the potential of −0.3 V(SHE).

The corrosion graph with coordinates of sodium hydroxide concentration–temperature (Figure 21) delimitates the likely range of AP for the elimination of corrosion cracking and the mitigation of uniform corrosion.

The greatest aggressiveness is shown by 50% sodium hydroxide solution; however, in this solution, AP is successful up to the temperature of 80 °C. At lower concentrations, AP can be effective even in pressure equipment where temperature exceeds the boiling point under atmospheric conditions.

AP of carbon steel in the sodium hydroxide solution is feasible in both the solutions used in the technology of aluminum oxide production and in the presence of chlorides and sulfides, that is, in solutions used in the paper and cellulose production process.

The aggressiveness of potassium hydroxide is higher compared with sodium hydroxide, and the scope of usability of unprotected carbon steel is narrowed for the same concentrations by 20–30K from the perspective of both the uniform corrosion and corrosion cracking. The polarization properties of carbon steels in potassium hydroxide solutions do not differ much from those of solutions of sodium hydroxide. Even the potential ranges of corrosion cracking are similar.

4.24.7.7 Melts

If the corrosion in a melt is controlled by electrochemical process and the melt has a sufficient ion conductivity, AP can mitigate corrosion attack in this environment as well. The specific conductivity of melts of inorganic salts and hydroxides usually exceeds 100 S m^{-1}. Stainless steel can be anodically passivated in $NaOH–Na_2SO_4$, $NaOH–Na_3PO_4$, $NaOH–KCl$, $NaOH–NaCl–Na_2CO_3–NaNO_3$, and NaOH melts at temperatures up to 1000 °C.

Glass is electrically melted by alternating current and molybdenum electrodes. Problems with the corrosion of heating electrodes arise when the glass melt contains ions of metals, such as lead, arsenic, or antimony, which reduce at the electrode surface along with the oxidation of molybdenum. The reduced metal can form compounds with molybdenum, which further accelerates the corrosion of the electrodes. Laboratory experiments proved that a protective layer forms on the molybdenum surface during the anodic polarization in the glass melt, which protects the electrode surface against corrosion, and at the same time, does not overly constrain the passage of alternating current that electrically heats the glass melt. The specific conductivity of the glass melt strongly depends on the type of glass; values at the refining temperature typically range from 20 to 50 S m^{-1}.

4.24.7.8 Electroless Nickel Plating Baths

The reason for AP in electroless (chemical) metal plating baths is the necessity to avoid undesirable deposition of metals on the walls of the metal plating equipment rather than corrosion protection.

The electroless nickel plating baths are the most widespread. The deposited coating is an alloy of Ni–P, or Ni–B, according to the type of the used reduction agent. Especially, sodium hypophosphite (NaH_2PO_2) or sodium tetrahydridoborate ($Na[BH_4]$) is used as a reduction component of the baths.

Electroless nickel plating is an electrochemical process, in which reduction reactions lead to the formation of nickel and hydrogen, and oxidation reactions turn hypophosphite to phosphate, or phosphate. These reactions optimally proceed at temperatures from 90 to 95 °C.

Reactions can proceed at any surface showing a catalytic effect and enabling a charge transfer. The idea of using anodic polarization to protect the walls of the production equipment from the deposition of nickel was brought in the mid-1960s by German authors.

Anodic polarization can be used only for materials that do not suffer from corrosion (get passivated) and upon which the oxidation of solution elements is restricted. Electroless metal plating baths contain substances of a reduction nature, and therefore, the oxidation reaction upon the surface of the used material must have a high overvoltage.

Considering the nickel plating baths, these requirements are complied with by stainless steels and titanium within the entire range of pH values. In addition to that, nickel can be used in alkaline baths.

The spontaneous nickel deposition process starts at temperatures exceeding 60 °C, which is the temperature limit of the effective use of AP. The specific conductivity of nickel plating baths ranges from 3 to 30 S m^{-1} at operation temperature according to the composition. The interval of protection potentials for stainless steel in the environment of electroless nickel plating baths depends on the type of the bath, but for most acidic baths, it ranges from −0.25 to 0.8 V(SHE), the optimal potential interval is 0.5–0.8 V(SHE).

The passive range of stainless steels is wider than that indicated by the interval of protection potentials, and the corrosion rate within this range is negligible. The upper potential limit of the protection interval is given by the substantial growth of current resulting from the oxidization of the solution components, probably of the hypophosphite to phosphate, while the lower limit lies right above the starting point of spontaneous deposition of metallic nickel (−0.35 V (SHE)). The actual exploitable range of potentials is narrower, since the spontaneous potential of passivated stainless steel corresponds to ~0.25 V(SHE). Without polarization, this potential remains stable at maximum for several hours in the operation conditions. Then, nickel deposits on the walls, and the potential shifts in the negative direction to the value held by the metallic surface self-plated with nickel (−0.35 to −0.44 V(SHE)).

Current densities passing through the anodically protected surface of stainless steel at protection potential represent the rates of suppressed oxidation of the solution components rather than the corrosion rate.

The range of titanium protection potentials is wider and the protection current is lower than that of stainless steel. The overvoltage of anodic oxidation of hypophosphite is higher on passive titanium. Even the resistance of passive titanium against nickel deposition without AP is higher. It is possible to anodically protect stainless steels in baths containing chlorides and fluorides, but the interval of protection potentials is narrower. The use of titanium in baths containing fluorides is precluded.

4.24.8 Industrial Applications of AP

Detailed information on industrial applications can be found in monographs[6–9] on AP and in surveys in journals[5,10–13] and other sources[27,34]

4.24.8.1 Sulfuric Acid Coolers Made of Stainless Steel

A great deal of heat is released in the production of sulfuric acid and this heat must be transferred by the cooling of the acid circulating in the production equipment. Mostly, it is acid with 93% or 99% concentration, and in some cases, even lower (up to 75%). The acid is predominantly cooled from 90 to 40 °C and the maximum temperature is limited by the corrosion resistance of the cooling set. The first and the most widespread coolers of this type to date are vertical and horizontal shell and tube anodically protected heat exchangers with water in pipes and acid flowing in the anodically protected intertubular space[13,27,28,33] (Figure 23).

The construction of heat exchangers with water as cooling medium with acid in pipes is less frequent. Sporadic are data on anodically protected desk coolers; more data can be found regarding spiral coolers.[29,30] AP is also used for air coolers.[11,14,28] Even the tubes for acid transportation are anodically protected.[31,32] Cathodes are mostly made of either stainless steel or nickel alloys[48]; reference electrodes are either made of mercury sulfate or platinum.

A competitive solution to the AP of common austenitic stainless steel coolers is the use of high-silicon stainless steels that resist without AP.

The installations of anodically protected coolers of 75–78% sulfuric acid[13] in plants processing calcining gases from ferrosins production (Figure 24) are rather unusual due to the threshold concentration and temperature.

Figure 23 Anodically protected stainless steel heat exchangers for cooling of 93–98 wt% sulfuric acid.

Figure 24 Anodically protected stainless steel heat exchangers for cooling of 75–78 wt% sulfuric acid.

4.24.8.2 Stainless Steel Equipment Operating in Environment Containing Sulfuric Acid

The AP was described for transportation stainless steel vessels, measuring vessels, neutralization vessels for sulfonic acid, hydrolysis vessels, hydroxylammoniumsulfate storage vessels, heating coil, and turbocoolers of 55–65% sulfuric acid. Stainless steel was also used for the anodically protected vessel for storing pure sulfuric acid (94–99%) at temperatures up to 40 °C (Figure 25).

4.24.8.3 Other Anodically Protected Equipment Made of Stainless Steels

The industrial application of AP was described for storage vessels of technical concentrated phosphoric acid, reactors for the production of combined fertilizers containing chlorides,[34] and sodium thiocyanate evaporator.[34]

4.24.8.4 AP of Stainless Steel in Chemical (Electroless) Nickel Plating Bath

The vessels for chemical nickel deposition are numerous groups of anodically protected industrial installations. Instead of corrosion resistance, the AP prevents, in this case, the undesirable deposition of nickel on the stainless steel tank walls. Anodically protected titanium tanks are also used for current-free nickel plating. AP has become a standard equipment of operation lines for chemical nickel plating.[13,35] Due to the passage of current, nickel deposits on a cathode usually made of stainless steel. Stainless steels, where nickel spontaneously deposits, serve as a reference electrode. Nickel can be regularly removed from electrodes mechanically as well as by dissolution in nitric acid.

4.24.8.5 Carbon Steel Storage Vessels for Concentrated Sulfuric Acid

In addition to corrosion protection, the AP of sulfuric acid storage tanks made of carbon steel ensures high purity of the stored acid. The AP keeps the iron content in the stored acid on the ppm level, while in the case without AP, there are tens of ppm. Cathodes are made of stainless steel, reference electrodes are either mercury sulfate or platinum. There are a

Figure 25 Anodically protected tank for storing pure sulfuric acid (94–99%) at temperatures up to 40 °C.

number of literature data on AP of these vessels.[13,36] For waste acid, it deals only with the reduction of the corrosion rate.

4.24.8.6 Carbon Steel Equipment for Alkaline Environments

In case of anodically protected carbon steel storage tanks of sodium hydroxide, change of potential in the passive area leads to values, at which intergranular SCC is eliminated.[11,13,37] Susceptibility to corrosion cracking can be eliminated in potassium hydroxide.[5,28] Cathodes can be made of nickel, reference electrodes of mercury oxide.

Tubular evaporators are complicated pressure vessels operating with AP in the sodium hydroxide environment.[5,28] The AP was also used for the protection of steel equipment in the production of aluminum oxide.

4.24.8.7 Cellulose Boilers and Other Equipment in Paper and Cellulose Industry

Batch and continuous digesters made of carbon steel[38–41] and a Kraft liquor tankage[42–44] are the main anodically protected objects. Reference electrodes are silver sulfide or molybdenum. The electrochemistry of Kraft liquors is complicated because of multiple oxidation states of sulfur compounds (thiosulfate, polysulfide). Potential–current dependencies have the shape of I–III (Figure 2) in this corrosion system. For batch digesters, it is necessary to rate the direct current sources for periodic passivation.

AP is the most effective protective measure against SCC and it is possible to overcome erosion–corrosion problems. The industrial success of AP resulted in many commercial installations in North America and Finland (Savcor[27]).

4.24.8.8 Liquid Fertilizer Storage Tanks

The AP of carbon steel in liquid fertilizer containing ammonium nitrate is described in literature[13]; however, it is not used much in operation any longer. If we compare the AP with other alternatives of the corrosion protection of steel-welded equipment, we will find out that operation-wise, the protection is simpler if ammonia leakage is avoided so that the pH of the solution does not drop below 7.5 and the steel surface is spontaneously passive.

AP is used for ammonium carbonate fertilizers containing amonium nitrate and for ammonia–water storage tanks, and in the production of ammonium carbonates.[45]

4.24.8.9 Equipment Made of Other Metallic Materials

The AP of a titanium exchanger was described for the viscose production process, in which diluted solutions of sulfuric acid containing other substances are used.

Documented information about the industrial application is available also for molybdenum heating electrodes in glass melt.[46,47]

References

1. Edeleanu, C. *Metallurgia* **1954**, *50*, 113–116.
2. Lawrence, C. K.; Engle, R. F. Preventing corrosion of ferrous metals in solutions of electrolytes. U.S. Patent 2,377,792 June 5, 1945; Inhibiting corrosion of ferrous metals by ammoniacal solutions of NH_4NO_3. U.S. Patent 2,3667,996 January 9, 1945.
3. Novakovskii, V. M.; Levin, A. I. *Dokl. Akad. Nauk. SSSR* **1954**, *99*, 129–132.
4. Tomashov, N. D.; Chernova, G. D. *Dokl. Akad. Nauk SSSR* **1955**, *104*, 104–107.
5. Gräfen, H.; Herbsleb, G.; Paulekat, F.; Schwenk, W. *Werst. Korros.* **1971**, *22*, 16–31.
6. Makarov, V. A. *Korrozia i zashchita ot korrozii*; VINITI: Moskva, 1974; Vol. 3, pp 84–152, (in Russian).
7. Riggs, O. L.; Locke, C. E.; Hamner, N. E. *Anodic Protection*; Plenum Press: New York, 1981.
8. Kuzub, V. S. *Anodic Corrosion Protection*; Khimiya: Moscow, 1983 (in Russian).
9. Novak, P. *Anodic Corrosion Protection*; SNTL: Prague, 1987 (in Czech).

10. Agafonova, N. N.; Makarov, V. A. *Prot. Met.* **1989**, *25*, 531–543.
11. Gräfen, H.; Kuron, D.; Paulekat, F. *Werst. Korros.* **1991**, *42*, 643–651.
12. Kuzub, V. S.; Makarov, V. A.; Novitskii, V. S. *Prot. Met.* **1991**, *27*, 652–657.
13. Novak, P.; Mokra, M. *Koroz. Ochr. Mater.* **2006**, *50*, 7–13.
14. Paulekat, F.; Gräfen, H.; Kuron, D. *Werkst. Korros.* **1982**, *33*, 254–262.
15. Vicentini, B.; Sinigaglia, D.; Taccani, G. *Werkst. Korros.* **1971**, *22*, 916–924.
16. Foroulis, Z. A. *Anti-Corros. Method. Mater.* **1980**, *27*, 5–13.
17. Bartek, J.; Novak, P. *Scientific Papers of ICT Prague* **1987**, *B32*, 187–203; CA *107:66512*.
18. Bochkareva, I. V.; Ivanov, V. T.; Makarov, V. A.; Novitskii, V. S. *Prot. Met.* **1992**, *28*, 312–316.
19. Bochkareva, I. V.; Ivanov, V. T.; Makarov, V. A. *Prot. Met.* **1991**, *22*, 390–396.
20. Makarov, V. A.; Novitskii, V. S.; Artamonova, N. M. *Prot. Met.* **1991**, *27*, 841–845.
21. Ivanov, V. T.; Makarov, V. A.; Bolotnov, A. M. *Prot. Met.* **1992**, *28*, 955–960.
22. Bolotnov, A. M.; Ivanov, V. T. *Russ. J. Electrochem.* **1996**, *32*, 637–640.
23. Bolotnov, A. M.; Ivanov, V. T. *Prot. met.* **2001**, *37*, 173–176.
24. Novak, P.; Bystriansky, J.; Bartel, V. *Werkst. Korros.* **1982**, *33*, 94–98.
25. Novak, P.; Stefec, R.; Franz, F. Proceedings of Eurocor 77, London, 1977; pp 89–95.
26. Bochkareva, I. V.; Ivanov, V. T.; Makarov, V. A.; Makhmutov, M. M. *Prot. Met.* **1989**, *25*, 65–73.
27. Company files of Noram Engineering, Canada; Mercad Ltd., Canada; Aker Kvaerner Chemetics, Canada; MECS Inc., USA; Nantong Fareast Chemical Equipment Co Ltd., China; eKS GmbH, Germany; Savcor Group Ltd Oy, Finland.
28. Von Baeckmann, W.; Schwenk, W.; Prinz, W. Eds. *Handbook of Cathodic Corrosion Protection*, 3rd ed.; Gulf Publishing Company: Houston, TX, Elsevier Science 1997; Chapter 21.4, pp 474–488.
29. Xu, D.; Li, J.; Zheng, J.; Zhang, Z.; Tao, Y.; Xiao, S. *Zhongguo Fushi Yu Fanghu Xuebao* **2002**, *22*, 133–137.
30. Lebet, R. *Ochrona przed Korozja* **1995**, *38*, 12–14.
31. Kuron, D.; Paulekat, F.; Graefen, H.; Horn, E. M. *Mater. Corros.* **1985**, *36*, 489–501.
32. Wang, Y.; Gao, P.; Shen, G.; Wen, S.; Wang, T. *Liusuan Gongye* **2002**, *2*, 27–30.
33. Bhaga, D. *Sulphur* **1980**, *147*, 32–33, 39–43.
34. Kuzub, V. S.; Makarov, V. A. *Proceedings 1st Soviet-Japan Seminar on Corrosion and Protection of Metals, Moscow 1977*; Nauka, Moscow, 1979; pp 96–120.
35. Mark, T. *Jahrbuch Oberflächentechnik* **2006**, *62*, 55–65.
36. Shim, W. W.; Munro, J. I. *Mater. Perform.* **2000**, *39*, 22–26.
37. Podval, J.; Filasova, A. *Koroz. Ochr. Mater.* **1993**, *37*, 7–8.
38. Wensley, A. C. *Tappi J.* **1996**, *79*, 153–160.
39. Nadezhdin, A.; McDonald, R. *Pulp& Paper Canada* **1999**, *100*, 44–48.
40. Wensley, A. *Proceedings of Corrosion 2001, paper 01423, 9p*, NACE International, Houston, 2001.
41. Wensley, A. Proceedings of Tappi Fall Technical Conference, Chicago, 2003; pp 555–593.
42. Singbeil, D.; Garner, A. *Mat. Perform.* **1987**, *26*(4), 31–36.
43. Munro, J. I. *Mat. Perform.* **2002**, *41*(2), 22–26, *41*(3) 24–28.
44. Munro, J. I.; Shim, W. W. Proceedings of Tappi Fall Technical Conference, San Diego, 2002; pp 689–699.
45. Kuzub, L. G.; Gnezdilova, V. I.; Smoroda, N. I.; Kovalinskaya, E. K.; Kuzub, V. S. *Soviet Mater. Sci.* **1989**, *24*, 89–91.
46. Susser, V.; Ladr, I. *Glastechnische Berichte* **1983**, *56*, 167–172.
47. Hwang, J. H.; Kim, C. Y.; Kwon, J. G. .; Kim, K. D. *Glass Technol.* **2005**, *46*, 142–145.
48. Rodda, J. R.; Ives, M. B.; Kish, J. R. *Mater. Perform.* **2005**, *44*(7), 20–23, *44*(8) 22–25.

4.25 Introduction to Control of Corrosion by Environmental Modification

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Abbreviations

CAR Corrosive agent removal
CI Corrosion inhibitor
CR Corrosion rate
IE Inhibitor efficiency
PBI Protective barrier inducement
RH Relative humidity

Symbols

C Concentration of species in solution
C_{crit} Critical concentration for effective inhibition by anodic passivating inhibitors
i_{corr} Corrosion current density
i_L Limiting current density for an electrochemical reaction, usually in the context of oxygen diffusion to a cathode
i_{crit} Critical current density required for passivation
θ Fractional surface coverage, where $\theta = 1$ is one monolayer

4.25.1 Introduction

Materials selection, substrate (surface) design engineering (e.g., by use of coatings), and environmental modification (e.g., application of a corrosion inhibitor (CI)) are three commonly accepted strategies for corrosion control. The first two of these approaches can be described formally as *ex situ*, and ideally would be sufficient for complete protection. Practically, however, cost-effective corrosion control typically requires the use of a relatively cheap material that serves the desired mechanical or physical function (e.g., commonly a carbon or low-alloy steel). In such cases, *in situ* environmental modification is often required to control the corrosivity of the ambient fluid (i.e., gas or liquid environment or atmosphere) in which a material is immersed. There are a variety of technologies available to achieve this end, and selection ultimately depends upon the specific details of the particular application, generally driven by the requirement to achieve acceptable performance for minimum cost. The scientific basis behind environmental modification can be divided into two fundamentally different underlying strategies:

- Corrosive agent removal (CAR): This involves deliberate modification of an environment in order to reduce its chemical and/or electrochemical activity towards a substrate material by removal of specific corrosive reagents.
- Protective barrier inducement (PBI): This involves the deliberate addition of a chemical species that interacts in some way with the corroding substrate so as to form a protective barrier that reduces the corrosion rate (CR) to an acceptable level.

It is important to note that these strategies may be combined together (and indeed also combined with one of the *ex situ* corrosion control methods – for example, the addition of corrosion inhibitors (CIs) to organic coatings) in order to achieve the desired performance. In this chapter, an introduction to the fundamentals of environmental modification for corrosion control is presented. Industrial practice is discussed in the following chapters of this section.

4.25.2 Corrosive Agent Removal (CAR)

The process of corrosion involves two simultaneous electrochemical reactions (i.e., the anodic and the cathodic), which occur necessarily at the same rate but at different physical locations, and which involve the transport of ionic current in an electrolyte, see Figure 1. Thus, the scientific basis for reducing the kinetics of the corrosion process involves interference with one or more of these electrochemical processes. From inspection of Figure 1, it can be deduced that there are three basic CAR strategies for reducing the rate of the electrochemical reactions associated with corrosion, they are:

- removal of the cathodic reactant (e.g., oxygen) such that the cathodic reaction is stifled;
- removal of the electrolyte solution (e.g., water) such that, in particular, the anodic reaction becomes stifled since metal ions have limited ability to be solvated; and
- reduction of the electrolyte conductivity such that a large resistance is developed between the anode and the cathode and, hence, the electrochemical corrosion current is stifled.

Determination of which fluid components to target is dependent upon both the environment and practical application. For example, it is not practical to deionize an oilfield seawater injection well system.

4.25.2.1 Gaseous Environments

Focusing on gaseous environments, a pertinent topic is corrosion of substrates exposed to the atmosphere. Common scenarios include: outdoors in the open air, indoor environments, packaging for long-term storage of materials, and mothballing of equipment for maintenance. While the first of these cannot be addressed by environmental modification, the other scenarios are amenable to CAR.

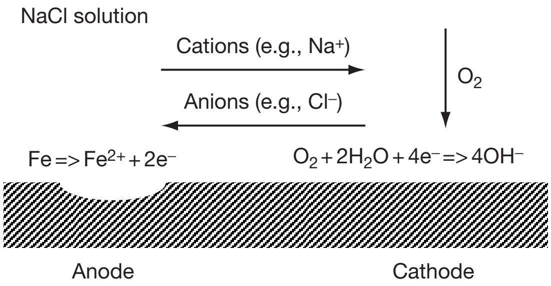

Figure 1 Schematic diagram of a corrosion process showing spatial separation of anode from cathode with corresponding migration of ions in solution and with oxygen as the cathodic reactant.

Gaseous atmospheric corrosion involves the condensation of moisture from the atmosphere onto a substrate. Typically, for a clean, uncontaminated, and polished surface in an atmosphere containing no gaseous or solid particle (aerosol) pollutant species, corrosion is minimal below a relative humidity (RH) of ~80%, where adsorbed water reaches a critical thickness of ~3–4 monolayers.[1] If the surface is roughened or has a porous structure (as in a corrosion product) then capillary condensation takes place at lower RH; where chemical salt contamination exists, is deposited, or forms on a surface by reaction, then water condensation will occur at the humidity of deliquescence of the salt. In all of these scenarios, corrosion is only of significance where the RH is greater than a critical value that depends on the surface condition (or contamination) of the substrate.[2,3] Corrosion can thus be suppressed by deliberate removal of water vapor from the atmosphere so as to reduce the RH to below the critical value for the onset of corrosion. RH can be calculated from the following expression:

$$\mathrm{RH} = \frac{p_{\mathrm{H_2O}}}{p^*_{\mathrm{H_2O}}} \times 100\% \qquad [1]$$

where $p_{\mathrm{H_2O}}$ is the water vapor partial pressure and $p^*_{\mathrm{H_2O}}$ the saturation water vapor partial pressure at the prevailing temperature. For a given absolute humidity (i.e., $p_{\mathrm{H_2O}}$) the RH falls with increasing temperature but rises with decreasing temperature. This explains the well known phenomenon of condensation on cold surfaces.

For 'technically' clean substrates, the critical RH for the onset of significant corrosion is generally between 50% and 60%. However, for surfaces contaminated with sea salt, the critical RH corresponds to the RH for deliquescence of magnesium chloride (~35%), while for historic artifacts derived from marine sources and, consequently, contaminated with chloride ion, the critical RH can be as low as 15% (the deliquescence RH for iron chlorides).[4]

For long-term storage of components, archaeological artifacts and for mothballing of equipment, environments of low RH are essential. For small components, this may be achieved by suitable packaging in materials with a low water vapor transmission rate, combined with a solid suitable desiccant. The familiar silica gel is commonly used; it functions best at around room temperature, and is capable of bringing RH down from 60–90% to ~40%. Activated alumina, quick lime (calcium oxide), montmorillonite clay, alumino–silicates (zeolites) are other solid desiccants that are used for such applications. For larger components, as well storage warehouses, it may be cost effective to consider mechanical dehumidification (i.e., air conditioning). Further information on desiccants can be found in BS 1133 Part 19.[5]

Occasional, but important, applications also exist for removal of corrosive gas fractions (including water vapor) from industrial processes by direct absorption. For example, triethylene glycol is often employed in natural gas production facilities to remove water content before the gas is transported away. Other gaseous species are also sometimes targeted in gas phase CAR, including carbon dioxide, sulfur dioxide, and hydrogen sulfide. The release of corrosive vapors from packaging materials is also an important consideration. For example, the degradation of cellulose (paper, wood, etc.) and polymeric packing materials may release aggressive agents such as acetic acid and hydrochloric acid vapor.[6] Detailed information on indoors corrosion and on corrosion due to packaging materials can be found in Donovan's book.[7]

4.25.2.2 Liquid Environments

Turning to CAR in liquid environments, water can be a major concern in nonaqueous systems. Thus, for scenarios where water is a nonessential constituent of the liquid, its removal is usually a desirable goal. For example, in oil production, water is commonly removed from the process fluid using separator vessels, which rely upon the different densities of oil and water; however, if the water exists as a stable emulsion then additional pretreatment is required. For some systems, it is preferable to retain a small amount of residual water in the nonaqueous medium, otherwise a protective passive film either may not be able to form, or may be unstable. Such environments include anhydrous liquid ammonia, where ~10 ppm water should be present to avoid stress corrosion cracking of steel[8] and chlorinated solvents, where a few ppm of water permits passivation and prevents the so-called 'bleeding corrosion' of aluminum.[9]

However, in aqueous environments, where water is the main component of the fluid or in those mainly nonaqueous environments where it is simply ubiquitous, then such a strategy is not feasible. Thus, CAR must target another relevant component of the environment. Noting, for example, that CRs in deionized water are generally lower than in potable water or seawater, a common strategy for aqueous corrosion control is to lower the electrolyte conductivity. The mechanism for this effect is as indicated in Figure 1; thus, a higher electrolyte resistance reduces the current flowing from anode to cathode. This may be simply achieved by specific removal of those (electrolyte) species that are able to form ions in solution by pretreatment of the water that will be used in the system. However, it is important to remember that water softening, often carried out to prevent scaling in systems, replaces calcium ions with sodium ions, and will often increase electrolyte conductivity. Deionization (or rarely nowadays, multiple distillation) is, therefore, the only reliable mechanism for achieving the desired reduction in anion and cation electrolyte concentration.

The most commonly used (and often most effective) method of CAR, especially in near-neutral aqueous solutions, is the control of dissolved oxygen levels as, under these conditions, it is the reactant for the rate-limiting cathodic reaction, that is:

$$O_2 + 2H_2O + 4e^- \rightarrow OH^-$$

At room temperature, the concentration of dissolved oxygen in water in equilibrium with air is ~8 ppm (0.2 mM). This value is sufficient to cause appreciable corrosion of unprotected carbon steel (i.e., in the range ~0.2 to $\gg$ 1 mm year^{-1} depending on fluid flow rate). A typical aim is to lower the CR to an acceptable level, that is, below ~0.1 mm year^{-1}. A good 'rule of thumb' that will generally achieve an acceptable CR for carbon steel equipment in flowing seawater is to reduce the dissolved oxygen content to 20 ppb (~0.0006 mM) or below,[10] which is readily achievable by mechanical deaeration.

The concentration of dissolved oxygen in water can be reduced by physical methods, chemical methods, or a combination thereof. Physical methods (often called mechanical deaeration) include heating the water, as O_2 solubility decreases with increasing temperature. In boiler systems, water heating is often combined with vacuum deaeration and/or gas sparge stripping. The former process involves lowering the gas pressure above the water hence leading to a reduction in dissolved gas content, while in the latter technique, a counter-current of gas (e.g., nitrogen, steam) mixes intimately with the water replacing dissolved O_2.

Chemical methods for removal of dissolved O_2 are commonly known as oxygen scavengers and function by reacting directly with residual O_2 to form another, more innocuous, species. Commonly they are only economic in closed systems such as boilers. Traditional oxygen scavengers suitable for low-to-medium pressure boilers include sulphite anions (SO_3^{2-}) and tannins.[11] The former reacts as follows:

$$SO_3^{2-} + \frac{1}{2}O_2 \rightarrow SO_4^{2-}$$

The sulfite is added either as sodium sulfite (Na_2SO_3), or ammonium bisulfite (NH_4HSO_3). Note that commensurate with a reduction in oxygen level, the use of sulfite will result in an increase in the quantity of dissolved solids in the system (as sulfate) and consequent increase in electrolyte conductivity. For high pressure and high performance boiler systems (such as in power generation), alternative oxygen scavengers are required that leave no residue. Traditionally, hydrazine has been used for this purpose, reacting as follows:

$$N_2H_4 + O_2 \rightarrow N_2 + 2H_2O$$

However, the use of hydrazine is increasingly deprecated due to its toxicity. Alternatives include carbohydrazide, which reacts with oxygen to form CO_2, N_2, and H_2O.

Another solution species, which is important in determining corrosivity, is the hydrogen ion (H^+). As the concentration of this species increases, pH decreases, and the CR usually rises. The reason for the occurrence of this phenomenon for iron can be understood from **Figure 2**, which depicts a Pourbaix (E–pH) diagram for this substrate. Domains of thermodynamic phase stability for soluble species (i.e., regions of corrosion), insoluble species (e.g., oxides), and the metallic phase (i.e., where oxidation of the metal is thermodynamically impossible) are displayed. Corrosion can be greatly suppressed if the pH is controlled (raised for iron according to **Figure 2**) to maintain the material within a domain in which a solid phase has significant thermodynamic (or kinetic) stability, that is, in a region of passivity. Thus, water treatment often includes a deliberate reduction in the level of hydrogen ions by the addition of a base such as ammonia, carbonate, or hydroxide, to maintain passivity of the metal.

For more details on water treatment, especially for boiler feedwaters, the reader is referred to the relevant chapter of this section.

4.25.3 Protective Barrier Inducement (PBI)

PBI involves *in situ* substrate/fluid interface modification to impede one or more steps in the corrosion process, for example, metal dissolution. Typically, such surface engineering is achieved through addition of one, or more, chemical reagents to the system, which affect synthesis of a protective substrate adhered layer.

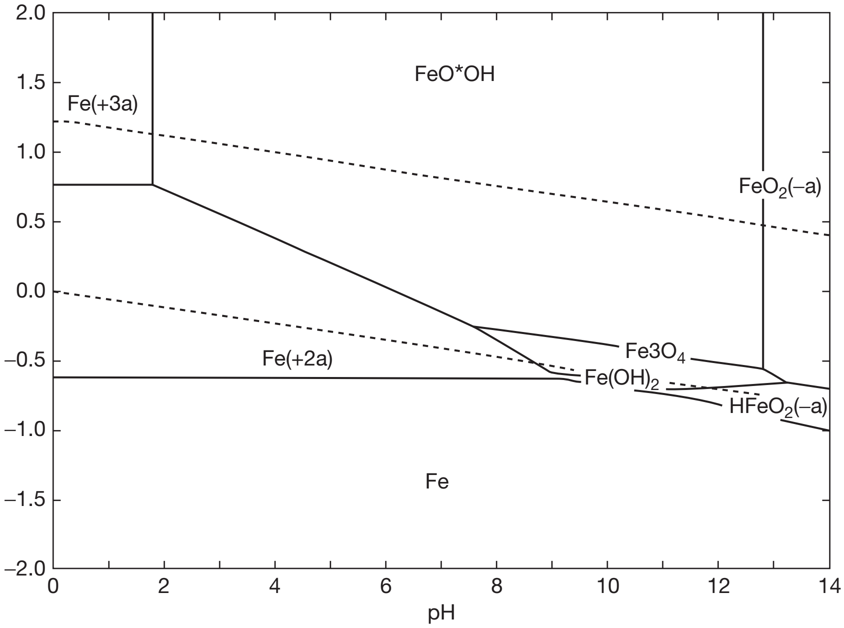

Figure 2 Pourbaix diagram for iron, drawn for a metal ion concentration of 10^{-5} M.

One can also consider cathodic protection to be a form of PBI (e.g., in the formation of calcareous films in sea water) but this topic will not be discussed further here as it is well covered in other sections.

One route to *in situ* protective layer formation is through initiating precipitation of low solubility inorganic compounds out of solution, such as calcium carbonate ($CaCO_3$). If the resulting solid forms a substrate bound scale, displaying low porosity/permeability, it can provide significant protection against corrosion. To stimulate the deposition of such a layer, there must be a change in the environment, so that the concentration of the scaling compound in solution exceeds its solubility. This shift may be affected by introducing more of a component of the scaling compound to the aqueous phase, for example, to promote growth of $CaCO_3$ scale, one could add either Na_2CO_3 or $Ca(OH)_2$. Another option is pH modification. Typically, the pH is raised through, for example, addition of NaOH to encourage scaling. These approaches have been applied in practice to control corrosion in potable water supplies where there are lead/copper pipes and few, if any, acceptable alternatives.[12] In other engineering applications, scale formation is undesirable, since it can interfere with the intended process, for example, greatly reduces the efficiency of heat exchange surfaces. A more detailed discussion of these matters can be found elsewhere in this section.

Alternatively, PBI can be accomplished through addition of chemicals known as CIs to the fluid environment. In BS EN ISO 8044:2000[13] the definition of such a species is:

> chemical substance that when present in the corrosion system at a suitable concentration decreases the corrosion rate, without significantly changing the concentration of any corrosive agent.

This rather succinct description may be augmented by adding that these substances decrease the CR by bringing about a change at or near the substrate surface, that is, they induce a protective surface barrier. The exact nature of this barrier varies with both the identity of the CI and the environment. For example, it may comprise either a 2-D monolayer or submonolayer comprising a single molecule or ion thickness, or a macroscopic 3-D film. Note that in the ISO definition, species such as oxygen scavengers are not considered to be CIs, as they do significantly change the concentration of a corrosive agent, i.e., they remove the O_2. Some authors, incorrectly, do not make this distinction.

Specific inhibitive species are further defined on the basis of one or more characteristics, including the dimensionality of the induced barrier. The terms ‘adsorption’ and ‘film-forming’ are used to classify inhibitors that induce 2-D and 3-D layers, respectively. Other characteristics by which CIs can be categorized include the following:

Organic/Inorganic – indicates the composition of a CI using the conventional chemical terminology for compounds.

Anodic/Cathodic/Mixed – specifies which electrochemical reaction is stifled by the CI; a mixed inhibitor interferes with both anodic and cathodic processes.

Oxidizing/Nonoxidizing – denotes whether or not dissolved oxygen is required for the inhibitor to function efficiently. As discussed later, this terminology is usually restricted to anodic inhibitors operating in near-neutral solutions.

Safe/Dangerous – refers to how corrosion proceeds at inhibitor concentrations that are insufficient for effective protection. For a *dangerous* inhibitor, the CR rises abruptly to approximately the same as, or greater than, that of the uninhibited system and localized corrosion (e.g., pitting) can occur. However, neither local corrosion nor a step-wise increase in rate, occurs for a *safe* inhibitor; rather there is gradual increase in the CR (which is not localized as pitting) as the concentration drops.

An alternative system for describing inhibitors is to indicate the environment in which they operate. Typically, a clear distinction exists between CIs for acidic or for near-neutral conditions, as protection mechanisms are usually quite different for these two types of environment. These differences are revealed for substrates immersed in aqueous solutions in the next two subsections.

4.25.3.1 Corrosion Inhibition in Aqueous Acidic Solutions

In sufficiently acidic conditions, the primary corrosion reactions are:

$$M \rightarrow M^{n+} + ne^- \text{(anodic reaction for the `}n\text{'-valent metal `M')}$$

$$2H^+ + 2e^- \rightarrow H_2 \text{ (cathodic reaction of hydrogen ion reduction)}$$

Often these reactions take place in the absence of any significant surface films (oxides, hydroxides, or salts) on the metal, due to the solubility of such layers at low pH. CIs for this situation are normally of the adsorption type, that is, they form a 2-D monolayer/submonolayer adsorbed directly onto the metallic substrate. Typically, organic molecules are employed,[14] although strongly adsorbing inorganic species such as iodide are also effective in reducing CRs in acidic conditions.[15] A few examples of the many organic molecules employed as CIs are depicted in Figure 3.

A variety of factors influence how effectively an organic adsorption CI protects a substrate. Two of the most important parameters are the strength of substrate bonding, and the fraction of the surface covered. Normally, increasing either of these quantities will improve the inhibitor performance, or, more quantitatively, inhibitor efficiency (IE). IE, which is a general term used for all inhibitors, is defined as:

$$\mathrm{IE} = \frac{\mathrm{CR}_{\mathrm{unhib}} - \mathrm{CR}_{\mathrm{inhib}}}{\mathrm{CR}_{\mathrm{inhib}}} \times 100 \qquad [2]$$

where $\mathrm{CR}_{\mathrm{unhib}}$ is the uninhibited CR, and $\mathrm{CR}_{\mathrm{inhib}}$ is the inhibited CR.

Concerning substrate bonding of organic CIs, it is useful to consider the molecule/ion to be constructed from a tail group that is normally hydrophobic and a head group that binds the molecule to the surface. As to the precise nature of the surface bonding, it is convenient to divide it into two distinct types, namely electrostatic and covalent. The former interaction arises due to attraction between the ionic charge or dipole on the CI species, and the electrical charge at the metal–electrolyte interface. The second type of bonding, covalent, involves electron transfer/sharing between the CI and the surface.

Electrostatic substrate bonding is most commonly exhibited by CIs having the formula $\mathrm{NR}_4^+\mathrm{X}^-$, with the cationic fragment acting as the primary inhibitive species. The simplest of these molecules are N-alkyl quaternary ammonium salts, for which the R groups are alkyl chains ($\mathrm{C}_n\mathrm{H}_{2n+1}$) of various lengths. Methyl groups are usually present to facilitate surface binding (head group), together with longer chains (tail group) oriented toward the corrosive solution. Clearly, the net charge at the substrate surface must be negative to enable NR_4^+ adsorption, and these species may either bond directly to the hydrated metal surface or through negatively charged adsorbed species (e.g., Cl^-, SO_4^{2-}).[16]

Covalent substrate bonding of organic CIs occurs through electron-rich head groups. Most often they are nitrogen or sulfur (or other Group V/VI elements) containing functional groups, although π-electron systems (e.g., C–C triple bonds and aromatic rings) are also effective. The bonding strength exhibited by the head group is determined by its electron density and polarizability, that is, the degree to which electrons can be donated to the substrate. These attributes depend not only on the identity of the functional group itself, but also upon the overall structure of the inhibitor molecule. For example, it has been shown for a number of aromatics that addition of ring substituents modifies inhibition performance.[17,18]

Turning to the surface coverage of an organic CI, usually this is related to its concentration in solution by standard adsorption isotherms. For example, the Langmuir isotherm relates the fraction of surface covered relative to a full monolayer (θ) to bulk solution concentration (C) by:

$$\theta = \frac{KC}{1 + KC} \qquad [3]$$

where K is a constant. On the basis of this expression, increasing bulk solution concentration will lead to greater surface coverage, as shown in Figure 4. Furthermore, assuming that corrosion only occurs on inhibitor free surface, IE (%) may be obtained from

$$\mathrm{IE} = 100 \times \theta \qquad [4]$$

Thus, increasing bulk solution inhibitor concentration will lead to more effective inhibition, albeit with

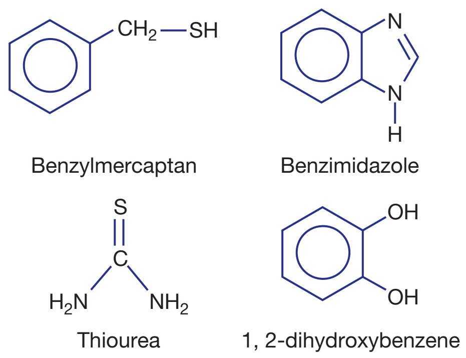

Figure 3 Examples of lower molecular weight organic CIs.

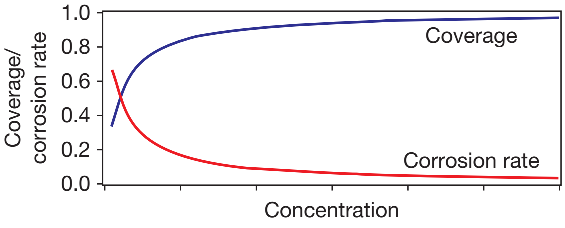

Figure 4 Plot of fractional surface coverage and corrosion rate as a function of bulk solution corrosion inhibitor (CI) concentration. Curves have been obtained using the Langmuir adsorption isotherm.

diminishing returns for increments at higher concentrations due to the nature of the Langmuir isotherm. However, this expression for IE and θ is often not strictly valid. On the one hand, the CR of inhibitor-covered parts of the substrate may not be zero, but rather just significantly reduced. Furthermore, full monolayer coverage may not be required to maximize corrosion suppression, if the inhibitive species preferentially adsorbs at electrochemically active sites (anodic or cathodic). It has also been reported that in certain cases CIs work better at lower coverage than at higher coverage (see, e.g., Singh).[19]

Of course to curtail corrosion, adsorbed organic monolayers/submonolayers must not only be present but must in some way retard the rate of the anodic and/or cathodic corrosion processes. The inhibitive species may entirely cover the surface, but still preferentially interfere with only one of the half reactions. It is, in principle, relatively straightforward to differentiate between an anodic and a cathodic inhibitor by measurement of variation in corrosion potential with time upon addition of the inhibitor. Thus, if the corrosion potential increases (decreases) then the CI is anodic (cathodic), while little change indicates a mixed inhibitor. Further mechanistic insight is not obtainable from a study only of the potential shift. However, more detailed investigation may be carried out by potentiodynamic polarization, along with surface analysis techniques. There are a number of proposals for how an organic CI may function in acidic solution, including:

Reaction site blocking – prevents bound metal atom(s) from taking part in corrosion reactions.

Formation of diffusion barrier – restricts diffusion of ions/molecules to/from metal surface. More likely to be operative for larger CIs (e.g., long hydrocarbon chain tail groups), or for alkynes that polymerize on the surface forming a blocking film.

Participation in electrode reactions – interferes with usual reaction pathway. A diagram indicating how an inhibitor might modify the anodic dissolution mechanism is displayed in Figure 5.

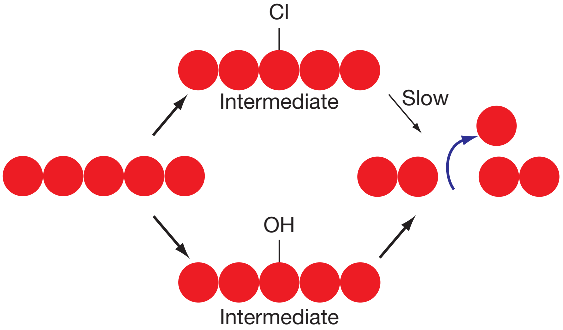

Figure 5 A diagram suggesting how a CI may interfere with anodic metal dissolution, slowing down this reaction by forming an alternative intermediate surface complex.

4.25.3.2 Corrosion Inhibition in Aqueous Near-Neutral Solutions

In aqueous near-neutral solutions, the anodic corrosion reaction remains metal dissolution, but the primary cathodic reaction becomes:

$$O_2 + 2H_2O + 4e^- \rightarrow OH^-$$

for aerated solutions (as illustrated in Figure 1). Also, unlike at low pH, the anodic/cathodic reactions usually occur in the presence of surface films (oxide, hydroxide, or salts). Under these conditions, CIs are typically of the film-forming variety. Typically, they are identified as being either anodic or cathodic, since these two types function rather differently, interfering with anodic metal dissolution and cathodic oxygen reduction, respectively. Inhibitor additions to deaerated solutions are not considered here, as CRs are usually sufficiently low (see previous section).

Anodic inhibitors for aqueous near-neutral solutions, sometimes known as passivating inhibitors, control the anodic dissolution of metals by inducing formation of a passive oxide film on the metal surface (typically of nanometer thickness). Their action is substrate specific, that is, an effective inhibitor for one metal is unlikely to be effective, or may even aggravate corrosion, for another metal. For carbon steels, which are of greatest interest practically, anions of various weak acids are effective, including chromate, nitrite, molybdate, and benzoate.

These anodic inhibitors can be further classified as oxidizing or nonoxidizing, depending upon whether or not dissolved oxygen is required for their operation. Chromate and nitrite are both oxidizing inhibitors, whereas molybdate and benzoate are nonoxidizing. Given the low CRs normally encountered in O_2 free near-neutral aqueous solutions, this division may appear to be of little use beyond academic interest. However, the employment of oxidizing inhibitors can prevent corrosion in areas exhibiting depleted dissolved O_2 concentration (e.g., in a crevice) in otherwise aerated systems.

Concerning performance of these anodic inhibitors, in contrast to the adsorption inhibitors for acidic solutions, CR does not vary smoothly with concentration. Instead, there is an abrupt decrease in CR at a critical concentration (C_{crit}), as illustrated schematically in **Figure 6**. The numerical value of C_{crit} is dependent upon the identity of the inhibitive species and substrate, as well as other environmental variables. For example, greater aggressive ion concentrations (e.g., Cl^-, SO_4^{2-}) usually increase C_{crit}. Typically, above C_{crit} the corrosion remains minimal and approximately constant, although some studies have shown a return to larger CRs at higher inhibitor concentrations (see, for example, Kolman and Taylor).[20] These inhibitors should also be labeled as dangerous, due to the sudden increase in CR below C_{crit}.

The existence of a C_{crit} for the onset of effective inhibition can be understood from the E–log i diagram shown in **Figure 7**. This plot is typical of carbon steel in aerated near-neutral aqueous solution, that is, the cathodic curve displays a limiting current density (i_L), and the anodic curve displays active and passive regions. As illustrated, increasing the inhibitor concentration results in a decrease in the critical current density (i_{crit}) required for passivation. However, spontaneous inhibitor induced passivation ($i_{corr} \rightarrow i'_{corr}$) is only achieved once $i_{crit} < i_L$, which requires a sufficient concentration of inhibitor (i.e., C_{crit}). Thus, there is a sudden onset of effective inhibition at a C_{crit}. The plot also indicates that there is sharp increase in the corrosion potential upon passivation, which is consistent with experimental studies.[21] It should be noted that some CIs (e.g., nitrobenzoate) can also increase i_L, enabling passivation to occur even with relatively large values of i_{crit}.

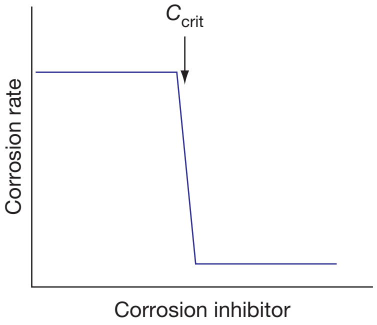

Figure 6 A schematic plot of corrosion rate versus inhibitor concentration for an anodic passivating inhibitor. C_{crit} is indicated.

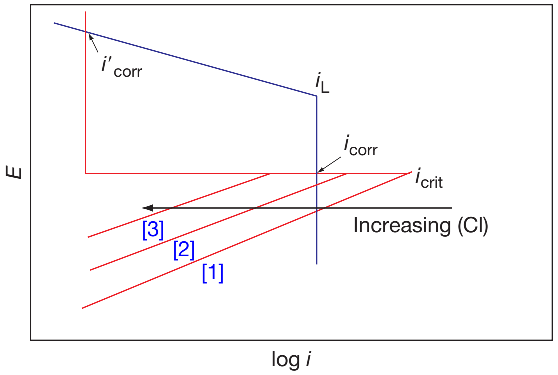

Figure 7 Schematic E–log i diagram for carbon steel in aerated, neutral solution. Red (blue) lines are anodic (cathodic) curves. It illustrates what happens to the corrosion rate as the concentration of anodic CI is increased in steps ([1]→[2]→[3]). On going from [1]→[2] the corrosion rate stays the same (i_{corr}), but further increasing [CI] to [3] leads to a huge drop in corrosion rate (i'_{corr})with the metal entering the passive region.

Concerning the precise mechanisms by which these anodic inhibitors induce passivity, limited real insight has been gained to date, although there is a great deal of speculation. Even the composition and structure of the passive films are not clear in many cases, which is essential input for nanoscale mechanistic understanding. However, CI roles likely include one or more of the following:

- catalyst for the formation of a passive film;
- reagent for the formation of a passive film;
- plugging active pores in an existing film with insoluble compounds so as to induce passivity;
- preventing the adsorption of aggressive anions; and
- reducing the rate of dissolution processes.

Cathodic inhibitors for aqueous near-neutral solutions typically reduce the rate of cathodic oxygen reduction by precipitating out an insoluble surface film, which restricts oxygen diffusion to the metal surface. Often, but not always, the films are rather thick (approx. 100 nm–few mm), and form largely independently of substrate identity. To be protective these layers must adhere well to the surface and have low porosity/permeability, as well as lack electronic conductivity, otherwise the cathodic reaction would occur on the surface of the film.

The prototypical film-forming cathodic inhibitor is a soluble salt containing, for example, Zn^{2+} cations, that results in the formation of a relatively insoluble, electrically insulating $Zn(OH)_2$ film with precipitation driven by the local rise in pH at a cathode. Importantly, and contrary to some perceptions, chromate ion, as well as being an anodic inhibitor at higher concentration, also acts as an extremely effective cathodic inhibitor at lower concentration, due to surface reduction of the CrO_4^{2-} anions to form highly insoluble $Cr(OH)_3$.

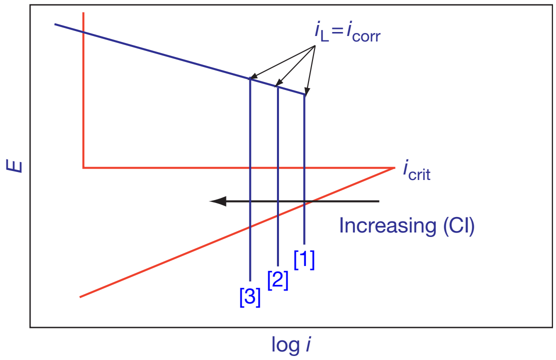

Figure 8 Schematic E–log i diagram for carbon steel in aerated neutral solution, illustrating the effect of increasing the concentration of a film-forming cathodic CI. Red (blue) lines are anodic (cathodic) curves. As the concentration increases ([1]→[2]→[3]) i_L, and thus i_{corr}, decreases.

Other species that can act as cathodic inhibitors include phosphonates and orthophosphates.

In contrast to anodic passivating CIs, there is no C_{crit} for cathodic inhibitors, rather the CR gradually reduces as its concentration increases. Again, this trend may be understood from considering changes in E–log i curves as a function of inhibitor concentration. As illustrated in Figure 8, increasing the cathodic inhibitor concentration reduces i_L, since in an aerated near neutral solution, it is determined by the transport of oxygen to the surface. As, under these conditions, $i_L = i_{corr}$, the CR also decreases.

4.25.4 Final Remarks

In the previous subsections, we have provided an introduction to CAR and PBI under typical conditions. No attempt has been made to give a complete review of the considerable volume of knowledge and ongoing research in this area. For example, we do not make specific mention of volatile CIs, although they can be an effective adjunct to CAR for various storage and packaging applications.[7,22] We have also restricted ourselves to the effect of a single inhibitive substance, whereas in many cases a mixture of inhibitors is used, which can display synergistic behavior. However, we believe we have provided enough information so that readers new to this area have sufficient insight into the basics of the following chapters in this section.

References

1. Picard, A.; Fang, H. *Metrologia* **2004**, *41*, 333–339.
2. Vernon, W. H. J. *Trans. Faraday Soc.* **1931**, *27*, 255–277.
3. Gdowski, G. E.; Estill, J. C. In *Scientific Basis for Nuclear Waste Management XIX;* Murphy, W. M., Knecht, D. A., Eds.; Materials Research Society Symposium Proceedings, 1996; 412, pp 533–538.
4. Greenspan, L. *J. Res. Natl. Bur. Stand* **1977**, *81A*(1), 89–96.
5. BS 1133–19: 1986: Packaging code – Use of desiccants in packaging.
6. Clarke, S. G.; Longhurst, E. E. *J. Appl. Chem* **1961**, *11*, 435–443.
7. Donovan, P. D. *Protection of Metals from Corrosion in Storage and Transit*; Ellis Horwood: Chichester, 1986.
8. Farrow, K.; Hutchings, J.; Sanderson, G. *Br. Corros. J.* **1981**, *16*(1), 11–19.
9. Bretherton, N.; Dawson, J. L.; Thompson, G. E.; Moreland, P. J.; Winterton, N. *Corros.Sci* **1993**, *35*, 205–211.
10. Oldfield, J. W.; Todd, B. *Desalination* **1979**, *31*, 365.
11. Revie, W.; Uhlig, H. H. *Corrosion and Corrosion Control, An introduction to Corrosion Science and Engineering*, 4th ed.; Wiley-Interscience: London, 2008; Chapter 18, p 317.
12. Karalekas, Jr.; Peter, C.; Ryan; Christopher, R.; Taylor; Floyd, B. *Govt. Eng.* **2007**, 42–43.
13. BS EN ISO 8044:2000: Corrosion of metals and alloys. Basic terms and definitions
14. Schmitt, G. *Br. Corros. J.* **1984**, *19*(4), 165–176.
15. Jeyaprabha, C.; Sathiyanarayanan, S.; Muralidharan, S.; Venkatachari, G. *J. Braz. Chem. Soc* **2006**, *17*(1), 61–67.
16. Fuchs-Godec, R. *Colloids Surf. A: Physicochem. Eng. Aspects* **2006**, *280*(1–3), 130–139.
17. Akiyama, A.; Nobe, K. *J. Electrochem. Soc.* **1970**, *117*(8), 999–1003.
18. Tan, Y. S.; Srinivasan, M. P.; Pehkonen, S. O.; Chooi, S. Y. M. *Corros. Sci.* **2006**, *48*, 840–862.
19. Singh, I. *Corrosion* **1993**, *49*(6), 473–478.
20. Kolman, D. G.; Taylor, S. R. *Corrosion* **1993**, *49*(8), 635–643.
21. Al-Refaie, A. A.; Cottis, R. A.; Lindsay, R. *NACE Corrosion 2009;* NACE International: Houston, 2009; Paper No. 09282.
22. Bastidas, D. M.; Cano, E.; Mora, E. M. *Anti-Corros. Method M* **2005**, *52*(2), 71–77.

4.26 Chemical Treating in Oil and Gas Production

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Abbreviations

API American Petroleum Institute
CA Corrosion allowance
CRA Corrosion resistant alloy
HIC Hydrogen-induced cracking
HSE Health and Safety Executive
ICDA Internal Corrosion Direct Assessment
ISO International Standards Organization
KPI Key performance indicator
LPR Linear polarization resistance
MEG Methyl ethyl glycol
MIC Microbiologically influenced corrosion
NACE National Association of Corrosion Engineers
NDT Non-destructive testing
QA Quality assurance
RBI Risk-based inspection
SCADA Supervisory Control and Data Acquisition
SHE Safety, health and environment

SRB Sulfate-reducing bacteria
SSCC Sulfide stress corrosion cracking
TQM Total quality management

4.26.1 Introduction

Chemical treatments are employed in many industries to control various corrosion and operational problems. The oil and gas production and refining industries use 'treating' to describe the injection of corrosion inhibitors, biocides, scale control chemicals, oxygen scavengers, etc. into process streams, produced fluids, and hydro-test waters with the objective of mitigation of corrosion risks from carbon dioxide, hydrogen sulfide, oxygen, and bacteria. Treatment success, both technical and financial, requires selection of suitable chemical packages along with control of dose rate to achieve the required concentration in the process stream plus regular monitoring of physical assets, including injection equipment to ensure optimal control of the management system performance. Details of the role of corrosion management in oil/gas production from concept design to operations is provided in a separate chapter of this volume[1] and provides a wider context of the use of treating as part of the strategic and tactical requirements for oil field assets.

Corrosion in petroleum industry equipment is controlled by fluid chemistries, water content, pressures, temperatures, and flow conditions that are in turn determined by past geological conditions in oil/gas reservoirs, the rate of extraction, and use of injection water for enhanced recovery. Stable chemical equilibria are disturbed as reservoir fluids are extracted and may result in increased scaling tendency and even enhanced hydrogen sulfide concentrations in produced fluids. Exported crude oils may contain sulfur compounds and other contaminants that cause corrosion under high temperatures found in refinery operating conditions.

Reservoir fluids contain hydrocarbon phases, gases such as methane and ethane, and oils of varying composition depending on the age/type of formation and original organic material source. Other organic reservoir components, such as acetic acid, often accelerate corrosion, although they can also lead to improved oil wetting properties decreasing corrosion rates due to an increase in oil wetting of metal surfaces. Formation waters, the aqueous/brine phase in the reservoir, often contain dissolved salts, such as calcium carbonate, barium sulfate, sodium sulfate, and sodium chloride. Chlorides and sulfates can cause pitting corrosion, whilst some dissolved salts (such as calcium carbonate/barium sulfate) may give rise to scaling conditions in some equipment. The major corrosion constituents are the acidic gases, carbon dioxide, and hydrogen sulfide that dissolve in both the oil and water phases, but cause corrosive electrolytes when dissolved in the water phase.

Overall corrosion reactions can be summarized by the following reactions.

For CO_2:

$$\underset{\text{iron}}{Fe} + \underset{\text{carbonic acid}}{H_2CO_3} \rightarrow \underset{\substack{\text{iron}\\ \text{corbonate}}}{FeCO_4} + \underset{\text{hydrogen}}{H_2}$$

For H_2S:

$$\underset{\text{iron}}{Fe} + \underset{\substack{\text{hydrogen}\\ \text{sulfide}}}{H_2S} \rightarrow \underset{\substack{\text{iron}\\ \text{sulfide}}}{FeS} + \underset{\text{hydrogen}}{H_2}$$

For CO_2, corrosion damage is typically seen as metal wall thinning and shallow pitting. Under high velocity conditions, deep elongated 'pits' may be observed; an erosion type of attack sometimes referred to as flow assisted localized corrosion. Iron carbonate corrosion products precipitate as semi-protective films or scales that assist in the control of CO_2 corrosion.

For H_2S, the low solubility of iron sulfide results in the formation of black corrosion product films that are more effective at protection than iron carbonate films, particularly at higher H_2S concentrations. However, the film is an efficient cathode, which can lead to intense pitting of unprotected areas. Hydrogen sulfide may also cause hydrogen damage in susceptible steels (the iron sulfide film causes atomic hydrogen produced in the corrosion reaction to diffuse into the steel). Typical hydrogen damage of susceptible steels includes embrittlement, hydrogen induced cracking (HIC), hydrogen blistering, and sulfide stress cracking.

Physical changes will also occur as produced fluids undergo pressure decrease when they rise up production tubulars, through well head/choke valves, pass along flow lines and manifolds and through gas–oil separation plant/equipment. Pressure decrease in the tubulars/reservoir to below the bubble point of the hydrocarbon gas leads to large increases in gas volumes leading to bubbly flow and even to the erosive conditions of slugging flow, **Figures 1** and 2. In addition, the combination of temperature and pressure decreases may cause deposition of scales, and lead to underdeposit corrosion. Corrosion

Figure 1 Erosion corrosion of a tubular (mesa corrosion).

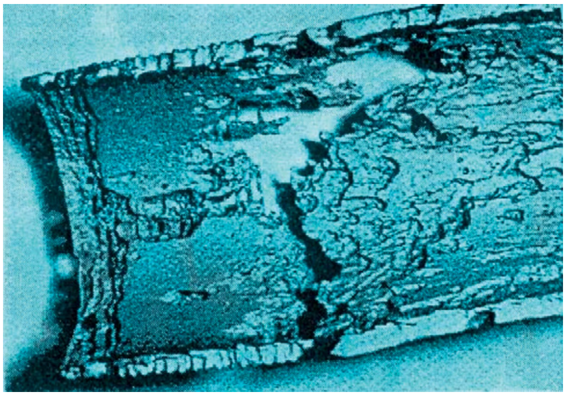


Figure 2 Erosion downstream of a tubular joint in a sour system.

processes, Figure 3, and bacteria present under deposits are difficult to treat because chemicals cannot easily diffuse through the scale or sludge found at the bottom of pipelines and process vessels; these deposits include mill-scale deposits, loose scale crystals/corrosion products.

In many applications, corrosion control is only one objective since control of scaling/microorganisms/fouling in downhole/field/refinery applications may be of equal or greater importance. Production economics, including factors such as plugging of reservoir strata/the hazard from a build-up of radioactive strontium scale in process plant, or microbial contamination including 'souring' of a reservoir or fouling of equipment may be of greater specific concern than that of corrosion. The majority of corrosion observed in pipelines is at the 6 o'clock position due to water drop out and deposits with corrosion, the oil and gas phases at the upper sections is normally assumed to be 10% of the bottom water wet section. However, it has been found that with wet gas lines/lines containing glycol/methyl ethyl glycol (MEG) that is pH stabilized, the concentration of acetate from the formation water will affect the concentration of acetic acid in condensed water in the top of the line. At too high a pH, the stabilized MEG may also give precipitation of $CaCO_3$ and $MgCO_3$.

Figure 3 Pitting corrosion found under deposits in a pipeline.

In general, corrosion is often a life limiting factor for equipment, particularly c-steel constructions, and corrosion inhibition is required to ensure the design/operation life is achieved. This also means that clean surfaces, free from deposits, biofilms, and nonprotective scales are needed so that treating chemicals are able to diffuse to and adsorb on surfaces. Ideally, the metal surface should be free from mill-scale at start-up, and chemical (acid) cleaning may be used as part of the commissioning process especially for welded vessels fabricated from corrosion resistant alloys. Pipelines with their large surface areas can produce significant quantities of sludge during the first years of operation as the air formed mill-scale produced during line steel manufacture is progressively replaced by iron carbonate/iron sulfide. In many cases, the sludge build up prevent a cleaning pig run. Also, iron sulfide is pyrophoric giving rise to disposal issues. A preferred option is to sweep blast the pipe internal during the shop application of the external coating process.

The general term chemical treating includes:

- **Control of corrosion of metallic components** by corrosion inhibitors, particularly c-steel and low alloy fabrications, such as lines, vessels, columns, heat exchangers, storage tanks, and in hydrotest fluids, but can also include corrosion resistant materials when acid treatments are employed for descaling equipment, acidizing rock formations, postfabrication cleaning, and repassivation.
- **Control of biological growth** to minimize biofouling and microbiologically induced corrosion (MIC) during hydrotest and operation.
- **Control of scales** by scale inhibitors to prevent plugging of pores in strata, blocking of lines and equipment, decrease of heat transfer at heat exchanger surfaces.
- **Control of fouling** by dispersion, sequestration, chelation, and detergents to minimize formation of sludge/precipitates/deposits in lines and equipment.
- **Control of wax** precipitation in production equipment and reservoirs.
- **Control of dissolved oxygen** by oxygen scavengers in hydro-test treatments and downhole water injection systems.
- **Control of emulsions** in oil–gas separation equipment by emulsion breakers as an aid to oil/water separation processes, also includes antifoam and antisludge agents.
- **Control of pH** by caustic injection into condensate and MEG/hydrate control chemicals.

Typically, the chemicals employed have surface active functional groups containing sulfur or nitrogen (e.g., amines, amides, imadazolines, quaternary ammonium salts), that are able to adsorb onto a metal surface and displace water, modify a growing salt crystal, or kill/restrict bacterial and fungus growth. Often, several chemicals are added to a system due to different problems. As well as providing their specified functionality they may also affect the interfacial conditions between liquid phases. For example, some surface active chemical mixtures may produce stable oil in water or water in oil emulsions (by micelle formation) that often result in down stream problems, including foaming and formation of tight emulsions. Other surface active chemicals are able to destabilize water in oil emulsions (emulsion breakers) or oil in water emulsions (reverse breakers), and these are employed to improve the separation processes in production equipment.

In practice, treating must be viewed as part of an organization's strategy to mitigate the effects of corrosion and enhance system performance. Successful management of the treating process is one of the primary aims of a corrosion team. Such teams may comprise various specialists including a corrosion engineer, chemist, biochemist, as well as production, maintenance personnel who have responsibility for the dosing and repair of injection systems. Effective chemical treating requires that ownership of the process and its boundaries must be clearly defined as part of the asset management structure. Typical duties involve selection, testing of chemicals, dosing, and monitoring, with reporting and decision making being key elements in the management process.[2] Most oil/gas production and refinery systems would be unable to achieve economic viability without chemicals such as inhibitors to control erosion–corrosion produced by multiphase slugging flow in pipework or filming amines as used in column overheads/condensers in refineries. The market for these chemicals is estimated at 3–6% of operational costs, of the order of millions of dollars per year.[3]

Section 4.26.2 of this chapter introduces some common themes, basic concepts, terminology, and issues relating to the use of chemicals, injection equipment, and monitoring. These include batch treatments of lines with corrosion inhibitors, and biocides, where a slug of chemical trapped between two pigs/spheres is employed, or when a scale control–corrosion inhibition 'squeeze treatment' is used downhole. Continuous inhibition is generally preferred in fluids with a high water content, such as treatment of multiphase fluids/water lines.

Corrosion inhibitors are addressed in Section 4.26.3, including the impact of local conditions, such as fluid composition, throughput, and water cut, on the type of inhibitor package employed. Section 4.26.4 considers the control of scale and deposition of fouling deposits. Control of bio-fouling and MIC, including monitoring and serial dilution, is outlined in Section 4.26.5. This chapter concludes with management aspects of treating processes.

4.26.2 Background

4.26.2.1 Treating Terminology

Formulations of vendor chemical treatment packages are commercially confidential with respect to the details of the type of compounds employed, although general information on the generic chemicals used (e.g., amine, quaternary amine) are provided together with data sheets on the chemical analysis performed, for example, UV/IR spectroscopy, that is then used for QA/QC purposes. The packages are designed for particular applications and specific environments that are typically characterized by the process fluid water content or water cuts for crude oil lines/gas phase applications. Thus, the terms typically employed include: *water soluble* (clear solutions), *oil soluble* (clear solutions), *oil or water dispersible* (cloudy solutions), *oil and water insoluble* ('gunkers'), and *gas phase* (low volatility/filming inhibitors).

Treating packages not only contain active inhibitor compounds but also contain additives that assist by providing solubility and dispersibility, that is, surfactants and demulsifiers that aid performance in the field. For example, dispersibility of an oil soluble inhibitor is increased by blending it with a surfactant that assists dispersion of oil soluble inhibitors into both the oil and water phases. An increase in emulsion tendency, formation of micelles, or microemulsions can present operating problems in separation equipment, and some corrosion inhibitor–biocide mixtures can produce emulsions in water–oil systems that are very hard to break. A demulsifier may, therefore, have to be added into the processing train to help oil and water separate. The emulsion tendency is a chemical's ability to disperse one liquid phase into another liquid phase. Solvents prevent separation of active ingredients, make chemicals less viscous for injection into the production system, and maintain the chemical in liquid form during storage. Solvents also lower the pour point, the minimum temperature at which the chemical remains a liquid.

The solubility of a chemical is the ability to dissolve in solution, but for compounds with limited solubility, the degree of dispersability is used. For example, some treating chemicals are not fully soluble in either the oil or water phases and must be dispersed largely in one phase. Oil soluble-water dispersible inhibitors readily mix with most crude oils and have various degrees of dispersibility in fresh, brackish water, or brines. Dispersibility helps inhibitors to be carried by fluids to the wet metal surfaces where they absorb, displace water, and form oil-wet films that resist corrosion. Water soluble corrosion inhibitors form inhibitor films that are not as persistent as the oil soluble corrosion inhibitor films, hence continuous injection is almost always needed for effective corrosion control in fluids with a high water content–high water cut.

Surfactants are added to corrosion inhibitor packages to help clean metal surfaces. However, a major factor during operation is that preexisting air formed iron oxide films are progressively replaced by reaction with CO_2/H_2S containing fluids. This means that large quantities of mill scale will be lost during the first few years of operation, particularly in large diameter, long distance pipelines leading to significant deposits/sludges of mixtures of oxides, carbonates, and sulfides. The maintenance of a clean surface from the start requires regular cleaning pig runs, a crucial procedure in some pipelines. Clean metal surfaces increase the effectiveness of almost all corrosion inhibitor treatments. In some equipment fabricated in corrosion resistant alloy, a precommissioning cleaning treatment followed by repassivation may be advisable before the introduction of process fluids.

Water-in-oil oilfield emulsions are droplets of water dispersed in oil or condensate. In low water cuts, water droplets become emulsified in oil due to mixing energy as fluids are produced from a formation, and are further mixed at valves and chokes. Surfactants will enhance this process, and may come from the crude oil or be introduced as part of the treating package. Emulsions may start to break down within a pipeline and this process is needed to achieve the oil–water separation process. Three steps are involved: flocculation, coalescence, and settling, see **Figure 4**. Flocculation is the process in which water droplets gather into groups. The droplets are surrounded by surfactant films that keep them apart. Coalescence is the process in which the surfactant film breaks and allows a group of droplets to become one larger droplet. The larger droplets settle to the bottom because water is heavier than oil. These processes are responsible for the progressive water drop out at low spots in lines as both temperatures decrease away from the mixing at the well head valve but also as water cuts increase in produced fluids. Emulsions are also created when the crude is washed to remove salt at the refinery. Given enough time, almost any emulsion will separate into oil and water phases. However, some emulsions do not separate, due to stabilization by fine solids like clays and iron sulfide.

Demulsifier chemicals, often called emulsion breakers, are continuously added to emulsion streams to speed up the separation process. Demulsifiers must thoroughly mix with the emulsion to work properly. Oil field separation vessels are added to production systems to allow efficient oil–water separation after demulsifier treatment. Demulsifiers or antifoam agents are sometimes added to organic inhibitors to prevent the formation of stable emulsions.

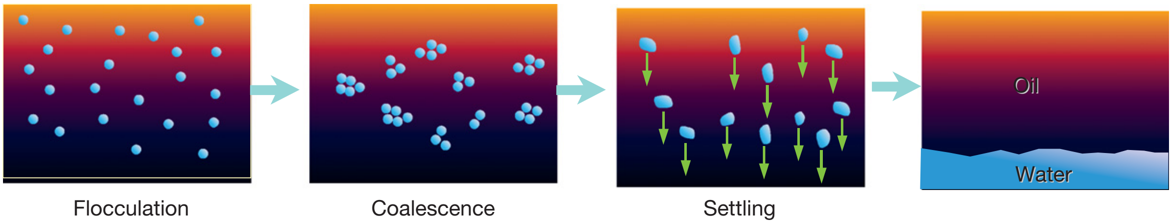
In oil field operations, water that has been separated from oil will contain some emulsified droplets of oil. These types of emulsions are called 'reverse emulsions’ or oil-in-water emulsions. The most common causes of reverse emulsions are the improper use of an oil demulsifier, excessive demulsifier treatment, or improper sizing or operation of water separation vessels. Removal of oil from water is often required to meet disposal regulations. Reverse emulsion breaker chemicals are added to water to gather or flocculate the oil droplets into larger droplets. Larger droplets of oil will float to the top of the water. Reverse emulsion breakers must thoroughly mix with the water so it will contact the oil droplets. Provision for injection of chemicals at process plant has to be made both for emulsion control and also for inhibition of export lines and water return lines, Figure 5.

4.26.2.2 Field Applications

Treating chemicals can be injected either continuously or in batches, depending on the application, system operating conditions, and fluid compositions, as well as performance versus costs. Continuous injection is generally preferred for aqueous fluid systems and multiphase fluid lines, particularly with high water cuts, and the gas phase of wet gas lines. Batch treatment is sometimes used for downhole treatments if technical or economic considerations preclude continuous injection. This may involve a ‘squeeze treatment’ in a similar manner to an acidizing treatment of a rock strata, but the aim is to allow inhibitor to slowly desorb from the strata back into produced fluids. Batch treatment is also used in special cases where a slug of biocide is trapped between two scraper pigs or spheres for application of a persistent inhibitor onto the surface of wet gas lines.

4.26.2.2.1 Continuous treatments

Continuous dosing in high water content systems is typically employed for corrosion inhibition, scale inhibition, oxygen scavenging, and to break emulsions.



Flocculation Coalescence Settling

Figure 4 Water in oil emulsion leading to water drop-out in lines.

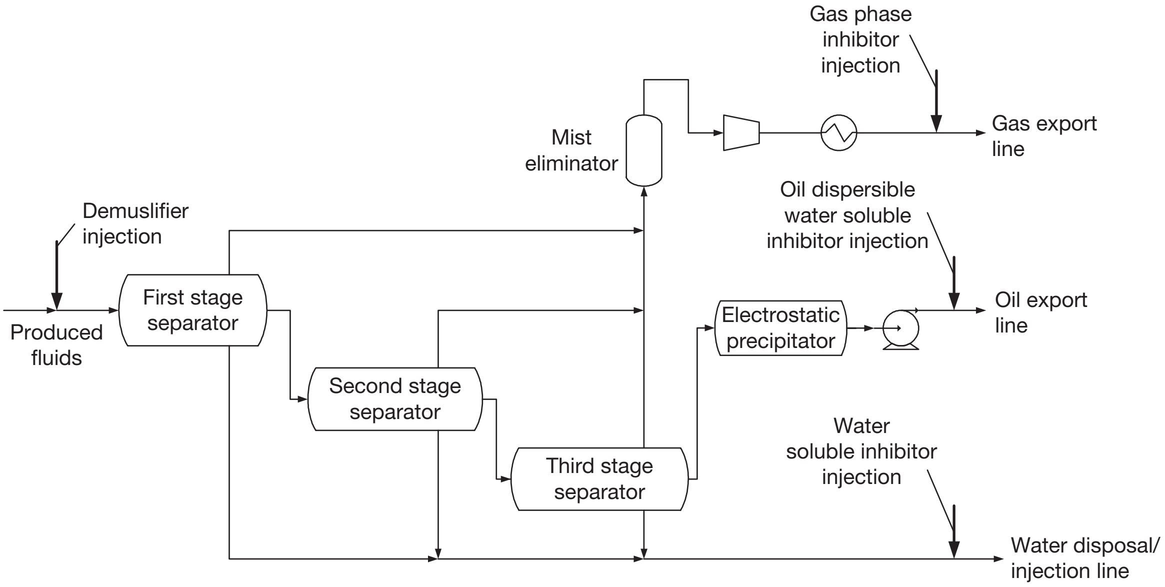


Figure 5 Typical chemical/inhibitor injection locations.

Continuous inhibition is a preferred method of application, particularly for wet systems, and where erosion–corrosion is anticipated. It can be used for downhole and topside equipment, including wellheads, separation facilities, flowlines, pipelines, etc. In processing trains, the inhibitor may be carried mainly by one stream (usually the separated water) and further continuous injection of an inhibitor into the other streams (exported gas and oil phases) may be required after separation. Continuous injection of gas phase inhibitors is also used for lines and equipment, see Figure 6.

The injection location is usually as far upstream as practicable to enable the inhibitor to reach as much of the equipment surface as possible. Common injection points in the field include: (1) downhole, (2) at the wellhead, (3) individual flow lines, (4) manifolds/gathering lines, trunk lines, separation plant, and (5) export lines. One concern is that many chemicals are corrosive when concentrated and can cause damage around the injection point, regular inspections are needed as recommended in API 570 *Inspection, Repair, Alteration, and Rerating of In-Service Piping Systems* to prevent failures of the type shown in the figure. Such failures have also been responsible for refinery fires, for example, Ras Tanura and South Humberside, that resulted in significant financial/production losses, see Figure 7.

In practice, down hole injection is difficult and prone to problems as liquid inhibitor has to be passed down a thin 'spaghetti' tube positioned in the annular space between the casing and the tubes. The inhibitor then goes through a valve into the tube just above the packer. All equipment below this injection point is not protected by inhibition and should be fabricated from corrosion resistant materials. Gas phase inhibitors used in gas lift operations are typically introduced under pressure down the annulus. In many cases, the flow conditions and differences in metallurgy between tubes (seamless/pierced billet) and flow lines (welded rolled plate) means that the down hole may be less of a concern and, therefore, the inhibitor is often added at the well-head.

Types of injection pumps include pressure injection systems (use of a nitrogen pressurized vessel with gravity feed), metering pump injection (positive displacement where a varying stroke length or varying speed controls the pump flow rate), flow proportional injection (produced fluid flow rate controls the injection rate, the pump is stopped when production stops). In high risk systems, a back-up pump is vital with shut-off alarms to increase reliability. Standard skid mounted equipment is used whenever possible to reduce costs and increase reliability. The supplier of the inhibitor injection system should provide

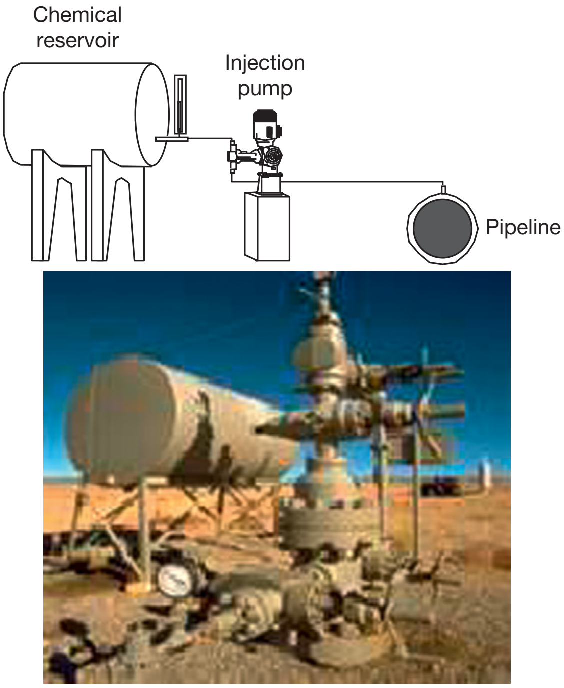


Figure 6 Chemical injection into line/well.

Figure 7 Failure of line at injection point. *Corrosion Threats Handbook – Upstream Oil and Gas Production;* Energy Institute of Oil and Gas: London, 2008.

evidence, in the form of field experience or a component reliability analysis, that the required up time/inhibitor availability can be achieved.

Continuous corrosion inhibitor treatment often begins with a high concentration of chemical that ensures rapid development of an inhibitor film on all metal surfaces. After the high initial concentration, a lower concentration of inhibitor is injected to maintain the bulk fluid concentration needed to repair the adsorbed inhibitor film.

The advantages of continuous treatment are:

- It supplies chemical at all times.
- It is the most cost-effective method to treat many systems such as pipelines, process lines and equipment, and cooling water systems.
- The chemical injection rate may be optimized to control operating problems.

The disadvantages of continuous treatment are:

- Chemical injection pumps require a reliable power source.
- Chemical injection pumps must be periodically monitored and maintained.
- Chemical drums/tanks that supply chemical injection pumps must be filled periodically.

4.26.2.2.2 Batch treatments

Batch treatments are typically employed for biocide treatment of seawater lines and periodic inhibitor dosage of wet gas lines where there is a risk of top of the line corrosion in stratified flow, or where a highly persistent treatment is required to provide protection for 2–3 months. The slug of concentrated chemical is trapped between two gel pigs/spheres/product separating pigs, see Figure 8, and the line pressure is used to transport it through the line. The time of contact of the chemical with a section of the pipe wall is determined by the length of slug and flow rate.

Batch treatment is sometimes used down-hole when technical or economic constraints preclude continuous inhibitor injection either by application of a persistent corrosion inhibitor onto tubular walls or more usually by means of a squeeze treatment. The persistency of batch inhibitors needs to be tested in the laboratory and verified in the field to ensure batch treatment viability.

Squeeze treatment uses the producing formation as a chemical reservoir with the aim of providing a dose similar to continuous treatment, see Figure 9. In squeeze treatments, a large volume of corrosion inhibitor/scale control inhibitor is pumped down the tubing with enough overflush to force inhibitor into the producing formation. The inhibitor adsorbs onto the formation and is slowly produced back from the formation. A successful squeeze treatment results

Figure 8 Gel pigs, spheres, and product separating pigs employed to trap a slug of treating chemical.

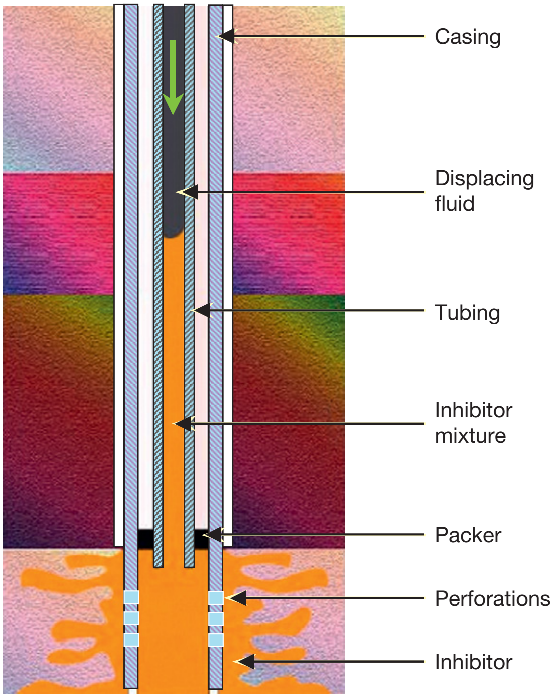


Figure 9 Schematic of squeeze treatment.

in an almost continuous return of inhibitor that can last for several months. Squeeze treatments can be applied in wells with sufficient porous and permeable producing zones. The major concern with inhibitor squeeze treatment is the possibility of plugging the formation. There is little danger of formation damage when squeezing scale inhibitors. Some corrosion inhibitors cause formation clays to swell. Laboratory tests with formation core samples may be used to determine if this will be a problem.

The advantages of batch treatment are:

- Provides treatment where continuous treatment is difficult.
- Protection of pipelines operating in stratified flow, when inhibitor distribution to the top of the line cannot be ensured by other means.
- In combination with continuous inhibition for very severe or upset conditions.
- Protection of process vessels which have long residence time, and that would require impractically low continuous injection rates, for example, low temperature separator vessels.
- Batch treatments with biocides are more cost-effective than continuous treatments.
- Squeeze treatment allows continuous treatment without expensive down-hole delivery systems.
- The chemical is available where it is needed.
- Less manpower required to check on chemical treatments.

The disadvantages of batch treatment are:

- A significant portion of the chemical may be wasted.
- Corrosion and bacteria are not continuously controlled between treatments.
- Wells are taken off production for several hours.
- Squeeze treatment can plug or damage the producing formation.
- The high cost of treatment.
- The chemical returns from the formation must be monitored.

4.26.3 Corrosion Inhibition

The use of inhibitors in the field and process equipment is defined in terms of the metal and the corrosive environment. Packages that protect one metal, c-steel, may not protect another, stainless steel. Similarly protection of a metal in, for example, acidic solutions (CO_2/H_2S corrosion) may not work in neutral solutions, particularly when dissolved oxygen is the corrodant. Various commercially available corrosion inhibitor packages have been developed for use in water systems, gas systems, oil field production systems, and refineries.

4.26.3.1 Inhibition Processes

Corrosion inhibitors work by one or more of the following mechanisms: precipitated films that visibly coat and protect metal surfaces (calcium salts in potable water, zinc salts in cooling waters), passive oxides which combine with corrosion product films to protect metal surfaces (silicates and molybdates in cooling systems), and adsorbed monolayers (organic molecules in oil/gas systems). The first two mechanisms, rely on relatively inexpensive inorganic salts, are used mainly in cooling towers, boilers, and fractionation units. The adsorption type of organic inhibitor is employed in oil field systems, and to prevent overhead corrosion in some refinery units (e.g., use of filming amines) are organic inhibitors. Inorganic inhibitors are further divided into anodic and cathodic classifications that describe the polarization of electrochemical corrosion process that are modified by the inhibitor action. Organic film-forming inhibitors (amines, amides, and imadazolines) block both the anodic and cathodic processes, although most tend to mainly polarize the anodic reaction as observed by an increase in corrosion potential. Note that although cost effective water treatments typically use inorganic compounds these often are more effective in combination with small additions of organic chemicals to provide a synergistic effect.

Inhibitors for near-neutral and alkaline environments in the presence of oxygen decrease the rate of the oxygen transport/rate determining step by the formation of an electronically nonconducting film on the metal surface (cathodic inhibitors). Inhibitors for oxygen-free near-neutral solutions, as may be found, for example, in oil production, cause the steel to form or retain a protective oxide film which acts as a barrier to metal dissolution, so that the corrosion rate is now controlled by the anodic process (anodic passivating inhibitors). Anodic inhibitors effectiveness relies on maintenance of a passive oxide film on the metal surface and includes both oxidizing inhibitors (nitrite, etc.) and nonoxidizing that require dissolved oxygen (phosphate, benzoate, borate, carbonate, hydroxide, molybdate, etc.). Insufficient dosage of anodic inhibitor may cause localized corrosion (e.g., pitting).

In acid environments, both metal dissolution and hydrogen evolution reactions are under activation control and can occur in the absence of surface films of oxides or corrosion products, because of their solubility in acid. Even a small reduction in the kinetics of either process will reduce the corrosion rate. Inhibitors for acid solutions usually function by adsorption on the metal surface, and typically contain elements in Groups V or VI of the periodic table, for example, N, P, O, S, or As, which possess lone pairs of electrons which can be donated to the metal to form a chemical bond by chemisorption. The tendency is to use long chain nitrogenous inhibitors (amines) and imidazolines. Exact mechanisms are not fully understood, but chemisorption appears to occur at active sites and physisorption at the remainder of the surface. The organic inhibitor molecules can be modified to increase their solubility or dispersibility in brine. These modifications include adding more polar groups to each inhibitor molecule.

Adsorption type inhibitors usually contain N or S atoms with an attached organic chain (typically C12–18) that determine the solubility, and are usually aliphatic (straight chain) fatty acid derivatives. Most metal surface in contact with an aqueous solution is covered with adsorbed water molecules and the unshared electrons in the polar N group of the inhibitor forms a chemisorption type bond with the metal surface. Organic inhibitors also physically adsorb to the metal surface but this is weaker than chemisorption. Some molecules also have an ability to attract each other and form a 2-dimensional monolayer across the metal surface. The chemisorption bond displaces water molecules (4–8 per inhibitor molecule) and other corrosive agents from the metal surface. These processes are described by standard adsorption isotherms (Langmuir, Tempkin, etc.) of inhibitor solution concentration (*c*) versus a function of the surface coverage (Θ) at various temperatures. The adsorption process can be visualized as formation of covalent bond between metal and polar group along with displacement of adsorbed water molecules, nonpolar or aliphatic end of molecule orientated outwards encouraging adsorption of a hydrophobic oil layer as illustrated in Figure 10.

Organic inhibitors include *mono amines*, typically used in refinery overheads and hydrotest packages, *diamines*, more efficient in oil systems than monoamines, *amides*, poly ethoxylated compounds made with differing oil and water solubilities (solubility increases with amount of ethylene oxide, acetic, oleic, dimeric naphthenic, or phosphate salts), and *imidazolines and derivatives*. Most exhibit at least partial solubility or dispersibility in both oil and water.

Water soluble inhibitors are required for fresh and brine waters, typically quaternary amines, amine salts, or salted imidazolines, see Figure 11. Water soluble corrosion inhibitors form a protective film on metal surfaces in sweet or sour environments but the inhibitor films are not as persistent as oil soluble corrosion inhibitor films. These tend to desorb at high temperatures and may salt out (lose solubility) in brines that contain a high concentration of total dissolved solids (TDS). Continuous treatments are almost always needed for effective corrosion control.

Oil soluble inhibitors tend to be long chain primary amines, imidazolines, fatty acids, and phosphate esters. These packages are also more effective at higher temperatures and high velocities.

Oil soluble-water dispersible inhibitors are normally used in oil wells and gas condensate wells and readily mix with most crude oils in sweet or sour

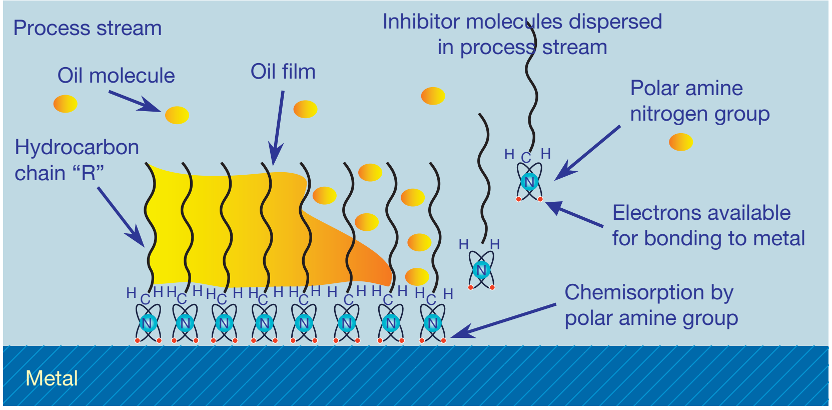


Figure 10 Schematic of adsorption inhibitor processes.

systems. They also have various degrees of dispersibility in fresh, brackish, or brine water. Higher concentrations of water dispersible inhibitors are usually needed as production increases and water break through occurs. The inhibitors form oil-wet films that resist corrosion under most conditions.

Batch treatment inhibitors are either oil soluble or 'gunkers' in order to achieve better persistency when water-wet. In wet gas lines, continuous injection of gas phase inhibitor is often applied in conjunction with periodic batch treatment.

Gas phase inhibitors are usually low molecular weight amines that have a high vapor pressure.

4.26.3.2 Inhibitor Performance

The performance of inhibitors is often defined by their efficiency based on the corrosion rate with and without inhibition, with the input data being obtained from corrosion coupons, and/or portable instrumentation (electrical resistance/electrochemical polarization resistance) using probes inserted into the process line or test solution. Inhibitor efficiency can be calculated from the following expressions:

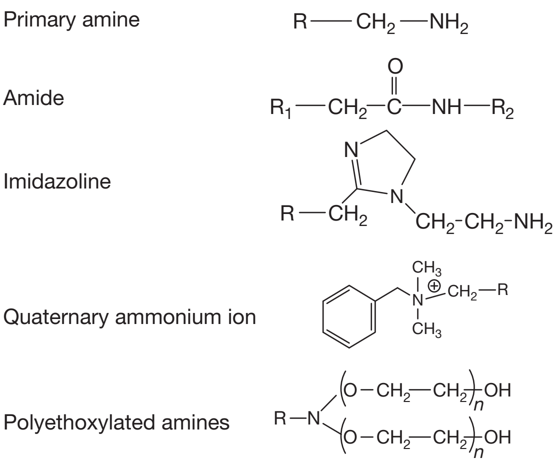


Figure 11 Basic structures of adsorption corrosion inhibitors.

For weight loss:

$$\%\ \text{Inhibitor Efficiency} = \left[1.00 - \frac{\text{Weight loss (with inhibitor)}}{\text{Weight loss (without inhibitor)}}\right] \times 100$$

For corrosion rates:

$$\begin{array}{c}\text{Inhibitor}\\ \text{efficiency}\end{array} = \frac{\text{Rate without} - \text{Rate with}}{\text{Rate with}} \times 100$$

N.B. 100% efficiency = no corrosion, 0% efficiency = no effect of 'inhibitor.' Inhibitor efficiency is also used often as a measure of the surface coverage as illustrated in **Figure 12**, where 100% efficiency corresponds to a surface coverage of one, and 0% efficiency to zero surface coverage.

The graph in **Figure 12** shows that for an adsorption type inhibitor the coverage (or efficiency) can be increased by increasing the bulk concentration in the fluid, and conversely, reducing the concentration reduces the efficiency. In practice, there is a balance between performance and cost but also the actual corrosion rates obtained are an important consideration. The efficiency required varies greatly from system to system. For example, pipeline designed some 25 years ago reflected a degree of conservatism and often assumed inhibitor efficiencies of 60–85%. However, improvements in vendor inhibitor formulations are based on experience at, for example,

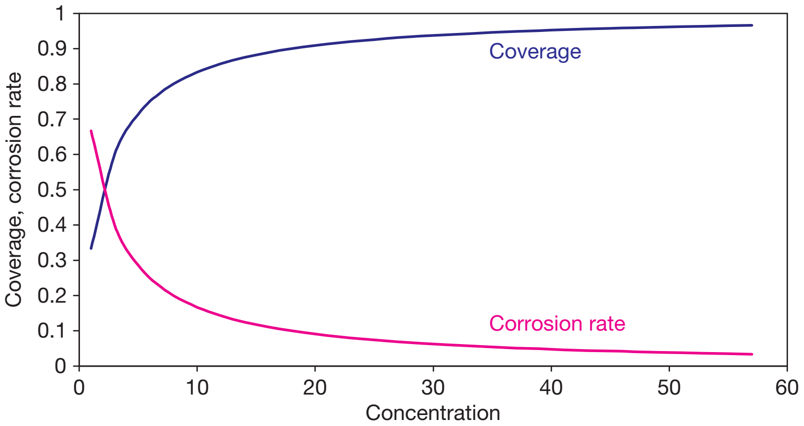


Figure 12 Relationship between inhibitor efficiency, surface coverage, and bulk concentration.

Prudhoe Bay from 1996 onwards shows that a field corrosion inhibitor efficiency of 98% for multiphase flow lines can be obtained. The use of an inhibitor efficiency of greater than 95% for design purposes is a high risk strategy that requires effective monitoring and corrosion management processes, but is achievable in practice. Some authors[4] consider 80% or 90% minimum efficiency obtained in the laboratory as a hypothetical assumption, since correctly chosen inhibitors can have efficiencies in the field of >99.9%, that is, inhibition ratios of 10^3–10^6 (the inhibition ratio is the corrosion rate without inhibitor/corrosion rate with inhibitor). The purpose of efficiency measurement is as a tool to provide a ranking of candidate packages and is used to select inhibitors prior to field testing/application.

A second but important practical consideration is the corrosion inhibitor availability[5] (A), that is the time the inhibitor is present in the system at the required dosage, where $A\% =$ the time the inhibitor is added divided by the lifetime × 100%. The design corrosion allowance (CA) is then defined as:

$$\mathrm{CA_{total}} = \mathrm{CA_{inhibited}} + \mathrm{CA_{uninhibited}}$$

The CA would be given by:

$$\begin{aligned}\mathrm{CA} = {} & (\mathrm{CR_{inhibited}} \times A\% \times \mathrm{Lifetime}) \\ & + (\mathrm{CR_{uninhibited}} \times [1 - A\%/100] \times \mathrm{Lifetime})\end{aligned}$$

The design stage assumption is that inhibition can decrease the corrosion ($\mathrm{CR_{inhibited}}$) to between 0.1 and 0.3 mm year^{-1}, that is, practical values that would have to be reviewed once field data trends were obtained. The availability concept emphasizes the criticality of inhibition downtime in high risk systems and uses realistically achievable corrosion rates that focuses attention on the importance of maintaining and managing the dosage/inhibitor supply chain.

Partitioning of inhibitors between the oil and water phases is also an important consideration as the practical aim is to achieve a required concentration of inhibitor in water phases where corrosion occurs. As the water cut increases during production, the inhibitor will distribute itself at different concentrations in the water and oil phases. The volume fractions of the phases are important factors in establishing partitioning between oil and water phases as the theoretical basis is given by:

If

$$C_o V_o + C_w V_w = C_t \text{ and } C_w/C_o = P$$

where C is concentration, V is volume fraction, w is water phase, o is oil phase, t is total fluids, and P is partitioning coefficient (water/oil).

Then

$$C_w = C_t P/(V_o + PV_w) \text{ and } \mathrm{C_o = C_t/(V_o + PV_w)}$$

Some operators specify a recommended inhibitor concentration in the water phase which is a sound practical consideration. Experimental data on inhibitor partitioning is then used to estimate the necessary concentration in the total fluids for a given water cut. Thus, a preferentially water soluble component ($P > 1.0$) will have a higher concentration in the water phase than a preferentially oil soluble component ($P < 1.0$).

Selection of an inhibitor requires consideration of several factors:

- The nature of the operating environment and the operating conditions.
- The materials requiring protection.
- Possible interactions between chemical additives.
- The efficiency of an inhibitor.
- Possible adverse effects of inhibitor on other aspects of the operation.
- Environmental effects of the inhibitor.
- The physical properties of the inhibitor.

4.26.3.3 Inhibitor Testing

A range of test procedures are available to assess inhibitor packages for various applications, including Bubble Test for initial screening, rotating cylinder electrode (RCE) for various flow conditions, segmented welds for low conductivity fluids, autoclave tests for high pressure/high temperature conditions. Such methods and procedures, along with others, have been developed over the years for assessment of oil industry inhibitors, but not all are routinely performed, rather a limited number of basic and reproducible tests have been adopted. A North Sea oil industry sponsored program of testing during the mid-1980s identified the Bubble Test, the Rotating Cylinder, and Jet Impingement as being able to provide the basis of a test protocol. The study provided statistical evidence of the reliability and reproducibility of electrochemical measurements in the establishment of corrosion rates and provided the basis of published work in this area.[6,7]

4.26.3.3.1 Bubble test

The test is designed for rapid screening of inhibitors using brine solutions (simulated or field samples) as the test fluid held in an easily cleaned glass vessel containing between 150 ml and 1 l of test solution. The test is carried out at room pressure (1 atm), with a sparge gas being bubbled through the solution using a mixture of a carbon dioxide/hydrogen sulfide/nitrogen concentration that simulates the field partial pressures of CO_2/H_2S. The vessel is sealed with water traps and purged of air prior to test solution introduction, test temperatures range from ambient to boiling. Samples of degassed crude may be introduced to form an oil layer if there are concerns regarding acetates, etc. The solution is magnetically stirred to ensure mixing but the shear stresses are low, <1 Pa.

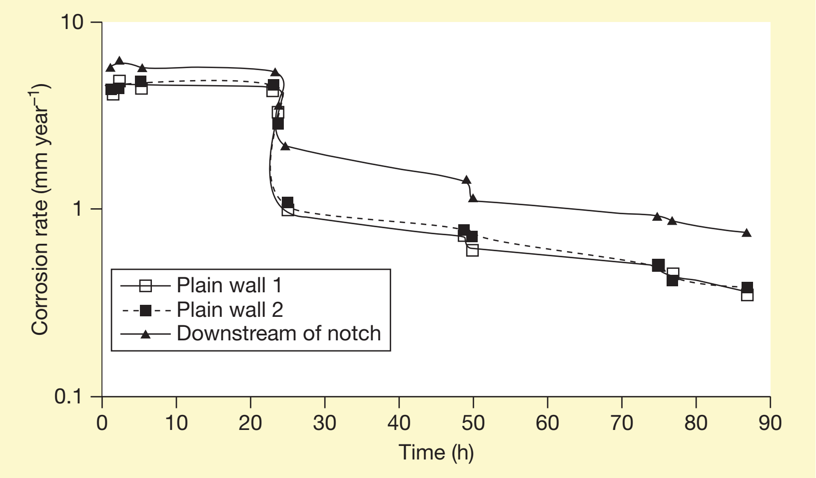
The normal procedure is to establish a base line corrosion rate, after a few hours but often over 24 h, using standard electrodes and test probes prepared by a rigorous degreasing/abrading/cleaning procedure. The base results give the uninhibited corrosion rate and this also identifies any samples that have a poor/out of specification preparation. The inhibitor must be soluble or dispersible in both hydrocarbon and water, it is added at the required dose rate and the inhibited corrosion rate obtained typically after a further 24 h from which the inhibitor efficiency is determined.

Bubble tests are almost always the initial screening tests because they are simple, easy to carry out, and reliable, if based on electrochemical measurements but are restricted to ~1 bar total pressure and <100 °C. They cannot reproduce high temperature–pressure systems, but nonetheless can still be an effective initial screening methods for such systems.

4.26.3.3.2 RCE test/flow loops

These tests are designed to reflect actual system wall shear stresses found under stratified flow conditions in pipelines. Many studies have demonstrated the validity of the approach based on standard hydrodynamic correlations, so that suitably designed equipment will give similar results from the two methods. Both can be pressurized but the RCE is often more convenient due to ease of operation and cleaning. Electrochemical measurements are normally employed or electrical resistance measurements in high hydrocarbon systems. Measurements can be made on a cylindrical electrode that forms part of the rotating shaft, but electrode probes positioned in the wall of a cylindrical test cell can also be employed, provided the electrode is machined to the wall profile and that a relatively small annulus is used to contain the test fluid so that the flow conditions are similar on the rotating cylinder and wall.

Figure 13 illustrates typical data from a dynamic test and shows that the two types of test give



	Concentration of inhibitor A		
	10 ppm	20 ppm	30 ppm
Flow loop	85%	92%	97%
RCE	85%	92%	97%
Fixed electrode rotating cylinder: Flush electrode	88%	93%	94%
Notch electrode	73%	83%	85%

Figure 13 Comparison of flow loop and RCE test data showing inhibitor efficiency tests and the effect of simulation of downstream of erosion pits.

compatible results provided the fluid to wall shear stresses are the same and enables pipeline conditions to be simulated. If inhibitor dose rates are sequential, the increased test can define the effect of concentration on performance. Base line uninhibited corrosion rates were established over the first 24 h, then inhibitor was injected at increasing dose levels of 10, 20, and 30 ppm. The RCE design can also be modified to assess the effect of inhibition downstream of a simulated erosion pit–local flow disturbance. The table shows the test data expressed as inhibitor efficiency as obtained from a flow loop test, an RCE, and autoclave rotating cylinder tests (higher rates) compared to efficiency under local turbulence conditions. The inhibitor did not perform as effectively under more turbulent intensity conditions.

4.26.3.3.3 Inhibitor persistency

There are always times when, for some reason, inhibitor dosage ceases and it is then important that protection persists for some time until inhibitor injection is reestablished. However, it is not a widely studied property, and therefore underestimated, particularly for high risk systems. Different inhibitors can show very different persistency as shown in **Figure 14**. The bubble test and jet impingement tests are employed, and by changing the fluid compositions, after an inhibitor film is first established, the persistency can be evaluated. The initial base line data and efficiency after 24 h were obtained using an RCE and inhibitor and then the persistency assessed by substitution of the inhibited test solution with fresh but already sparged fluid. The test indicates how quickly the corrosion rate returns to the original uninhibited rate. In the case of the quaternary amine package, there is a rapid increase in corrosion rate when inhibitor dosing is stopped, although complete loss of protection does not occur in the test. In the second case, the carboxylate amine, there is a good response as the inhibitor appears to be retained and redistributed on the metal surface.

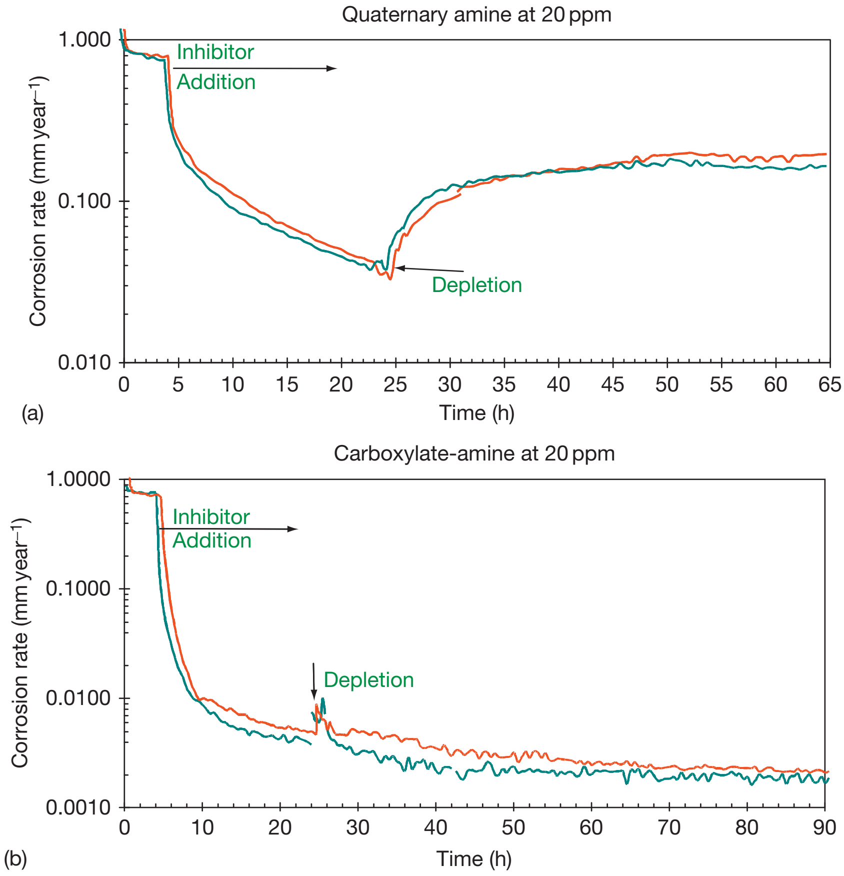


Figure 14 Electrochemical test data showing initial uninhibited corrosion rate, inhibition, and persistency check.

4.26.3.3.4 Jet impingement

The test is designed to give high shear stresses, but the quantification of shear stress is not as well-established as for flow loops or the RCE. It is also possible to obtain the high shear stresses normally associated with erosion–corrosion by use of a pulsed gas bubble injection into the feed to the impinging jet.

4.26.3.3.5 Inhibition of weld corrosion

This form of accelerated CO_2 attack is of particular concern in condensate lines and low conductivity waters. Nickel containing welds used in oil field fabrications to provide the required strength are cathodic. However, the high nickel content of the corrosion product film gives rise to different corrosion kinetics and films compared to the low alloy steel plate, which when combined with the high resistance of the electrolyte means that the normal galvanic protection derived from the weld being coupled to the more anodic parent plate does not occur and the weld may be preferentially attacked.

Some inhibitor packages can increase the rate of weld metal corrosion as they are less effective in the presence of the high nickel content corrosion product, but careful selection of an appropriate inhibitor can mitigate the problem. The test procedure is to section a weldment into five electrodes – weld metal, heat affected zones (HAZ), and parent plates and then reassemble the sections into a test electrode, Figure 15. Electrochemical corrosion rates are obtained via five zero resistance ammeters each connected to an electrode segment from which the individual rates of corrosion and galvanic coupling currents can be determined, Figure 16.

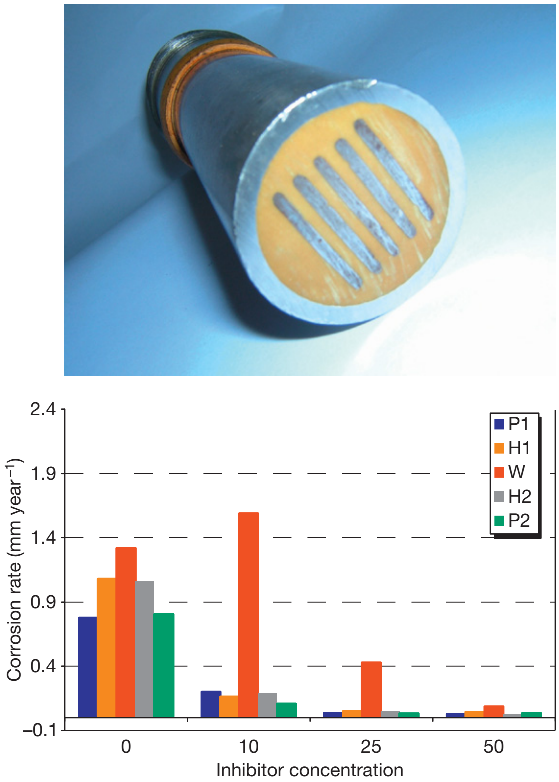


Figure 15 Preferential weld corrosion probe and inhibitor performance test data.

4.26.3.3.6 Autoclave tests

These are normally the final tests to replicate field conditions as they are expensive and usually restricted to inhibitors that are expected to be effective as based on previous and simpler tests. Typically employed to assess combined high temperature–pressure conditions and may also incorporate RCE and jet impingement, as well as electrochemical monitoring. Autoclave tests can be considered as being under full system condition simulation, with the test variables, fluid chemistry, $ppCO_2$, ppH_2S, shear stress, temperature and monitoring, subject to feasibility study Wt loss, LPR, and Ceion probe.

4.26.3.3.7 Compatibility

Compatibility with other production chemicals must be considered not only to control emulsions but also to prevent failures that have occurred due to loss of performance of some of the oilfield chemicals. In general, a compatability test will be concerned with assessment of emulsion stability, where a sample of untreated degassed crude is mixed with a sample of brine (field or synthetic) to which is added a known amount of treating chemical to give a similar concentration as will be employed in the field. The mixture is shaken and the time taken for the oil/water emulsion to break is noted. The effect of treating chemical mixtures on corrosion performance is also important. In the case shown in Figure 17, the corrosion inhibitor and other chemicals were found to be incompatible because of the effect of the biocide.

4.26.3.3.8 Field deployment

There are many issues related to field deployment activities and the reader is referred to the *European Federation of Corrosion Document Number 39, The Use of Corrosion Inhibitors in Oil and Gas Production*[8] for full details. In particular, problems can include: preparation of inhibitors for injection, such as dilution and mixing, deaeration–gas blanketing; the introduction

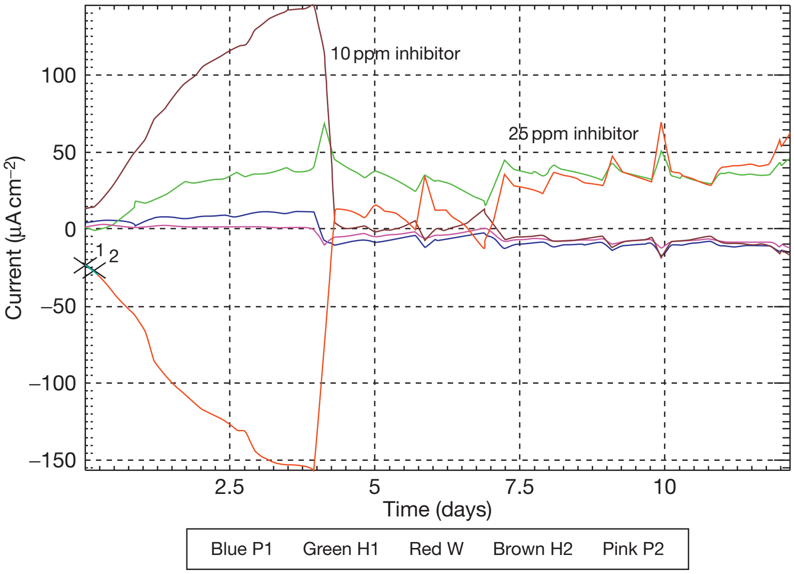


Figure 16 Effect of inhibitor dosing with time and increased dosage.

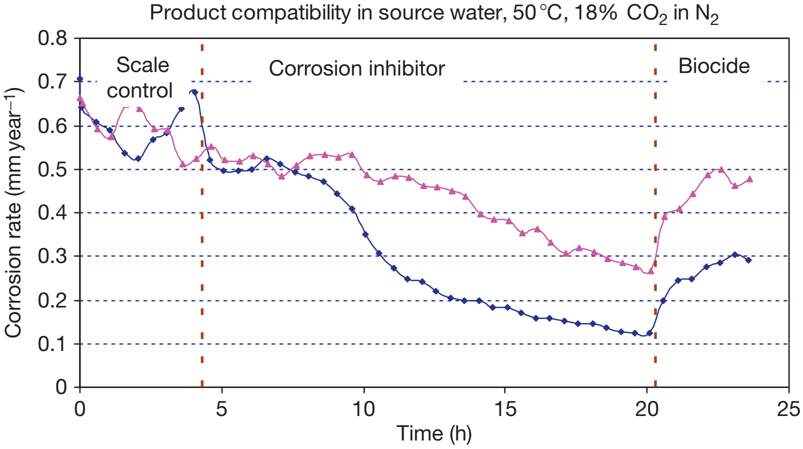


Figure 17 Effect of chemical additions on corrosion.

of atmospheric oxygen into chemical storage tanks or into water used to dilute 'neat' inhibitor is a prime cause of problems. Many chemicals are corrosive when supplied as concentrates and the injection equipment is usually constructed from 316 stainless steel. Preparation of facilities and pipelines for inhibition; improved performance is achieved in clean systems; therefore, cleaning and descaling may be required, for example, use of specially designed, adjustable scraper pigs, provision for removal of solids at pig traps, and use of specialist cleaning contractors.

Operation and maintenance of injection equipment must be managed with overall coordination of maintenance, housekeeping, and inspection activities allocated to a supervisor who has responsibility for updating the records; note that high corrosivity systems may require >95% up-time on injection equipment. Monitoring and inspection are key activities in corrosion inhibition management and asset integrity strategies. Regular corrosion monitoring/corrosion inspection to obtain trend data is the only means to ensure inhibition is effective. Inspection is also used periodically to ensure the integrity of production equipment, including export pipelines. Monitoring and the recording of all available parameters, including production rates, water cuts, and inhibitor consumption, are required to ensure that the program is operated and managed correctly.

Clean metal surfaces increase the effectiveness of almost all corrosion inhibitors; consequently, an initial cleaning treatment may be advisable before the introduction of a corrosion inhibitor system. Corrosion inhibition is also less effective in old, corroded, and pitted pipelines or facilities and in systems that contain large amounts of debris. Dosages may have to be increased or the system cleaned; in some cases, a scale inhibition program may have to be implemented in addition to the corrosion inhibition program. The inhibitor may not perform as anticipated in the field or there may be poor management of the dosage leading to lower than required inhibitor availability.

4.26.4 Scale Inhibition/Control

Scales, sometimes referred to as hard fouling, can plug reservoirs and equipment in production systems, flowlines, and pipelines. Scales can also affect the thermal efficiency of heat exchangers and boilers (an increase in the design fouling factor). Scaling and fouling by deposits–corrosion debris are both typically controlled by similar treating packages. The aim is to minimize operating problems (poor heat transfer, plugging) and aid corrosion control (under deposit corrosion) by use of scale control chemicals (phosphonates, phosphate esters, polymers). Note that prevention of scale formation on oil field lines may result in more fine crystals or sludges being carried downstream to oil and gas separation plants, see Figure 18.

Scale can inhibit or promote corrosion. Hard, nonporous scales may sometimes protect metal surfaces from electrolytes and prevent corrosion. For example, the addition of calcium salts helps to control corrosion ('red water' in desalination potable water) and other soft water distribution systems by deposition of calcium carbonate. Loose or porous scales can create concentration cells that accelerate corrosion in boilers, cooling systems, and production equipment. Since corrosion usually occurs under scales, particularly on heat transfer surfaces, it is better to prevent and remove a scale whether or not it protects the metal.

4.26.4.1 Scale Inhibitor Application

Scale inhibitors must always be present to stop scale formation. Batch treatments with scale inhibitors are NOT effective. Scale inhibitors are usually continuously injected at low concentrations (5–25 ppm). Scale inhibitors can react with calcium and iron in produced water to form a scale. This usually occurs at the point where a concentrated scale inhibitor is added to the system. If the scale inhibitors are diluted with fresh water, this problem can be prevented. Scale inhibitors may also be injected in the middle of the flowline so they are quickly diluted.

4.26.4.1.1 Scale treatment chemicals

Inorganic Phosphates – They contain a P–O–P group and have a tendency to adhere to the surfaces of scale crystals and prevent further crystal growth. They are effective at low concentrations: 2–5 ppm for $CaCO_3$; 10–12 ppm for $CaSO_4$; and >50 ppm for $BaSO_4$. The most common examples are sodium hexanetaphosphate and sodium tripolyphosphate. Inorganic phosphates have certain disadvantages. They revert from metaphosphate to orthophosphate at temperatures above 60 °C. Reversion makes the scale

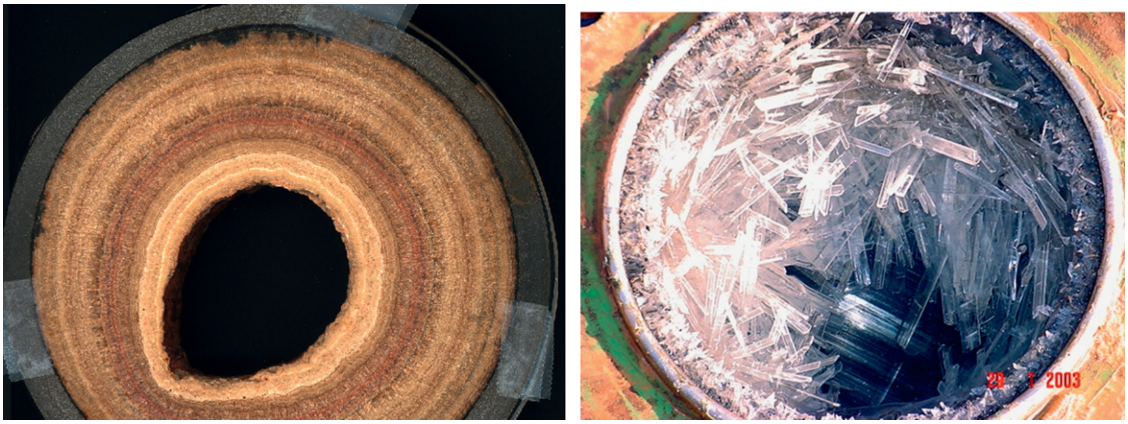


Figure 18 Oil field scales formed in flowlines.

inhibitor ineffective. Reversion occurs slowly with age and in low pH solutions. Inorganic phosphates were used extensively before organic phosphonates, phosphate esters, and polymers were discovered. Because of the disadvantages of inorganic phosphates, organic type scale inhibitors are used more often. The organic scale inhibitors described below prevent crystal growth much like inorganic phosphates.

Organic Phosphate Esters – Phosphate esters have excellent scale inhibiting properties and are thermally stable up to 82 °C or 93 °C.

Organic Phosphonates – They are more thermally stable than phosphate esters. The reason is that the phosphorous is directly bonded to the carbon atom in phosphonate inhibitors. An example is amino trimethylene phosphoric acid (ATMP). ATMP acid derivatives are stable at all pH conditions up to 230 °C. ATMP acid derivatives are used extensively in scale inhibition squeeze programs for oil producing wells.

Organic Polymers – They are effective against calcium carbonate, calcium sulfate, and barium sulfate. They have excellent thermal stability. Examples of organic polymers are polymaleates, polymethacrylates, and polyacrylamides, see Table 1.

4.26.4.1.2 Scale control

The mechanisms of scale control are complex but include:

- Threshold inhibition (hardness stabilization) aims to prevent creation of crystal nuclei (enable scale forming salts to exist in an over-saturated form), a kinetic process that allows the creation of submicroscopic nuclei.
- Crystal modification (growth control) due to adsorption/incorporation of scale inhibitor molecules or ions, this result in decreased growth and cohesion between deposited particles.
- Sequestration (chelation), the use of chemicals that complex or chemically bond to dissolved salt ions and remove them from precipitation reactions.
- Anionic dispersion (destabilization theory), the dispersion chemical, usually a highly anionic polymer, adsorbs onto a slightly anionic scale particle and increases the charge density causing the particles to remain in suspension in the water.

4.26.4.2 Scale Predictions

The tendency for a water to 'scale' is dependent on the calcium carbonate concentration (that is its 'hardness'), the pH and total alkalinity, dissolved solids, and temperature. When the solubility product of a scale forming material is exceeded, it can form a scale. The scaling tendency (the probability that scale will form) increases as the amount of supersaturation increases. Calcium carbonate forms when carbon dioxide is released from solution. This usually occurs when the pressure decreases. Calcium carbonate scale commonly forms in producing wells and associated flowlines in some fields. These scales can form in production equipment and interrupt operations. Normally, produced waters contain calcium ions (Ca^{2+}), bicarbonate ions (HCO_3^-), and carbon dioxide (CO_2). When CO_2 is evolved, the pH of the solution increases. The bicarbonate ions dissociate to form carbonate, CO_3^-. The carbonate reacts with calcium to form $CaCO_3$, which precipitates as it is relatively insoluble.

$$\begin{aligned} Ca^2 + 2HCO_{3^-} &\rightarrow Ca^2 + 2CO_3^{2-} + 2H^+ \\ &\rightarrow CaCO_3 + CO_2^+ H_2O \end{aligned}$$

The scaling tendency of $CaCO_3$ increases as the temperature increases.

For pH between 6.5 and 9.5, the chemical equilibrium is given by:

$$PH_{sat} = (pK_2 - pK_s) + pCa + pAlk$$

A basic indictor of scaling, the *Langelier Index:*

$$Ls = pH_{act} - pH_{sat}$$

shows when $Ls < 0$, the water is corrosive and nonscaling and when $Ls > 1$ it is scaling.

Table 1 Organic scale treating chemical mechanisms

Treating chemical	*Threshold stabilization*	*Crystal distortion*	*Complexation/chelation*	*Dispersion*
Low molecular weight polymers	X	X		
Phosphonates	X	X	X	
Phosphate esters	X			
Organic polymers		X		X
Modified organic		X		X
Polyphosphates			X	
Chelates			X	

Another index, the *Ryzner Stability Index:*

$$Rz = 2pH_{sat} - pH_{act}$$

indicates that the solution is for $Rz < 6$ – increasingly scaling; $Rz > 7$ – not scaling; $Rz > 8$ – increasingly corrosive.

In cooling waters, scale control can be achieved by modifying the pH – for example, acid dosing thereby ensuring good heat transfer in equipment but this then requires improved corrosion inhibition of the cooling water. In potable water systems, scaling on metal surfaces is desirable to reduce corrosion rates by formation of a barrier layer. Thus, if such waters do not naturally possess a scaling tendency, as determined by the Langelier Saturation or Ryznar Stability Indices, lime may be added to raise the calcium levels until calcium carbonate scaling forms on the pipe surfaces. Dezincification, that is, the selective dissolution of zinc from brass alloys used in water distribution systems, is also reduced by lime addition. It should be noted that the water output produced from a desalination plant is normally mixed with a small volume of sterilized seawater or groundwater to principally produce a palatable product. If this is done, the water may have sufficient scaling tendency without the need for further lime additions.

In oilfield systems, particularly where commingling takes place, the concern is to inhibit scale formation to prevent plugging of wells, flowlines, plant, or the reservoir. The potential of forming ‘hot’ radioactive scale is another hazard (radium related radioactivity), possibly as coprecipitants with $BaSO_4$ scale. Contaminated equipment may require specialized handling, and this would have an impact on the maintenance cost. Applicable scale inhibitors should be applied to limit excessive scale build-up and reduce the impact of such radioactivity.

For a more complete prediction of scaling in systems and reservoirs, sophisticated codes are available based on the equilibrium chemistry of the major ionic components present in the brines/waters. Below, some of these are outlined.

Petrotech MultiSCALE Code – this Norwegian University code, developed with support from Statoil, Saga Petroleum, and Norsk Hydro predicts the simultaneous precipitation of the respective scaling species. The code computes the equilibrium concentrations of Ca, Sr and Ba sulfate, and Ca and Fe carbonate scales, in addition, the code predicts FeS and halite precipitation. The user can allow the program to select the ‘stable phase’ for $CaSO_4$ precipitation or choose whether gypsum or anhydrite is to be considered.

OKU Code – the OKSCALE Prediction Model computes the equilibrium concentrations separately for $CaCO_3$ and sulfates of Ca, Sr, and Ba. All the sulfates are considered simultaneously; the user can choose whether gypsum or anhydrite is to be considered. The program has been upgraded following lengthy and detailed empirical $SrSO_4$ and $CaCO_3$ solubility determinations conducted by the OKU research group. The program calculates CO_2 fugacity either from the associated gas composition (CO_2 mole % level) or from a dissolved CO_2 value.

RICE Code – a Pitzer based model which utilizes the Peng-Robinson EOS to calculate fugacity coefficients. This model predicts the simultaneous precipitation of the respective scaling species. The code computes the equilibrium concentrations of Ca, Sr and Ba sulfate, and Ca and iron carbonates. In addition, it will predict halite, FeS, ZnS, and CaF_2 precipitation.

Such scale prediction programs are not by themselves definitive, rather they give an indication that a problem may occur. The level of precipitation predicted in many cases can be higher than that observed in a system. The levels of precipitation predicted are based on equilibrium solubility data, but these data do not take into account reaction kinetics. Furthermore, prediction accuracy is not just a function of modeling limitations, much depends also on the quality of the data input. If brine compositional data is inaccurate, possibly due to poor analytical technique or more commonly due to poor sample handling, then the computer prediction data will be devalued. Often brine analysis is conducted on samples many hours after sampling, transient changes occur, and precipitates may form. Results may be reported for filtered samples, without thought for the precipitate removed. Clearly unstable species, such as HCO_3^-, should be determined on-site; dissolved CO_2 levels should be determined on pressurized bomb samples.

The results of a typical PREDICTIVE study of a field whose water chemistry indicates a significant probability of barium sulfate scale when sea water injection is employed is shown in Figure 19, with the likely concentrations and scaling tendency plotted against seawater breakthrough. There is also a possibility of microbiological build up as water breakthrough increases.

Figure 19 illustrates the likely changes with continuing water injection leading to an increase in the barium sulfate and water profile with production time. Initially, the scaling will be calcium carbonate, but then it is the barium scale profile that predominates and the squeeze treating chemical would

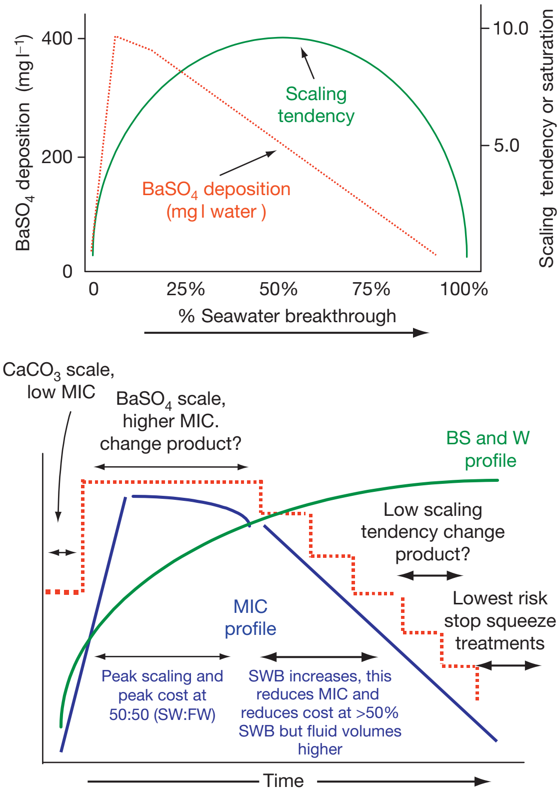


Figure 19 Predicted scaling tendency (mass and supersaturation) over the life cycle of a well described by the sea water injection), scaling and MIC profiles compared to the barium scale and water profile over the field life.

have to be changed for these new peak conditions. The MIC also reaches a peak, hence, this is the most costly period with the chemicals having to control both scale and MIC; compatibility issues would also have to be addressed. Further changes in chemicals can be anticipated later in field life.

It is important to understand that the precipitation of an insoluble salt crystal does not always result in scale deposition; much depends on the system parameters, dynamics, and the presence of crystal interacting chemistries. Precipitates (particularly if oil-wet) may to some degree be transportable. Nevertheless, scaling predictions should be used as an indicative tool to test sensitivities and estimate trends. However, careful consideration needs to be given to interpreting the outputs; generally, the predictions can be assumed to be a worst case.

Testing for scale formation is by:

(i) Static mixing tests – NACE TM0397, 0197, 0374
Advantage – Simple quick tests mix the waters and weigh deposits or analyze for scale species, Ca, SO_4, Ba, simple measure of efficiency.
Disadvantage – Does not evaluate crystal modifiers on an even basis.

(ii) Dynamic tube blocking tests.
Dynamic laminar flow used to examine growth mechanisms (scale and/or microbiological fouling) using a strata core sample, temperature >100 °C possible, allows examination of systems under pressure.

4.26.4.3 Squeeze Application

Core flood assessment used to determine inhibitor return profile isotherm by means of a model squeeze treatment, 'SQUEEZE V' to determine various parameters: squeeze life, concentrations, shut in period, postflush, see Figure 20. Effectively a sensitivity study but the model must be optimized after first treatment. Variations in: local temperatures, flow rates, precise scale inhibitor mechanism (precipitation/adsorption) will influence the model and actual response.

4.26.4.4 Scale Inhibitor Selection

Typical program includes:

- Monitor changes in well, water composition, and physical conditions data. Carry out scale prediction modeling to assess scale risk throughout production system, surface, and subsurface.
- The scale inhibitor candidate products are tested for performance and compatibility.
- Brine/chemical compatibility, various field water/sea water ratios to test for inhibitor/brine compatibility, static inhibitor adsorption tests on reservoir core (if for squeeze application).
- Efficiency performance test.
- Static bottle tests.
- Dynamic loop.
- Thermal stability tests for application >130 °C.
- Production chemical interference tests with candidate scale inhibitor.
- Review of inhibitor performance data.
- Select product.
- Core flooding and squeeze modeling.

4.26.4.5 Scale Removal

Mechanical – rod out the scale from heat exchangers, 'scraping'/'pigging' of lines.

Chemical methods – calcium carbonate is soluble in hydrochloric acid, acetic acid, formic acid, and sulfamic acid. Iron carbonate, iron oxide, and iron sulfide are also soluble in hydrochloric acid. The HCl must contain a sequestering agent (e.g., acetic acid, oxalic acid, gluconic acid, or citric acid) to prevent precipitation of iron. Gypsum ($CaSO_4.2H_2O$) is insoluble in acids. However, gypsum can be converted to another scale that is soluble in acid. Ammonium bicarbonate or sodium carbonate converts gypsum to calcium carbonate. Potassium hydroxide converts gypsum to calcium hydroxide. Both calcium carbonate and calcium hydroxide are soluble in acid. If the scales are covered by waxes, the waxes should be removed with organic solvents first. Waxes are not soluble in acids. Mechanical methods must be used to remove barium and strontium sulfate from tubes. An attempt should not be made to dissolve barium or strontium sulfate with acid because they are less soluble than casings and liners.

4.26.5 Treating for MIC

Bacteria cause two major operating problems:

Biofilms – bacterial growths that can reduce flow rates and cause plugging.

Localized corrosion – due to environment changes, usually under biofilms and deposits, see Figure 21.

The most common forms of bacteria found in natural waters used in oil and gas production/refining facilities are slime forming, and most are aerobic (often called general aerobic bacteria, GAB): *Pseudomonas, Flavobacterium, Alcaligenes, Bacillus,* and *Aerobacter–Sphaerotilus–Gallionella.* The bacteria responsible for many corrosion problems are the anaerobic sulfate reducing bacteria (SRB): *Desulfovibro, Desulphotomaculum,* and *Desulfobacter.* Some SRB can be found in aquifiers having been present for millennia. Other bacteria are oxidizing bacteria and convert sulfide to sulfur/sulfate or oxidize ferrous to ferric and are commonly found in waste water systems and are responsible for degradation of concrete, for example, *Thiobacillus* and *Beggiatoa.* Further details of microbial issues can be found in Stott[13].

4.26.5.1 Bacteria Monitoring Techniques/Serial Dilution

Samples acquired to estimate populations of free floating bacteria (planktonic) found in fluids, and bacteria attached to surfaces (sessile) are analyzed using similar techniques that comprise a *serial dilution step* followed by an *incubation step* with the concentration of bacteria estimated from changes observed in the sample bottles[9]. More specifically, the technique estimates bacteria concentration (bacteria/ml) by taking a 1 ml sample of the source water and injecting it into 9 ml of a sterile broth media in small, capped bottles. The solution in the bottle is mixed well and 1 ml is extracted using another syringe and the extracted fluid is injected into a second bottle and

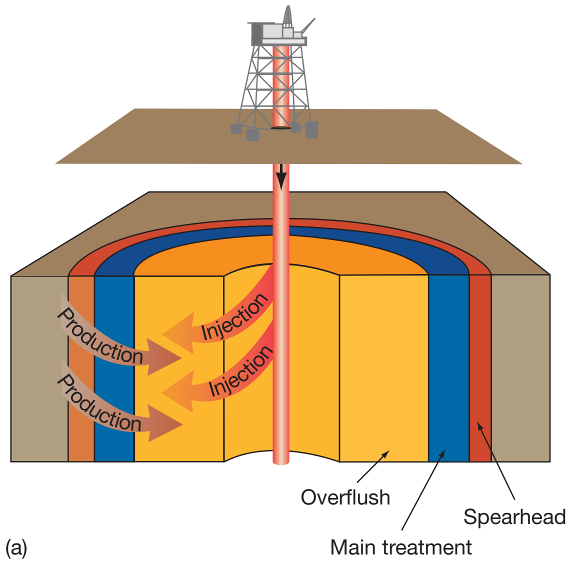


Figure 20

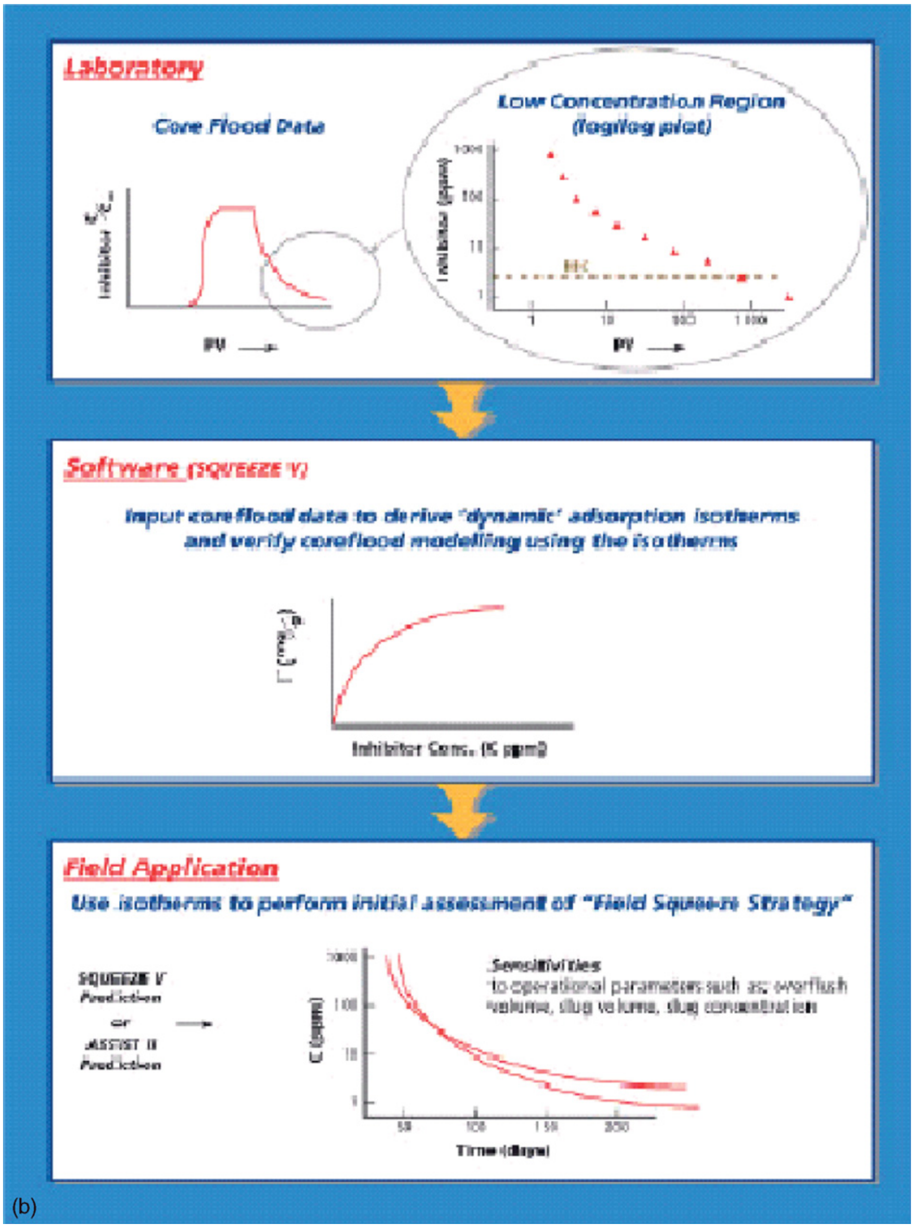


Figure 20 Continued. Illustration of squeeze application into reservoir.

the same procedure is followed until all six bottles are inoculated. The media contains nutrients and a carbon source with either saline or fresh water. For GAB, the carbon source is dextrose. For SRB, the carbon source is lactic acid together with an iron salt or an iron nail. At the end of the incubation period, the SRB population density in the original sample is determined to the nearest order of magnitude by the number of vials in each dilution series that turn black due to bacterial sulfide production. Tests in which five bottles turned black suggest that the water sample contains a bacteria count of between 10^4 and 10^5 bacteria/ml, see Figure 22. The SRB bottles are incubated for 28 days. GAB bottles are incubated for 5 days. Current standards prescribe an incubation period for SRB as a minimum of 28 days, but a very good indication of the SRB count can usually be obtained after 10–14 days of incubation. It can be assumed that if the planktonic bacteria count is high, the sessile bacteria count is also high somewhere in the system. However, a low planktonic count does not suggest that the sessile count is low.

Figure 21 MIC pitting in an iron sulfide film, morphology of micropits within larger pits. Reproduced from Stott, J. D. F. Microbial Environments. In *Corrosion*; Elsevier: London, 2009; Vol. 2.

Figure 22 Serial dilution test for SRB, five dilutions contain bacteria indicating a heavy infestation.

Ideally, the serial dilution part of the test should be carried out within a few hours of obtaining the subject samples (typically done on site), however, that is frequently not possible. The results become less reliable with increasing time from sampling. Total viable bacteria counts are usually much higher than SRB counts, with planktonic counts of up to 10^5 per ml are common in many natural waters and industrial systems. Higher population densities than 10^5 per ml probably indicate a significant build up of slime somewhere. In biocide-treated systems, total viable bacteria counts should be several orders of magnitude lower than in the untreated water. The incubation period for total viable bacteria counts is only ~3 days, considerably shorter than SRB. Therefore, these counts can give a useful early warning of any problem with biocide-treatment efficiency. GAB populations greater than 10^4 bacteria/ml are considered significant.

4.26.5.2 Biocide Treatments

Biocide treatments control bacteria numbers (measured by counting the population density), and the first stage of biocide selection is a laboratory evaluation of candidate biocides using a 'time-kill' test. These tests use a series of biocide dilutions combined with injection of known populations of the bacteria. After the completion of laboratory tests for biocides for a given application (which should include economic considerations and chemical compatibility tests), a program of site monitoring is recommended. The site monitoring should ensure that the chemical injection rate is giving the correct concentration of biocide and is changed when water throughput rate is altered. The monitoring should identify any major perturbations of the system which may affect biocide efficiency. Such perturbations include changes in contact time, flow rates, temperature, pH, use of a new chemical (e.g., corrosion inhibitor, scale inhibitor, or oxygen scavenger), or shutdown periods.

4.26.5.3 Biocide Application

The purpose of biocide treatment is not to kill all bacteria in the system but to control bacteria and economically minimize their effects on corrosion and water quality. Biocide performance is based on success in controlling sessile bacteria, although initially planktonic counting is employed to screen several biocides. Then the biocides that successfully pass this test are tested further for their impact on sessile bacteria (N.B. to acquire sessile samples, growths are carefully scraped or sonically removed. The bacteria population is related to the surface area of the coupon studs with results being reported as bacteria per square centimeter.)

Typical biocide packages are based on:

- Primary amines – cocoamine acetate,
- Diamines – cocodiamine acetate,
- Quaternary amine salts – dialklyl-benzyl ammonium chloride,
- Aldehydes – formaldehyde, glutaraldehyde, acrolin,
- Chlorinated phenols, and
- Oxidizing agents – chlorine, bromine (hypochlorite–hypobromite mixture) usually produced by electrolysis of seawater or brine.

Chlorine dosage has the disadvantage that the water may contain reducing agents with a chlorine demand, where chlorine is consumed by reaction with organic matter and pipework, whilst ammonia will form chloramines. The chlorine demand must be accounted for and the system is overdosed to a free chlorine 'residual' of typically between 0.2 and 0.5 ppm. Chlorination is not suitable for systems with a high chlorine demand or extensive (several km) exposed carbon steel pipework as the high dosage levels required at the inlet can lead to enhanced corrosion risks, possible stress corrosion cracking of austenitic steel.

There are essentially two classes of biocide treatment, viz. continuous, low level dosing with oxidizing agents and 'shock' treatment using organic biocides. These are often employed together for seawater injection systems where an initial dose of chlorine kills some bacteria and seed macrofouling. The water is then deaerated, removing chlorine and dissolved oxygen and then a batch dose of biocide is periodically sent down the line. Biocide batch treating of water systems controls bacteria with a higher biocide concentration and a shorter contact time. A typical offshore seawater injection system for example, would have continuous use of electrolyzed sea water to control macroorganisms (seed shell fish, etc.) and partially control bacteria followed by batch treatment with glutaraldehyde (e.g., $1500\,\mathrm{mg\,l^{-1}}$ twice weekly) for 1 h, and subsequently, to prevent the development of a dominant bacteria strain with a quaternary ammonium-based bactericide (e.g., $500\,\mathrm{mg\,l^{-1}}$ for 1 h).

Developing a biocide treatment strategy to maintain control of microbial populations is an iterative process. If insufficient biocide is dosed, a greater proportion of the microbial population will recover between dosing than being killed during dosing and the population trend will increase with time. Increasing the dosing regime may then lead to a situation where kill is exactly matched by recovery. Further improvements can lead to an overall reduction in population where kill exceeds the recovery rate. This will lead to a reduction of corrosion in the fluids which is the aim of the biocide treatment strategy.

An alternative method to chemical biocide treatment is ultraviolet sterilization, with the disadvantage that it carries no residual protection into systems and does not sterilize sessile bacteria on the metal surfaces. Treatment is only effective against planktonic (free floating) microorganisms in completely optically clear water. Any entrained particles will shield the SRB from the action of the UV radiation. Also, any scale formation or solids deposition on the optical window (even a very thin film) will severely limit the effectiveness of the treatment.

4.26.6 Management of Treating Programs

The use of chemical treating is a strategic decision made during the design stage in the case of corrosion, usually due to the selection of the use of c-steel or low alloy steel in preference to corrosion resistant alloys but in the case of scaling based on reservoir and injection water chemistries. The implications are that provision must be made for the positioning of injection locations, chemical storage, and chemical monitoring facilities. Details of many of these issues can be found in the oil and gas management chapter.[1] In many cases, the need to introduce chemical treating arises during operations due to adverse processing conditions, increased maintenance for cleaning/descaling, or is the result of corrosion damage of equipment found by routine inspection. This change will need a reassessment of corrosion, integrity, and operational issues as well as the sourcing, installation, commissioning, and operation of all associated activities concerned with the treatment programs.

In general, safety, health, and environmental (SHE) polices plus operational and commercial concerns control the development of chemical treating strategies and treating management.[2] The purpose of the treating programs must be clearly stated together with their likely impact on corrosion, asset integrity, maintenance, and operations. There are obvious costs associated with treating – the initial investment or capital cost, personnel recruitment, training, chemical costs, use of contractors or consultants but also benefits – the ability to operate effectively within highly aggressive environments, to push operating envelopes, and improve overall performance. Effective management requires a transparent framework for these activities with the management process involving a series of logical steps as illustrated by the management process flow sheet shown in **Figure 23**.

The inputs to the flow chart are the treating issues and their impact on maintenance of asset integrity (SHE) and improvement in performance (business outcomes). There are two outputs from the management process, the tactical, which is effective mitigation of the risks from corrosion, scaling, and microbiological infections (decreased rates of corrosion damage, less plugging of strata and equipment) and a continuous improvement of the management process (less risks from leakages or hazards from corrosion, fouling, fracture, wear, plus increased throughput at lower costs). Although this second outcome is a normal requirement of any quality

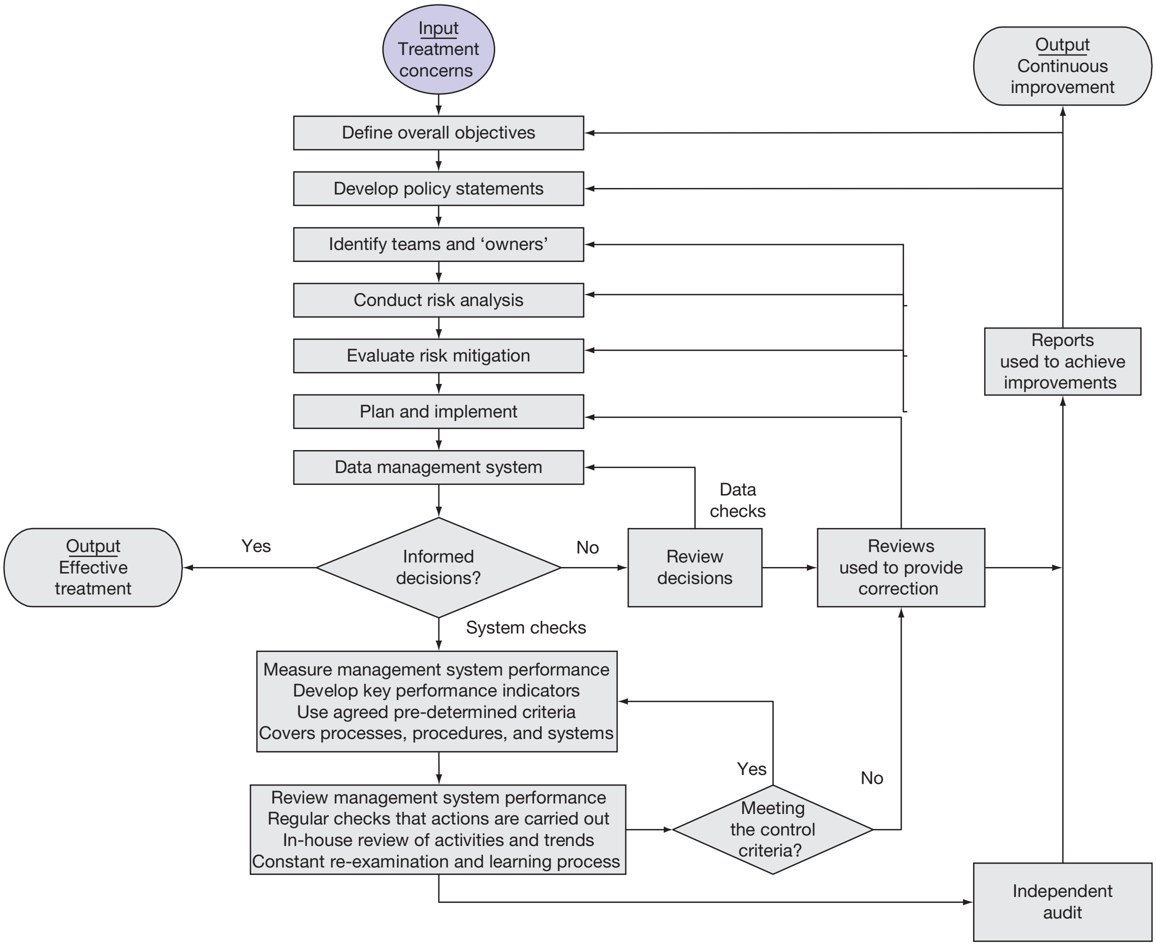


Figure 23 Steps in a risk-based treatment management process.

system and the management of SHE issues, it has not received widespread acknowledgment in the management of oil and gas assets or treatment management. This is in spite of the fact that asset management, including chemical treating and corrosion management, requires that products are recovered at lowest possible costs commensurate with meeting SHE requirements.

The flow sheet was developed using a risk-based approach for corrosion management,[2] with the decision-making step based on reputable field data as a key factor in development of strategies. The risks are from both physical and chemical processes (corrosion and scaling) and from management processes often referred to as human errors, when catastrophic failures occur. J. Reason[10] considers that key factors in many industrial equipment failures are due to *latent conditions*, which promote the likelihood of active failures by the creation of local factors that then promote errors. Latent conditions are defined here 'as undiagnosed or unrecognized flaws or defects in data, data management, systems, documents, procedures and guidance or standards that give rise to human errors.' The need to meet design and operational specifications, including no leaks, minimum unscheduled down time, cost effective production means regular reviews and audits including the development of performance indicators based on acceptable criteria. These audits are also a means of identifying latent conditions in the management system. A continuous improvement approach also has benefits in the control of operational issues – day-to-day activities, monitoring, chemical dosing, etc.

The objectives of a treating program must be transferred through from design to operations and should be encompassed in a policy statement from the senior management. The boundaries and ownership of the program must be clearly defined, as a number of individuals, specialists, teams, and vendors are likely to be involved. Hence, responsibility and

Table 2 Typical activities, responsible personnel, and implications

What	*Who*	*Comments*
Corrosion data	Operators/inhibitor supplier	For all monitored locations – last period and yearly trends
Analysis of data	Corrosion engineer	Is corrosion controlled?
Chemical consumption	Inhibitor supplier/ purchasing	Last period and trend
Chemical problems	Production chemist	Compatibility with other chemicals, water quality
Production rates	Operations	Last period, forecasts with emphasis on impact on chemical usage
Equipment on line availability	Operations/maintenance	Specify cause of outing, duration, cost of repairs
Processing information	Operations	Possible interference of inhibition with processing
SHE performance	Facilities/process	Targets, results (e.g., water discharge compliance)
Operators comments	Operations	Nonspecific problems, issues, suggestions for improvement
Targets for next period	All	Include technical, commercial issues

accountability may become less obvious as projects and operations develop. This is illustrated by a list of activities and personnel involved, see Table 2.

4.26.6.1 Inhibition Risks and Mitigation by Monitoring

One approach is to continuously monitor a number of process parameters (e.g., flow rate, water cut, temperature, etc.) and then be ready to alter the corrosion inhibition conditions appropriately. The concern is that there is no direct measure of metal loss. However, such a strategy may be appropriate in low risk systems where regular corrosion inspections can adequately identify wall thickness change. A more proactive and efficient approach, essential with high risk systems, is to identify the corrosion rate increase and its cause, such as an increase in water cut/process parameter change, as quickly as possible and respond to it immediately. Methods that use insert probes/spool pieces, such as the newer electrical resistance techniques and linear polarization resistance measurements (LPRM) are typically employed but sensitive ultrasonic transducers, permanently attached to the equipment have been used, as have iron counts to determine metal loss rates.

A risk assessment is a normal step in any business activity, and operating companies address inhibition risks differently depending on the type and age of equipment, location, types of fluids, constraints, and experience. There is also an increasing emphasis worldwide for organizations to adopt a risk-based approach to facility integrity and corrosion management, including the management of inhibition programs. Inhibition risks are typically associated with:

- maximum expected uninhibited corrosion rate;
- required inhibitor efficiency;
- required inhibitor availability;
- risks of erosion corrosion (flow regime and velocities);
- risks of pitting/under deposit corrosion;
- temperature that may cause loss of inhibitor performance and scaling;
- precorrosion (old or new system);
- available corrosion allowance (CA) and required life; and
- access for repairs and replacements.

The BP approach to assessment of inhibition risks for pipelines is summarized in the tables that list the categories for a typical 20-year design life with a maximum of 8 mm CA and indicates that inhibition is typically employed when the corrosion rate exceeds 0.5 mm year^{-1}. CRAs are used where the uninhibited corrosion rate is >6 mm year^{-1}. Note that the evaluation includes inhibitor availability, the percentage time, the injection of corrosion inhibitor occurs, and also the likely monitoring and inspection requirements to ensure adequate management of the system and to maximize integrity, see Tables 3 and 4.

Monitoring is a risk mitigation method that is used to confirm that inhibition, biocide, etc. are actually controlling the hazards (corrosion, fouling) to an agreed and acceptable rate. Monitoring can detect out of compliance, provide operators with sufficient reaction time to implement remedial action, such as repair of injection equipment, change operating procedures, change dose rate, and/or inhibitor/biocide/scale control package. Common corrosion monitoring methods include:

- chemical/biochemical analysis of fluid samples for changes is composition, water cuts, inhibitor residuals, planktonic bacteria;

Table 3 Example of a corrosion inhibitor risk evaluation

Risk category	*Maximum required availability*	*Maximum expected uninihb. corr. rate (mm year^{-1})*	*Comment*	*Proposed category name*
1	0%	0.4	Benign fluids, corrosion inhibitor use not anticipated. Predicted metal loss may be accommodated by corrosion allowance	Benign
2	50%	0.7	Corrosion inhibitor probably required, but with expected corrosion rates there will be time to review the need for inhibition based on inspection data	Low
3	90%	3	Corrosion inhibition required for majority of field life, but inhibitor facilities need not be available from day one	Medium
4	95%	6	High reliance on inhibition for operational lifetime. Inhibitor facilities must be available from day one to ensure success	High
5	>95%	>6	Carbon steel and inhibition is unlikely to provide integrity for full field life. Select corrosion resistant materials or plan for repairs and replacements	Unacceptable

Table 4 Monitoring and inspection requirements for different inhibitor risks

Corrosion inhibition risk	*Overall system requirements*	*Inhibitor injection system*	*First inspection schedule*	*Monitoring of subsea lines*
Category 1	Does not rely on corrosion inhibition	No requirement	Inspection determined by previous operation of similar systems	Process monitoring of fluids
Category 2	Inhibition not used in early life but is available when conditions change, i.e., increased water cuts	Commissioning without shutdown	As category 1	Standard inspection techniques at accessible points
Category 3	Inhibition not available due to logistics problems but must be operated as soon as possible	Commissioned as soon as practical and incorporate level device and flow monitor into injection system	Early inspection as determined by anticipated corrosion rates	As category one plus weight loss coupons, ER/LPR probes and occasional intelligent pig runs
Category 4	Corrosion control working on day one. Inhibitor and dose rate preselected	As category 3	As category 3	As category two plus FSM or UT mats system. Continual logging for all monitoring devices
Category 5	Assumes technical, SHE, and financial factors answered satisfactorily requirements as category 4	As category 3	As category 3	As category three plus increased inspection frequency

- ion counts (regular chemical analysis to provide trends);
- corrosion coupons (weight loss and detection of pitting, scales, bio-films);
- insert probes/spool pieces (electrical resistance/modern versions electrochemical – linear polarization resistance/electrochemical impedance/electrochemical noise/galvanic coupling);

- hydrogen probes (electrochemical, beta foils);
- FSM (field signature method) for metal loss/erosion pitting trends;
- ultrasonic strips (UT Mats) for metal loss trends; and
- erosion/sand probes.

Down-hole inspections of tubulars use wireline operations, including calliper surveys and ultrasonic examinations, complemented by visual and wall thickness UT measurements during work-overs. The inspection data, as with process plant examinations (RBI) should be correlated with the on-line corrosion monitoring. The same is true of in-line inspections where the condition of larger diameter pipelines is typically obtained by 'intelligent' pigging, usually magnetic flux measurements. Pipe geometry and vibration monitoring using a 'semi intelligent pig' (SAAM), which operates on the principles of measuring, recording, and detecting any changes in vibration level as the pig travels along the pipeline has also been used to correlate operations with field effects.[11] In addition, the differential pressure levels are detected and recorded along with axial acceleration and temperatures. This type of study demonstrates the importance of correlation of field data in the management process.

Further details on monitoring, including chemical analysis can be found in the Chapter on Oil and Gas Management.[1] The actual methods employed in any specific application will depend on the type of corrosion and the inhibition risk involved.

Tactical planning of the treating programs requires formulation of plans, specifications, assessment of chemicals, likely dose rates, and costs. Performance indicators will have to be developed for all activities, see EFC 39[7] for details.

4.26.6.2 Monitoring and Data Management

Water cut is an important operational parameter that must be monitored; the inhibitor dose rate and partitioning properties must be balanced to achieve optimal inhibitor concentration in the field. These are examples of field data that are continuously being collected and analyzed. Other parameters include the persistency of batch inhibitors that needs to be verified in the field to ensure the viability of the batch treatment. Corrosion monitoring is NOT a replacement for condition monitoring (e.g., use of inspection, intelligent pigs for pipelines, downhole wireline surveys), but an adequately monitored and well-managed chemical treatment program can provide cost benefits by optimizing the inspection frequency. Process interruptions, such as shutdowns, acid returns, and sand deposits due to loss of gravel packs require their own special set of precautions to prevent continuing corrosion damage in downstream operations.

Data collection is an integral part of any system that forms part of a chemical treating program. Data must also be properly stored to allow easy access for retrieval and analysis. Data are only useful when they are converted into information that can be employed to manage the corrosion. Monitoring for corrosion is only one aspect of managing the total inhibition system. For example, certain types of corrosion monitoring (e.g., weight loss coupons) only reveal an adverse change in the process after it has happened, often a significant time afterwards. These warnings are retrospective and reactive as metal loss has already occurred. Online data used to control chemical treatments require monitoring from chemical analysis, probes/spool pieces plus retrieval of appropriate process data, such as flow rates, temperatures, and fluid compositions from Supervisory Control and Data Acquisition (SCADA) systems. Conversion of data into information requires correlation of various datasets, analysis of trends, and extraction of information related to performance and cost benefits. An IT benchmark product such as *Amulet* has been employed for the management of corrosion data from various offshore and onshore production facilities/refining/oil field treating chemicals as illustrated in the figures. Not only should actual dose quantities of chemical be listed but these should be translated into dosage (ppm) by correlating with actual production rates. In many instances, an audit will show that the quantities of chemical ordered, delivered, in store or received by the field do not correlate with the specified dose.

Inhibition data such as corrosion rates should be correlated with other processing parameters, such as production rates and water cuts, to provide economic information for management. For example, chemical spend based on chemical performance and not dosage or usage targets, see Figure 24. Essentially this converts technical data to money to provide performance measures and criteria, enables compliance to be measured, and benchmarks similar assets. Other parameters could include cost per Ml water processed, cost per MW power, cost per barrel of seawater injected. A typical case is a $1.6 million per year saving achieved on a $5.6 million chemical spend as a result of online corrosion data management.

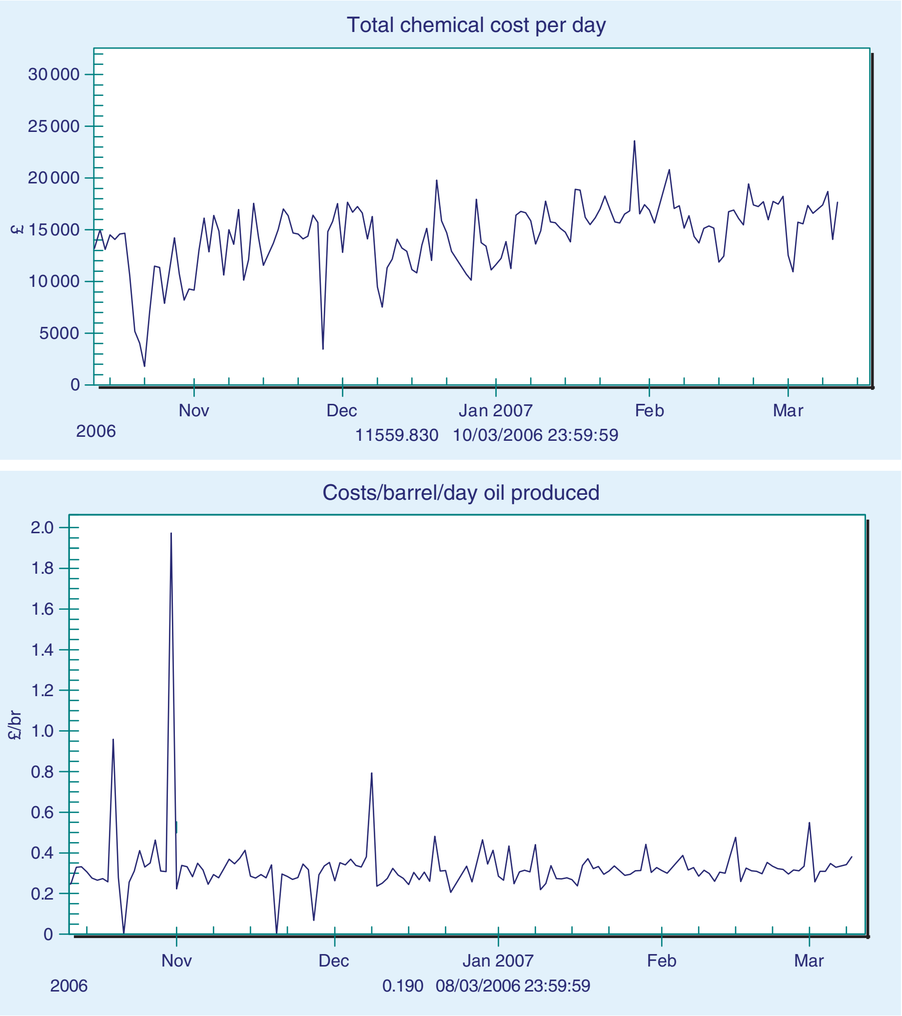


Figure 24 Comparison of chemical costs per day and per barrel of oil produced, courtesy A. N. Rothwell. Reproduced from Smith, C.; Murphy, B.; Flockhart, S. In *Corrosion'07*; NACE International: Houston, 2007; Paper No 330.

Management of treating programs relies on good decision making that requires information on field performance. This can only be obtained from data analysis that in turn means input of adequate field data. Without adequate data, there is no information and no effective chemical management control.

Further information on various aspects of the review and audit processes can be found in 'Guidance for corrosion management in oil and gas production and processing'[12] that also indicates normative requirements for the UK industry. The strategic decision to use chemical treating of a c-steel system has implications for other materials, such as some corrosion resistant alloys and Ti/Ti alloys. Also, the use of an alliance strategy with a chosen vendor has benefits in terms of a focused program with shared cost savings but ownership of equipment and field data, etc. has to be agreed prior to contract award.

It is also important to establish technical authority for chemical treating during design, commissioning, and operations and also to ensure that all relevant information is transferred from design to operations. Roles and responsibilities of all personnel have to be clearly defined, especially in large assets where chemical treating involves many disciplines, specialists and operational/maintenance staff, operators, technicians, and managers. System failures usually involve issues associated with data, handling, interpretation, issuing of reports and/or latent conditions within the management system, decision-making or audits for continuous improvement.

References

1. John, D. G.; Dawson, J. L.; Oliver, K. Corrosion Management in the Oil and Gas Industry. In *Corrosion;* Elsevier: London, 2009; Vol. 3.
2. Dawson, J. L. Corrosion Management Overview. In *Corrosion;* Elsevier: London, 2009; Vol. 3.
3. Chemical costs www.corrosioncost.com/pdf/oilgas.pdf
4. Crolet, J.-L. Progress in the Understanding and Prevention of Corrosion, EFC Conference, Barcelona 1993; pp 473–497.
5. Hedges, W.; Paisley, D.; Woollam, R. In *Corrosion 2000, June 2001*, NACE International: Houston, TX, 2000; pp 40–44; Paper No. 34.
6. Dawson, J. L.; Miller, R. G.; John, D. G.; Gearey, D.; King, R. A. In *Corrosion'88*; NACE International: Houston, TX, 1988; Paper No. 361.
7. Webster, S.; McMahon, A. J.; Paisley, D. M. E.; Harrop, D. *Corrosion Inhibitor Test Methods*, Sunbury Report No. ESR 95.ER.054, November 1996, Sunbury, B. P.: UK.
8. Palmer, J. W.; Hedges, W.; Dawson, J. L. *The Use of Corrosion Inhibitors in Oil and Gas Production, European Federation of Corrosion Document Number 39*; Institute of Materials: London, 2004.
9. Standard Test Method, TM0-194-94, *Field Monitoring of Bacterial Growth in Oilfield Systems*; NACE International: Houston, Texas, 1994.
10. Reason, J. T. *Managing the Risks of Organizational Accidents*; Ashgate Publishing Ltd: England, 1997.
11. Smith, C.; Murphy, B.; Flockhart, S. In *Corrosion'07*; NACE International: Houston, 2007; Paper No 330.
12. *Guidance for corrosion management in oil and gas production and processing*; Energy Institute: London, May 2008.
13. Stott, J. D. F. Microbial Environments. In *Corrosion*; Elsevier: London, 2009; Vol. 29.

4.28 Boiler and Feedwater Treatment

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Glossary

Attemperation The process for reducing and controlling the temperature of superheated steam.

Cation conductivity The measurement of the electrical conductivity of a water sample after it has been passed through a strong acid cation resin that is in the hydrogen form.

Decarbonator A degasifier used to remove carbon dioxide.

Desuperheat Removing superheat from steam typically by injecting high-purity water or steam condensate.

Duct burner A means of auxiliary firing in many combined cycle plant heat recovery steam generators (HRSG’s).

Feedwater heater A heat exchanger used to raise the feedwater temperature. Low pressure feedwater heaters are typically located ahead of the deaerator; high pressure feedwater heaters are typically located after the deaerator.

Mud drum The lower drum in a boiler circuit that acts as a point of recirculation and collects solids for removal by bottom blowdown.

Mud drum attemperator A steam to water heat exchanger located in the mud drum used to control steam temperature.

Specific conductivity The measure of the ability of water to conduct an electric current. Often related to the dissolved solids content of the water.

Steam blanketing A condition in a boiler tube where the steam water mixture stratifies into separate layers. This is more likely to occur in an inclined tube.

Sweetwater condenser A heat exchanger that cools a portion of generated steam so that the resultant condensate can be used for attemperation of the superheated steam.

Abbreviations

ASME	American Society of Mechanical Engineers
AVT	All volatile treatment
AVT(O)	All volatile treatment, oxidizing
AVT(R)	All volatile treatment, reducing
ED	Electrodialysis
EDI	Electrodionization
EDR	Electrodialysis reversal
EDTA	Ethylenediaminetetraacetic acid
EPRI	Electric power research institute
FAC	Flow accelerated corrosion
JIS	Japanese Industrial Standards
NTA	Nitrilotriacetic acid
ORP	Oxidation reduction potential
OT	Oxygenated treatment
RO	Reverse osmosis
TDS	Total dissolved solids
VGB	Vereinigung Grosskraftwerk Betreiber (Germany)

4.28.1 Introduction

Water is abundant on our planet. However, very little is suitable for human consumption (potable) without pretreatment. It is very rare that even potable quality water is suitable for makeup water to a boiler system without additional pretreatment.

There are many technical organizations around the world that publish guidelines on recommended feedwater and boiler water specifications. There are the European Standard[1] and the Vereinigung Grosskraftwerk Betreiber (VGB)[2] in Europe, the American Society of Mechanical Engineers (ASME)[3] and Electric Power Research Institute (EPRI)[4] in the United States, and the JIS[5] in Asia. These guidelines are generally developed by a consensus of committee members that can include equipment manufacturers, industrial equipment operators, water treatment companies, and experienced consultants. Some of these guidelines focus more on a particular segment of the industry than another. For example, the EPRI guidelines focus on boiler systems in the electric utility industry, whereas ASME focuses on boiler systems in industrial applications. Others may try to cover the entire scope of boiler applications. These guidelines are, for the most part, very general, and only in rare cases do these guidelines specify a treatment chemistry or treatment chemical to use. This is because the actual treatment chemistry used is a function of the makeup water quality available, the desired steam purity to be produced, and economic considerations. For instance, the ASME guidelines relate steam purity to the appropriate boiler water limits but do not specify feedwater purity in terms of total dissolved solid content. This is an economic decision left to the individual boiler system operator to decide how much is invested in the pretreatment system to purify the water as opposed to higher blowdown rates to maintain the boiler water dissolved solid limits. The EPRI guidelines are an example of such an exception from these more general types of guidelines, in that they are intended for a very specific audience of a narrowly defined type of boiler system – in this case, the electric utility industry.

Finally, since these guideline committees are continually updating their guidelines based on the most current information available and the latest operating experience, they will only be referenced in the chapter. For actual guidelines, the most current relevant issue of the chosen guideline should be obtained for use in a particular boiler system.

This chapter addresses the subject of makeup water, feedwater, boiler water, and steam and condensate treatment in steam boiler systems. Feedwater by definition is the combination of returned condensate and fresh makeup water (Figure 1). This combination can

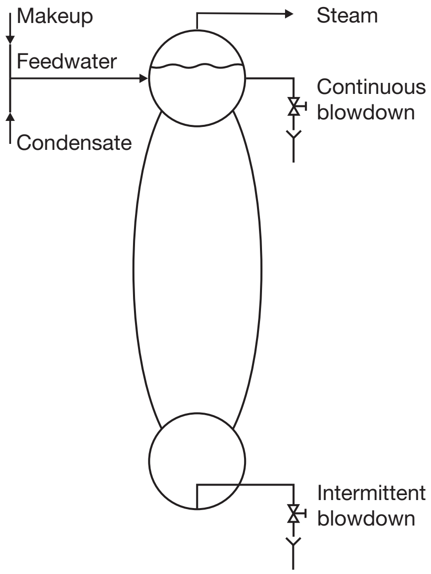

Figure 1 Schematic of typical boiler flows.

range from 0% to 100% in industrial steam-generating systems, in which the steam-generating system is generally part of an industrial or manufacturing plant. Figure 2 is a typical field-erected water tube industrial boiler. Notably different are steam-generating systems in the electric utility industry, which are dedicated only to the production of electric power and have condensate return rates consistently greater than 95% of the feedwater by design. Figure 3 is a typical drum-type utility boiler.

4.28.2 Make up Water Treatment

The type of pretreatment will dictate the necessary further chemical treatment that the water will require prior to use in the particular steam-generating system. The possible types of pretreatment are

clarification,
cold lime softening,
hot lime softening,
zeolite (ion exchange) softening,
demineralization,
reverse osmosis (RO).

Clarification is used to reduce the suspended solids of the water; cold lime, hot lime, and zeolite softening are used to reduce only the hardness, that is, the calcium and magnesium content of the water; reverse osmosis (RO) and demineralization are used for a more effective reduction of the total dissolved solids content of the water.

When precipitating processes for hardness removal such as cold or hot lime softening are used as pretreatment, the effluent water pH is inherently high, in excess of a pH of 10.0. pH control is a very important aspect of water treatment to protect the materials of construction of these systems. A secondary benefit of these precipitation processes is the partial reduction of the water's silica content. When these precipitating processes are used to reduce water hardness, it is important to remember to measure the total hardness of the effluent water. This involves an acid digestion step, as opposed to the normal soluble hardness tests, since there can be suspended solids of hardness in the effluent from these systems that the soluble hardness test would not detect and must be accounted for in the chemical treatments applied.

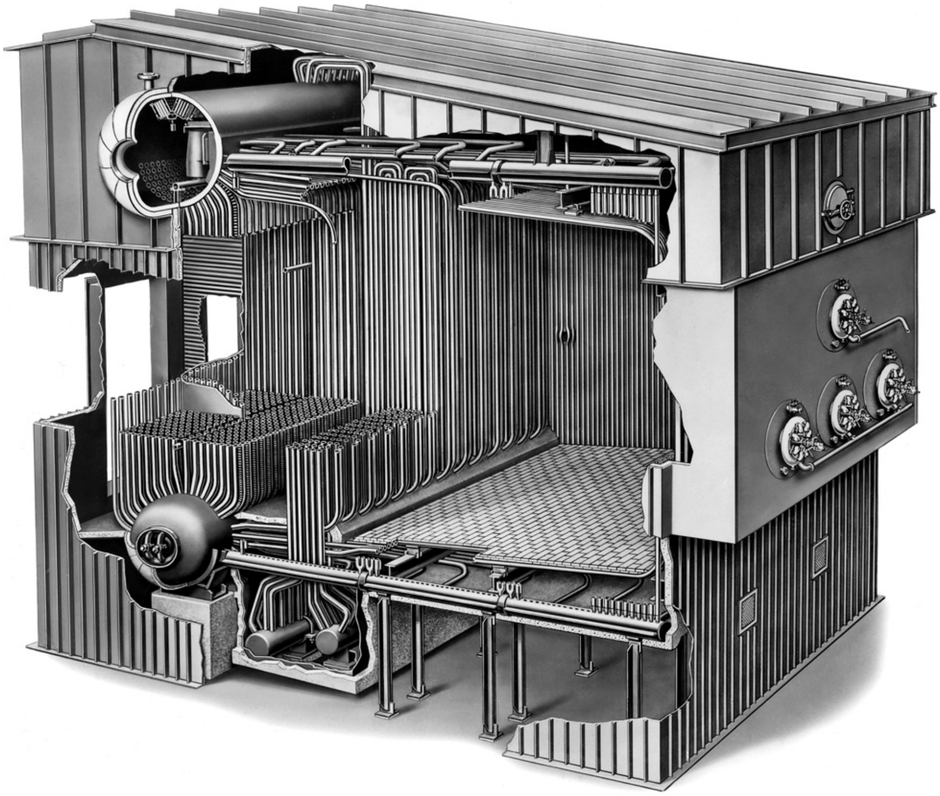

Figure 2 Field erected water tube industrial boiler.

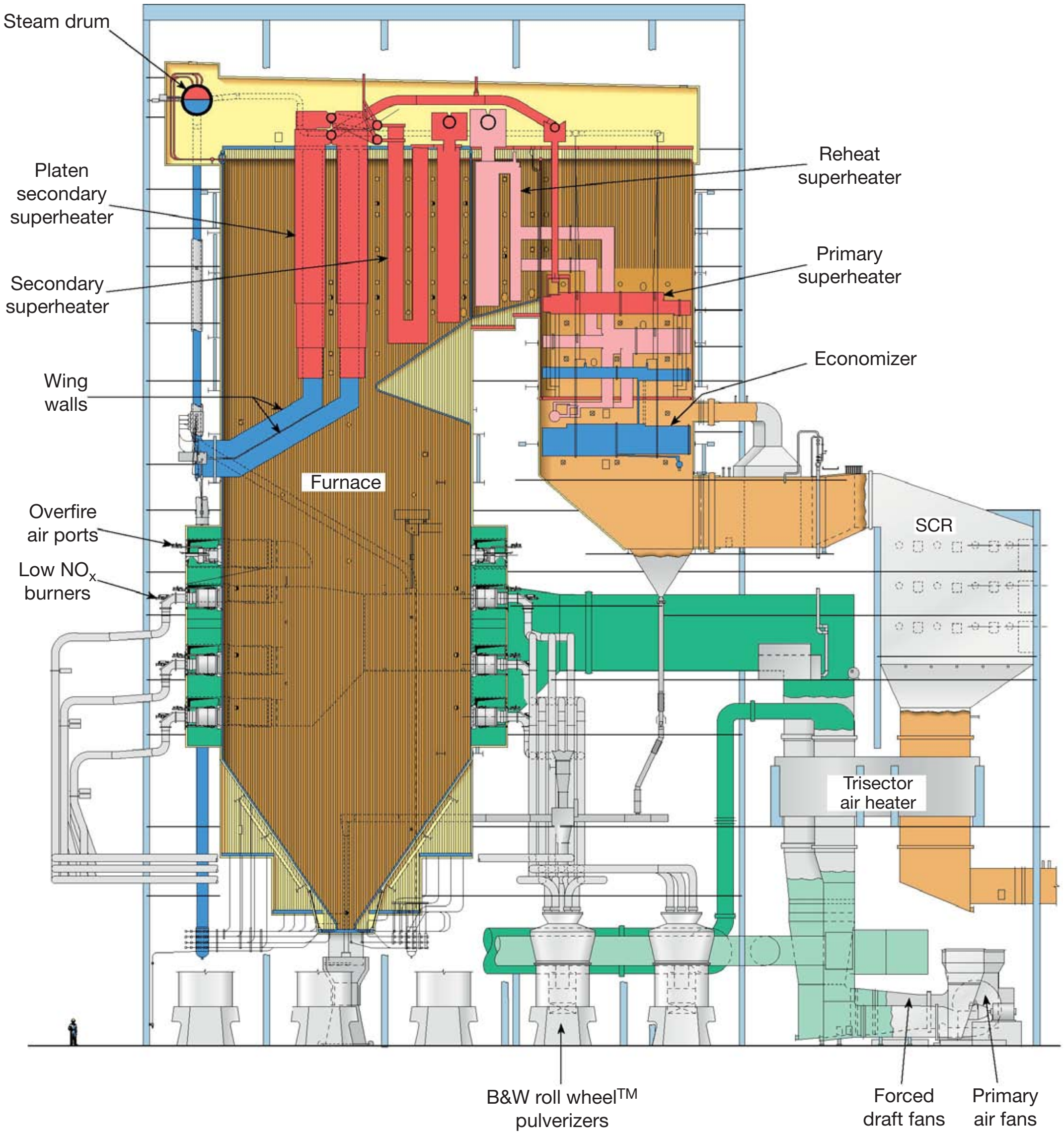

Figure 3 Natural circulation drum type utility boiler.

Softened makeup water is generally acceptable for lower-pressure boiler systems. Higher-pressure systems will require more purified water such as that treated by RO or a demineralization processes. A high percentage of condensate return in the feedwater can also produce high-purity feedwater.

Zeolite softening, an ion exchange process using strong acid cation resin in the sodium form, can also be used to remove the hardness from the water. This process can be applied in conjunction with one of the precipitating softening processes or alone. Ion exchange softening can also include a dealkalizer for the alkalinity reduction of the makeup water. This is typically done using anion resin in the chloride form, but several configurations are possible.

Conventional ion exchange demineralization of makeup water typically involves a two-bed demineralization system. Most common is a strong base cation resin bed in the hydrogen form, followed by a strong base anion bed in the hydroxide form. There may or may not be a decarbonator in between. There are many configurations of these systems available, which vary from cocurrent to counter current regeneration configurations. They may also include alternative resin types, weak acid resin, or weak base resin with multiple cation and anion units, depending on the starting water composition, the final desired water purity and local economics. For the highest water purity requirements, a mixed-bed resin unit is applied at the end of the process.

RO, a membrane-based water purification system, can be used to reduce the total dissolved solids content of the water. There are numerous configurations of the RO process available that can be chosen based on the water's composition to be treated, the level of effluent purity required versus the percentage of recovery required and the local economics of chemical cost, power cost, and labor cost. The details of these systems are beyond the scope of this chapter and will not be addressed in this chapter. The reader is directed to numerous literature sources available on these topics for specific information.

RO, a semipermeable membrane process, reduces the dissolved substances in water, but this removal is not complete, and effluent or permeate may not yet be suitable for boiler makeup water. A conventional mixed-bed resin polisher, electrodialysis (ED), or some modification of this process can follow the RO.

ED is a membrane process in which mineral salts and other ions are transported through ion-permeable membranes from one solution into another under the influence of a direct current electrical potential. Electrodeionization (EDI) is a modification of the ED process that combines ED with self-regenerating mixed-bed ion exchange resins installed between the membranes. Electrodialysis reversal (EDR) is another modification of ED in which the electrical field is periodically reversed to provide a self-cleaning process that can run at increased recovery rates.

Though these electrochemical processes are available commercially and are capable of producing high-purity water, they are rarely used in the boiler makeup water treatment application and are more likely to be seen in the microchip manufacturing industry. Conventional mixed-bed resin deionization is much more common in the production of high-purity boiler makeup water.

4.28.3 Feedwater Treatment

Corrosion protection in the feedwater system is generally achieved by mechanically and chemically removing dissolved oxygen from the feedwater and buffering the feedwater pH into a range suitable for the system materials of construction. Feedwater must generally be deaerated for industrial steam boiler applications, but there are special circumstances in which full deaeration is not recommended. These are discussed separately.

4.28.3.1 Dissolved Oxygen Control

Dissolved oxygen removal from the feedwater is typically accomplished in a deaerating heater or deaerator in which steam is used to remove the dissolved oxygen from the feedwater. Each of these pieces of equipment has its own dissolved oxygen removal efficiency. In some very low-pressure applications, there may only be a feedwater tank in which makeup water and condensate are mixed, which may or may not be actively steam sparged or otherwise heated to try to remove the dissolved oxygen.

The goal of the mechanical deaeration process is to reduce the dissolved oxygen content of the feedwater to less than 7 ppb for a system using a true deaerator. Dissolved oxygen in the feedwater can cause pitting corrosion damage of the feedwater system components. More complex feedwater systems can include both low- and high-pressure feedwater heaters in addition to an economizer.

Additionally, vacuum degasifiers or deaerating condensers can be used for dissolved oxygen removal. Recently, a semipermeable membrane process[6] has also been developed to reduce the dissolved oxygen content of water. These membrane systems have been used in laboratory environments for more than 25 years but have only recently become commercially feasible for industrial applications. This membrane process can use a combination of vacuum and stripping gas arrangements to deaerate the water. The membrane modules can be arranged in series to produce ppb level oxygen concentrations in the final water. These membranes, dependant on the pH of the water, can also remove carbon dioxide. RO pretreatment is recommended ahead of the gas membrane to prevent fouling. A conventional deaerator also provides only limited removal of carbon dioxide, based on the pH of the water.

After any of these mechanical/thermal deaeration processes, a chemical oxygen scavenger can be applied to further reduce the dissolved oxygen content of the feedwater (Table 1).

Sodium sulfite is the most common chemical oxygen scavenger used in low-pressure boiler systems. It is also available in a catalyzed form, which increases the speed of reaction with the dissolved oxygen. This can be important when the mechanical

Table 1 Oxygen scavengers used in steam-generating systems

Scavenger	*Primary reaction*	*Comments*
Hydrazine	$N_2H_4 + O_2 \rightarrow 2N_2 + 2H_2O$	Toxicity and handling issues
Hydrazine decomposition	$3N_2H_4 \rightarrow 4NH_3 + N_2$	At temp. >200 °C
Sodium Sulfite	$2Na_2SO_3 + O_2 \rightarrow 2Na_2SO_4$	Also $NaHSO_3$, $Na_2S_2O_5$, NH_4HSO_3
Carbohydrazide	$(H_2N\text{-}NH)_2CO + 2O_2 \rightarrow 2N_2 + 3H_2O + CO_2$	Forms hydrazine at temp. >150 °C, NH_3, N_2, and H_2 on decomposition
N,*N*-Diethylhydroxylamine	$4(CH_3CH_2)_2NOH + 9O_2 \rightarrow 8CH_3COO- + 9H^+ + 2N_2 + 6H_2O$	Frequently fed with hydroquinone, acetic acid, CO_2, acetaldehyde, NH_3 at temperatures above 275 °C
Hydroquinone	$C_6H_4(OH)_2 + 1/2O_2 \rightarrow C_6H_4O_2 + H_2O$	Acetates, CO_2 decomposition products, toxicity issues
Erythorbate	$C_6H_4O_6 + 1/2O_2 \rightarrow C_6H_5O_8 + H_2O$	CO_2, lactic acid, decomposition products
Methyl ethyl ketoxime	$2CH_3(C_2H_5)CNOH + O_2 \rightarrow N_2O + 2CH_3(C_2H_5)CO + H_2O$	Frequently fed with hydroquinone, NH_3, CO_2, ketones, aldehydes on decomposition

deaeration process does not provide sufficient residence time. Sodium sulfite is a nonvolatile inorganic compound that does contribute dissolved solids to the feedwater and the boiler water. This dissolved solids contribution prevents its use in feedwater that is to be used as attemperator spray or desuperheat spray for steam temperature control, as these solids would become impurities in the steam.

The control of sodium sulfite is generally based on maintaining a sulfite residual concentration in the boiler water. This can be a problem in a system where the feedwater system deaeration process and chemical injection point do not provide sufficient residence time and temperature for the chemical oxygen scavenging reaction to be completed prior to the feedwater entering the steam drum of the boiler. Oxygen scavengers and dissolved oxygen can coexist in the feedwater, in such a situation, pitting corrosion can occur. Because of the dissolved oxygen's high volatility, the oxygen preferentially goes into the steam phase when the feedwater enters the boiler steam drum, leaving the unreacted sulfite residual in the boiler water.

Another point of oxygen ingress into the system not to be overlooked is a leak path through the boiler feed pump seals. It is wise not only to monitor the temperature and pressure operating conditions of the deaerating device for proper operation but also to periodically measure the feedwater dissolved oxygen content directly at the boiler or economizer inlet.

Sodium sulfite can also produce some acidic gaseous decomposition products, such as sulfur dioxide, that will be carried out of the boiler in the steam. This can be significant at boiler operating pressures above 4.1 MPa g (600 psi g). These decomposition products can cause low steam condensate pH.

Hydrazine is another available oxygen scavenger that has been used primarily in higher-pressure boiler applications. It is a volatile compound that can be used in feedwater that is used for steam temperature control by attemperation or desuperheating. However due to its status as a suspect carcinogen, its use in industry has declined. When it is used, a closed feed system is typically required.

Given these health concerns, alternatives to hydrazine have been developed. The most common of these are carbohydrazide, erythorbate, diethylhydroxylamine, hydroquinone, and methylethyl ketoxime. Many of these oxygen scavengers also function as passivating corrosion inhibitors. Each is an organic compound that has its own temperature limitations. Decomposition products can vary from only carbon dioxide to several organic acids and other organic compounds. Some decomposition products are more undesirable than others, and the amount of these decomposition products can be application-specific, depending on system temperatures and metallurgy. Each application should be evaluated based on the benefit provided versus the potential undesirable effects of the decomposition products. As a note, commercially available erythorbate can be either in the acid form or in the sodium salt form. The sodium salt form is nonvolatile, which restricts its use if the feedwater is used as spray attemperation or in desuperheating.

4.28.3.2 pH Control

Feedwater pH adjustments to slightly alkaline conditions are used to minimize corrosion of the feedwater system piping and components, and the resultant corrosion product transport to the boiler. Caustic, neutralizing amines or ammonia are commonly used for this task. Obviously, caustic cannot be used where the feedwater is used as spray attemperation for steam temperature control. The more common amines in use are morpholine, cyclohexylamine, monoethanolamine, diethanolamine, and methoxypropylamine.

4.28.3.3 All Volatile Treatment (Reducing) (AVT(R))

The feedwater target pH range is a function of the feedwater system metallurgy. In the past, a target pH range of 8.8–9.2 had been specified for feedwater systems containing mixed metallurgy – typically heat exchanger components constructed of copper alloys. Recent work[7–9] has shown that reducing conditions in the feedwater system, an oxidation–reduction potential (ORP) of −300 to −350 mV at 25 °C (77 °F), measured between a Pt electrode and a Ag/AgCl (saturated KCl) reference electrode, at the deaerator inlet, are necessary to minimize copper corrosion and corrosion product transport in these mixed-metal feedwater systems. This work showed that the feedwater pH is a secondary control parameter, which should be restricted to a pH range of 9.0–9.3. EPRI has used the terminology AVT(R), all volatile treatment (reducing) to describe this treatment chemistry. In practice, many systems are not able to reach these low levels of ORP, but copper corrosion and copper corrosion product transport have been successfully reduced in some systems with feedwater ORP levels of even −200 to −100 mV at 25 °C (77 °F), measured between a Pt electrode and a Ag/AgCl (saturated KCl) reference electrode.

This treatment chemistry is expected to reduce corrosion production transport to the boiler system for all operating pressure boiler systems, but is most critical for the very high-pressure boiler systems used by the electric utility industry, where at their operating pressures (>16.4 MPa g (>2400 psi g)), copper has volatility properties into the high-pressure saturated steam and has caused deposition problems in the high-pressure steam turbine. This deposition in the steam turbine can limit steam throughput and megawatt output. Although the consequences of high copper corrosion product transport to most industrial boiler systems are not as dire as in the very high pressure electric utility boiler systems, only more frequent chemical cleaning of the boilers may be required; this new information on copper corrosion and strategies to minimize it should also be applied to industrial mixed metallurgy feedwater systems.

Theoretically these reducing conditions should be maintained by lay up practices even when the system is out of service, to prevent the reversion of the more protective, more reduced form of copper oxide, cuprous oxide, Cu_2O, formed in service, to the more oxidized and less protective form of copper oxide, cupric oxide CuO. Based on the actual circumstances of the out-of-service period, it may not be practical to maintain a reducing environment.

This work[7,8] also showed that the desired reducing environment could not be achieved by the addition of excessive amounts of a chemical reducing agent such as an oxygen scavenger to compensate for a mechanical problem in the system such as a malfunctioning DA or high levels of air in leakage into a condenser or hotwell.

For an all-steel metallurgy feedwater system, the feedwater pH target range is somewhat more alkaline pH = 9.3–9.6. For most industrial boiler feedwater systems, definitely those with softened water make up even those with demineralized make up water or high percentages of condensate return, it is still advisable to fully deaerate the feedwater and treat the system with a chemical oxygen scavenger to prevent dissolved oxygen pitting corrosion damage to the feedwater system components, as previously discussed.

4.28.3.4 Flow Accelerated Corrosion

In boiler systems in dedicated electric utility service, where the typical percentage of condensate return in the feedwater is over 95%, the feedwater most likely will be pure enough to make the system susceptible to flow accelerated corrosion (FAC) damage.[10–13] FAC is a corrosion mechanism that can cause corrosion damage and failures in feedwater systems including economizers, feedwater heaters, and piping. EPRI has compiled a significant amount of information on this topic as it relates to boiler systems in dedicated electric utility service.[14]

FAC is a very localized damage mechanism that affects predominantly areas of flow turbulence in the feedwater system. It is a primarily hydrodynamic phenomenon that prevents the formation of the normal protective oxide (magnetite) coating to form on carbon steel and prevent any further metal loss. FAC is a process whereby the normally protective oxide surface dissolves into a moving fluid. The most susceptible systems are typically all-steel, and employ very high-purity feedwater, due to the purity prerequisite of the steam purity required by the steam turbine in these systems. A significant amount of research has been done on this topic in power plants and is very well documented.[14] FAC is possible at a water temperature range of 100–250 °C (212–482 °F), but there seems to be a maximum susceptibility at about 150 °C ± 28 °C (300 °F ± 50 °F). Even though FAC is primarily a hydrodynamic phenomenon, those mechanical parameters that control velocity and turbulence are fixed and not easily changed in an existing system. The research work has identified two water chemistry parameters that influence FAC behavior that can be optimized – feedwater pH and ORP.

4.28.3.5 All Volatile Treatment (Oxidizing) (AVT(O))

EPRI has developed a feedwater treatment philosophy for boilers in the electric utility service industry that has been termed AVT(O),[4] all volatile treatment (oxidizing), to minimize the potential for FAC in these systems. With AVT(O) treatment, no chemical oxygen scavenger is fed and a nominal amount of dissolved oxygen, (typically $<10\ \mu g\ l^{-1}$, <10 ppb) is considered acceptable. This is expected to result in an ORP of -50 to $+50$ mV, measured between a Pt electrode, and a Ag/AgCl (saturated KCl) reference electrode. This condition is considered less susceptible to FAC than the completely oxygen deficient-reducing conditions of AVT(R) in this high-purity feedwater. Feedwater cation conductivity required for AVT(O) is less than 0.2 mS cm^{-1}.

All the discussion on ORP measurement of feedwater up to this point has been regarding the measurement of the ORP of a sample cooled to room temperature, 25 °C (77 °F). Room temperature ORP measurements have had problems with a lack of sensitivity and response. The capability to measure the feedwater ORP at system temperature has been developed, AT ORP™ (originally known as @T ORP™).[15,16] The potential is measured against an external pressure balanced reference electrode (Ag/AgCl//0.1 N KCl). This technology is much more responsive to system changes that affect ORP. These at temperature ORP measurements can be made at feedwater temperatures up to 260 °C (500 °F).

Feedwater pH is another chemistry parameter that affects FAC, and for an all-steel feedwater system, typically the more alkaline the better ($pH > 9.2$ up to about 10.0). Even though the feedwater system may be all-steel, there may be a copper alloy condenser that could limit the feedwater pH adjustment to prevent yellow metal attack of the condenser that can occur when ammonia is the alkalizing agent or a decomposition product.

This near-neutral ORP control, AVT(O), is quite acceptable for high-purity boiler feedwater systems such as those in the electric utility industry, in which the level and consistency of feedwater purity is high. Industrial boiler feedwater systems employing high-purity feedwater are also potentially susceptible to FAC, but the possible chemistry-related corrective actions are not nearly as clear. In industrial boiler systems, even when make-up water is demineralized, the required level of purity for this treatment – <0.2 mS cm^{-1} – is rarely achieved. Additionally, because of the lower percentage of condensate return and the very significant potential for constant low levels and periodic high levels of contamination, feedwater purity can be very inconsistent. For these industrial systems, the simultaneous presence in the feedwater of dissolved oxygen and any feedwater contamination provides the potential for oxygen pitting damage of the feedwater system, especially heat exchanger components, such as an economizer. From the existing research work, it is unclear how pure feedwater must be in order for dissolved oxygen to act as a corrosion inhibitor rather than cause the pitting damage common in industrial systems. From the experience with AVT(O) and oxygenated treatment (OT), feedwater cation conductivity of <0.2 and <0.15 mS cm^{-1} respectively are conditions in which dissolved oxygen acts as a corrosion inhibitor. But even the OT guidelines recommend ceasing oxygen feed and going to an AVT(O) treatment when cation conductivity exceeds 0.3 mS cm^{-1}. There are no further guidelines for acceptable higher levels of cation conductivity in the feedwater for AVT(O). OT is discussed in the next section.

This FAC mitigating philosophy of AVT(O) near-neutral ORP can also be accomplished in industrial systems by feeding a very low level of one of the available organic oxygen scavengers/passivators. In this treatment scheme, the oxygen scavenger/passivator is not fed in the stoichiometric ratio to scavenge the dissolved oxygen but rather is fed at a rate to passivate the steel and provide the neutral ORP target. The feedwater concentration needed to accomplish this ORP is unique to each of the scavengers (hydroquinone, erythorbate, carbohydrazide, diethylhydroxylamine, methylethyl ketoxime). In this treatment, when there is an excursion in the chemistry or dissolved oxygen concentration due to mechanical problems, the scavenger feed is able to compensate. We note that sodium sulfite, although it is an oxygen scavenger, cannot be used for this purpose, as it does not appear to have any passivating properties for steel.

Finally, monitoring feedwater ORP does not supply quantitative information regarding FAC, only qualitative information. It has been found that measuring the soluble iron concentration of the feedwater[17–19] at various points in the system can provide more quantitative information regarding FAC. Given that FAC is a very localized damage mechanism related to flow turbulence, it is important to sample the feedwater before and after a feedwater system component with a large surface area subjected to local flow turbulence for this soluble iron testing. Such a component is typically an economizer or feedwater heater with heat transfer surfaces constructed of carbon steel. Detecting a significant increase in the soluble iron content of the feedwater between the inlet and outlet indicates a potential for FAC in the system. Then optimizing feedwater treatment chemistry parameters (feedwater pH, ORP/oxygen scavenger feed) individually and reviewing their impact on the change in feedwater soluble iron content demonstrates the potential impact that feedwater chemistry changes can have on FAC in the feedwater system.

As soluble iron in the water is relatively unstable, soluble iron determination requires careful sample handling to minimize the potential to oxidize the soluble iron in the sample. Feedwater dissolved oxygen content should be less than 20 ppb, and it has been found that it is best to take the sample directly into the reagent to preserve the iron in the soluble state. There have been a number of different ferroin compounds used to determine iron spectrophotometrically.[17,18] One of the most widely used compounds is 3-(2-pyridyl)-5-6-bis (4-phenylsulfonic acid)-1,2,4-triazine, monosodium salt. The test procedure involves collecting samples directly into an acid-cleaned, iron-free container containing the ferroin reagent. Stainless steel sample lines are required.

Even though this soluble iron testing gives a more quantitative picture of the FAC susceptibility of a system and this information can be used to optimize feedwater chemical treatment, it cannot identify a specific feedwater system component that could be experiencing a particularly high local rate of FAC damage. For this reason, it is still recommended that such a system have periodic nondestructive testing performed on susceptible components (tees, elbows, piping, downstream of valves, flow orifices, etc.) especially those that are in the more prone temperature environment, with water at 150 °C ± 28 °C (300 °F ± 50 °F).

It has been found that in most cases, feedwater chemistry optimization has been able to reduce FAC rates in high-purity industrial boiler feedwater systems prone to FAC but not eliminate them, even in some cases where the treatment has been converted to AVT(O). But as the research work[10] on FAC has shown, commercially available low-chrome alloys (>1% chromium content) are much less susceptible to FAC than carbon steel. Replacing a carbon steel component found to be thinning due to FAC with one of these low-chrome alloy alternatives has eliminated future FAC damage in all but the most extreme situations.

4.28.3.6 Oxygenated Treatment

OT[20–25] is a feedwater treatment developed for once-through boilers in the electric utility industry in Germany in the 1960s. Prior to OT, these boilers were treated with all volatile treatment (AVT) using ammonia and hydrazine. With this conventional AVT treatment, these boilers required frequent chemical cleaning to prevent the accumulation of corrosion products from the feedwater system (primarily iron oxide) in the boiler. These deposits caused pressure drop increases in the boiler's flow circuitry and insulating deposits on high heat transfer areas of the boiler, which could lead to overheating damage.

A once-through boiler is an inherently high-purity feedwater system, since the feedwater purity must meet the steam turbines steam purity requirement. Most of the once-through boilers in Germany operate at subcritical pressures, whereas most of the once-through boilers in the United States operate at supercritical pressures. Most of these systems have all-steel feedwater systems and full-flow condensate polishing.

In these systems, it was found that low levels of dissolved oxygen added to this high-purity feedwater acted as a corrosion inhibitor, producing a more protective oxide on the steel than conventional AVT. This reduced corrosion product transport to and accumulation in these boilers. Most of the once-through boilers in operation worldwide today have now been converted to OT. Some boilers on OT treatment in

Germany have never required chemical cleaning. Once-through boilers in the United States that have converted to OT have significantly extended the time required between required chemical cleanings.

Typical control parameters for OT are a feedwater cation conductivity of less than 0.15 mS cm^{-1}; feedwater pH and dissolved oxygen can be controlled by either what is termed the neutral method, which involves maintaining the pH in the range of pH 7–8 and a dissolved oxygen content of 50–250 μg l^{-1} (50–250 ppb), or the combined method in which the feedwater pH is 8–9 and the dissolved oxygen content is 30–150 μg l^{-1} (30–150 ppb). Only ammonia can be used in this treatment as the alkalizing treatment chemical; dissolved oxygen degrades the more complex amines, increasing the cation conductivity.

OT is only occasionally used on high-pressure drum-type boilers because they rarely have the prerequisite feedwater system metallurgy and the consistent level of feedwater purity required, which typically requires a full flow condensate polishing system. Finally, the required chemical cleaning requirements for drum-type boilers that do meet the metallurgy and feedwater purity requirements are already quite long; therefore, OT does not provide the same economic benefit as it does to once-through boilers. OT for these drum boilers could provide a benefit regarding FAC potential in their feedwater systems, but this benefit is also provided by the AVT(O) feedwater treatment.

4.28.4 Boiler Water Treatment

4.28.4.1 Residual Phosphate Treatment

Boiler water internal treatment options are dependant on the type of makeup water pretreatment, percent condensate return, and boiler operating pressure. For softened makeup water systems, one of the most common internal treatments is residual phosphate treatment, a precipitating treatment for the hardness contaminants in the feedwater.

This treatment chemistry is designed to purposefully precipitate the feedwater hardness contaminants into more desirable, less adherent forms than if they precipitated on their own in the boiler due to their retrograde solubility characteristics. The intent is to precipitate calcium as basic calcium phosphate and magnesium as magnesium hydroxide by maintaining an appropriate boiler water orthophosphate residual and a free hydroxide concentration. The orthophosphate concentration must be measured on a filtered boiler water sample.

A synthetic organic polymer or naturally occurring organic material such as lignins or tannins may be used to help disperse the resultant precipitated suspended solids. The precipitated calcium and magnesium contaminants, though in a more desired form, are still difficult to remove from an operating boiler via the continuous blowdown. This is because they are entrained in the boiler's internal circulation between the downcomer and riser circuitry, which is many times the flow rate of the steam that the boiler actually produces. This circulation continually passes the particulates past the high heat transfer areas of the boiler, where they can form deposits. Suspended solids caught up in the boiler's internal circulation are also not removed very effectively by a boiler's intermittent blowdown system (mud drum blowdown), if the boiler has this capability. Because of the limited effectiveness of the boiler blowdown systems in removing suspended solids, the success of residual phosphate treatment is very much dependent upon minimizing the hardness contaminants in the feedwater and potentially cleaning the boiler, chemically or mechanically, periodically, to control deposit accumulation in the boiler.

Residual phosphate chemistry is controlled by maintaining an orthophosphate residual in the boiler water that is chosen as a function of the boiler's operating pressure, Table 2. Free hydroxide levels in the boiler water are typically maintained at a level of three times the boiler water silica concentration to aid in maintaining silica mineral solubility in the boiler water. In higher-pressure boiler applications (>4.1 MPag (>600 psi g)) where volatile silica transport into the saturated steam is a concern, or anytime the steam being produced is for use in a condensing steam turbine, maximum boiler water silica concentrations are maintained to limit the silica concentration in the saturated steam to the specified limit for the turbine (typically 10–20 μg l^{-1} (10–20 ppb)) silica in the steam).

4.28.4.2 Steam Purity

Boiler water total dissolved solids are maintained at or below a maximum value to control the overall purity of the saturated steam required. More stringent steam purity limits are required for that steam when it is to be used in a condensing steam turbine application as opposed to a process heating application. With the exception of silica, which has vaporous solubility characteristics in saturated steam, all other nonvolatile species of concern in boiler applications at less than

Table 2 Typical control limits for residual phosphate treatment

Boiler water component (ppm)	*Drum pressure (psi g; MPa g)*			
	150 (1.0)	*300 (2.1)*	*600 (4.1)*	*900 (6.2)*
TDS (max)[a]	4000	3500	3000	2000
Phosphate (as PO_4)	30–60	30–60	20–40	15–20
Hydroxide (as $CaCO_3$)	300–400	250–300	150–200	120–150
Sulfite	30–60	30–40	20–30	15–20
Silica (as SiO_2) max[b]	100	50	30	10

[a] The limits on TDS will vary with the design of the boiler and with the needs of the system with regard to steam purity.

[b] Example silica values are listed but if silica volatility is a concern, such as condensing steam turbine applications, available pressure dependant and pH dependant control curves on boiler water silica concentration should be used. Silica may be carried at higher levels if there are no condensing turbines in the cycle. In any case, maintain an OH/SiO_2 ratio of at least 3/1 to inhibit silica deposition.

13.7 MPa g (2000 psi g) end up in the steam as a result of mechanical carryover of boiler water droplets that pass through the mechanical separating equipment in the steam drum. Therefore, the steam purity is directly proportional to the boiler water purity.

The restrictions on boiler water total dissolved solid limits to maintain the same steam purity do vary with boiler operating pressure and are more restricted at higher operating pressures because the mechanical steam/water separation process is more efficient when the density difference between the steam and water phases is greater.

Sodium salts and copper oxides, considered nonvolatile at lower operating pressures exhibit volatility characteristics above 16.4 MPa g (2400 psi g). This mode of transport into the steam must also be considered and controlled by the appropriate measures to maintain the desired steam purity.

In addition, when attemperation is used for final steam temperature control, the impact of that attemperation water on the final steam purity must also be considered, in the design stage as well as while diagnosing steam purity problems. The potential sources of attemperation water are feedwater (if it is pure enough), condensate and a sweetwater condenser. A sweetwater condenser is typically a shell and tube heat exchanger that condenses saturated steam with incoming feedwater. That condensed saturated steam is then used as attemperation water for steam temperature control. Each of these sources of attemperation water can be potentially contaminated and impact on steam purity. A mud drum attemperator may also be used for steam temperature control. This is typically a heat exchanger located in the mud drum. By design, there is no intended contact between the steam and the boiler water, but in the event of a leak in the exchanger boiler water can contaminate the steam.

4.28.4.3 Chelant Treatments

Realizing the shortcomings of residual phosphate chemistry in the way it handles feedwater hardness contamination (precipitation), alternative treatment chemistries were developed.

The first was the use of chelants to solubalize the hardness contaminants. The most common chelants used were ethylenediaminetetraacetic acid (EDTA) and nitrilotriacetic acid (NTA). Both EDTA and NTA form soluble complexes with calcium and magnesium that are stable to relatively high temperatures, up to 6.8 MPa g (1000 psi g). The removal of hardness contaminants from the boiler, now in a soluble form, are no longer limited by the continuous blowdown's limited ability to remove suspended solids from the circulating boiler water. If the species in question is soluble in the feedwater, remains soluble in the boiler water and is nonvolatile, the continuous blowdown removes that species at 100% efficiency.

Theoretically, if the required stoichiometric ratio of chelant to hardness were maintained, there would be no accumulation of hardness-based deposits in the boiler. However in practice, there are variations in the level of hardness contaminants in the feedwater, and some overfeed must be applied continually to account for these variations. This overfeed is typically controlled to result in a small residual chelant concentration in the boiler water above that required for the actual hardness. It was found that this boiler water chelant residual must be controlled very tightly because high levels of the residual can result in corrosion of the boiler base material. This corrosion is most likely to occur in areas of high fluid velocity or turbulence in the boiler. For this reason, chelant residual control limits vary as a function of boiler operating pressure and range from about 1–5 mg l^{-1} (1–5 ppm). Chelants have been applied at boiler pressures over 6.8 MPa g (1000 psi g) early in their history but later were only commonly applied up to about 2.7 MPa g (400 psi g) for EDTA and about 6.2 MPa g (900 psi g) for NTA.

Today, chelants are rarely used for several reasons. NTA is classified as a suspected carcinogen, the potential corrosions problems, and challenges in controlling the required residual level and alternative treatment chemicals have been developed.

4.28.4.4 All Polymer Treatment

Technically, the ability of the chelant chemistry to maintain the solubility of feedwater hardness contaminants is a much more effective way to control hardness deposit accumulation in boiler systems than residual phosphate treatment. Synthetic organic polymer chemistries have been developed that also have chelating abilities for hardness control. These are based typically on polyacrylate or polymethacrylate polymers. Such synthetic organic polymers can be applied in what is termed an all-polymer treatment, the purpose of which is the same as the chelant chemistry: form a soluble complex with calcium and magnesium and maintain that soluble complex at boiler water conditions to allow for the efficient removal of these contaminants from the boiler in the continuous blowdown as dissolved solids. In addition to the ability of these polymers to maintain soluble hardness contaminants, they are typically anionically charged, whereas suspended solid contaminants such as iron oxide tend to be cationically charged. The polymers also have the ability to disperse particulate contaminants. This dispersion minimizes their ability to agglomerate into larger particles as well as adhere to the heat transfer surfaces of the boiler. But as a suspended solid, there is still the same physical limitation on the ability of the continuous blowdown to remove even these dispersed contaminants from the boiler.

There are many synthetic organic polymers in use in boiler water treatment. It is important to note that not all of these polymers have chelant properties relative to calcium and magnesium, and it is only those that do that can be used as an ‘all-polymer’ treatment for feedwater hardness contamination. And even those polymers that do have this chelating ability must be of an appropriate molecular weight for the boiler operating pressure and saturation temperature to function as intended. Polymers that do not have the chelant properties with respect to hardness tend to act only as dispersants and therefore do not have the same effectiveness in handling feedwater hardness contamination.

Even though the polymers used in the ‘all-polymer’ technology have chelant properties, they are much weaker chelants than EDTA or NTA. As much weaker chelants, the need to control the excess polymer residual relative to the hardness is much less critical. However as with all solubalizing treatments, the potential for corrosion of the boilers base material must be recognized and an appropriate control strategy used.

As there are many synthetic polymer treatments on the market today and most are offered as proprietary treatment chemistries by water treatment companies, hopefully the end user can ask the appropriate questions based on the information provided, such as what the purpose and abilities of their available products are and what the control limits and control strategies are, to decide while choosing between various offerings to best meet his/her needs.

Polymeric dispersants are also used within other treatment philosophies, such as in chelant treatments to disperse iron oxide contaminants and in residual phosphate treatment to disperse the resultant calcium and magnesium precipitated suspended solids. In these cases, however, the concentration of the polymers to hardness is much less than the stoichiometric requirement to solubalize the hardness, and as such they only act as a dispersant and do not compete with the primary intended purposes of the chelant or phosphate chemistry.

In industrial boiler systems, there have been many mixed treatment chemistries that have had mixed success – chelant/polymer, chelant/phosphate, polymer/chelant/phosphate, etc. There are too many to address specifically.

4.28.4.5 Coordinated Phosphate Treatment

In the past, it was more common to find high-purity feedwater in only high-pressure boiler applications >6.8 MPa g (>1000 psi g). Today the use of high-purity makeup water in low-pressure boilers is much more common.

Coordinated phosphate chemistry[26] was developed as a response to caustic embrittlement failures of boiler drums. In the early days of boiler water treatment, prior to the development of efficient make-up water pretreatment systems, coagulation internal treatments were used. This type of treatment used soda ash (Na_2CO_3) to precipitate the hardness salt contaminants into the desired form and then added organic materials (tannins and lignin) to condition this precipitated material (sludge) where hopefully it would settle in the mud drum and be removed from the boiler via the intermittent blowdown (mud drum blowdown) practice.

The use of soda ash introduced high levels of alkalinity, including free hydroxide or caustic alkalinity, into the boiler water, and at that time boiler drums were constructed by riveting rolled sections of steel plate together. These mechanical joints were prone to leaking. When a leak did occur, the leaking boiler water containing free hydroxide would flash to steam, resulting in very high local caustic concentrations at the site of the leak. Carbon steel is susceptible to stress corrosion cracking failure when it is highly stressed and in contact with high concentrations of caustic. The geometry of the riveted construction provided a location of stress concentration, and the flashing boiler water provided the environment that resulted in the potential for stress corrosion cracking or caustic embrittlement failure of the steel. In the early days of boiler water treatment, these embrittlement failures and sometimes resultant boiler explosions were not uncommon, and there were fatalities. Coordinated phosphate chemistry control was developed as a chemical solution to this problem. Coordinated phosphate chemistry balances the boiler water pH and orthophosphate concentration to a maximum Na:PO_4 molar ratio of 3.0:1 to theoretically prevent the formation of free hydroxide in the boiler water. For control, a minimum Na:PO_4 ratio of 2.2:1 is chosen to buffer low pH concerns. It is important to note that the Na:PO_4 molar ratio used in this treatment as well as the other high-purity phosphate chemistries is not determined by directly measuring both the boiler water sodium and phosphate concentration and calculating the ratio but rather is determined by measuring the boiler water pH and orthophosphate concentrate and then plotting that data on a graph similar to Figure 4.

The reason for this is that in most boiler systems, there are neutral sodium salts present that do not affect the boiler water pH. There can also be contaminants in the makeup water such as organic materials that can decompose to form organic acids in the boiler water, affecting boiler water pH but with no contribution of sodium.

With this in mind it is also important to realize that what affects the boiler water pH and phosphate relationship is that which is added intentionally as the treatment chemicals and that other contaminants may concentrate in the boiler water and affect pH (organic materials in the makeup water or sodium leakage [NaOH] from the make up demineralizer). Sodium salts of various phosphate species and sodium-to-phosphate molar ratios and sodium hydroxide may have to be used to buffer the pH into the desired control range in these situations.

4.28.4.6 Congruent Phosphate Treatment

Caustic problems in boiler systems were not totally alleviated by the adoption of coordinated phosphate chemistry. This was thought to be due to the

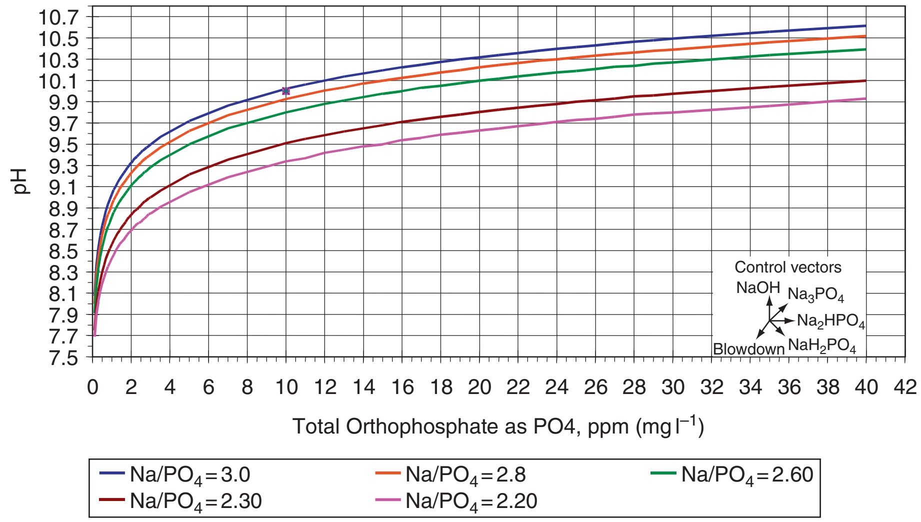

Figure 4 pH vs. PO_4 graph at different Na/PO_4 molar ratios.

solubility characteristics of sodium phosphate salts – a characteristic known as incongruent precipitation. Studies[27] showed that precipitation of phosphate from a high temperature (300 °C, 572 °F) sodium phosphate solution having a Na:PO_4 molar ratio greater than 2.85:1 always results in an increase in the Na:PO_4 ratio of the remaining solution, toward or further into the free caustic region above the 3.0:1 ratio boundary. Conversely, when phosphate is precipitated from a solution having a Na:PO_4 ratio less than 2.85:1, the Na:PO_4 ratio decreases in the remaining solution, further away from the free caustic region. With a solution Na:PO_4 ratio of exactly 2.85, the Na:PO_4 ratio in the precipitated phosphate solids is identical, that is, congruent.

Subsequent studies showed that at higher temperatures, the congruent point could be at a Na:PO_4 ratio as low as 2.6:1. Again, control is based entirely on the relationships of boiler water pH and orthophosphate concentration, endeavoring to keep their plotted coordinates within the appropriate zones on a control diagram (see **Figure 1**).[28] Congruent phosphate[29] then is a refinement of the original coordinated phosphate treatment with new boundaries on the Na/PO_4 molar ratio; a maximum ratio of 2.6:1 and a minimum ratio of 2.3:1. The actual PO_4 concentration control range is typically chosen based on boiler operating pressure and the degree of control capability in the plant and the consistency of feedwater quality (purity). Generally, higher phosphate control ranges (10–20 mg l^{-1} (10–20 ppm)) at lower boiler operating pressures and lower phosphate control ranges (5–10 mg l^{-1} (5–10 ppm) at higher boiler operating pressures are employed.

When the chosen PO_4 control range is less than 2 mg l^{-1} (2 ppm) in the boiler water, the effect of ammonia or neutralizing amines must be taken into account due to their effect on the boiler water pH measurement at room temperature.

Even though boiler drums are constructed using welded joints today, most industrial boilers operating at less than 6.8 MPa g (1000 psi g) are constructed with mechanical roll expanded joints to connect the tubes between the steam drum and the mud drum. Therefore, there is still the possibility of a local caustic embrittlement failure of the drum if one of these mechanical joints were to leak and the boiler water contained free hydroxide. Congruent phosphate chemistry provides a level of protection for these boilers from this failure mechanism and would be a preferred choice provided the feedwater purity requirements are met and the boiler is not experiencing phosphate hideout behavior (see the following section) due to the congruent phosphate treatment.

4.28.4.7 Phosphate Continuum Treatment (Formerly Equilibrium Phosphate Treatment)

Congruent phosphate programs can be difficult to control because of phosphate hideout.[30] Phosphate hideout is the simultaneous decrease in the phosphate concentration of the boiler water and an increase in boiler water pH during a load or heat flux increase. Hideout return is the reverse during a load decrease – phosphate concentration increases and boiler water pH decreases. Equilibrium phosphate control solves this problem and has therefore gained acceptance with electric utility drum boiler operators.

As phosphate hideout occurs, the phosphate concentration in the bulk boiler water is reduced down to very low remaining equilibrium levels. The boiler water phosphate might drop from a normal 5 mg l^{-1} (5 ppm) down to 2 mg l^{-1} (2 ppm) or even less during hideout. Attempts to maintain the original boiler water phosphate levels by adding phosphate during hideout are usually futile, because ongoing hideout simply continues to remove boiler water phosphate down to the equilibrium level.

In the past, phosphate hideout had been thought to be associated with the retrograde solubility behavior and incongruent precipitation behavior of sodium phosphates, but laboratory research work[31] has shown that phosphate hideout is actually the temperature-dependent reaction of low Na:PO_4 molar ratio compounds in the boiler water with magnetite. These reactions are significant when boiler water Na:PO_4 molar ratios are 2.3–2.6:1, but are essentially nonexistent when the boiler water Na:PO_4 molar ratio is greater than 2.85:1.

During phosphate hideout, phosphate wastage of the boiler metal can result due to the concentration of low Na:PO_4 molar ratio materials in high-heat flux zones. Maracite ($NaFePO_4$) and/or Iron Phosphate ($FePO_4$) are the residual corrosion products found on boiler tubes damaged by the phosphate wastage mechanism.[32]

Phosphate hideout and phosphate wastage are more likely at higher boiler operating pressures but are also possible in lower-pressure boilers with high local heat fluxes. Phosphate wastage corrosion predominantly occurs in conventional boilers operating at greater than 13.8 MPa g (2000 psi g), although it has been seen in an industrial boiler operating at 6.9 MPa g

(1000 psi g) that was experiencing steam blanketing. It is also common in vertical shell-and-tube steam generators; these are commonly unfired process boilers with flat tube sheets and deep oxide sludge deposits on the tube sheet, which is generally at the inlet of the highest process gas temperature. In addition, heat recovery steam generators (HRSG) commonly used in combined cycle plants with duct burners are also prone to phosphate hideout and the potential for phosphate wastage, especially when duct burners are in use.

Equilibrium phosphate control[30] makes no attempt to carry boiler water phosphate concentration above its hideout equilibrium level. Equilibrium phosphate levels vary from boiler to boiler, depending on the severity of hideout conditions and must be determined by testing for each unit. EPRI has recently revised and renamed the Equilibrium Treatment philosophy to what is now termed Phosphate Continuum Treatment[4] as illustrated in Figure 5. The maximum Na/PO_4 ratio control boundary is a Na/PO_4 equal to 3.0 plus 1 mg l^{-1} (1 ppm) NaOH and the minimum Na/PO_4 control boundary is $Na/PO_4 = 3.0$. Additionally, there is a minimum pH = 9.0 and a minimum boiler water orthophosphate concentration of 0.2 mg l^{-1} (0.2 ppm).

For mixed-bed makeup water systems with no significant sodium leakage and low organic contamination of the makeup and condensate, only trisodium phosphate and caustic soda (when needed) are recommended for Phosphate Continuum Treatment. Monosodium, disodium, and polyphosphates should not be needed. But for many industrial boiler systems that can have significant sodium leakage from the makeup system or significant organic contaminants in the makeup water or condensate, a wide range of $Na:PO_4$ molar ratio treatment chemicals might be required to maintain the desired control in a particular boiler system situation.

Phosphate continuum treatment does include the presence of free hydroxide in the boiler water and therefore does present the known concerns associated with caustic in boilers. There is the potential for under deposit caustic gouging in the boiler, the potential for stress corrosion cracking of steam system components in the event of boiler water carry over and the potential for embrittlement damage to the drums if the boiler has mechanical rolled tube joints if one were to leak.

4.28.4.8 All Volatile Treatment

AVT[33,34] helps achieve sufficiently high pH to protect boiler steel without introducing any dissolved solids. It is based on the use of entirely volatile, solid-free chemicals, such as hydrazine or carbohydrazide for oxygen scavenging, plus neutralizing amines or ammonia for boiler water pH control. AVT may be used in drum boilers that have the appropriate feedwater purity and is the only program that can be used in once-through boilers. In drum boilers, AVT may be used for simplicity where phosphate hideout has caused control

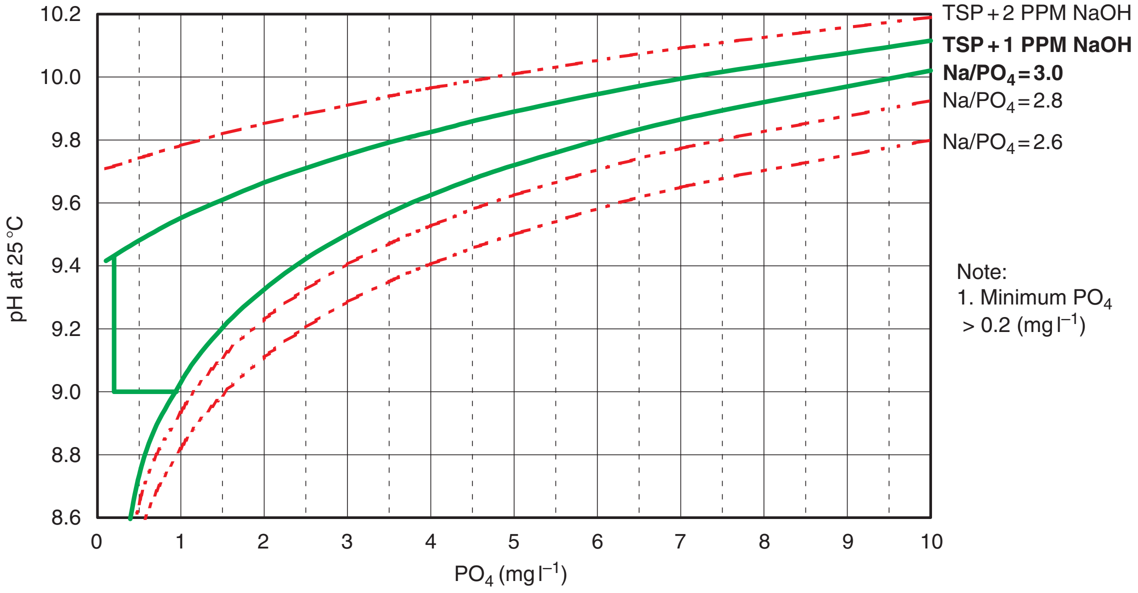

Figure 5 Phosphate continuum control chart.

problems on phosphate-pH control programs or where ultra pure steam is required.

A disadvantage of all-volatile treatment for drum boilers is that the boiler water is unbuffered and thus subject to extensive and rapid pH excursions in the event of feedwater contamination. Prompt detection and remedial action is required in the event of any feedwater contamination. A condensate polishing system, either for continuous polishing or for start-up and emergency polishing, is very desirable. Some utilities do operate high pressure drum cycles on AVT without the benefits of polishers, but their systems have extensive instrumentation that allows immediate remedial action to be taken in the event of cycle contamination (including feeding phosphate until the problem is resolved). A mixed-bed polisher is essential in the makeup system.

The AVT program control is simple and highly effective as long as feedwater quality is maintained. Feedwater contamination of an otherwise solid-free system produces undesirable effects immediately. With essentially no buffering capacity in the system, boiler water pH values can reach free acidity levels ($pH<4.3$) very rapidly following contamination. This is particularly true in systems using seawater or brackish water for condenser cooling.

Cation conductivity measurements of the boiler water are used to monitor any dissolved solids contamination of the cycle. Cation conductivity is also preferred for condensate and feedwater monitoring since it is very sensitive to changes in dissolved solids concentrations and is not affected by changing the amine or ammonia levels. Specific conductance is used primarily to monitor the level of ammonia or neutralizing amine present in the cycle.

Continuous pH monitoring of the boiler water is desirable, as pH provides another indication of a contamination problem. Boiler water pH values will typically be lower than the feedwater pH because of the volatilization of the amine or ammonia from the boiler water; pH control in the feedwater cycle will vary with cycle metallurgy.

4.28.4.9 Caustic Treatment

Sodium hydroxide alone can also be used as the solid alkali in internal boiler water treatment for pH control. It is a common practice in high-pressure drum boilers in the United Kingdom, and many of these are high-pressure drum boilers in the electric utility service industry.[4,35] A typical boiler water pH control range is 9.0–9.4. Caustic can still be very corrosive to carbon steel under concentrated conditions, such as under porous metal oxide deposits on a boiler's heat transfer surfaces, and can cause under deposit corrosion damage. It is therefore very important to keep the boiler's heat transfer surfaces clean by minimizing the feedwater corrosion product transport into the boiler and periodic chemical cleaning. There is also a concern that chloride contamination may increase this corrosion potential, and individual operators have also restricted boiler water chloride limits.

4.28.5 Condensate Treatment

Condensate is a very valuable commodity (resource) in a boiler system, not only because of its energy content but also because of its high purity. Therefore, the more condensate that can be returned as part of the boiler feedwater, the more efficient the economics are of operating the boiler system.

As condensate is very pure water, very small amounts of contamination can render it extremely corrosive and unsuitable as feedwater. One of the more common contaminants that can depress the pH of the condensate is carbon dioxide. Carbon dioxide can originate from the bicarbonate alkalinity in the makeup water, which decomposes at boiler operating pressure, contributing the carbon dioxide to the steam or from air in leakage into the system. The latter is most likely to occur when the pressure in the condensate system is at or below atmospheric pressure.

In addition, organic materials in the makeup water can decompose in the boiler water, resulting in the formation of low molecular weight organic acids such as acetic, formic, and glycolic acids. These organic acids have volatility characteristics that are a function of pressure. All are considerably stronger acids than carbonic acid and will increase the demand for the neutralizing amine treatment that is commonly employed to neutralize acids and so elevate the condensate pH. Hydrogen sulfide and sulfur dioxide, the products of decomposition of the sodium sulfite oxygen scavenger, that can occur at boiler operating pressures >4.1 MPa g (>600 psi g), can also depress condensate pH and contribute to the amine demand. Depressed pH conditions of the condensate can cause significant corrosion damage to condensate system components.

Dissolved oxygen either not removed by the deaeration processes or that has leaked into the system at points where the pressure is at less than atmospheric pressure can also cause corrosion damage in the condensate system.

Ammonia can also be considered a contaminant in the condensate if there are copper alloys in the condensate system that can be attacked by the ammonia.

Chemically, four types of treatment are used for condensate system corrosion control: ammonia or neutralizing amines, filming amines, oxygen scavengers/metal passivators, and nonamine filming treatment.

Neutralizing amines and ammonia are volatile, alkaline compounds that are added to either the boiler feedwater or the steam. They function by volatilizing into the steam and redissolving into the condensate. The amines and ammonia chemically neutralize the carbonic acid or any other acid present in the condensate. Then they raise the pH of the condensate to minimize the corrosion of the materials of construction of the condensate system. The most common neutralizing amines in use today are cyclohexylamine, morpholine, diethylaminoethanol, methoxypropylamine, and monoethanolamine. Each has a unique volatility and basicity characteristic.

Industrial boiler systems can have very extensive and complex steam/condensate systems. Complex steam systems that operate at multiple pressure levels, especially where high-pressure condensate is flashed to produce additional low-pressure steam, can concentrate a single treatment amine to one part of the system while simultaneously depleting its concentration in another part of the system due to its unique single, pressure-dependent vapor-to-liquid distribution ratio characteristic. This leads to a situation in which some parts of the complex system can be undertreated, even though from the pH measurement of the combined condensate sample the system appears to be sufficiently treated. The common solution to this situation is the use of an amine treatment product – that may be a combination of multiple amines, each with a different vapor-to-liquid distribution characteristic. In the most complex steam systems, satellite feed to a particular point in the system may still be required to provide adequate corrosion protection. In a simple steam condensate system such as the typical electric utility situation, a single amine or ammonia may provide adequate protection. But there have been many cases where a low volatility amine or the industrial multiple amine philosophies of treatment have provided better protection as measured by a reduction in corrosion product transport, in even the simple system.

Neutralizing amine treatment does not provide protection for the system from dissolved oxygen attack. The feed of an oxygen scavenger/passivator to the condensate can protect the system against dissolved oxygen attack. Sodium sulfite is typically not used for this application since it contributes nonvolatile solids. More typically, one of the volatile organic oxygen scavenger/passivator materials can be used in this application. Preferably though, the source of the oxygen in leakage should be found and corrected.

There can also be situations in which the carbon dioxide content of the steam is so high because of the natural bicarbonate alkalinity of the makeup water, and that treating the condensate with neutralizing amine technology is prohibitively expensive. In this case, a filming amine technology can be used. In the filming amine treatment, the carbon dioxide is not neutralized, but the filming amine forms a nonwettable barrier on the condensate system components preventing the low pH condensate from coming into contact with the materials. Filming amines also provide protection from dissolved oxygen attack. The amount of filming amine required is related to the surface area of the system. Octadecylamine is a commonly used filming amine. Filming amines have the ability to move corrosion products from the surface of the piping. It is therefore advisable to start with low dosages, which are gradually increased until residual limits are met. There are also proprietary filming amines.

There may be restrictions on amine concentrations in steam when there is contact of that steam with food or food products, when the steam is used for humidification of air or when it can contact certain catalysts used in industrial processes. A nonamine filming corrosion inhibitor technology[36] has been developed for when there is a prohibition on amines in the treated steam.

There are also mechanical means of treating condensate to remove contaminants and preserve its purity for reuse. If corrosion products – typically iron oxides and copper oxides – exist as suspended solids in the condensate, they can be filtered out. Cartridge filters can be used. Condensate polishers, an ion exchange process in which strong acid cation resin is in the sodium or amine form in industrial situations, act primarily as a filter but can also remove hardness that may have come from cooling water contamination of the condensate. In electric utility boiler situations where condensate temperatures are considerably lower, mixed-bed resin polishers (typically a mixture of strong acid cation resin in the hydrogen form and strong base anion resin in the hydroxide form) are used.

These can be deep bed regenerable units or they can be of the powdered resin, one-time-use type. In addition, high gradient electromagnetic filters have been used to remove corrosion products of iron and some copper that are magnetic.

As a final alternative, contaminated condensate can be discarded or diverted rather than returned to the system. The condensate diversion system (condensate dumps) is a system of sensors, valves and piping to detect the contamination of the condensate and divert it to waste. These condensate diversion systems must be properly engineered to detect and divert the contamination in a timely manner to prevent the contamination of the feedwater. This technique is only applicable to systems where the makeup water system capacity can compensate for this lost condensate.

4.28.6 Boiler Treatment During Out-of-Service Conditions

Boilers constructed out of carbon steel and low chromium alloys up to about 9% chromium content are prone to corrosion at ambient temperatures in contact with untreated, typically aerated, water. The maximum corrosion rate occurs where carbon steel is in contact with a water–air interface. This water–air interface occurs when an operating boiler is taken out of service and the vents are opened to the atmosphere during the cooling process and air displaces the condensing steam. Even if the boiler is drained at this point, depending on the boiler design configuration there may be areas of the boiler that do not drain completely. In addition, in many boiler designs that incorporate superheaters and reheaters, heat transfer surfaces can be of a pendant or other design configuration that is inherently nondrainable. Nondrainable components require special treatment if a wet lay-up method is employed. Water purity must be very high – condensate or demineralized quality – and any treatment chemicals used in the water must be volatile.

Guidelines[37,38] are available for the proper treatment of a boiler in the out-of-service condition. The goal of the guidelines is to use a procedure that generally eliminates the air–water interface. This can be accomplished in a number of ways – by draining the boiler under a positive nitrogen pressure or draining the boiler and installing a desiccant, for example. The appropriate procedure depends on many variables, including the configuration of the boiler and the expected duration of the out-of-service period.

4.28.7 Miscellaneous (But Important) Comments

Proper sampling is a prerequisite of effectively monitoring a system. Effective monitoring of the makeup water, feedwater, boiler water, steam, and condensate is necessary to control deposition and corrosion within the system. No matter how accurate or precise the analysis of a sample obtained is, if the sample is not truly representative of the stream being sampled, the results are useless.[39] Effective monitoring requires a proper sampling system, adequate sample system purging, the required sample velocity, and appropriate sample handling.[40]

A particular case in point is sampling steam to determine its purity. Isokinetic sampling nozzles and procedures are required.[41] When sampling superheated steam, sample cooling considerations are especially important. The distance between the sampling nozzle and the primary cooler must be minimized – no more than 7 m (20 ft) – and any sample line length between the nozzle and the cooler must be insulated.

The proper sampling and analysis of condensate is especially critical, because of its inherent high purity and the volatility characteristics of both the treatment chemicals and some of the contaminants it might contain.

A stainless steel injection quill must be used to inject treatment chemical into the system. Concentrated treatment chemicals in contact with carbon steel at elevated system operating temperatures present a corrosive situation for the carbon steel. A properly designed and installed chemical injection quill admits the chemical into the fluid stream, so that it is properly diluted in the stream.

References

1. Water-Tube Boilers and Auxiliary Installations-Part 12: Requirements for Boiler Feedwater and Boiler Water quality. CEN European Committee for Standardization Brussels: Belgium, EN 12952-12:2003, 2003.
2. VGB Guideline for Feedwater, Boiler water and Steam of Steam Generators with admissible operating Pressure >68 bar. VGB Kraftwerkstechnik GmbH, Essen, Germany, VGB-R 450 L, 1988.
3. Consensus on Operating Practices for the Control of Feedwater and Boiler Water Chemistry in Modern Industrial Boilers, CRTD-Vol.34. American Society of Mechanical Engineers, New York, NY, 1994.
4. Dooley, R. B.; Shields, K. J. *Power Plant Chem.* **2004,** *6(3).*
5. Japanese Industrial Standard, Water Conditioning for Boiler Feed Water and Boiler Water, JIS B 8223, Japanese Standards Association, 1989.

6. Miller, B.; Munoz, J.; Wiesler, F. Proceedings of the International Water Conference, Pittsburgh, PA, 2005; paper no. IWC-05-79
7. Dooley, R. B., Shields, K. J., *Power Plant Chem.* **2004**, *6(10).*
8. Dooley, R. B., Castle, J. E., Zhdan, P. A. *Power Plant Chem.* **2005**, 7(9).
9. Palmer, D. A., Benezeth, P., Simonson, J. M. *Power Plant Chem.* **2004**, 6(2).
10. Bignold, G. J.; de Whalley, C. H.; Gabert, K.; Woolsey, I. S. CERL single phase erosion corrosion studies under boiler feedwater conditions. Proceedings of EPRI Workshop, 4/15-15/1987, Washington, DC.
11. Flow accelerated corrosion. Port R.D.: NACE, 1998.
12. Banweg, T. *Flow Accelerated Corrosion in Industrial Boiler Feedwater Systems.* Canadian Pulp and Paper Association, Montreal, Canada, 1998.
13. Erosion Corrosion in Power Plants, Single & Two Phase Flow Experience, Prediction, NDE, Maintenance and Remedial Measures. IWC 89-22.
14. Flow Accelerated Corrosion in Power Plants, TR-10611, Electric Power Research Institute, Pleasant Hills, CA.
15. Hicks, P. *Power Plant Chem.* **2007**, *9*(5), 301–312.
16. Hicks, P.; Grattan, D.; White, P.; Bayburt, K. *Power Plant Chem.* **2007**, *9*(6), 324–336.
17. Stookey, L. L. *Anal. Chem.* **1970**, *42*(7), 779.
18. Fowee, R. NACE paper 218 1991.
19. Godfrey, M. R.; Chen, T. Y.; Eisner, I. E. NACE, 1995.
20. Resch, G.; Odenthal, H.; Epselo, D. *VGB Mitt.* **1965**, *79*, 228–240.
21. Freier, R. K., Cover layer formation on steel by oxygen in neutral salt free water. VGB Speisewassertagung, Sonderheft, 1969; pp.11–17.
22. Bohnsack, G. Teil 1, VGB Kraftwerktech **1973**, *53*(6), 382–393; Teil 2, VGB Kraftwektech **1973**, *53*(7), 472–481.
23. Busik, A. VGB Kraftwerktech **1982**, *62*(1), 36–41.
24. Bursik, A. Proceedings of the International Water Conference, **1986**, Vol. 47, pp. 226–233.
25. Banweg, A.; Clark, S. D.; Bohnsack, G. NACE, Corrosion 92, paper no. 148.
26. Whirl, S. F.; Purcell, T. E. Proceedings of the International Water Conference, Pittsburgh, PA, **1942**.
27. Panson, A. J., et al. *J. Electrochem. Soc.* **1975**.
28. Thaler, J. O.; Sinha, P. K. *Power Eng.* **1986**.
29. Marcy, V. M.; Halstead, S. L.; *Combustion* **1964**.
30. Stodola, J. Proceedings of the International Water Conference, Pittsburgh, PA, 1986; paper no. 27.
31. Gray, L. G. S.; Wiwchar, B.; Tremaine, P. R.; Stodola, J. NACE Corrosion 92 paper no. 417.
32. Herro, H. M.; Banweg, A. NACE Corrosion 95, paper no.498.
33. Bursik, A.; Jensen, J. P.; Staudt, U. Proceedings of the International Water Conference, Pittsburgh, PA, 1996; paper no. 38.
34. Bursik, A. Gruszkiewicz, M. *Power Plant Chem*; **2004**, *6*(11).
35. Ball, M. *Power Plant Chem.*; **1999**, 1(2).
36. Cicero, D. M. Proceedings of the International Water Conference, Pittsburgh, PA, **1997**.
37. Consensus for the Lay Up of Boilers, Turbines, Turbine Condensers and Auxiliary Equipment, CRTD-Vol. 66, American Society of Mechanical Engineers, New York, NY.
38. VGB Guidelines, VGB-R116H, VGB Technische Vereinigung der Grosskraftwerksbetreiber, 1981.
39. Pocock, F. J., Personal communication, Babcock and Wilcox Research and Development Division, 1979.
40. Consensus on Operating Practices for the Sampling and Monitoring of Feedwater and Boiler Water Chemistry in Modern Industrial Boilers, CRTD-Vol. 81, ASME, Three Park Ave., New York, NY.
41. Annual Book of ASTM Standards. section 11, D-1066, Practice for Sampling Steam, American Society for Testing and Materials, Philadelphia, PA, 2004.

4.29 Corrosion Inhibitors: Other Important Applications

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4.29.1 Introduction

Corrosion inhibitors are used in a wide range of industrial applications. In this chapter, their employment in processing with acids, mining operations, paints and coatings, construction materials, processing electronics packaging, display, and storage is discussed.

4.29.2 Processing with Acids

Acids are extensively used in acid pickling, industrial acid cleaning, acid descaling, oil well acidizing, and manufacturing processes in different industries. Inhibitors are used in acid solutions in order to minimize corrosive attack on metals. The selection of suitable inhibitor depends on the type of acid, concentration of the acid, temperature, flow velocity, the presence of dissolved inorganic or organic substances, and the type of metallic material exposed to the acid solution. The most commonly used acids are hydrochloric, sulfuric, nitric, hydrofluoric, citric, formic, and acetic acid.

4.29.2.1 Acid Pickling

Metals or alloys subjected to painting, enameling, galvanizing, electroplating, phosphate coating, cold rolling, and other finishing processes must have a clean surface free from salt or oxide scale. In order to remove the unwanted scale such as mill scale rust, the metal is immersed in an acidic solution known as the acid pickling bath. After the scale is removed by dissolution, the acid may attack the metal. In order to minimize the attack of the metal, and consumption of the acid, corrosion inhibitors are added to the pickling solution.

Hydrochloric acid is commonly used in the pickling bath. Large-scale continuous treatment such as metal strip and wire pickling and regeneration of depleted pickling solutions are the advantages in using hydrochloric acid instead of sulfuric acid. Other acids, such as nitric, phosphoric, sulfamic, oxalic, tartaric, citric, acetic, and formic acid are used for special applications.

The choice of inhibitor depends on the purpose of acid pickling. If the pickling is for the purpose of removal of mill scale from hot-rolled steel, then the acid concentration, temperature, pickling time, and the type of steel will dictate the selection of the inhibitor. In the case of pickling with HCl, up to $200\,\mathrm{g\,l^{-1}}$ are commonly used at 60 °C with a pickling time of about 30 min, depending upon the type of steel and the steel mill operating conditions. Sulfuric acid at $200\text{–}300\,\mathrm{g\,l^{-1}}$ level and at temperatures up to 90 °C may also be used. These are severe conditions that require effective inhibitors.

The inhibitors used in pickling operations should possess the following requirements:

1. effective inhibition of metal dissolution,
2. lack of overpickling process,
3. effective at low inhibitor concentration,
4. effective at high temperatures,
5. thermal and chemical stability,
6. effective inhibition of hydrogen entry into the metal,
7. good surfactant properties,
8. good foaming properties.

The most important requirement is that the inhibitor minimizes metal dissolution even in the presence of dissolved salts such as ferrous sulfate that promotes metal dissolution. The corrosion rates of steel in 20% sulfuric acid at 90 °C and in 20% sulfuric acid containing 12% ferrous sulfate are 3100 and 5900 g m^{-2} h^{-1}, respectively. Although there exist inhibitors to counter the accelerating effect of ferrous sulfate, the pickling times are increased. In pickling in sulfuric acid at 60–90 °C to remove the mill scale, inhibitors of high thermal stability should be used. The inhibitors must be stable with respect to hydrolysis, condensation, polymerization, and hydrogenation by nascent hydrogen.

Pickling inhibitors should also minimize the entry of hydrogen into the metal. This aspect is not typically part of the protocol in the evaluation of the inhibitors, since no test involving hydrogen permeation measurement is performed to determine the effect of inhibitor on the kinetics of electrochemical production of hydrogen. Testing an inhibitor only for metal dissolution can be detrimental, as there is no direct relationship between inhibition of metal dissolution and inhibition of hydrogen entry into the metal.

Another important criterion is that the inhibitor should possess high efficiency at low concentrations for economic reasons. A good pickling inhibitor should also possess good surfactant and foaming properties. Usually, the inhibitors have poor surfactant and foaming properties, and therefore, wetting agents, detergents, and foaming agents are added to the commercial inhibitor formulation.

Wetting agents play an important role in facilitating the penetration of pickling acid into the cracks and fissures in the scale and help the removal of the scale. Thus, they are known as 'pickling accelerators.' Some wetting agents have degreasing properties and are known as 'pickling degreasing agents.' Wetting agents by themselves usually have no inhibitive effect. However, the chemical nature of the wetting agents determines whether they improve or decrease the inhibitive effect. Wetting agents and detergents help in producing clean metal surface after the pickling acid drains completely and the rinsing of pickled sample is improved. Wetting agents and detergents also possess foaming activity. When this is insufficient, additional foaming agents may be added to the inhibitor formulation. A stable foam blanket on the surface of the pickling bath reduces the acid spray and conserves heat. It is necessary that wetting agents, detergents, and foaming compounds function effectively over a wide range of temperature, acid concentration, and iron salt concentration. It is obvious that no single inhibitor can meet all the requirements of an effective inhibitor and hence commercial inhibitors are multicomponent mixtures, which in some cases may contain as many as thirty components. A typical inhibitor formulation consists of a mixture of an active inhibitor, wetting agent, detergent, foaming agent, solvent, and sometimes a cosolvent.

The active inhibitors used in acid pickling are generally mixtures of nitrogen-bearing organic compounds, acetylenic alcohols, and sulfur-containing compounds. The surface-active compounds may be anionics such as alkyl or alkyl phenyl sulfonates or alkyl sulfates with C_{10}–C_{18} alkyl chains or nonionics such as ethoxylated derivatives of higher alcohols, phenols, or alkylphenols. Nonionics are used when precipitation of iron is to be avoided.

Commercial inhibitor formulations are generally available in solution form. The solvent may be water or the acid in which the inhibitor is to be used. In cases where the inhibitor formulation is not sufficiently soluble, solvents such as methanol, isopropanol, or acetone may be added. Depending upon the amount of solvent or cosolvent, about 5–50 g of the inhibitor is used for 1 l of pickling acid. Corrosion inhibitors used for various metals in HCl containing pickling media are listed in Table 1.

Sulfoxides, sulfides, and thiourea compounds are generally used in a sulfuric acid medium. The common commercial inhibitor formulations consist of dibenzyl sulfoxide, dibenzyl sulfide, thiourea, and di-*O*-tolylthiourea. These inhibitors are effective at high temperatures. Some of the inhibitors used in a sulfuric acid pickling medium area summarized in Table 2.

Iron and steel are passivated in concentrated 65% nitric acid but dissolve in lower concentrations of this acid. Unlike hydrochloric and sulfuric acids, nitric acid is an oxidizing acid, and it is difficult to inhibit high and medium concentrations effectively. Some of the inhibitors used for a nitric acid pickling medium are listed in Table 3. Tables 4 and 5 indicate inhibitors for hydrofluoric acid and phosphoric acid pickling media, respectively. For these two acids, inhibitors are similar to those employed in HCl.

4.29.2.2 Scale Removal by Acids

Scale formation by circulating water or process compounds occurs in power plants, chemical plants, steel mills, paper mills, pipelines, compressor stations, and other industries. Scales or precipitates formed in heat exchangers, boilers, vessels, reactors, piping, and associated equipment reduce heat transfer and cause

Table 1 Inhibitors employed for various metals in HCl containing pickling media

Medium	*Metal or alloy*	*Inhibitor*	*References*
Hydrochloric acid	Iron, steel	Primary, secondary and tertiary amines, oximes, nitriles, mercaptans, sulfoxides, thioureas, and complexones	
	Copper, brass	Thiourea, benzimidazole, 2-mercapto-benzothiazole, phenyl thiourea	[1–4]
1 M HCl + 2.5% NaCl	Al and its alloys	Aliphatic, aromatic aldehydes, carboxylic acids, ketones, sulfonamides, sulfones, dihedric phenols, tetrazolinium compounds, formazan compounds, sulfoxides, aromatic sulfonic acids, cupferron, *N*-allyl thiourea, and dibenzyl sulfoxide	[5–7]
HCl + H_3PO_4 (1 N)		*p*-Thiocresol and sodium diethyl dithiocarbamate	
10% HCl		Mixture of aromatic aldehyde, 1 M urea/triethylamine/dodecylamine, > 1 M thiourea and 1-hexyn-3-ol together with alkyl sulfonates	[8]
Hydrochloric acid	Zinc	Inhibitors used for Al are satisfactory	
5.6 M HCl	Nickel	Thiourea and its derivatives *O*-tolylthiourea and sym-diisopropyl thiourea have 90% inhibition over a wide temperature range	[9]
Hydrochloric acid	Titanium and alloys	Copper sulfate, nitric acid and chromic acid at 0.5–1.0% act as inhibitors. Nitrobenzene, trinitrobenzoic acid, picric acid, benzene arsonic acid at 0.03–0.003 M. Condensation product of formaldehyde with aromatic at 0.003 M	[10–13]

Table 2 Inhibitors used in a sulfuric acid pickling medium

Metal	*Inhibitor and conditions*	*References*
Steel	2-mercaptobenzimidazole	[4]
	2-mercaptobenzimidazole + propargyl alcohol or 1-hexyn-3-ol improved performance	
	Sulfonium compounds at low temperatures	[14–16]
	Thiocyanates, thiourea, thicarbamates, mercaptans produce H_2S and hydrogen entry into metal. Hazardous mustard gas related compounds from thiourea should be guarded	[17]
	Amines or quaternary ammonium salts + halides $Cl^-/Br^-/I^-$ shows synergetic effect in the order $I^- > Br^- > C1^-$	[18]
	Alkylpyridinium salts, *p*-alkylbenzylpyridinium halides and *p*-alkylbenzyl quinolinium halides with alkyl = C_8–C_{12} with KI at 10^{-2} to 10^{-3} M at 20–60 °C in 5–30% H_2SO_4 give good inhibition	
	N-containing inhibitors along with SH^- from H_2S show synergistic effect	[19]
	Acetylenic alcohols (0.05–0.01 M). Acetylenic alcohols + halides	
	Corrosion rate in boiling H_2SO_4: 175 $g\,m^{-2}\,h^{-1}$. In 0.4% propargyl alcohol or 1-hexyn-3-ol: 1355 $g\,m^{-2}\,h^{-1}$. Upon introducing KCl 5–1.5 $g\,m^{-2}\,h^{-1}$ (synergism)	[20]
Copper, brass, aluminum	2-mercaptobenzimidazole + 1 hexyn-3-ol (may be used for boilers)	
Copper	Thiourea	[21–23]
Brass	Quinolines, azoles	[24–26]
Titanium	2,4,6-trinitrophenol, 5-nitroquinoline, 8-nitroquinoline, 0-dinitrobenzene, *n*-nitroacetanilide, nitrobenzene and picric acid Inhibitors at 0.01–0.001 M in 10% H_2SO_4 at 60 °C give good inhibition. In 1 M H_2SO_4 cresolphthalexon, thymolphthalexon, thymol sulfophthalexon at low concentrations and at 80 °C gives good protection	[27–30]

tube failure, plugging, or fouling of equipment. The solid deposits should be removed in addition to preoperational cleaning to remove oxide scales or organic coatings.

The scales may be either organic or inorganic in nature. Inorganic deposits are formed in heat exchangers or steam generations. Typically, these inorganic deposits consist of magnetite, hematite, iron sulfides, calcium, and/or magnesium carbonates, sulfates, phosphates, and silicates. Organic deposits consist of algae, slime, or moulds. The acids commonly used in scale removal are hydrochloric and hydrofluoric acid, in combination with ammonium bifluoride, sulfuric acid, nitric acid, sulfamic acid, citric acid, acetic acid, hydroxyacetic–formic acid mixture, and phosphoric acid.[61] Some inhibitors used in the removal of scales in hydrochloric acid are given in **Table 6**.

Hydrofluoric acid and ammonium bifluoride are usually added to hydrochloric acid solution to accelerate the removal of iron scales and silicate deposits.

Table 3 Inhibitors used in nitric acid pickling medium

Metal	*Inhibitor and conditions*	*References*
Ferrous metals	Propargyl mercaptan, propargyl sulfide, ethane dithiol, thioacetic acid, mercaptoacetic acid, diethyl sulfide, benzyl-2-methyl pridine thiocyanate and thiourea. Thiourea in low concentration because high concentrations promote corrosion	[31–34]
	Condensation product of hydroabietylamine with HCHO and an aldehyde of 2–6C atoms and 1-hexyn-3-ol	[35]
Copper	Aliphatic and aromatic amines and diamines	[36–45]
Brass	Aminophenols, aminobenzoic acids, heterocyclic amines, thiourea and derivatives, *p*-thiocresol. *O*-Chloroaniline, *O*-nitroaniline, and sym-diethyl thiourea (0.1–0.001 M in 30% HNO_3)	[46–50]
Titanium	In 20–70% HNO_3 at 190–230 °C, 5×10^{-5} wt% silicone oil reduced the corrosion rate from 1 to 10 mm $year^{-1}$ to a negligible value	[51]

Table 4 Inhibitors used in hydrofluoric acid pickling medium

Metal	*Inhibitor and conditions*	*References*
Ferrous	In 0.5–10 wt% HF, dibenzyl sulfoxide, C_{10}–C_{14} alkyl pyridinium salts, di-*o*-tolylthiourea, benzotriazole, mixture of thourea and Mannich base derived from rosin amine	[52–54]
Ferritic steels	In nitric acid + HF, 2–5% thiourea	[55]

Table 5 Inhibitors used in phosphoric acid pickling medium

Metal	*Inhibitor and conditions*	*References*
Steel	Benzyl quinolinium thiocyanate	[56]
Steel vessels	Transport of 50–116% H_3PO_4 – dodecylamine or 2-amino bicyclohexyl (0.03–0.10%) in KI (0.007–0.014%)	[57]
Aluminum alloys	Urotropin, *p*-toluidine in H_3PO_4 medium are effective inhibitors	[58, 59]
Titanium	Conc. H_3PO_4 – inhibited by $(NH_4)_2MoO_4 + K_2Cr_2O_7$	[60]

Table 6 Inhibitors used in scale removal in a hydrochloric acid medium

Metals/scales	*Inhibitor and conditions*	*References*
Scale of calcium and iron salts	5–15 wt% HCl at 80 °C. Mixture of imines, thiourea and alkynols	
Zinc	Mixtures of *N,N′*-dicyclohexylthiourea, ethyncyclohexanol, and polyaminomethylene phosphate	[62]
Carbon steel	Sulfonium compounds	[15, 16]
Scale in refineries	14% HCl containing 33–37 g l^{-1} of hexamethylene tetramine	[63]
Copper with a scale of magnetite in high pressure boilers	Mixture of thiourea or its derivaties and hexahydropyrimidine-2-thione	

Magnetite and hematite scales may be removed by hydrofluoric acid. Mannich bases, thiourea and its derivatives, and alkynols may be used as inhibitors in hydrofluoric acid medium.[54] The condensation product of diethyl and dibutyl thiourea with hexamethylene tetramine can also act as an inhibitor in HF medium for scale removal.[64]

Sulfuric acid at 5–15 wt% may be used to remove oxide scales. This acid cannot be used to remove calcium deposits because the product, calcium sulfate, is insoluble. Concentrated sulfuric acid in combination with nitric acid is used to remove organics, coke. Mixtures of quaternary ammonium compounds, alkynols, and sulfur compounds may be used for inhibition in a dilute sulfuric acid solution. Nitric acid is useful in cleaning stainless steel or plastic equipment. Inhibitors are not stable in the strong oxidizing nitric acid and are not used in the case of carbon steel or copper alloys.

Sulfamic acid is useful in the removal of calcium scales but not iron oxides. A mixture of sulfamic acid and sodium chloride can remove iron oxide scale through slow generation of hydrochloric acid. Sulfamic acid can be used in cleaning equipment containing copper, brass, stainless steel, and galvanized steel. Inhibitors at 10 wt% used in sulfuric acid medium may be used in sulfamic acid solution. Sulfamic acid is extensively used in cleaning evaporations in sugar mills made of cast iron with copper heat exchangers.

Citric acid is used in cleaning heat exchangers of nuclear plants, which are susceptible to chloride attack. Iron oxide scales can be removed by repeated treatment with citric acid. Inhibitors for sulfuric acid solutions can be used in citric acid medium.

Acetic acid may be used where chloride-free removal of carbonate scales in equipment made of aluminum is necessary. Inhibitors used in sulfuric acid find application in acetic acid medium. A mixture of 2 wt% of hydroxyacetic acid and 1 wt% of formic acid may be used to remove magnetite from high-pressure steam generators and superheater sections of boilers. Again, inhibitors functioning in a sulfuric acid medium may be employed here.

4.29.2.3 Acidizing Oil Wells

Acids are generally used in oil and gas wells to stimulate the oil or gas flow from the well and to remove any encrustations in the well. Acids such as hydrochloric acid are forced, under high pressure, through the hole into the rock formation to produce fractures around the hole. The fractures are then filled with sand in order to prevent the fractures from closing and allow the gas or oil to permeate. About 10–15 wt% of HCl is generally used. A mixture of hydrochloric and hydrofluoric acids is used when the formation is rich in silicate. It is necessary to protect the equipment from corrosion due to the acid by use of inhibitors. The inhibitors used should be stable up to 150 °C and in some cases, 260 °C. Some inhibitors used in acidizing oil and gas wells are given in Table 7.

Table 7 Inhibitors used during acidizing oil and gas wells

Inhibitor and conditions	*References*
Mixtures of nitrogen containing compounds, acetylenic compounds and surfactants C_{12}–C_{18} primary amines, cyclohexyl amine, aniline, methyl anilines, alkyl pyridines, benzimidazole, and rosin amine condensed with formaldehyde	[65]
Amines together with cuprous iodide	[66]
Propargyl alcohol or 1-hexyn-3-ol gives improved inhibition at high temperatures	[67]
Alkynoxymethyl amines.	
Acetylenic inhibitors together with ferrous ions gives rise to protective surface films due to iron catalyzed condensation and polymerization	[58, 68]

4.29.3 Mining Industry

In the mining industry, the three corrosive environments are (i) mine air, (ii) mine dust, and (iii) mine water. Mine air causes atmospheric corrosion of mining equipment to an extent determined by the composition of mine air, humidity, and temperature. Mine air is deficient in oxygen and contains significant amounts of oxides of sulfur and nitrogen. Sulfur dioxide results from burning coal, and oxides of nitrogen originate from the use of underground explosives. The oxides of sulfur and nitrogen combined with high humidity and temperature cause corrosion of mining equipment.

Coal mine dust contains pyrite in coal seams and gypsum, which is used for dusting in order to reduce the amount of combustible particles. The sulfur content of coal is corrosive to mining equipment. Sulfur dioxide, produced by the oxidation of pyrite, reacts with hygroscopic constituents and generates sulfuric acid, which attacks the metal.

Mine waters are unique in that they vary in composition from mine to mine. The pH values range from 2.8 to 12.3. Chloride values range from 5 to 10 500 ppm and sulfate ranges from 57 to 5100 ppm. Low pH, high chloride and sulfate content of mine water are conducive to severe corrosion.

Microbial corrosion can also be a problem. *Thiobacillus* species, such as thiooxydans, are common soil or water organisms. These entities oxidize sulfur, generating corrosive sulfuric acid. Sulfate-reducing bacteria generate hydrogen sulfide, which is also corrosive.

Mitigation of corrosion in the mining industry is done by the addition of (i) passivating inhibitors, (ii) precipitation inhibitors, and (iii) adsorption inhibitors. Chromates and phosphates are typical of passivating inhibitors and function by blocking the anodic reaction. These inhibitors are incorporated into the oxide film on the metal, thereby stabilizing the oxide film and preventing further dissolution. The concentration of the chromate inhibitor used is

Table 8 Inhibitors and their performance in acidic mine waters

Inhibitor	*Type*	*Performance*
Sodium silicate	Precipitation	Fair to good
Potassium oxalate	Precipitation	Fair to good
Sodium nitrite	Passivation	Good
Sodium molybdate	Passivation	Fair to good
Phosphonate–phosphate	Precipitation	Excellent
Phosphonate–silicate	Precipitation	Fair to good

critical because low concentrations give rise to underprotection resulting in pitting corrosion.

Precipitation inhibitors consisting, for example, of zinc salts block the cathodic reaction by precipitation at the cathode due to elevated local pH values. Pitting is not a problem, even though complete coverage is not attained, because the anodic sites are unaffected by the inhibitors and the number of unprotected cathodic sites are insufficient to promote anodic dissolution.

In general, organic inhibitors can be considered as adsorption inhibitors. The functional group in the inhibitor molecule such as amino, carboxyl, or hydroxyl readily absorbs on the metal surface forming a type of bond and blocks the anodic and/or cathodic sites.

The performance of some inhibitors tested in acid mine water are given in Table 8.[69] It should be noted that corrosion inhibition by potassium oxalate involves the formation of tris-oxalate iron complex, which is photosensitive. The complex decomposes in the presence of light to β-ferrous oxalate.

$$Fe^{3+} + 3C_2O_4^{2-} \rightarrow Fe(C_2O_4)_3^{3-}$$
$$Fe(C_2O_4)_3^{3-} \xrightarrow{hv} \beta - FeC_2O_4 + 4CO_2$$

The product of photochemical decomposition, β-ferrous oxalate, is deposited on the metal and protects the metal from corrosion. This is the first example of photochemical corrosion inhibition.[70]

Corrosion inhibitors have been used in corrosive wear loss of grinding balls in grinding Cu–Zn–Fe sulfide ore. Many inorganic inhibitors both as single component and binary mixtures were used and a binary mixture of sodium chromate and sodium carbonate reduced the corrosive wear of the grinding balls by 30%.[71]

4.29.4 Paints and Coatings

The primary function of an organic coating on a metallic structure is to provide a protective barrier between the metal and the external corrosive environment. Paints are used for both corrosion protection and cosmetic purpose. Usually corrosion inhibitors are incorporated in the primer. The inhibitors used in coatings can be anodic, cathodic, or mixed. Some examples of the inhibitors incorporated into coating formulations suitable for steel core are given in Table 9.[69]

Table 9 Inhibitors employed in coating formulations for steel core

Compounds
Calcium
Carbonate
Molybdate
Plumbate
Chromium
Barium potassium chromate
Basic lead silicochromate
Cadmium chromate
Zinc chromate
Lead
Basic silicoplumbate
Blue
Calcium plumbate
Carbonate (white)
Red
Titanate
Zinc
Chromate
Molybdate
Oxide
Tetroxychromate
Miscellaneous
Antimony oxide
Carbon black
Chalk
China clay
Iron oxide
Strontium chromate
Talcum
Titanium dioxide

Some of the components are used as fillers. Zinc and calcium molybdate are effective at low levels (~3%), and are nontoxic. These compounds may be used in place of chromates, which are toxic. Red lead protects the steel by combining with the corrosion products of iron. Red lead, zinc oxide, and calcium carbonate form soaps with linseed oil and then decompose in the presence of oxygen and water into a lead salt of azelaic acid, which promotes cathodic reduction of oxygen. This helps to stabilize the iron oxide film by maintaining a suitable potential. Calcium plumbate increases the pH and thus inhibits corrosion. The lead suboxide in oleoresinous coatings forms lead soaps on the metal surface and blocks the anodic sites by adsorption. Lead suboxide in linseed oil primer is found to penetrate the rust film and into crevices of rusted steel.

Inhibition by chromate-based pigments is similar to that of dissolved chromate, and this is supported by the slight solubility of the pigment.[72] Chromate ions are adsorbed onto the surface followed by the formation of a passive film containing Cr_2O_3 and Fe_2O_3. Both potassium chromate and zinc chromate protect the steel. Potassium chromate protects by interfering with the anodic reaction, while zinc chromate also forms a zinc hydroxide film inhibiting the cathodic reaction.

Zinc, along with cadmium and strontium, chromate has been used in the protection of aluminum involving crevices. These compounds are reduced at cathodic sites and hydrogen evolution is prevented. Disbonding of coatings is due to hydrogen evolution and addition of cadmium phosphate shows improved inhibition.

Chromates, such as zinc chromate, potassium or barium chromate, may be used as primers in various vehicles including linseed oil, long oil linseed penta-alkyd, double-boiled linseed oil for corrosion inhibition. Good protection was obtained with modified phenolic stand oil and epoxy ester primers, as confirmed by neutral pH, noble potentials, and formation of soap, which covers the zinc chromate causing water repulsion.

Some pigments based on lead, silicate, and phosphate, along with some applications, are given in Table 10.

The coatings discussed so far involve heavy metal compounds that are toxic with the exception of molybdates and phosphates. Thus, development of environmentally friendly coatings containing tannins has received attention. It is necessary that the fabrication of raw products, surface pretreatment and application of coating, use of coated structure, and recycling and elimination steps should be considered from the point of environmental impact. Tannins are used as corrosion inhibitors in water-based paints. Such paints can be applied directly on rusted objects without pretreatment, such as sandblasting.

The mechanism of protection by tannins in paints has been investigated by many studies.[77–83] An early proposal was the formation of an insoluble chelate complex at anodic sites.[78] The insoluble chelate complex may act as an insulator between anodic and cathodic sites because of the cross-linked structure of the complex.[79]

Tannins are also known to convert ‘active’ rust into nonreactive oxide such as magnetite.[80] The insoluble complex formed may act as a barrier for the diffusion of oxygen.[77] The action of tannins appears to depend upon the properties of paint-rust system and upon the amount of rust present.[81] X-ray photoelectron data and Mössbauer spectra showed an increase in the ratio of ferrous to ferric ions when the rust was treated with tannins.[82] Vacchini[83] showed the dissolution of rust by tannins and the formation of a complex that acted as a barrier for the diffusion of oxygen.

4.29.5 Construction Materials

Corrosion inhibition in reinforced concrete structures involves a single addition of the inhibitor. One this basis, the criteria for effective corrosion inhibition in concrete are that (i) the inhibitor should be soluble in mixing water to allow homogeneous distribution and not readily leachable from concrete;

Table 10 Some pigments in common use

Pigment	*Comments*	*References*
Red lead	Red lead in linseed oil used as primer for steel structures. Red lead oxide forms soluble soaps with vehicle	[73]
Lead silicochromate	Consists of silicate case coated with its own pigment. Anticorrosive due to lead and passivation due to chromate. Coating with this is comparable to red lead in linseed oil in protection. Protection of passenger car bottoms by using priming coats with the pigment achieved	[74]
Barium oxide–iron oxide	Developed for corrosion control of fertilizer plants. Corrosion protection is satisfactory	[75]
Zinc phosphate/barium phosphate primer	Nontoxic and promotes excellent intercoat adhesion. The primer converts the metal to metal phosphate. This primer reduces diffusion of ions through paint film. Zinc phosphates-iron oxide in linseed stand oil performed better than red oxide–zinc chromate in field tests	[76]

(ii) the inhibitor must be compatible with the aqueous cement phase, to render its full protection potential; (iii) the concentration of the inhibitor should not adversely affect the properties of the concrete; and (iv) the consumption rate of the inhibitor should be low.

The most extensively used inhibitor in concrete is calcium nitrite, although organic inhibitors have become prominent in recent years. Calcium nitrite has been used as an inhibitor for concrete on a large scale. Calcium nitrite provides corrosion protection in the presence of chlorides, does not affect the properties of concrete, and is readily available for commercial use in concrete.

Calcium nitrite, an anodic inhibitor, is thought to be responsible for the constant repair of weak spots in the protective iron oxide film as well as the following reactions:

$$2Fe^{2+} + 2OH^- + 2NO_2^- \rightarrow 2NO + Fe_2O_3 + H_2O$$
$$Fe^{2+} + OH^- + NO_2^- \rightarrow NO + \gamma - FeO{\cdot}OH$$

The nitrite ion is believed to compete with chloride and hydroxyl ions in the reaction with ferrous ions. As the nitrite ion helps to repair the flaws in the oxide film the probability of chloride attack at the flaws of the oxide film and dissolution of the oxide film as soluble chloro complexes of iron are minimized. Given that nitrite inhibitor is involved in repairing the oxide film and the oxide films are of the order of monolayers, nitrite is not consumed to a great extent.

Pozzolans (complex silicate of iron, aluminum, and calcium) are used to prevent corrosion by reducing permeability of concrete to chloride. Microsilica is one of the most effective pozzolans because its small particle size acts as a filler and increases its chemical reactivity. Calcium nitrite is compatible with microsilica and should provide corrosion protection in the presence of chloride. Calcium nitrite is also found to improve the performance of fly ash concrete and concretes containing slag. Calcium nitrite is also effective in the protection of cracked concrete.

Organic inhibitors have been used as an alternative to the commonly used calcium nitrite. The organic inhibitors, referred to as organic corrosion inhibiting admixtures (OCIA), adsorb on the metal surface through a polar functional group, while nonpolar hydrophobic groups repel the aqueous corrosive fluids and interact with each other to form a tight film of aggregates on the metal surface. The tight hydrophobic film is also impermeable to chloride ingress into the concrete.

The performance of organic amines and esters with both uncracked and precracked concrete samples has been compared with precracked samples treated with calcium nitrite.[84] The organic inhibitors lowered the corrosion rates to a significant extent. The onset of corrosion in samples treated with organic inhibitors occurred after 180 days, and the corresponding times were 30 and 5 days in the case of calcium nitrite treated samples and uninhibited samples, respectively. The ingress of chloride was highest in calcium nitrite treated samples and least in organic inhibitor treated samples. The higher chloride ingress in samples treated with nitrite is attributed to the accelerating effect of nitrite resulting in a more permeable concrete matrix. The blocking of pores by organic inhibitor results in low ingress of chloride in samples treated with organic inhibitor.

A mixture of glycerophosphate and nitrite showed synergistic behavior in the protection of steel in mortars.[85] Other inhibitors used in reinforced steel are ethanolamine,[86] poly alcohols, polyphenols, and sugars. Alkanolamine has been shown to be an effective inhibitor and to migrate through the pores when it is injected into the cavities.[87]

4.29.6 Processing Electronics Packaging, Paper Display, and Storage

Some organic compounds with vapor pressures in the range 10^{-2} to 10^{-7} mmHg volatilize and condense on the surface of a structure to be protected from corrosion in a closed space. These types of compounds are known as vapor-phase corrosion inhibitors; a list of common vapor-phase inhibitors, along with their vapor pressures, is given in Table 11. Vapor-phase corrosion inhibitors are particularly useful in impeding atmospheric corrosion. Atmospheric corrosion is expensive and results from individual or combined action of moisture, oxygen, and pollutants such as SO_2 and NO_2.

Most effective vapor-phase inhibitors consist of a weak volatile base and a weak volatile acid. Amine nitrites undergo hydrolysis and provide inhibition

$$R_2NH_2NO_2 \xrightarrow{H_2O} R_2NH_2^+ + OH^- + H^+ + NO_2^-$$

The pH of the medium is critical to the effective inhibition by vapor-phase inhibitors.

The application of vapor-phase inhibitors varies, depending upon the composition of the object to be protected, as well as the conditions of storage of the object. Storage conditions dictate the aggressiveness

Table 11 Common vapor phase inhibitors and their saturated vapor pressures

Substance	*Temperature (°C)*	*Vapor pressure (mmHg)*	*Melting point (°C)*
Morpholine	20	8.0	
Benzylamine	29	1.0	
Cyclohexylamine carbonate	25.3	0.397	
Diisopropylamine nitrite	21	4.84×10^{-3}	139
Morpholine nitrite	21	3×10^{-3}	
Dicyclohexylamine nitrite	21	1.3×10^{-4}	179
Cyclohexylamine benzoate	21	8.0×10^{-5}	
Dicyclohexylamine caprylate	21	5.5×10^{-4}	
Giuanidine chromate	21	1.0×10^{-5}	
Hexamethyleneimine benzoate	41	8.0×10^{-4}	64
Hexamethyleneamine nitrobenzoate	41	1.0×10^{-6}	132
Dicyclohexylamine benzoate	41	1.2×10^{-6}	210

of the treatment. The storage conditions requiring progressively more aggressive treatments are (i) enclosed nonventilated area; (ii) uncovered inside storage; (iii) covered outside storage; and (iv) uncovered outside storage.

Vapor-phase inhibitors are either oil or water soluble and applied in the form of powders, sprays, or impregnated papers and foams. A controlled-release inhibitor formulation can be employed, which is designed to release the inhibitor at a controlled rate over a specified period. Polymer encapsulation may be used for controlled release, where a rate-controlling membrane encloses a cavity that contains the inhibitor either dispersed or in solution. The membrane can be porous or nonporous and the inhibitor is in a reservoir in a fluid state that maintains a constant amount in the reservoir until an excess amount is released. This results in a steady-state release of the inhibitor that follows Fick's law.

In addition to encapsulation, the inhibitor can be dispersed in a polymer matrix, from which the inhibitor is extracted. There are two types of matrix device. In the first type, the release of the active inhibitor is controlled by diffusion through the matrix upon erosion of the matrix. In the second type, the release of the inhibitor is initiated by the penetration of some species, such as water, from the environment into the matrix. On reaction with water, the active inhibitor is released because of hydrolysis.

$$\text{Polymer} - \text{Inhibitor} \xrightarrow{\text{H}_2\text{O}} \text{Polymer} + \text{Inhibitor}$$

Some common examples of this type are esters, anhydrides, and acetals.

References

1. Kurilovich, T. I.; Klyuchnikov, N. G. *Ingibitory Korroz Met*. **1972**, *168*; *Chem. Abs*. **1975**, *83*, 210657j.
2. Desai, M. N.; Sheth, H. M. *Vidya* **1976**, *B19*, 118; *Chem. Abs*. **1978**, *88*, 40661q.
3. Desai, M. N.; Desai, S. T. *Chem. Concepts* **1978**, *5*(7), 15; *Chem. Abs*. **1978**, *89*, 219453.
4. Patel, M. N.; Patel, N. K.; Vora, J. C. *Chem. Era*. **1975**, *11*(5), 4; *Chem. Abs*. **1977**, *87*, 9998.
5. Horner, L.; Meisel, K. *Werkstoffe Korros*. **1978**, *29*, 654.
6. Makwana, S. C.; Patel, N. K.; Vora, J. C. *J. Indian Chem. Soc*. **1973**, *50*(10), 664; *Chem. Abs*., **1974**, *80*, 127351x; *Werkstoffe Korros*. **1973**, *24*, 1036.
7. Makwana, C. M.; Bhavsar, A. C.; Gandhi, D. C. *Chem. Era*. **1976**, *12*(4), 145; *Chem. Abs*. **1977**, *86*, 125613j.
8. Makwana, S. C.; Patel, N. K.; Vora, J. C. *Trans. Soc. Adv. Electrochem. Sci. Technol*. **1977**, *12*(1), 15; *Chem. Abs*. **1978**, *88*, 64933f.
9. Clark, P. N.; Jackson, E.; Robinson, M. *Br. Corros. J*. **1979**, *14*, 33.
10. Mansfeld, F.; Kenkel, J. V. *Corros. Sci*. **1975**, *15*, 767.
11. Tupikin, E. I.; Klyuchnikov, N. G.; Verzilina, M. K. *Izv. Vyssh. Ucheb. Zaved. Khim. Khim. Tekhnol*. **1974**, *17*(4), 514; *Chem. Abs*. **1974**, *81*, 32513.
12. Gerasyutina, L. I.; Tulyupa, F. M.; Karvaka, L. G. *Zashch. Mettalov*. **1978**, *14*(6), 719; *Chem. Abs*. **1979**, *90*, 158952e.
13. Tupikin, E. I.; Klyuchnikov, N. G.; Nemchaninova, G. L. *Zashch. Mettalov*. **1975**, *11*(3), 351; *Chem. Abs*. **1975**, *83*, 1055287.
14. Heiss, L.; Hille, M. (Farbwerke Hoechst AG) U.S. Patent 3,773,675, Nov. 20, 1973; *Chem. Abs*. **1974**, *80*, 148130.
15. Frenier, W. W.; Settineri, W. J. (Dow Chem Co.) U.S. Patent 3,764,543, Oct. 9, 1974; *Chem. Abs*. **1976**, *80*, 86674; U.S. Patent 3,969,414, July 13; *Chem. Abs*. **1976**, *85*, 123665.
16. Settineri, W. J.; Frenier, W. W.; Oswald, J. R. U.S. Patent 3,996, 147, Dec. 7, 1976; *Chem. Abs*. **1977**, *86*, 58948.
17. Klitgaard, J.; Blum, R. *VGB Krafwerkstechnik* **1978**, *58*(4), 303; *Chem. Abs*. **1978**, *89, 168203.*
18. Frumkin, A. N. *Z. Elektrochem*. **1955**, *59*, 807.
19. Iofa, Z. A. *Zashch. Metallov*. **1970**, *6*(5), 491; *Chem. Abs*. **1973**, *73*, 136607; *Zashch. Metallov*. **1972**, *8*(2), 139; *Chem. Abs*. **1972**, *77*, 55465a.
20. Allabergenov, K. D.; Kurbanov, F. *K. Zashch. Mettalov*. **1979**, *15*(4), 472; *Chem. Abs*. **1979**, *91*, 179255r.

21. Sorokin, V. I.; Romasenko, V. P. *Ukr. Khim. Zh. (Russ. Ed.)* **1974**, *40*(8), 804; *Chem. Abs*. **1975**, *83*, 67624p.
22. Kolevatova, V. S. *Zh. Prikl Khim. (Leningrad)* **1975**, *48*(10), 2216; *Chem. Abs.* **1976**, *84*, 10323f.
23. Kolevatova, V. S.; Korobkov, V. I. *Zh. Prikl. Khim.* **1976**, *49*(1), 86; *Chem. Abs.* **1976**, *84*, 127942y.
24. Ahmad, Z.; Ghafelchbashi, M.; Categh, S.; Jahanfar, S. *Met. Corros. Ind.* **1975**, *50*(599–600), 271; *Chem. Abs*. **1976**, *85*, 36459a.
25. Patel, N. K.; Patel, M. M.; Patel, K. C. *Chem. Era.* **1975**, *10*(12), 24; *Chem. Abs*. **1976**, *84*, 77811.
26. Patel, N. K.; Patel, M. M.; Patel, L. N.; Mehta, S. H. *Chem. Era.* **1976**, *12*(2), 46; *Chem. Abs*. **1977**, *86*, 32773.
27. Tupikin, E. I.; Klyuchnikov, N. G.; Verzilina, M. K. *Zashch. Metallov.* **1974**, *10*(1), 65; *Chem. Abs.* **1974**, *81*, 53488.
28. Tupikin, E. I.; Klyuchnikov, N. G. *Izv Vyssh Uchebn. Zaved. Khim Khim Tekhnol.* **1977**, *20*(5), 790; *Chem. Abs.* **1977**, *87*, 92514.
29. Gleizer, M. M.; Tseitlim, Kh. L.; Sorokin, Yu. L.; Isaenko, G. I.; Babitskara, S. M. *Zashch. Metallov.* **1976**, *12*(5), 629; *Chem. Abs*. **1977**, *86*, 94505.
30. Gerasyutina, L. I.; Tulyupa, F. M.; Gromova, N. L.; Koryaka, L. G. *Zashch. Metallov.* **1976**, *12*(2), 195; *Chem. Abs.* **1976**, *85*, 98142a.
31. Eberhard, J. F.; Oakes, B. D. (Dow Chemical Co.), US Patent 3,037,934, June 5, 1962; *Chem. Abs.* **1962**, *57*, 6970a.
32. Eberhard, J. F. U.S. Patent 2,963,439, Dec. 6, 1960; *Chem. Abs.* **1961**, *55*, 10294.
33. Uzlyuk, M. V.; Fedorov, Yu, V.; Pinus, A. M.; Tolstykh, V. F.; Panfilova, Z. V.; Shatukhina, L. I.; Miskidzh'van, S. *Zashch. Metallov.* **1977**, *13*(2), 212; *Chem. Abs.* **1977**, *86*, 162689j.
34. Mahan, J. E.; Stahl, R. A. (Phillips Petroleum Co.), US. Patent 2,769,690, Nov. 6, 1956; *Chem. Abs.* **1957**, *51*, 3430c.
35. Standford, J. R. (Nalco Chemical Co.), US Patent 3,585,136, June 15, 1971; *Chem. Abs.* **1971**, *75*, 83570h.
36. Desai, M. N. *Werkstoffe Korros.* **1972**, *23*, 483.
37. Desai, M. N.; Shah, V. K. *Corros. Sci.* **1972**, *11*, 725.
38. Desai, M. N.; Thanki, G. H. *J. Electrochem. Soc. India.* **1972**, *21*(1), 13; *Chem. Abs.* **1972**, *76*, 161550p.
39. Desai, M. N.; Joshi, J. S. *J. Inst. Chem. Calcutta* **1972**, *44*(4), 138; *Chem. Abs.* **1973**, *78*, 51603s.
40. Desai, M. N.; Thanki, G. H. *Labdev. Part A.* **1972**, *10*(2), 73; *Chem. Abs.* **1973**, *79*, 26416w.
41. Desai, M. N.; Rana, S. S. *Anti-Corrs. Methods Mater.* **1973**, *20*(5), 16; *Chem. Abs.* **1973**, *79*, 86712z.
42. Desai, M. N.; Rana, S. S. *Anti-Corros. Methods Mater.* **1973**, *20*(6), 16; *Chem. Abs.* **1973**, *79*, 11103m.
43. Desai, M. N.; Shah, D. K.; Gandhi, H. M. *Br. Corros. J.* **1975**, *10*(1), 39.
44. Desai, M. N.; Shah, D. K. *Vidya B.* **1976**, *19*(2), 226; *Chem. Abs*. **1978**, *88*, 77679c.
45. Desai, M. N.; Thaker, B. C.; Chhaya, P. M. *J. Indian Chem. Soc.* **1975**, *52*(10), 950; *Chem. Abs*. **1976**, *84*, 97026.
46. Desai, M. N.; Thanki, G. H.; Shah, D. K. *Anti-Corros. Methods Mater.* **1971**, *18*(10), 8; *Chem. Abs*. **1972**, *76*, 67228t.
47. Desai, M. N.; Thaker, B. C.; Patel, B. M. *J. Electrochem. Soc. India.* **1975**, *24*(4), 84; *Chem. Abs*. **1976**, *84*, 139675u.
48. Desai, M. N.; Rana, S. S. *Anti-Corros. Methods Mater.* **1973**, *20*(5), 16; *Chem. Abs.* **1973**, *79*, 86712z.
49. Patel, M. M.; Patel, N. K.; Vora, J. C. *India J. Technol.* **1974**, *12*(10), 469; *Chem. Abs*. **1975**, *82*, 78400t.
50. Patel, M. M.; Patel, N. K.; Vora, J. C. *J. Electrochem. Soc. India.* **1978**, *27*(3), 171; *Chem. Abs*. **1979**, *90*, 129380m.
51. Keller, H.; Risch, K. *Workstoffe Korros.* **1964**, *15*, 741.
52. Vosta, J.; Pelikan, J.; Smrz, M. *Workstoffe Korros.* **1974**, *25*, 750.
53. Pearlstein, F.; Weightman, R. F. US NTIS, AD Rep. AD-A 14163, 1975; *Chem. Abs.* **1976**, *84*, 183167.
54. Anderson, J. D.; Hayman, E. S., Jr.; Rodzewich, E. A. (Amchem. Products Inc.), U.S. Patent 3,992,313, Nov. 16, 1976, *Chem. Abs.* **1977**, *87*, 139496.
55. Maksimenko, M. N.; Podobaev, N. I. *Ingibitory J. Corros. Met.* **1972**, 78; *Chem. Abs.* **1976**, *84*, 48406.
56. Uzlyuk, M. V.; Fedorov, Yu. V.; Voloshin, V. F.; Panfilova, Z. V.; Shatukhina, L. I.; Aleinikova, L. G. *Zashch. Metallov.* **1973**, *9*, 446; *Chem. Abs*. **1974**, *80*, 51152.
57. Malowan, J. E. (Monsanto Chem. Co.) U.S. Patent 2,567,156, Sept. 4, 1951; *Chem. Abs.* **1952**, *46*, 876e.
58. Talati, J. D.; Pandya, J. M. *Anti-Corros. Methods Mater.* **1974**, *21*(2), 7; *Chem. Abs*. **1975**, *83*, 17561.
59. Talati, J. D.; Pandya, J. M. *Corros. Sci.* **1976**, *16*, 603.
60. Ignatov, B. P.; Anoshenko, I. P.; Pyaterikov, V. V.; Luk'vanova, G. I.; Nechepurenko, E. A. *Tr. Novocherk, Politek. Inst.* **1975**, *285*, 41; *Chem. Abs.* **1975**, *82*, 130921.
61. NACE Task Group T-3M-4. *Industrial Cleaning Manual*; NACE: Houston, TX, 1982; *Corros. Abs.* **1982**, *21*(6), 376.
62. Clark, H. D. (Universal Oil Products Co.) U.S. Patent 3,969,260, July 13, 1976; *Chem. Abs.* **1976**, *85*, 165428; U.S. Patent 3,979,311, Sept. 7; *Chem. Abs.* **1976**, *85*, 182249.
63. Frenier, W. W. (Dow Chemical Co.) U.S. Patent 4,310,435, Jan. 12, 1982.
64. Jones, J.; Geldner, J. (Metallgesellschaft AG): Ger. Offen. 2,616,144, Nov. 3, 1977; *Chem. Abs.* **1978**, *89*, 10126.
65. Constantinescu, A.; Cracium, D. C. *Rev. Coroz.* **1971**, *1*, 206; *Chem. Abs*. **1972**, *77*, 37989.
66. Keeney, B. R.; Johnson, J. W., Jr. (Halliburton Co.) U.S. Patent 3,773,465, Nov. 20, 1973; *Chem. Abs.* **1974**, *80*, 136319.
67. Keeney, B. R.; Johnson, J. W.; Jr. *Mater. Prot. Perfom.* **1973**, *12*(9), 13; *Chem. Abs*. **1974**, *87*, 104314.
68. Redmore, D. (Petrolite Corp.) U.S. Patent 3,997,293, Dec. 14, 1976; *Chem. Abs.* **1977**, *88*, 107770; U.S. Patent 3,998,883; *Chem. Abs.* **1977**, *87*, 84823; U.S. Patent 4,089,650; *Chem. Abs.* **1977**, *87*, 109012.
69. Sastri, V. S. *Corrosion Inhibitors*; Wiley: Chichester, UK, 1978.
70. Sastri, V. S.; Perumareddi, J. R.; Elboujdaini, M. *Corrosion* **2008**, *64*, 657.
71. Lui, A. W.; Sastri, V. S.; Elboujdaini, M.; McGoey, J. *Br. Corros. J.* **1996**, *31*, 158.
72. Naganathan, K.; Guruviah, S.; Rajagopalan, K. S. *Paint India Annual* **1965**, *15*(1), 78.
73. Guraviah, S.; Rajagopalan, K. S. *Paint India* **1968**, *16*(8), 28.
74. Selvaraj, M.; Guruviah, S. *Paint India* **1987**, *37*(8), 27.
75. Chakrabarthy, B. R.; Verma, K. M. *Corr. Prevent. Control* **1987**, *34*(5), 127.
76. Gomathi, H.; Chandrasekaran, V.; Guruviah, S.; Narasimhan, K. C.; Udupa, H. V. K. In Proceedings of the 2nd National Conference on Corrosion and its Control **1979**; p 205.
77. Seavell, A. J. *J. Oil Colour Chem. Assoc.* **1978**, *61*, 439.
78. Knowles, E.; White, T. *J. Oil Colour Chem. Assoc.* **1958**, *41*, 10.
79. Franiau, R. *Cong. Colloq, Univ. Liège.* 1973, 129.
80. Ross, T. K.; Francis, R. A. *Corros. Sci.* **1978**, *18*, 351.
81. Deslauriers, P. T. *Mater. Perform.* **1987**, *11*, 35.
82. Gancedo, J. R.; Gracia, M. *Hyperf. Interact.* **1989**, *46*, 461.
83. Vacchini, D. *Anticorr* **1985**, *9*, 9.
84. Nmai, C. K.; Farrington, S. A.; Bobrowski, G. S. *Concrete Int.* **1992**, 45–51.

85. Anoschenko, I. P.; Puzey, E. V.; Tulenev, A. N. In Proceedings of the 8th European Symposium on Corrosion Inhibitors, University of Ferrara, 1995; Vol. 1, p 609.
86. Wieczorek, G.; Gust, J. In Proceedings of the 8th European Symposium on Corrosion Inhibitors, University of Ferrara, 1995; Vol. 1, p 599.
87. Miksie, B.; Gelner, L.; Bjegovic; Sipos, L. In Proceeding of the 8th European Symposium on Corrosion Inhibitors, University of Ferrara, 1995; Vol. 1, p 569.
88. Balezin, A.; Belen'kii, S. M.; Aronson, Yu. P.; Belen'kaya, N. M. *Zashch. Mettalov* **1968**, *4*(4), 385; *Chem. Abs.* **1968**, *69*, 109104.
89. Riggs, O. L.; Morrison, K. L.; Brunsell, D. A. *Corrosion* **1979**, *35*, 356.
90. Oude-Alink, B. A. (Petrolite Corp.) U.S. Patent 3,984,203, Oct. 5, 1977; *Chem. Abs.* **1977**, *87*, 104314.
91. Berke, N. S. In ASTM STP 906; American Society for Testing and Materials, Philadelphia, PA, 1986, pp 78–91.

4.27 Environmental Modification for Cooling, Heating and Potable Water Systems

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4.27.1 Introduction

Water has a relatively high heat capacity. In fact, water has the second highest heat capacity of any known substance, after ammonia, and is slow to absorb and reject heat. These properties are because of hydrogen bonding at the molecular level and make water valuable in cooling and heating processes and systems such as heating, ventilation, and air conditioning (HVAC) systems. Water is commonly employed as a heat transfer fluid, that is, a vehicle for transporting heat to some distant point of use, or away from a process, or for the uptake/removal of heat via a heat exchanger, cooling tower, or similar device.

The water may be employed in liquid, gaseous (steam), or solid (ice) form, depending upon the specific process. For example:

- liquid water is employed for HVAC condenser cooling;
- steam is the medium for many boiler plants;
- ice can be used in HVAC thermal energy storage systems.

However, all water sources ultimately employed for industrial process or in HVAC system applications, and even potable grade water contain a variety of contaminants, and as a result of a combination of the contaminants (including dissolved oxygen), the specific process operating conditions, and the materials of equipment construction, the water can act as a scale-forming or corrosive fluid.

Various forms of modification and active control of the process environment are usually necessary to maintain operational efficiency and reduce the potential for corrosion, fouling, or premature system failure. This is usually achieved through the selective use of filters, softening equipment, certain nonchemical devices, pH management, and/or the addition of specialty chemical inhibitors, together with appropriate technical overseeing.

Other heat transfer fluids, such as ethylene or propylene glycol, may be used under certain circumstances, for example where the fluid in a pipe is exposed to freezing winter temperatures. After prolonged usage, glycols may become corrosive because of thermal breakdown or microbial action, and modification of the fluid by, for example, raising the pH and adding a chemical inhibitor, may be necessary.

Water is also vital to the existence of all life forms, where it acts as a vehicle for the transport of essential minerals and vitamins to all parts of the organism. In developed societies potable water is delivered under pressure through pipes, and these pipes (especially metal pipes) together with pumps, valves, etc. may also be subject to scaling, fouling, or corrosive action. Thus, modification and active control of potable water systems to prevent corrosion and other problems may also be necessary. Here, we may choose to use less corrodible materials of construction, employ potable grade phosphate or silicate chemicals (for corrosion control or threshold stabilization of scale-forming alkaline earth salts), or use approved disinfection processes, such as chlorination, bromination, ozonation, or the application of chlorine dioxide from an on-site generator.

The active modification of an aqueous heating, cooling, or process environment (and usually that of other heat transfer fluids) to prevent or minimize corrosion, scaling, or biological or inorganic fouling, together with the provision of appropriate monitoring and control is termed ‘water treatment.’

4.27.2 Heat Capacity and Latent Heat

It has already been stated that a major benefit of using water in cooling, heating, and potable water systems is because of its high heat capacity. As more heat energy is required to increase the temperature of a substance with high specific heat capacity than to increase the temperature of one with a low specific heat capacity, from an engineering design position it is convenient for water to be employed as a vehicle for the transport of heat.

The measure of the heat energy required to increase the temperature of a unit quantity of a substance by a certain temperature interval is known as the specific heat capacity (the symbol is c), also known simply as specific heat. When measuring specific heat capacity in science and engineering, the unit quantity of a substance is often in terms of mass: either the gram or kilogram. For example, the heat energy required to raise water’s temperature by 1 K (equal to 1 °C) is $4184\,\mathrm{J\,kg^{-1}}$ – the kilogram being the specified quantity. This is at a sea-level pressure of one standard atmosphere (101.325 kPa) – approximately a bar (which is 100 000 Pa) and a temperature of 15 °C. Scientifically, this measure would be expressed as $c = 4184\,\mathrm{J\,kg^{-1}\,K^{-1}}$.

- The specific heat capacity of liquid water is $4.184\,\mathrm{kJ\,kg^{-1}\,K^{-1}}$.

- The specific heat capacity of water vapor is 1.996 kJ kg^{-1} K^{-1}.
- The specific heat capacity of ice is 2.108 kJ kg^{-1} K^{-1}.

In the United States, which tends not to commonly use SI units, the specific heat of water is defined as the amount of heat necessary to increase the temperature of one pound of water by 1 °F, and is given as 1 British Thermal Unit (Btu).

When thermal energy is withdrawn from a liquid such as water, or a solid such as ice, the temperature falls, as in a chiller plant, a cooling tower, or an evaporative condenser. When you add heat energy the temperature rises, as in a boiler. If sufficient energy is withdrawn or added, a change of state can occur, as in a steam-raising boiler (steam generator). To go from liquid to solid, the molecules of a substance must become more ordered. To maintain the order of a solid, extra heat must be withdrawn. In the other direction, to create disorder on going from solid crystal ice to liquid water, extra heat must be added.

The enthalpy of vaporization (the symbol is ΔH_v), also known as the heat of vaporization or latent heat of evaporation, is the energy required to transform a given quantity of a substance into a gas. It is often measured at the normal boiling point of a substance, although tabulated values are usually corrected to 298 K.

The enthalpy of fusion (the symbol is ΔH_{fus}), also known variously as the latent heat of fusion, the enthalpy change of fusion, or the specific melting heat, is the amount of thermal energy which must be absorbed or evolved for 1 mol of a substance to change state from a solid to a liquid or vice versa. The temperature at which it occurs is called the melting point and at this point, extra energy is required (the heat of fusion).

- The heat of vaporization of water is 2260 kJ kg^{-1}.
- The heat of fusion of water is 333.55 kJ kg^{-1}.

In the United States, the latent heat of fusion is usually defined in non-SI units, and is given as the amount of heat required to change one pound of a given substance from solid to liquid state without change in temperature. It requires 144 Btu to change one pound of ice at 32 °F to one pound of water at 32 °F, the heat of fusion of ice being 144 Btu per pound.

Also, the latent heat of vaporization in non-SI units is defined as the amount of heat required to change one pound of a given substance from liquid to vapor state without change in temperature. It requires a considerable amount of additional heat energy (970 Btu) to change one pound of water from 212 °F to 1 pound of steam at 212 °F. This high energy input requirement is again because of hydrogen bonding, and results in steam occupying 20 600 times the volume of liquid water at 100 °C (212 °F). The steam, usually under high pressure, is available both as a medium for transporting heat energy and for mechanical work (as in steam engines, steam pumps, and for turning turbine blades in the generation of electrical energy).

In North American refrigeration and air conditioning applications, 1 'ton of cooling' is a common unit, and is 12 000 Btu h^{-1}. It is the amount of power needed to melt one ton of ice in 24 h, and is approximately 3.51 kW. Cooling towers, boiler plants, and chiller plants are commonly rated in tons.

4.27.3 The Use of Water in Industrial Cooling and Heating Systems and Potable Applications

Global withdrawal rates of freshwater continue to grow at more than double the rate of population growth.[1] Withdrawal rates of estuarine and salt water also continue to grow at a similar rate. Unfortunately, freshwater availability and distribution is not divided up fairly or evenly around the globe and this has created difficulties in developing countries.

Where water is conserved by being reused in industrial processes, such as employing treated waste water as a makeup stream for a cooling tower, there is a significant benefit in terms of a reduced need for potable grade water, but the contaminants create increased risks of corrosion and scale. Thus, to ensure clean waterside conditions and optimum operational efficiencies, active modification of the process environment is necessary to control the risks, yet still obtain the benefits of water recycling.

Slightly less than 5000 km^3 of freshwater is available globally for production of potable quality water and for general commercial and industrial applications[2] ($1\ km^3 = 264.2 \times 10^9$ US gallon). Half the world exists on only 95 l day^{-1} (25 US gallon per day) but in developed countries water consumption is much higher, for example consumption in the USA per capita is around 5.1 m^3 day^{-1} (1350 US gallon per day), of which personal use accounts for 0.53 m^3 day^{-1} (140 US gallon per day).[3,4] Much of the water consumed is used for agricultural purposes (typically 50–60% or more), especially irrigation, with water for industrial and potable use being significantly lower.

A closer look at, for example, the United States' estimated 408 billion gallons per day ($1.54 \times 10^9\ \mathrm{m^3\ day^{-1}}$) use of freshwater shows the following breakup[3,4]:

- Agriculture accounts for some 49% of this consumption (200 billion gallons per day), with 160 billion gallons per day being used for irrigation purposes (although water for irrigation in California may be as high as 80%).
- Public supply, delivering water to homes, businesses, and industry is some 11% (45 billion gallons per day).
- Self-supplied industrial users, together with mining, livestock producers, aquaculture, and domestic wells account for 7% (29 billion gallons per day).
- Thermoelectric power generation is the primary user of the balance of surface freshwater consumed, at around 134 billion gallons per day or 33% of the total.[5]

US thermoelectric power generators also use more than 61 billion gallons per day of saline water for once-through cooling. So, total water withdrawal rates for the US thermoelectric power industry are 195–200 billion gallons per day.[5] Most of this is used for cooling water duty, although some water is required for boiler feed, ash handling, and other functions. (Heavy industrial processors also withdraw significant quantities of saline water for once-through use – again primarily for cooling water duty.)

Wet cooling requirements are about 25 gal $\mathrm{kWh^{-1}}$ of electricity generated, although once-through cooling systems typically require 37.7 gal $\mathrm{kWh^{-1}}$, whereas recirculating cooling water processes only require 1.2 gal $\mathrm{kWh^{-1}}$.[6] This dramatic saving in water is the primary reason for the extensive and global use of cooling towers for all types of application. Again, however, the savings in water consumption also create a risk, as the contaminants present in the cooling water concentrate as 'pure' water evaporates from the tower and fresh makeup brings additional contaminants with it, which can reach saturation levels and result in scale, fouling and corrosion problems, if left uncontrolled.

Apart from the power industry, it can be seen that the various businesses and industry in the United States collectively use about 45 billion gallons of water per day ($170.3 \times 10^6\ \mathrm{m^3\ day^{-1}}$). Globally, water consumption for similar activities is perhaps 200 billion gallons per day ($757 \times 10^6\ \mathrm{m^3\ day^{-1}}$).

Often more than 50% of this total water consumption is for heating and cooling purposes, so there exists, not only a great opportunity for further reduction, recycling and reuse of water, but the potential for a wide range of scaling, fouling, and corrosion problems to develop! The risk of waterside problems are a constant threat to process operating efficiency and costs, and to the quality of potable water supplies, necessitating a proactive approach to modification and control of water system environments, that is, an active water treatment program.

Eight examples of heating, cooling, and potable equipment using water are shown in Photos 1(a)–1(h).

4.27.4 The Need for Water Treatment to Control Waterside Heating, Cooling and Potable Water Environments

Water treatment encompasses a wide range of technologies and activities designed to prevent serious corrosion, failures, and malfunction of equipment using or delivering water, and to ensure the heath and safety of operators and other personnel who may come into contact with or use the water.

Water is a universal solvent. Whenever it comes into contact with a foreign substance, there is some dissolution of that substance. Some substances dissolve at faster rates than others, but in all cases a definite interaction occurs between water and whatever it contacts. It is because of this interaction that problems occur in equipment such as boilers or cooling-water systems in which water is used as a heat-transfer medium. In systems open to the atmosphere, corrosion problems are made worse by additional impurities picked up by the water from the atmosphere and can have a devastating effect on equipment such as heat exchangers, cooling towers, valves, pumps, etc.

Corrosion alone is a major cause of failure and costly replacement of equipment and so is itself a good reason why water treatment is necessary. As a result, environmental maintenance, surveillance, and the application of water treating equipment, chemistries and controls are required of almost all water systems, including cooling towers and evaporative condensers, especially in view of the awareness of the risks of infection that may result from systems that are poorly designed, dirty, and/or badly maintained.

The risks of waterborne infection from bacterial organisms such as Legionella species are not limited to cooling systems, but can emanate from almost any type of building facility water systems, especially domestic hot and cold water services. Also, pools, spa baths, showers, and humidifier pans are sources of microbial contamination, as are HVAC systems that are poorly maintained or not cleaned on a regular basis. Microbial growth in HVAC water tanks and pans is distinct from, but may also be linked to problems developing in air handling systems – which typically involve mold organisms such as *Aspergillus* sp. or *Stachybotrus* sp. (the same organisms that can proliferate behind damp sheetrock walls and insulation).

For water treatment to be effective it is necessary to understand the problems water and its

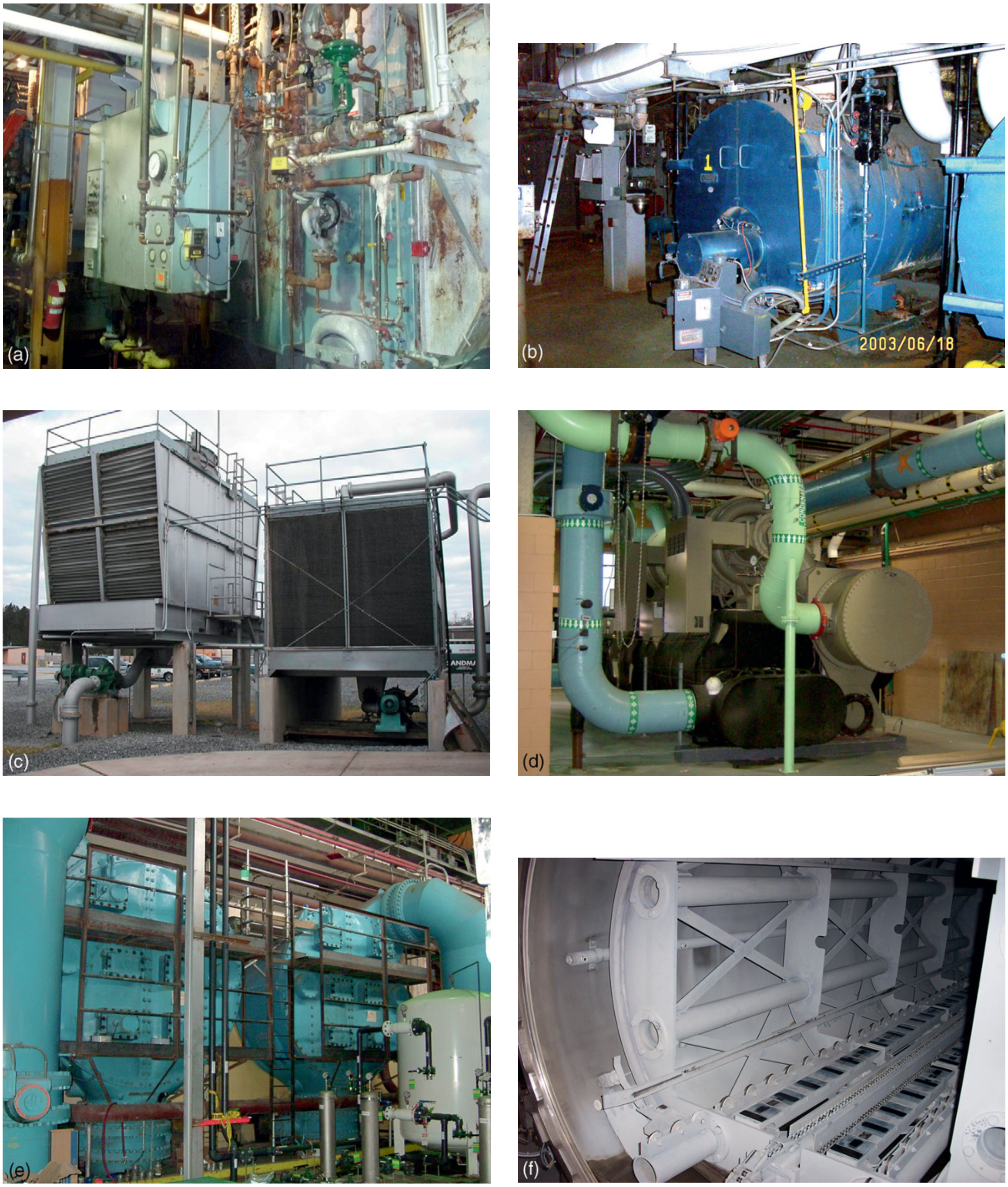

Photo 1 Continued

Photo 1 (a) D-type, 2 drum watertube boiler, (b) firetube boiler, (c) cooling towers, (d) chiller plant, (e) surface condenser, (f) retort cooker; (g) domestic water storage tanks, (h) hotel hot water storage vessels.

contaminants can cause, the mechanisms by which water causes these problems, and the effects that result. A review of the results of analysis of the contaminants in any particular water, plus a thorough understanding of the chain of cause and effect leads to a diagnosis of the potential or actual problems, and from there a solution may be found. The solution may be based on a 'standard' item of equipment, chemistry, or operational protocol or local environmental control, but is usually tailored in some way to meet the specialized and often unique operating conditions that may be found.

Corrosion is a pervasive problem and the direct losses because of corrosion of metals for replacement and protection globally are staggering, and as most costs studies available only look at the direct costs, the true costs are even higher. Indirect costs of corrosion include the costs of labor for repairs and corrosion management, temporary equipment, loss of revenue, and reliability. Annual direct costs because of corrosion in the United States have been reliably estimated at $276 billion in a study published by NACE International.[6] Examples of these costs include the following:

- drinking water and sewer water systems: $36 billion per year;
- production and manufacturing industry: $17.6 billion per year; and
- electrical utilities: $6.9 billion per year.

Another report, measuring the impact of corrosion in the US Department of Defense (DOD),[7] found that the annual cost of corrosion ranged from $10 billion to $20 billion in direct maintenance costs, with the annual cost of corrosion to Navy ships being $2.43 billion.

Protection against corrosion may include organic coatings, cathodic and anodic protection, use of more resistant alloys, and water treatment products (such as corrosion inhibitors) and services. Water treatment is usually focused on modifying the waterside environment by rendering the water less scale-forming or corrosive, and by use of inhibitors which act at the metal–water interface to form a passive chemical barrier composed of an oxide, carbonate, silicate, molybdate, hydroxide, phosphate, phosphonate, etc.

The formation of scale and deposits, sludges, and biological foulants are other problems that can increase operating costs, and reduce efficiency and the economical service life of equipment such as HVAC systems. There is no reason to believe that the maintenance and additional energy costs associated with scaling and fouling problems are not at least as high as those associated with corrosion. Photos 2(a) and 2(b) show the results of corrosion and deposition in pipes.

Scale formation is insidious and will interfere with the normal efficient transfer of heat energy from one side to the other of a heat exchanger. The degree of interference with this transfer of heat is called the fouling factor. Manufacturers' recommended design fouling-factor for air-conditioning chillers and condensers is usually 0.000 5. In HVAC systems, high fouling factors cause an increase in condensing temperature of the refrigerant gas which, in turn, increases energy requirements to compress the refrigerant at that higher temperature. It can be seen from Figure 1 that there is a significant increase in condensing temperature with increase in fouling factor.

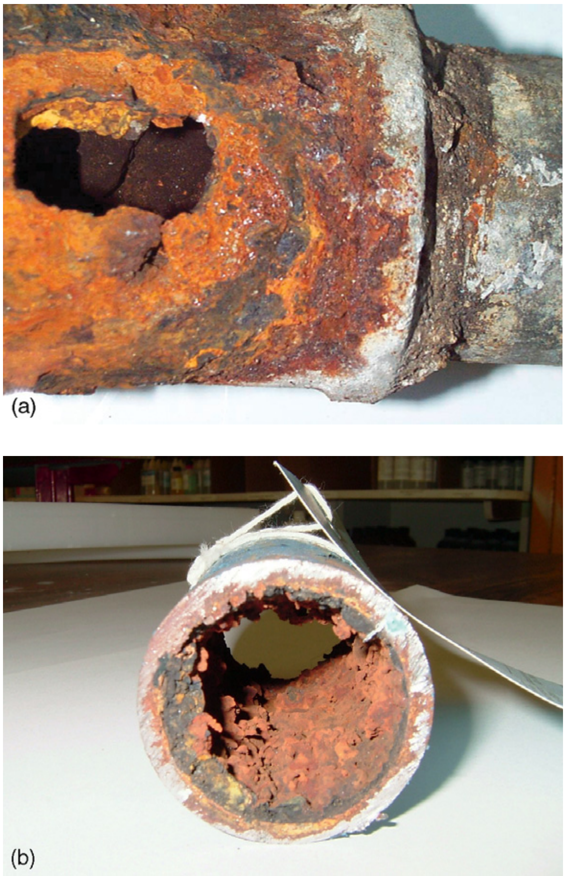

Photo 2 (a) Pipe metal wastage because of corrosion and (b) pipe deposits due primarily to scaling, but also corrosion.

Where scales or deposits occur in boilers, they are often also associated with under deposit and pitting-types of corrosion, and can consist of various substances including iron, silica, calcium, magnesium, carbonates, sulfate, and phosphates. Each of these, when deposited on a boiler tube, contributes in some degree to the insulation of the tube, which reduces the rate of heat transfer from the hot gases or fire through the boiler metal to the boiling water. This leads to an increase in the temperature of the boiler tube and can result in metal bulges, blisters, and eventually, boiler failure and possibly an explosion.

4.27.5 The Hydrologic Cycle and Water Chemistry

As discussed earlier, water and its contaminants are responsible for the corrosion of metals and formation of deposits on heat-transfer surfaces, which in turn reduce efficiency, waste energy, and increase costs. The effects of corrosion and deposits have been illustrated in the earlier pictures and in order to see how these problems can be prevented, it is first necessary to understand their basic causes, why and how they occur. This understanding starts with a review of the hydrologic cycle (see Figure 2).

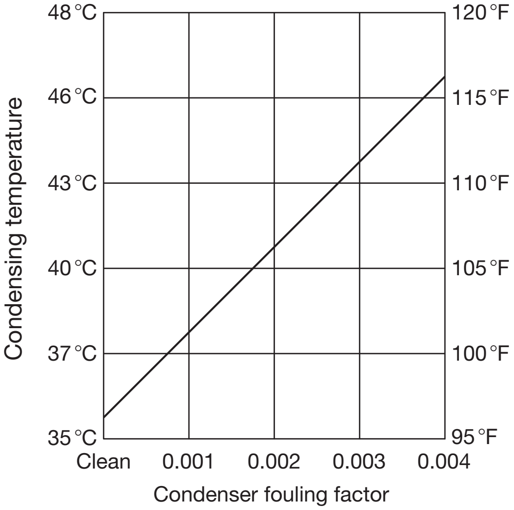

Figure 1 Effect of scale on condensing temperature.

The hydrologic cycle consists of three stages: evaporation, condensation, and precipitation, and begins when the rays of the sun heat surface waters on the earth, which vaporize and rise into the troposphere, a thin layer of air and moisture approximately 11 km (7 miles) thick surrounding the earth. Clouds of condensed moisture form in the troposphere and contact cold air currents when carried over land by the wind, causing precipitation, such as rain or snow. In this manner, water returns to the earth's surface, only to repeat the cycle. Throughout the hydrologic cycle, the water absorbs impurities.

The concentration of inorganic and organic contaminants, and greenhouse gases in the atmosphere varies depending on geographic location, the sources of pollution (such as basic industrial facilities, fossil-fueled utility power generators, and high density cities and their automobiles), and the weather patterns, including prevailing winds and air currents. Rainwater, containing these contaminants and dissolved gases, is often at a pH of below 7.0 (i.e., slightly acidic) and in contact with the earth surface, it will tend to dissolve and absorb many of the minerals of the earth via reactions including hydrolysis and hydration. The reaction rate with the earth's minerals

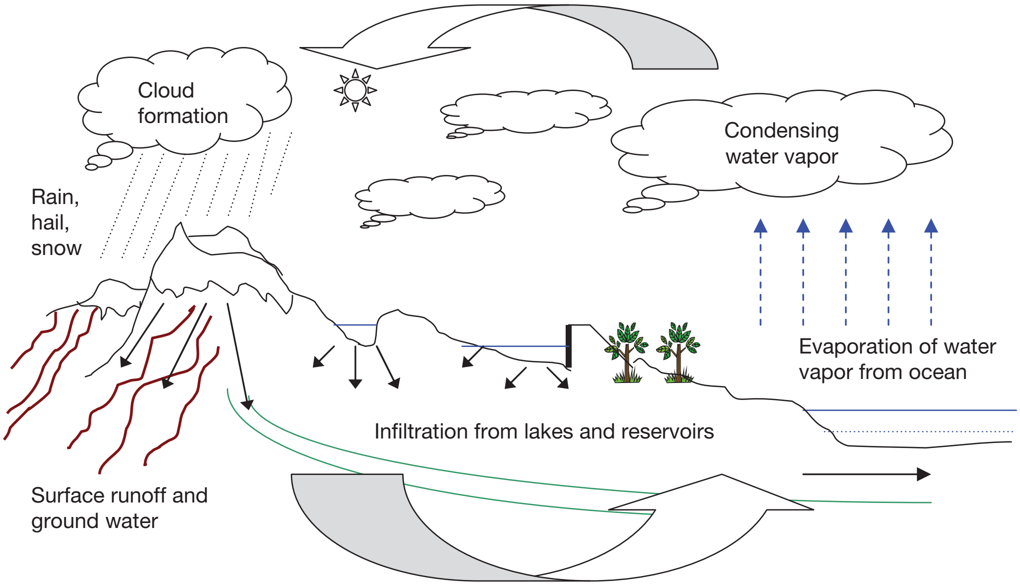

Figure 2 Hydrologic cycle.

(such as gypsum, calcite, dolomite, and quartz) is increased with more acidic rainfall, and calcium, silica, magnesium, iron, minerals, etc. are dissolved. As a general rule (although there are numerous exceptions):

- Surface water in lakes, rivers, streams, ponds, and reservoirs usually contain fewer minerals but more dissolved gases.
- Underground water supplies are a result of surface waters' percolation through the soil and rock, and usually contain higher concentrations of minerals and less dissolved gases.

While falling through the atmosphere, water dissolves gases such as oxygen, nitrogen, carbon dioxide, nitrogen oxides, sulfur oxides, and other trace elements and polluting chemicals. The quantity of dissolved gases in water is governed by Henry's Law of partial pressures, and the solubility of these gases in water decreases with increasing temperature. Gases found in water include the following:

- *Carbon dioxide.* In the earth's atmosphere carbon dioxide is considered a trace gas, and currently occurs at an average concentration of about 385 mg l^{-1} (parts per million) by volume or 582 mg l^{-1} by mass.[8] It is present in both surface and underground water supplies as a dissolved gas. Surface waters normally contain less than 10 ppm free carbon dioxide, while some ground waters may easily exceed that concentration. Carbon dioxide is readily soluble in water forming the weak acid, carbonic acid, as follows:

$$\underset{\text{Carbon dioxide}}{CO_2} + \underset{\text{Water}}{H_2O} \rightarrow \underset{\text{Carbonic acid}}{H_2CO_3}$$

Over the ordinary temperature range (0–30 °C) its solubility is about 200 times that of oxygen. Calcium and magnesium combine with carbon dioxide to form carbonates and bicarbonates. Larger amounts of carbon dioxide are absorbed from the decay of organic matter in the water and its environs. Carbon dioxide contributes significantly to corrosion by making water acidic. This increases its capability to dissolve metals in boiler plant (especially steam condensate systems, and cooling systems). The breakdown of calcium bicarbonate with the release of carbon dioxide under conditions of stress and increase of the concentration of contaminants, because of evaporation processes, are the primary reasons for the increase in cooling water pH during operation.

- *Oxygen.* Oxygen gas (dioxygen O_2) is the second most common component of the Earth's atmosphere taking up 21.0% of its volume and 23.1% of its mass and is essential for life. The allotrope ozone (trioxygen O_3) is produced in the upper atmosphere. It is very reactive and near the earth's surface it is a pollutant formed as a by-product of automobile exhaust.[9] However, oxygen is the basic factor in the corrosion process and is, in fact, one of the essential elements in the corrosion process of metals. Therefore, dissolved oxygen in water is important to us in the study of corrosion and deposits. In cold water it is present at 8–9 mg l^{-1}.

- *Sulfur oxides*. Sulfur oxide gases are present in the atmosphere as pollutants from the combustion of fuels containing sulfur, such as coal and fuel oil. In large urban areas, the quantity of sulfur oxides that are absorbed by surface water supplies and aerated waters used in cooling towers can be significant. Also when dissolved in water, sulfur oxides form acids which create a corrosive atmosphere.

SO_3	+	H_2O	→	H_2SO_4
Sulfur trioxide		Water		Sulfuric acid

- *Hydrogen sulfide*. The odor typical of rotten eggs, which is found in some water, is because of the presence of hydrogen sulfide. This gas comes from decaying organic matter and from sulfur deposits, and is a constituent of sewer gas, marsh gas, and coal gas. Hydrogen sulfide reacts with water to form hydrosulfuric acid, a slightly acidic solution. It can be present in water but because of its acidic reaction, it is very corrosive and must be removed or neutralized. Hydrogen sulfide forms when acidic water reacts with sulfide minerals such as pyrite (iron sulfide).

FeS	+	$2H^+$	→	Fe^{2+}	+	H_2S
Ferric sulfide		Acid in solution		Iron in solution		Hydrogen sulfide

- *Nitrogen oxides*. Nitrogen oxides are also present in the atmosphere, both naturally and from pollutants created by the combustion process. These also form acids when absorbed by water, and contribute to the corrosion process.

$3NO_2$	+	H_2O	→	$2HNO_3$	+	NO
Nitrogen dioxide		Water		Nitric acid		Nitric oxide

When rainwater, containing carbonic acid (resulting from the reaction between dissolved carbon dioxide gas and water), reaches chalk or limestone strata, it will dissolve some of the mineral forming the soluble salt calcium bicarbonate, as shown in the reaction below. The presence of this salt is of particular importance where water is employed for any type of heat transfer duty, as under heat load conditions it can quickly breakdown and produce scale on the heat-transfer surfaces. Scale inhibits the efficient transfer of heat and also provides an environment for problems of underdeposit corrosion to develop. Thus, modification of the local waterside environment ('water treatment') is required to prevent this common but costly problem.

CO_2	+	H_2O	→	H_2CO_3
Carbon dioxide (in the air)		Water vapor		Carbonic acid (weak acid)

H_2CO_3	+	$CaCO_3$	→	$Ca(HCO_3)_2$
Carbonic acid (rain)		Chalk or limestone (dissolves)		Calcium bicarbonate (mgl^{-1}solution)

Apart from the dissolved gases discussed above, contaminants in water will typically include various common dissolved minerals and/or salts. Some of the common minerals that may be dissolved in water include the following:

- silicates, for example, quartz, augite, mica, chert, feldspar, hornblende;
- carbonates, for example, calcite, dolomite, limestone;
- halides, for example, halite, fluorite;
- oxides, for example, hematite, ice, magnetite, bauxite;
- sulfates, for example, anhydrite, gypsum;
- sulfides, for example, galena, pyrite;
- natural elements, for example, copper, sulfur, gold, silver; and
- phosphates, for example, apatite.

Any or all the above may enter into solution as the mineral or a related salt, and are considered contaminants, although some of them may be desirable in potable water (to provide taste and minerals necessary for good health). Some common dissolved minerals and salts found in water include the following:

- calcium bicarbonate: $Ca(HCO_3)_2$;
- calcium chloride: $CaCl_2$;
- calcium sulfate: $CaSO_4$;
- calcium carbonate: $CaCO_3$;
- magnesium bicarbonate: $Mg(HCO3)_2$;
- magnesium chloride: $MgCl_2$;
- magnesium sulfate: $MgSO_4$.
- sodium bicarbonate: $NaHCO_3$;

- sodium chloride: NaCl;
- sodium phosphate: Na_3PO_4;
- sodium sulfate: Na_2SO_4;
- ferrous bicarbonate: $Fe(HCO_3)_2$;
- manganous bicarbonate: $Mn(HCO_3)_2$;
- silica: SiO_2;
- silicic acid: H_2SiO_3; and
- sodium silicate: Na_2SiO_3.

The concentration of these species are usually in the milligrams per liter (parts per million) range, and are regularly tested in all waters used in industrial cooling and heating systems. Also, pH and the various forms of alkalinity are tested. For potable use and more critical industrial and process applications, the water will be tested for trace organics present and other low-level contaminants – which may only be present in the microgram per liter (part per billion) range – as well as some of the dissolved gases. Table 1 is an example of a typical, but basic, water analysis report.

Common tests include the following:

- *Alkalinity.* Alkalinity is the quantity of dissolved alkaline earth minerals expressed as calcium carbonate. It is the measured carbonate and bicarbonate minerals calculated as calcium carbonate, as that is the primary alkaline earth mineral contributing to alkalinity. Alkalinity is also measured and calculated as the hydroxide when that is present. All natural waters contain some quantity of alkalinity. It contributes to scale formation because its presence encourages deposition of calcium carbonate or lime scale. However, the alkalinity content is important in modifying the corrosive behavior of water in both boiler plant and cooling system environments. Thus, titration of the various types of process waters found in heating and cooling systems for alkalinity concentration is regularly carried out by plant operators and water treatment company service providers. Calculation of the various forms of alkalinity can be obtained from using Table 2.
- *Phenolphthalein alkalinity* (P alkalinity) is that portion of the alkalinity titrated with acid to pH 8.2 end-point.
- *Total alkalinity* (or M alkalinity) is that portion of the alkalinity titrated with methyl orange to pH 4.2.
- *pH.* In practical terms, pH is the measure of the relative strength of acidity or alkalinity of water, and is a value calculated from the hydrogen-ion concentration in water. The pH scale is based on the negative decimal logarithm of the hydrogen ion activity in an aqueous solution and ranges from 0 to 14. Hence, because of the logarithmic nature of the scale, water with a pH value of 4.0 is 100 times more acid in strength than water with a pH value of 6.0. Water is corrosive, if the pH value is on the acidic side. It will tend to be scale-forming, if the pH value is alkaline. A pH of 7.0 is neutral and indicates a balance between acidity and alkalinity.

Table 1 Water analysis report sheet

Water Analysis:

Location	*Industrial water*	*City water*
Date of sampling		
Date of testing		
Parameter		
pH	9.2	7.5
P alkalinity, as $CaCO_3$ (mg l^{-1})	10	0
Bicarbonates, as $CaCO_3$ (mg l^{-1})	52	167
Carbonates, as $CaCO_3$ (mg l^{-1})	20	–
Hydroxides, as $CaCO_3$ (mg l^{-1})	–	–
M (total) alkalinity, as $CaCO_3$ (mg l^{-1})	72	167
Total hardness, as $CaCO_3$ (mg l^{-1})	159	149
Sulfate, as SO_4 (mg l^{-1})	181	
Silica, as SiO_2 (mg l^{-1})	7.7	10
Iron, as Fe (mg l^{-1})	0.3	0.1
Chloride, as NaCl (mg l^{-1})	23	187
Specific conductance (μS cm^{-1})	415	815
Total dissolved solids (mg l^{-1})	270	501
Molybdate, as Na_2MoO_4 (mg l^{-1})	–	–
Phosphate, as PO_4 (mg l^{-1})	1.0	0.1
Sulfite, as Na_2SO_3	–	–

pH is an important metric and increasing the concentration of dissolved minerals in a boiler water or cooling water, by permitting the release of steam or evaporation, results in a higher pH and less tendency for general corrosion processes to occur, but increases the risks of deposition of supersaturated salts.

By virtue of its logarithmic nature, pH is a dimensionless quantity. pH is defined in terms of the activity of hydrogen ions (H^+) in solution[10]:

$$\mathrm{pH} = -\lg[a(\mathrm{H}^+)] = -\lg[m(\mathrm{H}^+)\gamma_{\mathrm{m}}(\mathrm{H}^+)/m^{\ominus}$$

Table 2 Interpretation of ‘P’ and ‘M’ Alkalinity Titrations

Ions	*P = 0*	*P < M/2*	*P = M/2*	*P > M/2*	*P = M*
(OH)	0	0	0	2P – M	M
CO_3	0	2P	M	2(M – P)	0
HCO_3	M	M – 2P	0	0	0

Bicarbonates and hydroxides do not exist together. CO_2 does not exist with carbonates. ‘*P*’ Alkalinity = ½ carbonates and all hydroxides. ‘*M*’ Alkalinity = all hydroxides, carbonates and bicarbonates.

where $a(\mathrm{H}^+)$ is the activity of hydrogen ion (H^+) in aqueous solution; $\mathrm{H}^+(\mathrm{aq})$, $\gamma_{\mathrm{m}}(\mathrm{H}^+)$ are the activity coefficient of $\mathrm{H}^+(\mathrm{aq})$ (molality basis) at molality $m(\mathrm{H}^+)$; $m^{\ominus} = 1\mathrm{mol\ kg}^{-1}$, and is the standard molality.
Notes:

1. Molality is the number of moles of solute dissolved in 1 kg of solvent.
2. pH cannot be measured independently because calculation of the activity involves the activity coefficient of a single ion. Thus it can be regarded only as a notional definition.
3. The establishment of primary pH standards requires the application of the concept of ‘primary method of measurement,’ and involves the use of a cell without transference, known as the Harned cell.
   - *Hardness.* Hardness is the total calcium, magnesium, iron, and trace amounts of other metallic elements in water, which contributes to the ‘hard’ feel of water. Hardness is also calculated as calcium carbonate, because it is the primary component contributing to hardness. Hardness causes lime deposits or scale in equipment.
   - *Temporary hardness or carbonate hardness* can be removed by heating water to precipitate as carbonate salt (e.g., bicarbonates), equal to or less than the P alkalinity.
   - *Permanent hardness or noncarbonate hardness* is that portion of total hardness that cannot be removed by heating water (e.g., sulfate hardness), and is the difference between total hardness and total alkalinity.
   - *Iron, manganese, and alumina.* These dissolved or suspended metallic elements are present in water supplies in varying quantities. They are objectionable because they contribute to a flat metallic taste and form deposits. These soluble metals can react with oxygen in water exposed to the atmosphere, and form oxides which precipitate and cause cloudiness, or ‘red water.’ This red color, particularly from iron, causes staining of plumbing fixtures, sinks, and porcelain china and is a cause of common laundry discoloration.

- *Silica.* Silica is dissolved when water flows through sand or silica-bearing rock (such as quartz). Silica is the cause of very hard and tenacious scales that can form and cause severe heat-transfer problems. It is present, either dissolved in water as silicate or suspended in a very fine, invisible form, as colloidal silica.
- *Chlorides.* Chlorides are the sum total of the dissolved chloride salts of sodium, potassium, calcium, and magnesium present in water. Sodium chloride, which is common salt, and calcium chloride are the most common of the chloride minerals found in water. Chloride is a depassivating ion. It reduces the corrosion resistance of many metals, especially those that naturally and strongly passivate to form a protective oxide layer, such as stainless steels and aluminum, by attacking the passivated film.[11]

  High chloride waters will increase the risk of stress corrosion cracking in austenitic stainless steels (e.g., 304/304L, 316/316L) and will tend to increase both the general rate of corrosion and attack in localized areas, often causing pitting type corrosion. Corrosion from chlorides always tends to be more severe when the metal surface is shielded by foulants or semiporous deposits, such as silt and muds, as various forms of selective corrosion can take place with often very high concentrations of chloride forming under the deposit. The most logical environmental modification response, therefore, to using a makeup water source with high chlorides is to be scrupulous in maintaining clean metal surfaces in the cooling system. This can take the form of more frequent physical cleaning and the use of side-stream filters, polymer dispersants, and biodispersants. Raising the level of chemical inhibitor treatment is a further and usually beneficial response, although this may require a reevaluation of the cooling system economics.
- *Sulfates.* Sulfates are the dissolved sulfate salts of sodium, potassium, calcium, and magnesium in the water. They are present because of to dissolution of sulfate-bearing rock such as gypsum. Calcium and magnesium sulfate scale is very hard and difficult to remove and greatly interferes with heat transfer.

Sulfates are causative agents (along with oxygen, hydrogen, etc.) of the various types of concentration cell corrosion that results in pits, crevice attack, or tuberculation. They have reactions similar to chloride. In addition, and again similarly to chlorides, the presence of sulfate ions contributes strongly to increases in electrical conductivity and hence influences potential increases in corrosion rates. Sulfates are also involved in depassivation, especially where deposits or foulants are involved and can be reduced by selective microbial action (sulfate reducing organisms), that are almost always present in biofilms, producing deep pits of corroded steel.[11]

- *Total dissolved solids.* The total dissolved solids (TDSs) reported in water analyses are the sum of dissolved minerals including the carbonates, chlorides, sulfates, and all others that are present. The dissolved solids contribute to both scale formation and corrosion in heat-transfer equipment.
- *Suspended matter.* Suspended matter is finely divided organic and inorganic substances found in water. It is caused by clay silt and microscopic organisms, which are dispersed throughout the water, giving it a cloudy appearance. The measure of suspended matter is turbidity. Turbidity is determined by the intensity of light scattered by the suspended matter in the water.

4.27.6 Waterside Problems Resulting from Mineral Scales, Muds, and Sludges

Calcium carbonate scale is the most common and costly water-caused scaling problem encountered in industrial boilers, cooling systems, condensers, and HVAC equipments. Other scale components include calcium sulfate, phosphate, magnesium carbonate, iron, silica, and manganese. In most cases, scales contain a complex mixture of mineral salts because scale forms gradually and deposits the different minerals in a variety of forms.

Depending upon the specific boiler plant/cooling system/HVAC/potable waterside environment, mineral scales can develop on heat transfer surfaces in crystalline form (which is usually hard and tenacious) or in noncrystalline or amorphous form, which often is sludge-like and removable by high-pressure water jetting or similar cleaning process. Often, problems of scaling and deposits are accompanied by problems of corrosion as well. Corrosion can take place under scales and may be due, in part, to similar causes, such as a failure to preclean a water system, inadequate chemical treatment, or ongoing maintenance.

Many salts such as sodium chloride (table salt) are more soluble in hot water than in cold; however, calcium and magnesium salts have an inverse solubility and dissolve more readily and in greater quantity in cold water than in hot water. This property, as discussed earlier, is primarily responsible for the problem of mineral scale formation on heat-transfer surfaces in HVAC equipments. The high energy and maintenance costs that can result stems from the significant interference with heat transfer caused by water mineral scale deposits, corrosion, and the problems associated with the removal of scale deposits (usually requiring some form of acid cleaning).

As shown earlier, typically, calcium carbonate enters solution through the following reactions:

$$\begin{array}{ccccc} CO_2 & + & H_2O & \rightarrow & H_2CO_3 \\ \text{Carbon dioxide} & & \text{Water} & & \text{Carbonic acid} \\ \text{(in the air)} & & \text{vapor} & & \text{(weak acid)} \end{array}$$

$$\begin{array}{ccccc} H_2CO_3 & + & CaCO_3 & \rightarrow & Ca(HCO_3)_2 \\ \text{Carbonic} & & \text{Chalk or} & & \text{Calcium} \\ \text{acid} & & \text{limestone} & & \text{bicarbonate} \\ \text{(rain)} & & \text{(dissolves)} & & (\text{mgl}^{-1}\text{solution}) \end{array}$$

However, with the application of heat, the reaction reverses and because of the low solubility of calcium carbonate, carbonate scale develops as follows:

$$\begin{array}{cccccc} Ca(HCO_3)_2 & \rightarrow & CaCO_3 & + & CO_2\uparrow + & H_2O \\ \text{Calcium} & & \text{Heat} & & \text{Carbon} & \text{Water} \\ \text{bicarbonate} & & \text{Scale} & & \text{dioxide} & \end{array}$$

A list of some commonly found mineral components of deposits and foulants is given in **Table 3**.

4.27.6.1 Problems from Mineral Scales, Muds, and Sludges in Boilers

Scale in boilers is a direct result of precipitation of the calcium, magnesium, iron, and silica minerals present in the boiler feedwater and can be prevented by removing a portion or all of the scale-forming ingredients in the boiler water makeup supply with external water-softening equipment such as ion-exchange or lime/lime-soda softening. An example of scaled boiler tubes is shown in **Photo 3**.

Modification of the waterside environment will also require additional 'polishing' chemical treatments (internal boiler water treatment), usually on the basis

Table 3 Commonly found mineral components of deposits and foulants

Salt/oxide	*Mineral*	*Formula*
Calcium carbonate	Aragonite	$CaCO_3$
	Calcite	$CaCO_3$
Calcium phosphate	Hydroxyapatite	$Ca_{10}(OH)_2(PO_4)_6$
	Tricalcium phosphate	$Ca_3(PO_4)_2$
Calcium sulfate	Anhydrite	$CaSO_4$
	Gypsum	$CaSO_4{\cdot}2H_2O$
	Hemihydrate	$CaSO_4{\cdot}\frac{1}{2}H_2O$
Copper oxide	Cuprite	Cu_2O
Iron carbonate	Siderite	$FeCO_3$
Iron oxide	Haematite	Fe_2O_3
	α-Iron oxide (paramagnetic)	α-Fe_2O_3
	γ-Iron oxide (ferromagnetic)	γ-Fe_2O_3
	Lepidocrocite	$Fe_2O_3{\cdot}H_2O$
	Magnetite	$Fe_3O_4{\cdot}H_2O$
Iron sulfide	Troilite	FeS
Magnesium hydroxide	Brucite	$Mg(OH)_4$
Magnesium phosphate	Magnesium hydroxyphosphate	$3Mg_3(PO_4)_2{\cdot}Mg(OH)_2$
Magnesium silicate	Serpentine	$3MgO{\cdot}2SiO_2{\cdot}2H_2O$
Silica	Crystoballite	SiO_2
Zinc carbonate	White rust	$ZnCO_3$

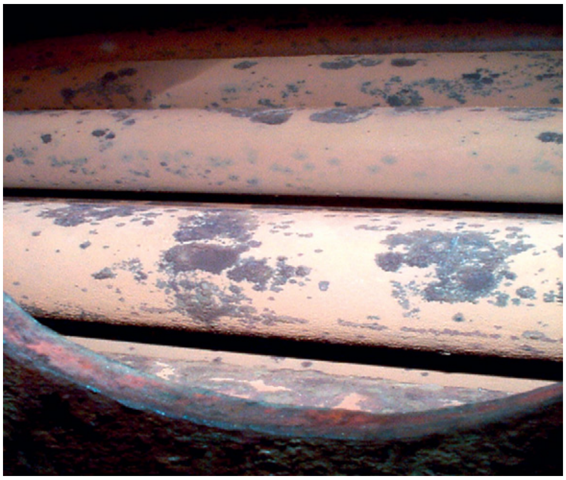

Photo 3 Scale on boiler tubes.

of phosphates, chelants, and/or organic polymers. Iron and combinations of iron with calcium and phosphate can form sticky, adherent sludge deposits in boilers and is caused by iron in the form of iron oxide or iron carbonate corrosion products, entering the boiler with the feedwater. It is a result of corrosion products from the sections prior to the boiler, such as steam and condensate lines, condensate receivers, deaerators, and boiler feedwater lines. Modification of the water-side environment may include the use of amine-based corrosion inhibitors added to the steam or condensate, which generally also neutralize carbonic acid in the condensate and raise the condensate pH.

Foulants in steam boilers usually consist of foreign contaminants present in the feedwater, including muds, oils, contaminants from a process, iron corrosion products from the steam system, and construction debris in new boiler systems. Mud or sludge in a boiler is usually a result of scale-forming minerals combining with iron oxide corrosion products and treatment chemicals, and are commonly controlled by using modern polymeric dispersants, which prevent adherence on heat-transfer surfaces.

In heating boilers, the most frequent foulants (other than sludge) are oil and clay. Oil can enter a boiler system through leakage at lubricators, fuel oil preheaters, or steam heating coils in fuel oil storage tanks. When oil enters a boiler it causes priming and foaming by emulsifying with the alkaline boiler water. Priming is the severe bouncing of the water level that eventually cuts the boiler off at low-water because of the wide fluctuation of this water level sensor. Oil can also carbonize on hot boiler tubes, causing not only serious corrosion from concentration corrosion cells but also tube ruptures as a result of overheating because of insulating carbon deposits and a departure from nucleate boiling (DNB). Whenever oil enters a boiler system, it must be removed immediately to prevent these problems. Modification of the boiler water system environment is usually done by blowing down the boiler heavily and often by additionally 'boiling out' with an alkaline detergent cleaner.

Clay is a less frequent foulant in heating boilers, but it can also form insulating deposits on tube surfaces. Clay enters a boiler with the boiler makeup water that is either turbid or contaminated with excessive alum, used as a coagulant in the clarification process, and has not been subject to filtration or any other makeup water pretreatment process. It can get dispersed during the use of chemical dispersants in the internal treatment of the boiler, but makeup water should be clear and free of any turbidity before it is used as boiler feedwater. Where turbidity and clay are a constant problem, modification of the boiler feedwater by filtration is required (An example is multimedia filtration).

4.27.6.2 Problems due to Mineral Scales, Muds, and Sludges in Cooling Systems

Scale deposits in recirculating cooling tower condenser water systems for HVAC air conditioning and refrigeration chillers are typically a direct result of precipitation of calcium carbonate, calcium sulfite, or silica minerals, because of an overconcentration of these minerals in water. The solubility or pH of saturation is exceeded and the minerals come out of solution. What a heat transfer equipment operator might commonly refer to as 'scale' can also include various corrosion products and foulants such as organic matter and mud or dirt.

Photo 4 shows an example of scaled and corroded condenser tubes.

Modification of the water circuit to prevent mineral scale should, therefore, include the following:

1. Sufficient dilution of the recirculating water to prevent the concentration of minerals from approaching the saturation point.
2. pH control to prevent the pH from reaching the pH of saturation of calcium carbonate.
3. Chemical treatments to inhibit and control scale crystal formation.

In addition to mineral scale, other recurrent problems in recirculating water systems include mud, dirt, debris, foreign matter, and organic growth – especially algae (in warm and sunny weather) and planktonic and sessile bacteria. Deposits of foreign matter plug narrow passages and interfere and foul heat-transfer surfaces, causing inefficient performance of the equipment and energy consumption higher than desirable.

Photo 4 Scaled and corroded condenser tubes.

A cooling tower is a natural air washer with water spraying over slats and tower fill, and washing the air blown through either naturally or assisted by fans. Depending on the location, all sorts of airborne dust and debris end up in cooling tower recirculating water systems. These vary from fine dust particles to pollen, weeds, plant life, leaves, tree branches, grass, soil, and stones. The fine particles of dust and dirt tend to collect and form a compacted layer in the condenser water system, especially in areas of low circulation and at heat-transfer surfaces. Minimizing these problems again requires modification of the specific waterside environment. It may call for a side-stream filter, screens to limit air-blown dust (say near a construction site), or the regular use of polymeric dispersing chemicals, antiscalents, biocides, and biodispersants.

4.27.6.3 Problems due to Mineral Scales, Muds, and Sludges in Closed-Loop Water Systems

Closed-loop systems contain a finite volume of water and evaporative processes do not take place, although minor water losses because of leaks will occur. Closed-loop systems will include engines under circumstances where they are employed in emergency/backup electricity generating systems and similar applications (e.g., standby diesel generators for hospitals, commerce, and general industry, and diesel engine utility power generators). Some closed-loop systems are not in fact 'closed' and may have, for example, a returned water receiver that channels a number of individual cooling water lines to a single point before being pumped across a heat-exchanger and around another loop.

As a general rule, all closed and semi-closed loop systems tend to suffer to some extent or other from iron and steel corrosion problems because of the prolific use of mixed metals, poor passivation, and limited maintenance. Therefore, one of the most common and difficult foulants found in closed systems is a black mud made up of compacted, fine, black magnetic iron oxide particles, which deposit at heat-transfer surfaces, and clog or block narrow passages in unit heaters, fan coil units, and cooling, reheat, and heating coils in air-handling units. This mud is a result of very fine wet particles of black magnetic iron oxide compacted into a dense adherent mud.

The interior of black iron piping, commonly used for recirculating water, has a natural black iron oxide protective coating ordinarily held intact by oil-based inhibitors used to coat the pipe to prevent corrosion during storage and lay-up. This natural iron oxide protective coating is called mill scale, a very general term which can be applied to any form of pipe scale or filings washed off the interior of the pipe. This mill scale film becomes disturbed and disrupted during construction because of the constant rough handling, cutting, threading, and necessary battering of the pipe. After construction, the recirculating water system is filled and flushed with water, which removes most of the loosened mill scale along with other construction debris. However, very fine particles of magnetic iron oxide will continue to be washed off the metal surface during operation, and in many instances this washing persists for several years before it subsides. Mill scale plugging can be a serious problem. It is best alleviated in a new system by thorough cleaning and flushing with a strong, low-foaming detergent–dispersant cleaner. This, however, does not always solve the problem. Even after a good cleanout, gradual removal of mill scale during ensuing operation can continue.

4.27.6.4 Problems due to Waterside-Surfaces Fouling in ‘New Construction’ HVAC Systems

All new HVAC systems can become fouled and contaminated with various forms of foreign matter during construction. It is not uncommon to find remnants of welding rods, beads, paper bags, plastic wrappings, soft drink can rings, pieces of tape, insulation wrappings, glass, etc. in the interior of HVAC piping and heat exchangers. Also, cement, mortar, metal filings, pieces of pipe, and other construction debris may be present. Oil and mill scale is usually found and can seriously foul and plug closed systems, and cause boiler tube failures if the oil is carbonized during firing. It should be noted that commonly found black iron pipe ‘scale’ is not, in fact, a mineral scale, but rather the oxides of iron (rust) produced during manufacture and storage. It is also called mill scale and can be slightly protective to the pipe against contaminants in water, but is not sufficiently nonporous for good protection.

It is necessary not only to clean out construction debris from the interior of new construction HVAC systems prior to initial operation, but also to modify the waterside environment by cleaning the metal surfaces of oil and mill scale naturally present on the pipe interior, then passivate the metal surface, and follow up with an initial feed of inhibitor chemicals. Cooling water systems and boiler must be cleaned thoroughly with an alkaline detergent–dispersant type of cleaner. Where the boiler is a steam raising plant, an alkaline boilout compound is used. All this takes place before implementing a maintenance chemical treatment and technical service overseeing program.

4.27.6.5 Problems due to Mineral Scales, Muds, and Sludges in Potable Water Lines

Water containing unusual turbidity or suspended matter is usually treated at the source by coagulation, clarification, and filtration so as to improve its quality. Turbidity is the cloudiness or haziness of a fluid caused by individual particles (suspended solids) that are generally invisible to the naked eye, similar to smoke in air. The measurement of turbidity is a key test of water quality. However some minor level of turbidity may still be present that will be acceptable if it does not affect potability. Therefore, the presence of excess levels of suspended matter and turbidity is not common in makeup waters to HVAC systems as the makeup water usually comes from a municipal or local source, over which there is an authority responsible for delivery of clear, potable quality water.

Where private well water and pond, or other non-public sources of water are available for use as makeup water to cooling water systems and boilers, it should be carefully examined for turbidity and suspended matter. Governments around the world have set standards for the allowable turbidity in drinking water. In the United States, the allowable standard is 0.3 NTU, with many utilities striving to achieve levels as low as 0.1 NTU.[12] When the supply is excessively turbid, modification by some form of clarification should be used to remove the suspended matter and reduce the turbidity to below 1 NTU. Modification examples include coagulation, settling, filtration, and/or fine strainers.

The more common problem with suspended matter and turbidity results from makeup water that is temporarily or occasionally dirty, which may occur when the local water authority is cleaning sections of a distribution main, installing new mains, or when water mains are cut into during some nearby construction project. These deposits consist mostly of iron oxide corrosion products and dirt, clay, or silt.

4.27.7 Problems of Corrosion including Microbial Induced Corrosion

Corrosion occurs very rapidly in heat-transfer equipment because of the presence of heat, corrosive gases and dissolved minerals in water, which stimulate the corrosion process. Corrosion mechanisms can be concentrated locally to form a pit or crack, or under local environmental conditions, extend across a wide area to produce general deterioration. The local corrosive conditions may be caused by use of dissimilar metals, excess of oxygen, short- or long-term stress (such as that at points of welds, bends, and elbows), and excessive or prolonged heat, or thermal shock.

Although specific corrosion problems, such as the various types of differential aeration mechanisms, hydrogen embrittlement, and flow assisted/accelerated corrosion (FAC) – especially in high-pressure utility boilers and heat recovery steam generator (HRSG) plants – can take place the most common forms of corrosion found in heat-transfer equipment include the following:

- uniform or general corrosion;
- oxygen pitting corrosion;
- galvanic corrosion;
- concentration cell or crevice corrosion;
- stress corrosion;
- erosion corrosion or impingement corrosion;
- condensate line corrosion or grooving corrosion;
- microbiologically influenced corrosion (MIC); and
- white rust.

In water systems, modification of a waterside environment to minimize corrosion will involve direct or indirect passivation of a metal surface, a change in pH, and use of oxygen scavengers (in boiler plants), and usually require small concentrations of corrosion inhibitors (especially in cooling systems).

4.27.7.1 Uniform or General Corrosion

General corrosion is found in various forms in HVAC and other heat-transfer equipment and can be seen as an overall deterioration of the metal surface, with an accumulation of rust and corrosion products in the piping and water boxes. For example, it might be present as a surface gouging or a uniform thinning of the tube metal on copper condenser tubes, or in boilers, as the total overall disintegration of a boiler tube metal surface in contact with boiler water.

This type of corrosion occurs when the process takes place over the entire surface of the metal, resulting in a uniform loss of metal rather than a localized type of attack. Iron and other metals are corroded by electrochemical reaction resulting in the metal going into solution in the water. The waterside environment will usually have some level of oxygen present, plus possibly dissimilar metals or areas of stress, together with dirt, and/or an accumulation of corrosion products over the surface of the metal. It is necessary, therefore, to limit corrosion of these metals by cleaning the system, passivating the metal surface, and by reducing the activity of both hydroxyl ions and hydrogen ions, that is, by developing a corrosion-free environment through the use of corrosion inhibitors.

4.27.7.2 Oxygen Pitting Corrosion

An important factor in corrosion processes is dissolved oxygen, and it may manifest itself in various forms of differential aeration corrosion and under-deposit corrosion processes, producing tubercles or other accumulations of rust and corrosion products. Specifically, oxygen pitting is characterized by deep penetration of the metal at a small area on the surface with no apparent attack over the entire surface, as in general corrosion. The corrosion takes place at a particular location on the surface and corrosion products frequently accumulate over the pit. These appear as a blister, tubercle, or carbuncle.

Localized pitting corrosion is a common problem and may result from a variety of contributory causes, such as deposits of foreign matter. However oxygen pitting corrosion differs somewhat from other forms of pitting corrosion in that it is caused solely by the presence of dissolved oxygen, which reacts with a metal, eventually forming the insoluble oxide and builds up a voluminous deposit of rust in the case of iron and steel.

Photo 5 shows an example of oxygen pitting corrosion in a sectioned length of boiler pipe.

Photo 5 Oxygen pitting corrosion.

In boilers, oxygen pitting occurs where the feedwater contains dissolved oxygen. The pitting is found on boiler tubes adjacent to the feedwater entrance, throughout the boiler, or in the boiler feedwater line itself. Modification of the feedwater often entails mechanical deaeration through the use of a vacuum or pressure deaerator. However, oxygen pitting can still develop in boiler feedwater lines following a deaerator, as low concentration of dissolved oxygen can be more corrosive in feedwater than higher dissolved oxygen content! Mechanical deaerators are not 100% efficient and none can produce a feedwater with zero oxygen. The lowest guaranteed dissolved oxygen content that deaerators produce is 0.005 $\mathrm{cm}^3\,\mathrm{l}^{-1}$. This trace quantity of dissolved oxygen is sufficient to cause severe pitting in feedwater lines or in boiler tubes adjacent to the feedwater entrance. In this situation, oxygen pitting is characterized by deep holes scattered over the surface of the pipe interior with little or no accumulation of corrosion products or rust, as there is insufficient oxygen in the environment to form the ferric oxide rust.

However, in utility peaking boilers or in cyclic operations, it may, in fact, be necessary to modify the waterside environment by adding a constant trace amount of oxygen (oxygenation treatment, OT) in order to maximize the maintenance of a protective magnetite film on the metal surface at the metal/water interface, and minimize the development of excessive quantities of corrosion product debris (‘crud’).

4.27.7.3 Galvanic Corrosion

Galvanic corrosion (dissimilar-metal corrosion) is an electrochemical process in which one metal corrodes preferentially, when in electrical contact with a different type of metal, and both metals are immersed in an electrolyte such as water. Typically in an industrial process water system or HVAC system, different metals of construction will be used, and more often than not they are not dielectrically insulated from each other, but are connected via a flange, valve, union, or brazed joint. Thus, when the two or more different types of metal come into contact with one another (as in the coupling of steel and copper in a heat-exchanger), a galvanic couple is set up, as the different metals have different electrode potentials. The electrode potential is the tendency of a metal to give up electrons and go into solution.

The system water electrolyte provides a means for ion migration, whereby metallic ions can move from the anode to the cathode. This leads to the anodic metal corroding more quickly than it otherwise would; the corrosion of the cathodic metal is retarded even to the point of stopping. The presence of electrolyte and a conducting path between the metals may cause corrosion, where otherwise neither metal alone would have corroded. Also, a single type of metal may corrode galvanically if the electrolyte varies in composition, forming a concentration cell.

The rate of galvanic corrosion is strongly influenced by the electrode potential difference between the dissimilar metals. The galvanic series is a list of metals in order of their activity, the most active being at the top of the list and the least active at the bottom. The further apart two metals are on this list, the greater will be the reactivity between them and, therefore, the faster the anodic end will corrode.

Methods for the modification of the waterside environment to control the rate of active galvanic corrosion include the following:

1. Eliminating the contact of dissimilar metals in an HVAC system by using insulating couplings or joints such as a dielectric insulator coupling, which interferes with the electron flow from one metal to the other.
2. Eliminating one or more of the essential elements required for galvanic corrosion to occur. This might require, for example, modifying the HVAC system design by changing one of the metallic materials of construction, such as zinc or copper.
3. The use of protective coatings and chemical corrosion inhibitors, which all provide a physical or chemicophysical barrier between the corroding metal and its environment.

4.27.7.4 Concentration Cell Corrosion or Crevice Corrosion

Concentration cell corrosion, like pitting corrosion, is a localized type of differential aeration corrosion rather than a uniform attack. It is a form of underdeposit corrosion or crevice corrosion, as it occurs under deposits or at crevices of a metal joint. Differential aeration cells can be caused by crevices, lap joints, deposits of foreign matter, dirt, organic matter, corrosion products, scale, construction debris, and moist insulation. Oxygen not only enables a corrosion reaction by maintaining a cathodic reaction, but it can promote one where there is a difference in the concentration of dissolved oxygen between two points of the same metal surface.

If the supply of oxygen is not uniform across a surface, then any regions that are depleted in oxygen will become anodic, for example within a crevice, at a joint or beneath a surface deposit. The remainder of the surface with free access to oxygen acts as a large cathodic area. Thus, where there is a difference in the concentration of dissolved oxygen at two points on a metal surface, the surfaces in contact with the solution containing the higher concentration of dissolved oxygen will become cathodic to surfaces in contact with a lower concentration of dissolved oxygen. Because the cathodic area is so much larger, severe local attack will occur in the small anodic region.

Additionally, where contaminants (such as chlorides or sulfates) are present in the water, these can concentrate under the deposit or in the crevice and rapidly increase the rate of corrosion – leading to gouging corrosion or pitting corrosion, where the anode will again suffer accelerated corrosion in the (oxygen) concentration cell. Thus, the rate of supply of oxygen or ion concentration will govern the rate and mechanism of rusting. With concentration cell corrosion, the corrosion reaction proceeds as in galvanic corrosion, as this differential also forms an electrode potential difference. Maintaining clean surfaces, in conjunction with chemical inhibitors can best prevent this form of corrosion.

In closed-loop systems where the water is, in fact, not closed but in contact with air (as in many plastic extrusion component manufacturing facilities, where various cooling water streams flow to a common receiving tank) concentration cells can develop and severe crevice corrosion can occur. Limiting contact with oxygen in the air by use of a physical barrier, such as a floating plastic sheet, is an option, but system modification will still require the addition of anodic or cathodic inhibitors to the water.

4.27.7.5 Stress Corrosion

Stress corrosion failure is a result of a corrosive environment and stresses and strains at the very point of failure. It is because of the combination of exposure of a metal to a corrosive environment and the application of stress on the metal, such as in stress-corrosion-cracking mechanisms involving various grades of stainless steel, where the alloy comes into contact with a corrosive, high-chloride concentration environment. It can also occur on condenser tubes and heat-exchanger tubes, from heat expansion that causes stresses in the metal at tube supports or tube sheets.

Stress corrosion is frequently seen on condenser tubes and boiler tubes in the area where the tubes are rolled into the tube sheets. In steam boilers, stress corrosion has been referred to as ‘necking and grooving.’ It is also seen as a circumferential groove around the outside of a firetube in a firetube boiler, where it enters the tube sheet. Usually it occurs at the hottest end of the tube, (i.e., at the beginning of the first pass against the firewall). Stress corrosion concentrates at the tube end because of strains from two sources. First, when tubes are rolled in, stresses are placed on the metal, expanding the metal to fit the tube sheet (and the stresses may be unrelieved). Second, when a boiler is fired, the heat causes rapid expansion of the tube, and consequently strains are greatest at the tube ends, which are fixed in the tube sheets. This actually causes a flexing and bowing of the tube, and sometimes the expansion is so severe that the tubes loosen in the sheets. During this bending of the tube, the natural protective iron oxide film formed at the tube ends tends to tear or flake off, exposing fresh steel to further attack. Eventually, the tube fails because of a combination of both corrosion and stress.

Reducing the risk of stress-corrosion in stainless steel alloys (and other types of alloy) starts with improved product selection and design. Also, it requires the removal or modification of the corrosive waterside environment – often through regular cleaning practices and the use of inhibitors. The problem of stress corrosion in boilers is reduced by more gradual firing practices, and by using proper inhibitors to correct the corrosive environment.

4.27.7.6 Erosion Corrosion or Impingement Corrosion

Erosion corrosion or impingement corrosion is the gradual wearing away of a metal surface by a combination of both corrosion and abrasion from an impinging water stream, such that the higher the velocity of the impinging stream, the greater the rate of erosion corrosion. Water moving rapidly through piping can contain entrained air bubbles and suspended matter, sand, or other hard particulates. These abrasive particles remove natural protective oxide films present on the surface of the metal and cause general corrosion of the exposed metal.

Unfortunately, this is not uncommon in cooling tower waters where such particles are extracted from the atmosphere so that in environments where high levels of particulates can enter the system (e.g., close to a construction site or in an open area where high winds are prevalent), modification of the water treatment program usually calls for the installation of a side-stream or fill-stream filter, plus perhaps a dispersant chemical.

A special kind of erosion corrosion that has become very prevalent in recent times, with the increased use of cogeneration and combined cycle power plants that utilize heat recovery steam generators (HSRG), is flow assisted or flow accelerated corrosion (FAC). FAC is a term originating with The Electric Power Research Institute (EPRI) for a condition that the industry has previous labeled with the more generic term erosion corrosion. EPRI defines FAC as “a process whereby the normally protective oxide layer on carbon or low-alloy steel dissolves into a stream of flowing water or a water–steam mixture.” It can occur in single phase and in two phase regions. EPRI has stated that the cause of FAC is water chemistry.[13]

Several variables contribute to this phenomenon including but not limited to velocity, pH, directional changes and geometry, temperature, chemistry, oxygen concentration, oxygen scavenger (reducing environment), and material composition. Two phase FAC can be differentiated from cavitation erosion by the evidence of ‘tiger stripes’ or ‘chevrons.’

Note: Cavitation erosion (CE) occurs downstream of a directional change, or in the presence of an eddy. Evidence can be seen by the presence of round pits and is often misdiagnosed as FAC. Like erosion, CE involves fluids accelerating over the surface of a material; however, unlike erosion, the actual fluid is not doing the damage. Rather, cavitation results from small bubbles in a liquid striking a surface. Such bubbles form when the pressure of a fluid drops below the vapor pressure, the pressure at which a liquid becomes a gas. When these bubbles strike the surface, they collapse, or implode. Although a single bubble imploding does not carry much force, over time, the small damage caused by each bubble accumulates. The repeated impact of these implosions results in the formation of pits. Also, like erosion, the presence of chemical corrosion enhances the damage and rate of material removal. Cavitation is not a property of the material, but a property of the system itself. The fluid pressure is determined by the size and shape of the vessel, not the material. While a stronger material can be highly resistant to cavitation, no metal is immune.[14]

4.27.7.7 Condensate Line Corrosion or Grooving Corrosion

Condensate corrosion or grooving corrosion is a particular, but very common, corrosion phenomenon of steam condensate lines in HVAC and industrial process equipment. The primary cause of condensate grooving is carbon dioxide. The dissolved carbon dioxide is a breakdown product of calcium bicarbonate in boiler feedwater – originating from the makeup water component of feedwater. The CO_2 gas is volatile and carries over with the generated steam in the boiler, then dissolves in the hot condensate, forming carbonic acid. Typically the pH of condensate may fall to perhaps as low as 5.5 or 6.0.

Condensate corrosion is found in steam condensate piping on all types of equipment, heat exchangers, steam-turbine condensers, unit heaters, steam absorption condensers, radiators, or any type of unit utilizing steam as a heat-transfer medium. It is a direct chemical attack by acidic steam condensate on the metal over which it flows, and is identified by the typical grooves found at the bottom of the pipe carrying the condensate.

The methods available to prevent this type of corrosion include removal of bicarbonate and carbonate alkalinity from the boiler makeup water (dealkalization) and use of carbonic acid neutralizers and filming inhibitors.

Usually, these inhibitors are amine-based. Food industries tend not to use amine-based corrosion inhibitors, for fear of odors or taints they may impart to the food in question; therefore, they may use sorbates and other inhibitors of similar chemistry — which, although ‘safe’ are not particularly effective, despite claims to the contrary. Often, the food company will prefer to suffer the consequences of condensate line corrosion rather than spent capital on a dealkalization plant or use amine inhibitors, some of which are permitted in the United States for the food manufacturing industry at certain maximum concentrations, under Code of Federal Regulations (CFR), §21, section 173.310.

4.27.7.8 Microbiologically Influenced/Induced Corrosion or Biocorrosion

The term 'microbiologically influenced corrosion' covers a wide range of corrosion processes that are initiated or promoted by microorganisms – usually chemoautotrophic bacteria (i.e., bacteria that obtain energy by the oxidation of electron-donating molecules in their environments). MIC is a very serious problem in all types of industry, affecting, for example, buried water, gas, and oil pipelines, as well as petroleum products and fuel storage tanks. Attack can take place on both the external and internal metal surfaces, with the microorganism living in the water phase (i.e., microorganisms in the water table can cause MIC on external metal pipeline/tank surfaces, and microorganisms in tank 'bottoms' can cause MIC of internal metal pipeline/tank surfaces, as well as damage the stored fuel or other product). Similarly MIC can affect industrial heating and cooling systems, potable water lines, and building HVAC systems. Photo 6 shows an example of MIC on a section of pipe.

There are many forms and mechanisms of MIC involving many types of microbiological organisms, both aerobic and anaerobic. MIC in water systems can be initiated by various major groups of organisms, and their biomass products (biofilm) such as the following:

- *Iron related bacteria (IRB).* IRBs include *Gallionellea ferrugine* (which oxidizes ferrous ions to ferric ions and manganous ions to manganic ions) and *Ferrobacillus* sp.
- *Sulfate reducing bacteria (SRB).* The genera *Desulfovibrio*, *Desulfomaculum* and *Desulfomonas* are both anaerobic microorganisms and reduce SO_4^{2-} to S^{2-} and H_2S.
- *Acid producing bacteria (APB).* These are mainly slime-forming microorganisms, and include *Acidithiobacillus thiooxidans*, which oxidize sulfur and sulfides to H_2SO_4, and *Acidithiobacillus ferrooxidans* which oxidize ferrous (Fe^{2+}) ions to ferric (Fe^{3+}) ions. Also, APBs include *Pseudomonas*, *Aerobacter*, and *Bacillus* spp. which exude various organic acids in their metabolic process, resulting in localized underdeposit and pitting corrosion, often resulting in pinholes in pipework.

Photo 6 MIC on a sectioned pipe.

Apart from bacterial slimes, biomass, or biofilm can be produced by other types of microorganisms, including algae, yeast, molds, and fungus. Slimes and biofilms can provide the environment for corrosion through establishment of concentration cells resulting in under deposit corrosion. Also, biological deposits in general act as traps and food for other organisms resulting in rapid growth. This complex matrix sets up a corrosion potential between adjacent areas of a metal surface that may have a different type of deposit. Additionally, biofilms provide a safe environment for organisms when attacked by biocides, especially those with limited penetrating ability, necessitating the additional use of biological penetrants or biodispersants to effect a good kill level in cooling water systems.

To control MIC it is important to understand the organisms and processes that cause it. Modification of the waterside environment will require periodic microbiological testing and use of specific types of microbiocides – usually a tailored program containing both an oxidizer and a nonoxidizer.

4.27.7.9 White Rust Corrosion

Many 'standard' cooling water system components, such as HVAC panels, basins, and complete cooling towers, are constructed of galvanized steel for ease of fabrication and low manufacturing costs. Galvanizing produces a zinc–iron intermetallic alloy in layers on a steel surface that acts as a corrosion-resisting coating. The zinc is anodic to steel and thus will provide cathodic or sacrificial protection to any small areas of steel that may be exposed (i.e., scratches, cut edges, etc.). Also, the passive, oxidized zinc coating provides a physical barrier in protecting the bulk of the steel surface from any direct contact with the environment. However, with the giving up of the use of sulfuric acid and chromate as a water treatment scale and corrosion-inhibiting chemical treatment program in most parts of the world over 30 years ago, a corresponding, and significant rise in white rust corrosion has been observed. It has become such a serious problem, especially in new construction, that many cooling tower manufacturers have turned to using glass fiber and plastics.

White rust corrosion is a problem where the fresh galvanized surface is not able to form a protective, nonporous, basic zinc oxide, especially where the surface is partially wetted or completely submerged in water. Deterioration begins when a localized corrosion cell is formed, leading to pitting corrosion, metal wastage, and reduced equipment life expectancy. White rust corrosion is often identified by the white, gelatinous or waxy deposit of a porous zinc-rich oxide complex, $3Zn(OH)_2 \cdot ZnCO_3 \cdot H_2O$. It is aggravated by the modern use of high-pH, high-alkalinity water chemistries, and in softer waters, especially when appropriate pretreatment passivation protocols have not been followed (a major problem in new construction).[15]

4.27.8 Problems of Microbiological Fouling

All water systems have the potential for the growth of microorganisms, and the production of slimes, biomass, or biofilm, which, not only present fouling and corrosion problems, but can also compromise the health and safety of workers and visitors. In cooling systems, spa baths, potable hot water lines, and calorifiers (hot water generator and storage tanks), the presence of slimes and biofilm can increase the risk of illness from, for example, Legionnaires' disease. Photos 7(a) and 7(b) below show microbiological fouling in a cooling system.

As noted earlier, microorganisms to be found in water systems can include not only bacteria, algae, yeast, molds, and fungus, but also unicellular protozoa (such as *Cryptosporidium*, *Paramecia,* and *Amoeba*).

Algal growths and biofilms are always found to some degree in open recirculating water systems such as cooling towers, evaporative condensers, air washers, and spray-coil units. Occasionally closed systems can become fouled with organic slimes because of foreign contamination (although the single biggest problem here is always corrosion, usually as a result of improper initial cleaning, passivation, and ongoing use of chemical inhibitors).

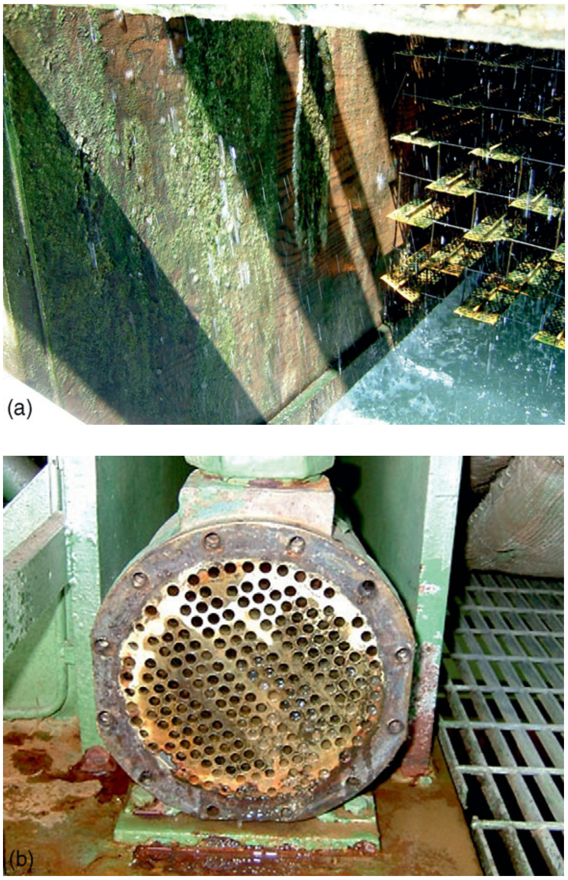

Photo 7 (a) Algal fouling on a cooling tower and (b) fouled and corroded heat exchanger.

Open cooling systems are constantly exposed to the atmosphere, and the local environment can contain dust, dirt and innumerable quantities of microscopic organisms such as algal cells and bacteria, which will enter the cooling systems because of the scrubbing of air during the evaporative cooling process. Also, because cooling water is exposed to sunlight, often operates at ideal growth temperatures, and contains nutrients, it provides a favorable environment for the abundant growth of biological organisms. The basic types of microorganisms found in cooling systems, and system environment modification methods are discussed below:

- *Algae.* The types of algae found in open recirculating water systems include the blue-green algae, green algae, and brown algae. Large masses of algae can cause serious problems by blocking the air in cooling towers, plugging water distribution piping and screens, and accelerating corrosion by concentration cell corrosion and pitting. Algae must be removed physically before a system can be cleaned as the mass will provide a continuous source of material for reproduction and biocides will be consumed only at the surface of the mass, leaving the interior alive for further growth. Modification of the cooling water environment will include screening sunlight from towers by use of distribution trough covers, and the periodic use of specific algaecides, such as tertbutylazine (TBZ).

- *Fungi.* Fungi usually require low alkalinity waters and can grow together with algae, as the algae living within the fungus mass are furnished with a moist, protected environment, while the fungus obtains carbohydrates from the algae. Fungi can attack wood contained in cooling towers, so treated wood is used. Also, biocides such as tris(hydromethyl)nitromethane (trisnitro) may be employed.
- *Bacteria.* There are hundreds, if not thousands, of potential types of bacteria that may be found in water systems, especially cooling water systems. Bacteria are microscopic unicellular living organisms that exhibit both plant and animal characteristics. They may be rod-shaped, spiral, or spherical in shape, and may be pathogenic or harmless to people. However, in general, the most troublesome organisms are the slime producers – iron bacteria, sulfate-reducing bacteria, etc.

Bacteria may be found free-floating in water (planktonic bacteria) and are relatively easy to kill, although persistent strains and rapid regrowth may develop if the kill-rate is not maximized. Bacteria growing within a biofilm (sessile organisms) are more difficult to kill.

In general, the control of microorganisms is undertaken by developing a protocol or program for the selective and periodic (or semicontinuous) addition of oxidizing and/or nonoxidizing pesticides (also called microbiocides or biocides). Nonoxidizing biocides include isothiazolinones, thiones, and gluteraldehyde. Oxidizing biocides include various chlorine and bromine donors, such as bleach, calcium hypochlorite, and dibromohydantoins. Additionally, cationic, anionic, and non-ionic biodispersants and special biocidal cleaners may be employed.

Monitoring by the use of simple site tests, such as dip-slides, is necessary to establish the concentration of planktonic and sessile organisms, kill rates, and regrowth rates. Under more difficult cooling water operating conditions, or where there may be resistance to certain pesticides or a reason to suspect the potential for the growth of pathogens, special testing is carried out in a microbiological laboratory.

4.27.8.1 Problems of Amplification of Pathogenic Bacteria

Pathogenic bacteria are disease-causing bacteria. Cooling tower waters and domestic hot water lines in particular, have ideal conditions for the growth of bacteria and other organisms, and can promote the growth of pathogenic strains, which may then give rise to infection and possibly death, for example the amplification of commonly found Legionella organisms in cooling water and domestic hot water, leading to the risk of illness from Legionnaires' disease. It is important to keep these systems clean and free of general bacterial contamination in order to inhibit growth of potentially pathogenic bacteria, as well as to prevent corrosion from slime-forming organisms. Photo 8 shows *Legionella* sp. amplifying in an amoeba.

Disease forming organisms that may grow in water systems that are not regularly cleaned, disinfected, or otherwise maintained may include the following:

- *Legionella pneumophila*, especially serotype 1. Responsible for Pontiac fever and Legionnaires' disease, a potentially fatal type of pneumonia.
- *Mycobacterium avium.* Responsible for nontuberculosis mycobacterium disease, also called hot-tub lung disease.
- *Pseudomonas* sp. Responsible for chronic respiratory infections and infections of the eye, skin, and soft tissue.

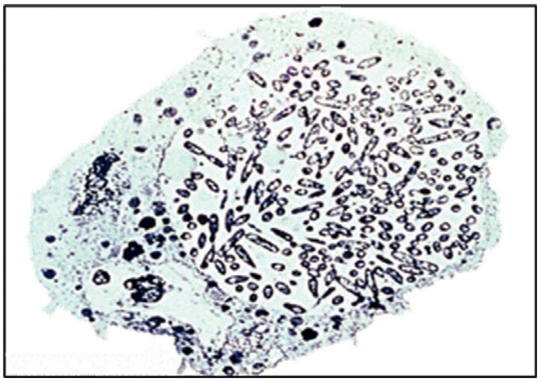

Photo 8 *Legionella* sp. bacteria in an amoeba.

- *Escherichia coli.* Responsible for septicemia and diarrhea.
- *Giardia lamblia.* Responsible for Giardiasis, producing diarrhea and abdominal cramps.

Modification of the waterside environment to prevent bacteria related problems means that all cooling systems should be drained, cleaned, and disinfected at least twice per 12-month period, irrespective of whether the cooling systems operate all year round or only on a summer cycle. Some countries mandate this approach by law. Others demand three cleanings and disinfection programs per year. In addition to good maintenance, a periodic risk assessment and ongoing surveillance program should also be instituted, and all records kept in a logbook. Implementation of a risk assessment program is an additional and necessary precaution for many facilities prior to starting up a new or winterized tower, or where design or location is suspect (e.g., poor drift elimination, or the tower is sited too close to a ventilation system's fresh air intake).

4.27.9 Evaluating and Modifying Waters for Use or Reuse in Industrial Processes and HVAC Water Systems

Municipally treated waters are of potable quality, but may require some form of treatment, such as reducing or modifying the concentration of minerals, salts, and other compounds present, before becoming suitable for industrial process applications. Surface waters and well waters drawn directly from source will inevitably require pretreatment, and recycled treated waste waters or reused industrial waters will, likewise, require pretreatment, regardless of the process application envisioned.

In general, treatment will take several steps, the first being a basic 'cleanup' using mechanical filtration, ion-exchange water softening, or similar capital intensive process. Next may follow a purification process, such as demineralization by ion-exchange or membrane process, or mechanical deaeration. Finally, an ongoing, maintenance chemical treatment program will be employed for 'polishing' purposes.

Cooling systems are generally accepting of a wide diversity of water sources and provided the water is reasonably consistent in quality, many industrial streams can be economically recovered and reused as tower makeup. However, as noted above, recoverable process waters will always require some measure of judicious pretreatment before being recycled for reuse in cooling systems, even if it is only to remove particulates, fats, oils, and greases (FOG) and heavy metals; and to make pH adjustments (say pH 7.0–8.5). Water used as a makeup source for steam boilers may need significant pretreatment, depending upon the boiler design and pressure. Generally, as boiler pressure rating increases, the makeup water employed will need to be further modified or 'purified' by removing most, if not all, measurable contaminants.

In industry, water is employed for innumerable applications, not simply for heating and cooling. It is required, for example, in dissolving, washing, cleaning, dying, rinsing, melting, quenching, stripping, scrubbing, desalting, plating, surface coatings, fermentation, dust control, process liquors, steam heating, drying, cooking, pasteurization, oil and gas abstraction, and domestic purposes. Additionally, excess water results from distillation, evaporator condensates, reverse osmosis (RO) reject, oil and gas production, boiler blowdown, chemical manufacturing, recovery of fibers and chemicals, straining, filtration, drainage, and a myriad of other process operations. This water may be treated and recycled, or reused for other types of process, or downstream applications.[16,17]

Any water considered for use or reuse in industrial processes and even for small, simple, HVAC water system applications must first be evaluated, if problems of corrosion and scaling are to be avoided or minimized. In general, we would need to consider the following:

1. An understanding of the process flows, operating conditions, materials balance, and volume/quality requirements.
2. A full understanding of the chemistry of the water under consideration, plus testing parameters, limitations, and costs. We need to know the chemical and physical characteristics, including pH, temperature, calcium, magnesium, alkalinity, silica, suspended solids, chlorides, sulfates, and the presence of potentially undesirable constituents, such as FOG, solvents, ammonia, soluble/insoluble iron, and heavy metals. Also, we may need to know the 5-day biochemical oxygen demand (BOD_5), chemical oxygen demand (COD) or total organic carbon (TOC) analysis.
3. We have to be able to interpret the data, in order to identify which contaminants may provide limiting factors regarding deposition, fouling, or corrosion of materials of construction (such as copper,

steel, heat-exchanger alloys, or concrete), and would thereby impact chemical treatment programs, cycles of concentration (COC), bleed discharge volumes, and ongoing costs.

4. We need to provide a robust and economic pretreatment design, ensuring that the treated water meets the desired or practical/useable/chemical/physical water quality specifications.
5. Where water is used for cooling purposes, we also need to consider further modification of the waterside environment by the operational protocols and the downstream chemical inhibitor treatment program(s) that will be used on a regular maintenance basis.

In order to keep water consumption as low as practically and economically possible, we need to consider COC (i.e., the ratio of concentration of TDSs in recirculating water to that of the make-up water employed). This requires us to consider corrosion, fouling, and deposition risks, as indicated by basic and ionic equilibrium model saturation indices or ion-association predictive modeling (see also Sections 4.27.13–4.27.15). However, the law of diminishing returns applies for any specific cooling system, beyond a certain COC number, the risk of waterside problems increases greatly as the reward of water savings progressively diminishes. A COC of 4× to 6× is often a good standard. There is seldom any significant benefit in raising COC levels to >10× unless the water is a lean acid water, with a minimum of minerals and other contaminants present, or a zero liquid discharge (ZLD) system is in place.[16]

4.27.10 Modifying Water by Selective Use of Standard Pretreatment Processes

The types of water contaminant pretreatment process under consideration will depend upon the degree of contaminant removal or modification required. Some examples of pretreatment equipment are shown in Photos 9(a)–9(d).

Although certain types and brands of 'nonchemical devices' ('gadgets') such as magnetic devices (not the same as a magnetic separator), electrostatic, pressure changing, or catalytic devices may be employed, these tend not to have mainstream acceptance. This is usually because of limited availability of peer-reviewed data and/or extravagant claims.

Examples of mainstream, 'standard' pretreatment processes include the following:

- *Alkalinity removal.* This process can be carried out via lime softening, sulfuric acid treatment, or ion-exchange dealkalization.

  A steam boiler that operates with makeup water containing excessive quantities of carbonate and bicarbonate alkalinity not only will develop excess alkalinity in the boiler (causing priming, foaming, and carryover), but also will generate large quantities of carbon dioxide as a result of decomposition of the carbonates and bicarbonates. This process results in an acid steam and condensate, which, as noted previously, causes severe corrosion of steam and condensate return lines. The alkalinity in these cases can be reduced by 90%, by passing the makeup water through a dealkalizer following the water softener.

  The typical dealkalizer plant contains an ion-exchange resin similar to the water softener with the capability of exchanging carbonate, bicarbonate, sulfate, and other anions for chloride, hence the name 'chloride anion dealkalizer' (i.e., a strong base anion (SBC) resin in the chloride form). Alternatively the dealkalizer can be a strong/weak acid cation (SAC/WAC) in the hydrogen form, plus degassing. In this type of plant, there is a reduction in dissolved minerals, leading to a reduction in boiler blowdown requirements and thus, energy savings.
- *Dirt, grit, sand, slime, algae removal.* This can be achieved by using a strainer, bag or cartridge filter, sand filter, multimedia filter, inclined plate clarifier (e.g., Lamella Gravity Settler), or conventional coagulation/sedimentation/clarification techniques. It is common practice to install strainers prior to pumps on open recirculating condenser water systems to protect the pump internals, vanes, shaft and impellers from large damaging flakes of rust, suspended dirt, or other foreign particles that can enter an open system. Similarly, strainers should be installed on closed systems as they are frequently plagued with suspended black magnetic iron oxide mill scale as well as foreign particles. The bag or cartridge strainer can be used as a coarse filter to remove larger particles before the pumps and heat exchangers.
- *Disinfection.* Here, we might consider ultraviolet light at 254 nm (UV), ozone, chloramines, chlorine dioxide, bleach, or emerging technologies such as photocatalytic anatase titanium dioxide (TiO_2), for example, TioxyClean™, etc.
- *FOG, solvent, and hydrocarbon removal.* Organics for example, benzene, toluene, xylene – BTX) can be removed using coalescers such as American

Photo 9 (a) Filters removing oil and organics from water, (b) twin ion-exchange water softeners with salt tank and chemical feed station, (c) demineralization and RO plant, (d) deaerator.

Petroleum Institute (API) separators, corrugated plate interceptors (CPI), or dissolved air flotation (DAF) units.[17] A secondary filtration system such as bentonite, organoclay, or similar full-flow media filter (e.g., Biomin™) may also be required.[18] Also advanced filtration/absorption processes may be used, although careful designs are needed as the rule of thumb is often that 50% of costs are incurred for the first 99% of contaminant removal, with the other 50% being spent on the last 1%.[19]

- *Hardness and/or silica removal.* This can be achieved through hot/cold lime and lime-soda softening or ion-exchange. An ion-exchange water softener is a synthetic zeolite softener containing an ion-exchange water softener resin. This ion-exchange resin adsorbs calcium and magnesium ions from the water passing over the resin bed. The resin at the same time releases sodium, hence the term 'ion exchange.' It is often not economical to use softeners for open cooling tower condenser water, evaporative condensers, chilled water and closed loops, hot water generators, and surface spray units, as these systems operate at pH values close to the neutral point, where the hardness can be kept in solution with the aid of antiscalents and pH control types of chemical treatments. However, chemical treatments will be required even if most of the hardness is removed.

Waters with a hardness of more than 300 or 400 mg l^{-1} require at least partial softening so that they can be used for cooling tower makeup water. With steam boilers, however, removal of hardness from the makeup water is nearly always required to remove the hardness, and prevent risks of excessive scale or sludge deposits on heat-transfer surfaces. With steam boilers, the determining factors are both the hardness and the amount of makeup water used. In low-pressure heating applications where steam is used for heating only and possibly small amounts of humidification requiring less than 10% of the steam generated, the boiler feedwater will consist of 90% or more of return steam condensate. In instances such as this, the makeup water will not require external hardness removal as the small amount of hardness entering the system can be controlled with internal treatment.

- *Heavy metal removal.* Metals such as iron, lead, nickel, chromium can be removed by coagulation and alkaline precipitation, or by use of carbamates. Also used is absorption on waste treatment residues (WTR – a lime-based product) or iron-coated olivine (a magnesium–iron silicate) – usually at a neutral to acid pH.
- *Iron and manganese removal.* Fe and Mn are common contaminants in many water sources and may be removed by use of aeration, coagulants, manganese greensand/permanganate techniques, or BIRM™ filters.
- *Removal of volatile organic compounds (VOCs), organics, ammonia, chlorine, color, turbidity, BOD, and COD.* A wide range of organics and other contaminants may be removed from water by using air scouring, activated carbon filters, bio-reactors, redox chemicals, or traditional activated sludge methods.
- *Wide-spectrum contaminant removal.* In addition to the above processes, various membrane techniques (e.g., microfiltration, EDI, RO) may be employed, either as stand-alone processes combined with deionization (DI) or as part of more complex pretreatment arrangements to remove oils, organics, etc.[19]
- *Mechanical removal of oxygen.* In many boiler plant installations, it is economical, necessary, or simply good practice to remove oxygen in the boiler feedwater by use of feedwater heaters or mechanical deaeration (prior to use of a chemical oxygen scavenger for final removal of corrosive gases), in order to prevent serious corrosion and pitting of steam boiler feedwater lines and boiler tubes. Whenever a steam boiler system is open to the atmosphere through vented condensate receivers, feedwater tanks, etc., the air absorbed will result in high quantifies of dissolved oxygen. This increases in direct proportion to the amount of makeup water used because the cold raw makeup water is high in dissolved oxygen, High levels of cold makeup water will not only increase the dissolved oxygen content, but also will lower the temperature of the feedwater in the return condensate tank, enabling more oxygen from the atmosphere to be dissolved in the feedwater. This happens because the solubility of oxygen in water is inversely proportional to temperature.

  Modification of the feedwater for oxygen removal is best carried out by using a deaerator. The mechanical pressure deaerator is a complex device that utilizes steam injection to scrub the incoming makeup water and condensate for removal of the dissolved corrosive gases, oxygen and carbon dioxide. In the deaerator, water is sprayed over inert packing or trickled through baffles or trays to break up the water and provide for intimate mixing of the feedwater with the incoming steam. The steam is injected counter to the flow of the incoming water, which drives the gases, oxygen and carbon dioxide upward out the vent. The vent releases only noncondensible gases and steam losses are at a minimum. Some deaerators can produce feedwater with dissolved oxygen content as low as 0.005 $cm^3\,l^{-1}$ (0.0072 ppm).[20,21]

4.27.11 Modifying Waterside Environments by Appropriate Metal and Alloy Materials Selection

Corrosion protection of metal surfaces contacting water is an ongoing management, maintenance, and control problem, as has been discussed elsewhere. However, better selection of appropriate materials at the design stage can help minimize initial corrosion risks; therefore, consideration of the galvanic series at the material selection stage is a useful exercise. Also, metals may only be vulnerable under very specific operating conditions; therefore, a simple galvanic series guide may not, by itself, be satisfactory and further investigation may be required. Simple things like flow rate, high cycles of concentration, or high chlorides may initiate corrosion problems.

Table 4 provides a limited corrosion vulnerability summary.

An example of the need for appropriate materials selection is when employing high chloride waters in cooling systems containing stainless steels, as it is well known that high chlorides will increase the risk of stress corrosion cracking in austenitic stainless steels (e.g., types 304/304L/316/316L) and will tend to increase general corrosion and attack in localized areas, often causing pitting type corrosion. Specifications for the upper limits of tolerance to chloride ions, where the cooling system contains a high percentage of 304L stainless steel (SS) or there is concern over vulnerability of stainless steel components, will typically designate 200 $\mathrm{mg\,l^{-1}}$ $\mathrm{Cl^-}$. Nevertheless, high natural chlorides can often be tolerated in recirculating water at levels of 600–800 $\mathrm{mg\,l^{-1}}$, and estuarine water users can find seasonal fluctuations raise the chloride in their systems to perhaps 800–1200 $\mathrm{mg\,l^{-1}}$ $\mathrm{Cl^-}$. This latter level is probably the maximum that can be tolerated under normal circumstances for 304-grade SS and requires good management if serious problems are to be avoided.[11]

Table 4 Corrosion vulnerability summary

Metal	*Type of corrosion risk in water*
Steel	Stagnant water tends to induce local attack Fouling induces concentration cell type corrosion High $\mathrm{Cl^-}$ and $\mathrm{SO_4^{2-}}$ tend to increase risks of pitting $\mathrm{O_2}$ saturated water may induce general corrosion Fouling and $\mathrm{SO_4^{2-}}$ induce corrosion from sulfate reducers Coupling with noble metal causes galvanic corrosion pH 4.0 induces rapid acid-induced wastage and pitting
Iron	Presence of some $\mathrm{O_2}$, plus deposits and low flow, stimulate tuberculation Soft water, low pH, $\mathrm{H_2S}$ can stimulate graphitization
SS	Vulnerable to depassivation from high $\mathrm{Cl^-}$ and $\mathrm{SO_4^{2-}}$ Residual or applied stress with $\mathrm{Cl^-}$ induces SCC.
Brass	Ammonia produces cracking & wastage. High velocity can induce erosion-corrosion (>6 fps) Uninhibited brass suffers dezincification
Zinc	High alkalinity causes white rust
Al	pH over 9.0 with $\mathrm{OH^-}$ causes rapid corrosion

The maximum chloride limit for 316-SS grades is generally set by technical organizations at 1000 $\mathrm{mg\,l^{-1}}$ but higher concentrations can sometimes be tolerated, and up to 5000 $\mathrm{mg\,l^{-1}}$ $\mathrm{Cl^-}$ have been reported in refinery water reuse programs.[17]

At chlorides concentrations of up to 3600 $\mathrm{mg\,l^{-1}}$, a duplex SS is recommended (e.g., 2205-grade) and seawater requires superaustenitic or superduplex SS grades.[27]

Where specific metals and alloys have been selected, part of the ongoing control of corrosion risk is to monitor corrosion rates *in situ* using test pieces, coupons, and various forms of test meters. An example of a corrosion test coupon is shown in Photo 10. The corrosion coupon test method has been described by the National Association of Corrosion Engineers (NACE) and is consistent with the ASTM standard 'Corrosivity Testing of Industrial Cooling Water (Coupon Test Method).' The test coupon is placed in the recirculating water system in a test coupon 'rack.' The corrosion test report will include the calculated corrosion rate in mils per year or micrometers per year and other pertinent data such as depth of pits, variations, and types of corrosion deposits.

In cooling systems, the results of corrosion monitoring can be usefully interpreted from Table 5.

4.27.12 Understanding Contaminant Saturation Problems as a Precursor to Modification of Waterside Environments by Chemical Inhibitors

In most sources of water, apart from estuarine water and seawater, calcium bicarbonate is usually the most abundant salt found; but it has only limited solubility

Photo 10 Corrosion test coupon.

Table 5 Guide to specifying and quantifying corrosion rates

Interpretation of cooling system corrosion rates

Description	*Rate (mpy)*	*Comment*[a]
Negligible	<2.0	Excellent. Very difficult to achieve.
Mild	2.0–4.0	Good. Acceptable for most situations.
Moderate	4.0–6.0	OK. Probably adequate protection.
High	6.0–8.0	Poor. Doubtful protection.
Severe	>10.0	Very poor. Probably unacceptable protection.

[a] For closed systems, same comments apply if steel mpy is 50% of above rates. For Cu and brasses the same comments apply if mpy is 10% of above rates.

and under conditions where concentration effects take place, as in a cooling system, it will break down to calcium carbonate and form troublesome crystalline scale or sludge deposits. This effect also takes place where heating occurs, as in a boiler, because of an inverse solubility.

Similar effects occur in seawater, where although sodium chloride will be present at levels exceeding 35 000 mg l^{-1} (ppm) calcium bicarbonate will be present only at approximately 400–420 mg l^{-1}; if the seawater is heated (as in a multistage flash evaporator for the generation of potable water), the calcium bicarbonate will again breakdown to form calcium carbonate scale. Of course, the sodium chloride salt presents another problem, one of corrosion, and it is common to find some form of corrosion associated with most scaling deposits. Scaling and deposition problems often occur in the same water system, and therefore modification of a waterside environment to control one problem must, of necessity, take into consideration the opposite problem at the same time.

Calcium carbonate ($CaCO_3$) can form as both aragonite and its polymorph, calcite, which has the same chemistry as aragonite, but a different crystal structure and shape. Aragonite is thermodynamically unstable at standard temperature and pressure, and tends to transform to calcite. Under most heating or concentration–effect conditions in water systems where amorphous or crystalline calcium carbonate scales develop, it is generally considered that calcite is preferentially formed, as it is the most stable form of crystalline calcium carbonate scale. This may simply be a measure of convenience rather than a fact always; however, it allows us to consider the concept of saturation of a salt or compound in water and the resulting effects of exceeding saturation level concentrations.

A water is said to be saturated with a compound (e.g., calcium carbonate, tricalcium phosphate, amorphous silica,) if it will not precipitate the compound and it will not dissolve any of the solid phase of the compound when left undisturbed, under the same conditions, for an infinite period of time. Water which will not precipitate or dissolve a compound is at equilibrium for the particular compound. Water from which a compound precipitates is supersaturated with respect to that compound. The precipitate is a foulant and may also cause crystalline scaling deposits to be formed. Calcite is the most common foulant. By definition, the amount of a calcium carbonate that can be dissolved in a water and remain in solution for this infinite period of time is described by the solubility product.

$$K_{sp} = (\mathrm{Ca})(\mathrm{CO_3})$$

where (Ca) is the activity of calcium; (CO_3) is the carbonate activity; K_{sp} is the solubility product for calcium carbonate at the temperature under study.

The degree of saturation of any compound (such as calcite) in water is described by the relationship of the ion activity product (IAP = (Ca)(CO_3)) to the solubility product (K_{sp}) for the compound as follows:

- If a water is undersaturated with a compound ($\mathrm{IAP} < K_{sp}$), then it will tend to dissolve the compound
- If a water is at equilibrium with a compound ($\mathrm{IAP} = K_{sp}$), then it will not tend to dissolve or precipitate the compound
- If a water is supersaturated with a compound ($\mathrm{IAP} > K_{sp}$), then it will tend to precipitate the compound.

The saturation index (or degree of supersaturation) describes the relative degree of saturation as a ratio of the ion activity product (IAP) to the solubility product (K_{sp}), such that[22,23]:

$$\mathrm{SI} = \frac{\mathrm{IAP}}{K_{sp}}$$

Under typical practical operating conditions, the solubility of calcium carbonate in CO_2-free water at 15 °C is estimated as only 14 mg l^{-1} and so modification of the waterside environment is required to prevent calcite scaling.[11] This usually requires the application of an antiscalent chemical. There are a

Anodic reactions:	*Cathodic reactions:*
1. $Fe \rightarrow Fe^{2+} + 2e^-$	1. $\frac{1}{2}O_2 + H_2O + 2e^- \rightarrow 2OH^-$
2. $Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2$	2. $2H^+ + 2e^- \rightarrow H_2\uparrow$
3. $4Fe(OH)_2 + O_2 + 2H_2O \rightarrow 4Fe(OH)_3$	

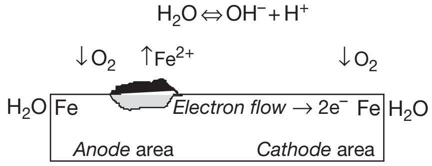

Figure 3 Corrosion reactions forming rust blisters over pit.

wide range of water treatment chemistries (polyacrylates, phosphonates, polymaleates, etc.) available in the market today and antiscaling inhibitor formulation blends based on one or more of these chemistries will typically be able to control the risk of fouling in strongly scaling waters where the calcite SI exceeds 100; and often 150.

For any water under specified operating conditions, the IAP and SI for a range of contaminants (and thus the risk of fouling) can be calculated using industry-available software programs.[24] These modern programs overcome the operational interpretation problems (such as a failure to take into account common ion effects) of early, noncomputerized indices, for example, the Langelier saturation index (LSI).

4.27.13 LSI and Related Indices as an Aid to Modification of Waterside Environments

In condenser water systems using recirculating cooling tower water or once-through cooling water, the water temperature is much lower than that in steam boiler or hot-water systems. At these lower temperatures most of the scale-forming minerals will remain in solution, but the tendency will be to deposit calcium carbonate (calcite) on the heat-transfer surfaces where there is a slight rise in temperature. Modification of a water to reduce the risk of fouling, scaling, and/or corrosion requires that certain analytical factors are considered. The primary factors that affect this tendency are the following:

- alkalinity;
- calcium hardness;
- pH;
- total dissolved solids; and
- temperature.

The higher the alkalinity of a particular water, the higher the bicarbonate and/or carbonate content. As these minerals approach saturation, they tend to come out of solution and precipitate as a calcite foulant or scaling deposit. Likewise, a higher concentration of hardness will increase the/tendency of calcium and magnesium salts to come out of solution. The pH value reflects the ratio of carbonate to bicarbonate alkalinity.

The higher the pH value, the greater the carbonate content of the water. As calcium carbonate and magnesium carbonate are less soluble than the bicarbonate, they will tend to precipitate as the pH value and carbonate content increase. Also affecting this tendency are the TDSs and temperature. The higher the solids content the greater the tendency to precipitate the least soluble of these solids. The higher the temperature, the greater the tendency to precipitate the calcium and magnesium salts because of their property of inverse solubility.

- *Langelier saturation index (LSI).* This, developed in 1936, is a calcium carbonate saturation index that is very useful in determining the scaling or corrosive tendencies of a water sample under investigation. It is based on the assumption that any given water with a scaling tendency will tend to deposit a corrosion-inhibiting film of calcium carbonate and hence will be less corrosive. By inference, water with a nonscaling tendency will tend to dissolve protective films and be more corrosive. This is not entirely accurate as other factors are involved in corrosion, but, although a relatively simple tool, it provides a valuable index in determining the tendency of water to directly influence scaling or corrosive actions.

  The LSI is on the basis of the pH of saturation of calcium carbonate. The pH of saturation (or 'saturation pH,' pH_s) of calcium carbonate (calcite) is the theoretical pH value of any particular water if that water is saturated with calcium carbonate, and is given by the formula below:

$$pH_s = (9.3 + A + B) - (C + D)$$

where $A = (\log_{10}[\mathrm{TDS}] - 1)/10$; $B = -13.12 \times \log_{10}(°C + 273) + 34.55$; $C = \log_{10}[Ca^{2+} \text{ as } CaCO_3] - 0.4$; $D = \log_{10}[\text{alkalinity as } CaCO_3]$
or

$$pH_S = 12.3 - (\log_{10}\mathrm{Ca} + \log_{10}\mathrm{TA} + 0.025\,\mathrm{Temp} - 0.011\,TDS^{\frac{1}{2}})$$

Table 6 Makeup water requirements decrease with increasing COC

Makeup water volumes based on an evaporation rate of 5000 $m^3 \, day^{-1}$

Bleed rate assumes no windage loss

COC	Bleed (m^3 day)	Makeup ($m^3 \, day^{-1}$)
2×	5 000	10 000
3×	2 500	7 500
4×	1 666	6 666
5×	1 250	6 250
6×	1 000	6 000
7×	833	5 833
8×	714	5 714
9×	625	5 625
10×	555	5 555

where Ca = calcium Hardness as ppm $CaCO_3$; TA = total alkalinity as ppm $CaCO_3$; Temp = Temperature as °C; TDS = total dissolved solids ppm.

To determine the Langelier index, the actual pH of the water must be measured, and the pH of saturation of calcium carbonate is calculated from a measure of the total alkalinity, hardness, TDSs, and temperature. Once the pH of saturation of calcium carbonate has been calculated, the LSI can be determined from the formula.

$$\mathrm{LSI} = \mathrm{pH} - \mathrm{pH_s}$$

A positive index indicates scaling tendencies; a negative one (by inference), corrosion tendencies as shown below:

- If LSI is negative: No potential to scale, the water will dissolve $CaCO_3$. An LSI of −2.5 is extremely corrosive
- If LSI is positive: Scale can form and $CaCO_3$ precipitation may occur. An LSI of +2.5 is extremely scale-forming
- If LSI is close to zero: Some risk of either/both scale/corrosion. Water quality, changes in temperature, or evaporation could change the index.

An LSI of 2.5 is approximately equivalent to a calcite saturation index (CSI) of 150

- *Ryznar index (Ryznar stability index, SI, RSI).* This is another useful tool for determining the scaling tendencies of water. This index is also on the basis of the pH of saturation of calcium carbonate and was intended to serve as a more accurate index of the extent of scaling or corrosion in addition to the tendency. This index was derived from the LSI by observation of actual cooling water conditions and is calculated as follows:

$$\mathrm{RSI} = 2(\mathrm{pH_s}) - \mathrm{pH}$$

where $\mathrm{pH_s}$ = pH of saturation of calcium carbonate, pH = actual measured pH of the water, RSI <6 the scale tendency increases as the index decreases, RSI >7 the calcium carbonate formation probably does not lead to a protective corrosion inhibitor film, RSI >8 mild steel corrosion becomes an increasing problem.

- *Puckorius scaling index (PSI).* LSI and RSI are limited in their absolute relevance as they do not account for two other critical parameters: the buffering capacity of the water, and the maximum quantity of precipitate that can form in bringing water to equilibrium. Puckorius attempts to quantify the relationship between saturation state and scale formation by incorporating into the index an estimate of buffering capacity of the water. However, it is debatable whether, in a practical situation, this additional estimate is of real value, as common ions effects still bring other factors into the overall situation. Common Ion effects are taken into account in IAP modeling, such as the various FrenchCreek® software programs.[24]

Water high in calcium, but with low alkalinity and buffering capacity can have a high calcite saturation level. The high calcium level increases the ion activity product and a plot of ion activity product against precipitate for the water would show a rapid decrease in pH as calcium carbonate is precipitated because of the low buffering capacity. Even small decreases in carbonate concentration in the water would significantly decrease the ion activity product because of the small quantity present prior to the initiation of precipitation. This water might have a high tendency to form scales because of the driving force but any scale formed would be a small quantity and practically unobservable. Thus, the water has the driving force but not the capacity and ability to maintain pH as precipitate matter forms. PSI is calculated in a manner similar to the RSI; however, Puckorius uses equilibrium pH rather than the actual system pH to account for the buffering effects:

$$\mathrm{PSI} = 2(\mathrm{pH_{eq}}) - \mathrm{pH_s}$$

where $\mathrm{pH_s}$ is the pH at saturation of calcite or calcium carbonate, $\mathrm{pH_{eq}} = 1.465 \times \log_{10}[\mathrm{Alkalinity}]$

$+ 4.54$, $[\text{Alkalinity}] = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-]$.

Interpretation of PSI is the same as for RSI.

- *Larson–Skold index (L-SI).* The L-SI indicates the corrosivity of water towards mild steel and is based on the evaluation of actual corrosion rates and the type of attack on mild steel lines transporting Great Lakes waters. The index is the ratio of equivalents per million (epm) of sulfate (SO_4^{2-}) and chloride (Cl^-) to the epm of alkalinity in the form bicarbonate plus carbonate[26]:

$$\text{L-SI} = (\text{epm}Cl^- + \text{epm}SO_4^{2-})/(\text{epm}HCO_3^- + \text{epm}CO_3^{2-})$$

Extrapolation of observed corrosion results to other waters, such as low or very high alkalinity waters, goes beyond the range of the original data. The index has proven a useful tool in predicting the aggressiveness of once-through cooling waters. The L-SI may be interpreted in the following way:

- L-SI = <0.8: Chlorides and sulfate probably will not interfere with natural film formation;
- L-SI = 0.8–1.2: Chlorides and sulfates may interfere with natural film formation and higher corrosion rates might be anticipated;
- L-SI ≥ 1.2 A tendency towards higher localized corrosion rates should be expected as the index increases.

4.27.14 Use of Contaminant Cycling Effects in Modifying Waterside Environments

The previous section discussed the problem of exceeding calcite saturation limits in water and the very real risks of producing scaling deposits. Calcite scaling risks tend to increase in waters with higher alkalinities, but conversely, the propensity for general corrosion tends to fall, because of the shielding effect of calcium carbonate foulant at the heat exchange surface. This reduced corrosion risk might be considered a benefit, and thus, it is common in both boiler waters and recirculating cooling waters to increase alkalinity levels as an aid to reducing corrosion.

In both steam raising boilers and cooling systems, evaporation of water takes place with makeup water replacing that lost by evaporation and, as the makeup waters will inevitably contain dissolved gases and mineral contaminants, concentration effects take place which can lead to an increase in contaminants, including alkaline salts. Of particular interest is that the concentration of (alkaline) calcium bicarbonate will increase, and where breakdown of calcium bicarbonate occurs there is a loss of (acidic) carbon dioxide leading to an increase in alkaline (protective) carbonates.

Thus increasing cycles of concentration can be a simple method of mitigating risks of corrosion. In any water system where evaporation occurs there are always constraints that limit the degree of concentration that can takes place, but this is usually well beyond the saturation limits for most scaling contaminants. Thus, operational limits are placed on the water system by periodically blowing down (bleeding off) some of the 'concentrated' water and replacing it with fresh makeup water. The overall effect is that for any specific water system, the cycles of concentration (COC), that is, the ratio of concentration of TDS in recirculating water to that of the make-up water, are maintained at a prescribed limit, appropriate for the water system in question. This limit may be from, say, 3–10 cycles for cooling systems, and from 10 to 100 cycles for steam raising boilers.

There is an additional benefit of maintaining an appropriately high COC in a water system, and that is that losses of water because of blowdown (bleed) are controlled and generally minimized, leading to an increase in operational efficiency and a savings in both water and chemical inhibitor costs. It should be noted that evaporation rates are not affected by COC. Table 7 shows the potential for water savings with increase in COC.

Typically, when calculating actual, theoretical, and practical COC in cooling system waters, because of the difficulties of testing for TDS in water, testing for chloride is carried out. Chlorides are very soluble and are not otherwise easily removed from the water. We know that COC relates to the increase in TDS over time in the recirculating water, as evaporation (E) of pure water takes place from the tower (providing the cooling effect) and is replaced by makeup water (MU) containing additional TDS. The record of past COC as well as the potential for improving future operating COC is often a vital key to technically improving water treatment management (adding value).

For any cooling system, there is a limit to the maximum COC that can be obtained. The limit is essentially on the basis of the loss of TDS-containing

Table 7 Contaminant limits in cooling waters

TAB result	*Evaluation*
0 to10^2 colonies per ml	Excellent control
10^2 to10^3 colonies per ml	Warning, but no serious fouling risk
10^4 to10^5 colonies per ml	10^4 is the maximum permitted for healthcare 10^5 is a typical maximum for commerce/industry
10^5 to10^6 colonies per ml	Unacceptable. Fouling anticipated. Also, a possible health risk
$>10^6$ colonies per ml	Serious risk of fouling and pathogens

water, that is, windage or drift (D), deliberate purge or bleed (B), and leaks. If all leaks and bleed can be halted, then:

$$\mathrm{COC_{max}} = \frac{E + D}{D}$$

Typically, $E = 1\%$ of water circulation rate (CR) per 10 °F ΔT.
where ΔT = temperature drop over tower, D is usually in the range 0.01–0.3% of CR for mechanical draft towers.

Also, considering bleed (B):

$$\mathrm{B} = (E/\mathrm{COC} - 1) - D$$

4.27.15 Modification of Waterside Environments by Chemical Inhibitors

In general, although a very wide range of chemical inhibitors is commonly available and employed in all types of water systems, the specific selection is based on the needs of the water system under consideration, and such needs may include, for example, green chemistry protocols, food industry requirements, or discharge regulations.

The selection of chemical inhibitors forms part of a water treatment program that is usually water system specific and generally thought of as an ongoing maintenance ‘polishing’ protocol. The inhibitor program is typically designed to also operate in conjunction with water treatment equipment, such as filters, softeners, or deaerators.

Modification of the waterside environment by chemical inhibitors will result in cleaner heat-exchange surfaces, relative freedom from corrosion and other problems, improved operational efficiencies, reduced cleaning and other maintenance issues, and increased asset lifespan.

4.27.16 Modification of Steam Boiler Waterside Environments by Chemical Inhibitors

The chemicals, equipment, and methods for inhibitor chemical addition, testing, and control required to optimize firetube (FT), watertube (WT) and other types of steam boiler system operations, to reduce the risks of corrosion, scaling, and fouling to accepted minimums must be tailored, not only to each system, but also to each geographic location, as the water quality and contaminant level will vary by location, and also by season. Implementation and optimization of chemical inhibitor programs need to be administered by qualified water technologists – usually those with an engineering or chemistry background.

The chemical inhibitors are usually referred to as ‘internal treatments,’ as opposed to ‘external treatments,’ by which is meant pretreatment equipment.

Modification of steam boiler water systems by chemical inhibitor programs is required to prevent the problems of corrosion, pitting, scale deposits, and erratic boiler operation because of priming, foaming, and carryover. To prevent these problems, correct blowdown and treatment must be applied. HVAC and space heating boilers also require similar modification, although operational conditions may not need to be so tightly controlled. Control over problems such as the supersaturation of dissolved solids, short and long-term overheating, and boiler priming (surging) rely at least as much on good operation. A summary of the most common problems and the chemistries used to modify the waterside environment follows.

- *Blowdown control.* Blowdown of a boiler is the spontaneous removal of some concentrated boiler water from the boiler under pressure. The recommended maximum concentrations of the impurities, which must be properly controlled, are generally specified by codes, insurance companies, or by industry standards or consensus (e.g., ASME Consensus). Actual operating experience will determine the true operational limits for any specific boiler operation.

The maximum allowable cycles of concentration can be maintained by blowing down the boiler water, in order to remove accumulated boiler water solids. The amount of solids present in the concentrated boiler blowdown water is equal to the amount of solids in the makeup water multiplied by the cycles of concentration. This can be expressed mathematically as

$$\text{Solids leaving} = BCX$$

where B is the blowdown, gal (l), C is the cycles of concentration, X is the total solids concentration of makeup water, mg l^{-1} (ppm).

The amount of solids entering the boiler with the makeup is expressed as

$$\text{Solids entering} = MX$$

where M is makeup water (l, gal).

As blowdown is designed to maintain a specific level of cycles of concentration, the specified level can be kept consistent only if the amount of solids leaving the boiler is equal to the amount of solids entering the boiler. This is expressed as:

$$BCX(\text{solids leaving}) = MX(\text{solids entering})$$

Solving this equation for blowdown B, we obtain:

$$B = \frac{M}{C}$$

This formula is used to determine a blowdown rate with respect to the makeup rate. In percent, it can be expressed as:

$$\%\text{Blowdown} = \frac{100}{C}$$

- *Control of priming, foaming, and carryover.* Priming of boiler water is the bumping and bouncing of the water level of the boiler during operation. Foaming, however, is a less violent activity and consists of the formation of small bubbles in the surface of the boiling water. Carryover essentially is the contamination of the steam with boiler water and is a result of priming and foaming. However, it can be a more subtle entrapment of boiler water with the steam, causing steam contamination without the evidence of priming and/or foaming. Most frequently, the causes of priming, foaming, and carryover are a result of contamination of the boiler water with oil or other foreign substances. Other causes are excessive solid accumulation because of the lack of blowdown, high alkalinity, over-treatment, and mechanical malfunction. Modification of the boiler water to reduce the problems of priming, foaming, and carryover will require adequate blowdown and certain adjunct antifoam inhibitor treatments – generally polyethoxylates.[21]
- *Corrosion control.* Control over boiler section system corrosion typically requires a combined approach that includes (following mechanical deaeration), oxygen scavenging, maintenance of passivated films, and pH and alkalinity control. Primary inhibitor chemistries encompass oxygen scavengers that include inorganics such as sodium sulfite and organics such as hydrazine. Sometimes, certain additional conjunctional inhibitor treatments are required, such as sodium nitrate for protection against embrittlement. Also, anodic corrosion inhibitor programs, which employ nitrite, silicate or molybdate chemistries, may be specified in light-duty multifunctional programs for HW heating and lower-pressure steam boiler systems. Additionally, tannin programs, on the basis of blends of certain natural (e.g., quebracho tannin) or synthetic tannins are used as corrosion inhibitors, as they provide a combination of oxygen scavenging, passivating and sludge conditioning functions.

Sodium sulfite is widely employed, and approximately 8 ppm is needed for every 1 ppm of oxygen. As a fairly high sulfite reserve is required (typically 20–50 ppm or more), additional sulfite must be added and so the general rule is 10 ppm of sodium sulfite per 1 ppm oxygen. The maintenance of a slight excess of the oxygen scavenger in the water provides assurance that there is no dissolved oxygen present. Complete water treatment formulations containing sodium sulfite for this purpose will also include a catalyst, ensuring that the reaction between the dissolved oxygen and the oxygen scavenger is instantaneous, even in cold water.

Hydrazine is not widely used as an oxygen scavenger because of its toxicity. Other oxygen scavengers currently used as a replacement for hydrazine include diethylhydroxylamine (DEHA), sodium erythorbate, carbohydrazide (CHZ), methylethylketoxime (MEKO), and hydroquinone (HQ). Typical reserves for these materials are very low, perhaps only 0.1–0.2 ppm.

Control over corrosion in the boiler section may also require the use of alkalinity boosters, based on alkali metal hydroxides. Feedwater pH is generally in the range 8.0–9.3. Boiler water pH will vary depending upon design and pressure rating. For lower pressures the pH will be 10.5–11.5 or 12. For higher pressures, the pH may only be 9.0–10.0.

Control over corrosion in steam and condensate line sections will need to manage the ingress of oxygen and the formation of carbonic acid, and perhaps deal with the corrosive effects of ammonia on copper – which may have been specified as a pH adjuster and steel corrosion modifier. Condensate treatments include neutralizing amines such as morpholine and filming amines such as octadecylamine (ODA), as well as the highly basic ammonia.

- *Scale and deposit control.* This requires control over primarily hardness salts and other scale forming minerals. Usually a water softener will be specified to soften all incoming makeup water, used as boiler feed. Internal inhibitors include coagulation and precipitation chemistries, chelants, polymers, and blends of all these types of chemicals.

  Coagulation and precipitation programs are widely used and employ various types of phosphates as a precipitant to provide control over the unwelcome deposition of hardness scales. Carbonates and polysilicates were once commonly used. Chemistries based on neutral and alkaline phosphates are now the primary precipitation programs. Where coagulation and precipitation programs are employed, specific polymeric dispersants are also required. In the presence of excess alkalinity, phosphate is precipitated as calcium hydroxy-phosphate or hydroxyapatite [$Ca_3(PO_4)_2 \cdot Ca(OH)_2$]. Magnesium with hydroxide alkalinity present in the boiler water will form the hydroxide, precipitating as brucite ($MgOH_2$). In these forms, the particles are more easily dispersed and held in suspension. It is vital to have adequate alkalinity. The basic coagulation and precipitation program includes a phosphate polymer combination used to maintain a sodium phosphate concentration in the boiler water at 20–60 mg l^{-1}, ensuring that all the calcium has precipitated as phosphate.

  Chelant programs, based on the use of ethylenediaminetetraacetic acid (EDTA) and nitrilotriacetic acid (NTA) chemistries, are commonly prescribed for both FT and WT boilers either as replacements for, or used in combination with, phosphate precipitation programs. They act as solubilizers, not precipitants. Chelants should not be used in excess of 2–3 mg l^{-1} free chelate because corrosion of iron can be accelerated in the boiler water. Excellent control over the presence of dissolved oxygen is vital, but chelants can provide a very clean boiler.
- All-polymer/all-organic programs are perhaps the most widely used hardness control products today. Very many specialty polymers are now available and widely used in every type and size of boiler. Typically, multifunctional blends are used as phosphate replacements, and act as dispersants and sludge conditioners. They also provide control over specific problems such as iron transport and silica scaling that can affect many industrial boiler systems. The type of polymers employed includes, polyacrylic acid and polyacrylates (PAA), sulfonated styrene/maleic anhydride (SS/MA), and an iron oxide dispersant, the second one (SS/MA) being an excellent $Ca_3(PO_4)_2$ inhibitor/dispersant where soluble Fe is absent. Also, the copolymer based on acrylic acid and 2-acrylamido-methylpropane sulfonic acid (AA/AMPS or AA/SA) is employed as a $Ca_3(PO_4)_2$ inhibitor/dispersant. Additionally, phosphinocarboxylic acid (PCA) chemistries are used as high temperature suspended-solids dispersants and $CaSO_4$ scale inhibitors. These polymers are also polyelectrolytes and distort the scale particle/crystal and its growth, rendering it less adhesive to heat-transfer surfaces and more readily dispersed with a reduced tendency to compact into a dense scale. Some modern polymers also sequester hardness similar to the chelants.

  Many permutations of dual- or multifunctional programs exist, on the basis of either chelant or phosphate chemistries, together with polymers and related organics. These types of program are widely employed.
- *Control over specific contaminants and higher pressure boilers.* Very specific polymers are used for control over silica, iron, and copper transport.

  Coordinated phosphate programs are employed where there is a need to avoid the formation of hydroxyl alkalinity (free caustic) in higher-pressure WT boilers. They require very careful management and control. Variant programs include congruent control and equilibrium phosphate treatment chemistries.

  All-volatile programs (AVPs) are also employed in higher-pressure boilers (generally power boilers) and utilize only volatile chemicals, such as ammonia, amines (such as diethylhydroxylamine, DEHA), and other vapor-phase inhibitors (VPIs).

4.27.17 Modification of Cooling System Waterside Environments by Chemical Inhibitors

Corrosion and deposits of scale, dirt, mud, organic slime/biofilms, and algae growths are the major problems encountered in open recirculating cooling water systems. There is a loss of water caused by both evaporation and windage drift. The water lost by drift will be of the same quality as the recirculating water; that is, it will contain the same amount of dissolved minerals and impurities. The water lost by evaporation, however, will be essentially pure water, devoid of mineral contaminants.

The evaporation of pure water vapor leaves the dissolved mineral contaminants behind in the recirculating water, and as discussed earlier, the water lost by evaporation is replaced by makeup water, containing dissolved minerals and impurities. As a result, there is an accumulation of minerals that constantly increases in the system as more makeup water is introduced. If the cycles of concentration of dissolved minerals are not controlled, eventually the recirculating water will become so saturated that the most insoluble salts will come out of solution and form a scale on heat-transfer surfaces or within other parts of the system. To avoid this, a risk–benefit condition exists, whereby some bleed off is given but COC is strictly limited.

If COC is raised, there are savings to be made in both water volumes and chemical inhibitors consumed. However, the risk of scaling and fouling increases, which can produce significant cost increase because of cleaning, loss of operational efficiencies, and additional maintenance, so a risk–benefit balance has to be calculated. This will be different for each and every type of cooling system, on the basis of system design acceptable maintenance costs, and water quality.

In open cooling water systems, oxygen cannot be economically removed with scavengers because these systems are constantly aerated and therefore, corrosion inhibitors that are effective in oxygen-containing environments must be employed. Also recirculating cooling water systems contain various types of metals and alloys, and inhibitors and environmental conditions maintained must be compatible with these multimetallic systems. A particular problem associated with these systems is galvanic corrosion caused by bimetallic couples and white rust.

Treatment of recirculating cooling water must first include control of the pH value for both scale and corrosion control – usually within the range of 7.5–9.5. Lower pH values tend to render the recirculating water excessively corrosive, while higher pH values will result in both amphoteric metal corrosion (as with zinc, brass, and aluminum) and scale-forming conditions. At this pH, modification of corrosion risk is controlled by corrosion inhibitors added to the recirculating water, which usually form a protective barrier on the metal surface either by chemical reaction with the metal surface or by physical or chemical adsorption on the metal surface. An actively corroding metal can be rendered passive though the use of inhibitors that react in this manner. There are many types and combinations of corrosion inhibitors used for open cooling water systems, on the basis of molybdate, zinc, phosphate, and potentially many dozens of organic-based inhibitor chemistries.

The most troublesome mineral scale is calcium carbonate as it is the least soluble of the salts present in the recirculating water. Alkalinity should also be limited to prevent precipitation of calcium carbonate scale. Alkalinity is present in the form of bicarbonates and carbonates which combine with calcium and magnesium to form calcium carbonate and magnesium carbonate. (Calcium carbonate, being less soluble than magnesium carbonate, will form first).

Alkalinity should be limited not only to prevent precipitation of calcium carbonates, but also to prevent high pH conditions, which may be damaging to some system components such as galvanized steel, brass, or cooling tower lumber. In many larger cooling systems operating with hard water, sulfuric acid is employed to reduce alkalinity by forming calcium sulfate, which is much more soluble than calcium carbonate by a factor of more than 100 times.

Smaller cooling systems operating with hard water may use fully or partially softened water. It is not a good idea to use fully softened water as the risk of corrosion increases significantly. In most modern cooling water program chemistries, calcium, in the presence of phosphonates and polymers, is employed as an anodic corrosion inhibitor.

Limits for common contaminants in recirculating cooling water is provided in Table 8.

Modification of the waterside environment will require control over cooling water chemistry. Notes are provided below.

- If the total hardness rises above 600 ppm, the LSI is likely to be above +2.5 to +2.8 and ion-exchange or lime-soda softening is required, ideally using an 80:20 ratio, soft:hard water blend. Alternatively,

Table 8 Evaluation of control over bacterial growths

TAB result	*Evaluation*
0 to10^2 colonies per ml	Excellent control
10^2 to10^3 colonies per ml	Warning, but no serious fouling risk
10^4 to10^5 colonies per ml	10^4 is the maximum permitted for healthcare 10^5 is a typical maximum for commerce/industry
10^5 to10^6 colonies per ml	Unacceptable. Fouling anticipated. Also, a possible health risk
$>10^6$ colonies per ml	Serious risk of fouling and pathogens

sulfuric acid and/or a special, stabilized phosphate or alkaline phosphate program must be used. All programs require a good understanding of chemistry and excellent monitoring and control.

- Usually, if the total hardness rises significantly, then the total alkalinity will also rise. If total alkalinity rises above 500 ppm, then the LSI is likely to be above +2.5 to +2.8 and dealkalization is required. (Commonly sulfuric acid is employed; also sulfamic acid for small systems). Alternatively, high stability tolerant, organic threshold/crystal modifier polymers are employed, as adjuncts to the chemical treatment program in place.
- Silica should not be permitted to rise above 120 ppm otherwise irreversible silica scaling will occur. The generally accepted limit is 150 ppm, but this is only in highly alkaline water systems (silica is more soluble in caustic alkaline waters, e.g., boiler water).
- In deep well waters, sulfate often comprises 50% or more of the total calcium hardness (i.e., if, for example, the calcium hardness is 350 mg l^{-1} (as $CaCO_3$) and the total alkalinity is, say, 200 mg l^{-1} (as $CaCO_3$), then the difference of 150 mg l^{-1} will most likely be because of calcium sulfate). Sulfate concentration in recirculating cooling water should not exceed 1500 ppm, unless a sulfate-stabilizing polymer is present. Maximum level to avoid irreversible sulfate scaling is 1800 ppm, as $CaSO_4$. Ideally use a sulfate stabilizer over 1200 ppm.

Chemical inhibitor chemistries employed as waterside environmental modifiers include the following:

- *Cathodic and anodic inhibitors*. Cathodic inhibitors, such as zinc, promote insoluble deposits that have an insulating effect and block the flow of electrons, limiting the cathodic reaction and hence anodic dissolution. Anodic inhibitors, such as nitrite, assist film repair over the metal at anodic sites and hence passivate these areas. When using anodic inhibitors it is vital to maintain correct concentration, as if the anodic sites are not completely blocked, the remaining exposed anodic area will be much smaller than before and preferentially and rapidly corrode, because of higher current densities at the anode sites, causing highly localized pitting attack and rapid perforation of sections.

  Molybdate inhibitors depend upon sodium molybdate as a weak oxidizer for ferrous metals, promoting a complex passive oxide film. Molybdates are used in combination with other inhibitors such as zinc, phosphate, phosphonates, and organics for synergistic effect to produce highly effective, synergistic corrosion inhibitor formulations. However, because of cost, the molybdate inhibitor blends are usually used at very low levels in open cooling water systems, typically maintaining less than 5–10 mg l^{-1} as sodium molybdate. In fact, because of the improvement in effectiveness of some novel organic chemistries, molybdenum may be present only at a 'tracer' level, as it is easily and accurately tested at low level and can act as an indicator molecule. Under these circumstances, the typical level in the cooling system is, perhaps, only 1.0–1.5 ppm as Mo. There is a secondary benefit, in that the Mo acts as a synergizer to enable other (organic) inhibitors, such as totyltriazole (TTA) for copper and hydroxyphosphinocarboxylic acid (HPCA), for iron/steel, to function better.

  Zinc, when combined with other inhibitors can provide very effective synergistic chemistries. Formulations might be based on zinc–silicate; zinc–phosphonate, zinc–molybdate, zinc–polyphosphate–organic, or zinc–organic–phosphate combinations. The zinc level in the cooling water is usually held to a maximum of 2–5 mg l^{-1}, depending upon the type of formulation. (The United States Public Health Service Drinking Water Standards limit the zinc of drinking water to 5.0 mg l^{-1}). In some cases, zinc discharged even at this level can be toxic to aquatic life. Some discharge criteria limit the permissible zinc concentrations to 1.0 mg l^{-1} zinc, or less. In this case, non-zinc inhibitors should be used.

  Phosphate inhibitors are used in neutral to slightly alkaline and moderately alkaline cooling water systems, combined with polymers to form formulated blends that inhibit the formation of phosphate sludge. With the development of very effective phosphate scale inhibitors and stabilizing dispersants (such as the copolymers of acrylic acid and sulfonic acid polymer, and sulfonated polystyrene and maleic acid) alkaline and stabilized phosphate based inhibitor programs have gained wide acceptance. The orthophosphate levels maintained vary from 5 to 20 $mg\,l^{-1}$. These inhibitors are most effective at high pH and alkalinity and are usually used at pH 8.0–9.0. The formulations require increased scale control from improved polymer and phosphate blends. The organic azole nonferrous metal inhibitors are also necessary for complete protection. Stabilized phosphate programs in various modifications are probably still the most widely used programs around the world, as they are relatively low cost. Generally, they are used in conjunction with sulfuric acid.

Orthophosphates at much lower levels (perhaps 1.5–3.0 $mg\,l^{-1}$) may be employed as threshold corrosion inhibitors in potable waters, where they inhibit the pickup of lead into the water, stabilize calcium present, and provide some protection against the corrosion of iron and steel pipes. The phosphates used are either phosphoric acid or sodium hexametaphosphate. Silicates can also be used in potable water systems, where they exhibit similar corrosion-inhibiting effects.

- *Organic Scale Inhibitors, Dispersants and Deposit Control Agents.* Starting with the development of polyacrylates in the 1960s, there is now a plethora of organic scale and corrosion inhibitors available today. Most water treatment formulations will contain several organic inhibitor chemistries blended in precise synergistic ratios to produce the most cost-effective inhibitor programs possible. Depending upon the water treatment company or technologist and the specifics of the cooling system, the total level of 'active' organic inhibitor chemicals present in the recirculating cooling water might be between 7.5 $mg\,l^{-1}$ and 30 or possibly 35 $mg\,l^{-1}$. This is much less than the level of contaminants and reflects the threshold control abilities of the chemicals. The chemicals provide a combination of effects to control corrosion, scale, and dispersion of minerals and salts. The effects include the following:
  - adsorption on the metal surface to control corrosion by film formation;
  - direct interference with the corrosion mechanism, so that the inhibitor becomes an integral part of the passivated metal surface;
  - chelation of metals, to solubilize them, thus preventing fouling (e.g., by Fe) and scaling (e.g., by Ca);
  - dispersion of minerals and salts by adsorption onto particulate surfaces, causing them to repel each other because of a like charge; and
  - scale inhibition because of modification of the growth of the crystal.

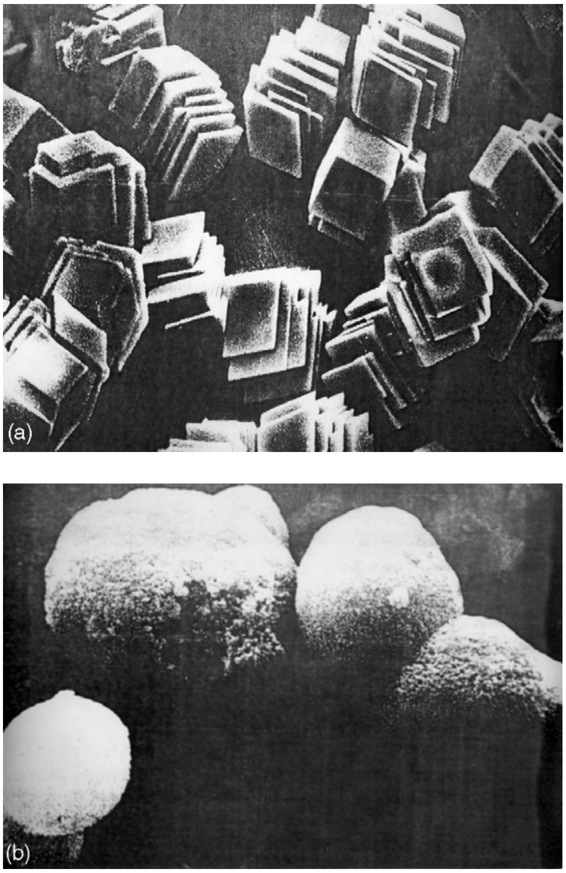

Photo 11 (a) Scale crystals modified by an organic inhibitor and (b) scale crystals also modified by an organic inhibitor.

Photos 11(a) and 11(b) show calcite crystals modified and distorted by organic inhibitors.

4.27.18 Types of Modern Organic Chemical Inhibitors Employed to Modify Cooling System Waterside Environments Against Risks of Scale, Fouling, and Corrosion Control

The various organic chemistries commonly employed today include[11,16]:

- *Polyacrylic acid and polyacrylates (PAA), 2000–3000 molecular weight (MW).* Used for lower-stress $CaCO_3$

scale inhibition and general dispersive purpose, or as a secondary support to other chemistries.

- *Polyacrylic acid and polyacrylates (PAA) 4000–5000 MW.* Used for lower-stress general dispersion of suspended solids.
- *Polymethacrylic acid and polymethacrylates (PMAA).* Used for general and $CaCO_3$ scale inhibition; also dispersion of suspended solids and iron (Fe) transport.
- *Polymaleic acid (PMA).* An excellent homopolymer chemistry for $CaCO_3$ and $CaSO_4$ scale inhibition under severe service conditions, but with limited dispersive powers.
- *Maleic acid/methyl vinyl ether (MA/MVE).* Used for $CaCO_3$ scale inhibition, with good stability in severe stress conditions and where chlorine is employed.
- *Acrylic acid/hydroxypropyl acrylate (AA/HPA).* Used as a $Ca_3(PO_4)_2$ inhibitor/dispersant and an iron oxides dispersant.
- *Sulfonated styrene/maleic anhydride (SS/MA).* Available in a variety of styrene/maleic ratios, and an excellent $Ca_3(PO_4)_2$ inhibitor/dispersant where soluble Fe is absent. Also, an iron oxides dispersant.
- *Acrylic acid/2-acrylamido-methylpropane sulfonic acid (AA/AMPS or AA/SA).* An excellent copolymer used as a $Ca_3(PO_4)_2$ inhibitor/dispersant and a Zn stabilizer.
- *Acrylic acid/sulfonic acid/substituted acrylamide (AA/SA/NI).* Used as an iron oxide dispersant. Also, as a Ca_3PO_4 and Zn stabilizer/dispersant, in the presence of iron, and under high-stress conditions.
- *Acrylic acid/sulfonic acid/sodium styrene sulfonate (AA/SA/SSS).* Used for $Ca_3(PO_4)_2$ inhibition/dispersion. Also, for calcium phosphonate control and Fe stabilization.
- *Maleic anhydride/ethyl acrylate/vinyl acrylate (MA/EA/VA).* A terpolymer, used as a $CaCO_3$ scale inhibitor and a thermally stable, general dispersant.
- *Aminotri(methylenephosphonic acid) (ATMP).* A phosphonate used as a lower-stress $CaCO_3$ scale inhibitor and building block-corrosion inhibitor for general duty.
- *1-Hydroxyethylidine-1, 1, diphosphonic acid (HEDP).* A standard $CaCO_3$ scale inhibitor and building block-corrosion inhibitor. It is reasonably Cl_2 resistant.
- *Phosphono-butane tricarboxylic acid (PBTC).* A $CaCO_3$ scale inhibitor and building block-corrosion inhibitor under high stress conditions.
- *Hydroxyphosphono acetic acid (HPCA).* A ferrous corrosion inhibitor, especially designed to be incorporated into 'all organic' programs.
- *Phosphonocarboxylic (sulfonated) copolymer (POCA).* A low phosphorus content, $CaCO_3$ scale inhibitor and corrosion inhibitor.
- *Phosphinocarboxylic acid (PCA).* A number of PCA materials have been designed as suspended solids dispersants, $CaSO_4$ scale inhibitors operating under high stress conditions, low phosphorus content, chlorine resistant, ferrous corrosion inhibitors, or zinc stabilizer and building block corrosion inhibitors (especially in soft water).
- *Tolyltriazole (TTA) or benzotriazole (BTA).* Azoles, used as corrosion inhibitors for copper and brasses.

Under higher-stress operating conditions (i.e., high heat-exchanger 'skin' temperatures, regular use of oxidizer biocides, low or high flow rates, high dirt loadings, etc.), improved inhibitor formulations, or higher concentration of inhibitors are employed – or both! Because different waters may require different types of inhibitor and the fact that all water systems are dynamic, with variable flow rates, stress-levels, and operating demands, it is necessary to have automatic adjustment of inhibitor concentrations, using feed and control equipment. Chemicals may be supplied in perhaps drums or totes and proportionally fed to a water system by means of a pump, which is actuated by some type of controller ranging from a simple timer to a web-based energy management device.

Photo 12 shows a supply of chemical corrosion inhibitor being fed to an industrial cooling water system for gas process application.

4.27.19 Modifying Cooling System Waterside Environments to Minimize Risks of Biological Fouling and MIC

Oxidizer and nonoxidizer chemistries are widely employed to control microbiological and algal growths in cooling systems, to prevent fouling and operational efficiency problems, to reduce health risks, and to prevent MIC. The major forms of biological organisms that thrive in cooling tower waters are bacterial slimes, algae, and fungi. The spores and seeds of these organisms are present in the atmosphere attached to particles of dust, dirt, pollen, and other airborne particulates. When washed out of the air at the cooling tower they find a favorable environment to grow and multiply. These growths cause serious problems of corrosion, fouling, and blockage, and accelerate buildup of deposits. Such growths not only interfere with

Photo 12 Chemical corrosion inhibitor feeding station.

water flow but also reduce heat transfer and increase energy losses.

Biological growths can be controlled by registered pesticides substances variously called microbiocides, slimicides, algaecides, and fungicides. Examples include the following[28]:

- *Sodium hypochlorite (Bleach).* Oxidizer. Sodium hypochlorite is supplied as a 11–13% available chlorine solution. Handling is not usually a problem, but the significant volumes required usually make bleach suitable for only smaller cooling systems. In water, bleach rapidly hydrolyzes according to the equation below:

$$\begin{array}{lclclcl} NaOCl & + & H_2O & = & HOCl & + & NaOH \\ \text{Bleach} & & \text{Water} & & \text{Hypochlorous acid} & & \text{Sodium hydroxide} \end{array}$$

Thus when bleach is used, hypochlorous acid is formed but also sodium hydroxide (caustic soda) tends to increase the pH. Therefore, extra vigilance may be needed if bleach is used in galvanized cooling towers. Bleach is usually dispensed two or three times per week by hand-adding a known volume, although the use of a timer-controlled pump, is a preferred alternative. Bleach can also be used in combination with sodium bromide solution to produce hypobromous acid.

- *Bromine.* Oxidizer. Bromine based biocides have been used as pesticides, disinfectants, algaecides, and slimicides for 40–50 years or more, in agriculture, the pulp and paper industry, once-through turbine condenser cooling, and the chemical industry. In the late 1970s and early 1980s, a major step forward came in cooling water treatment technology with the introduction of programs based on bromine release agents. This was primarily bromo-3-chlorodimethylhydantoin (BCDMH), which is available as granules and in various sizes of tablet (puck) and stick. Most bromine biocides employ chlorine in some form, as an 'activator' to produce the primary biocidal species hypobromous acid (HOBr). During the last 20 years, the use of programs based on bromine chemistry has become standard practice. Bromine/chlorine-based biocides have become internationally accepted as mainstream products for all types of cooling water systems, brewery pasteurizers, and many other process applications. Bromine/chlorine biocides are now available in many permutations of composition and form.
- *DBNPA.* Nonoxidizer. 2-2-Dibromo-3-nitrilopropionamide. Organo-bromine group. Effective, general-purpose bactericide but hydrolyzes rapidly above pH 8.0. DBNPA is suitable for bacterial slime cleanup where high levels of organics and biomass are present. It functions in conjunction with chlorine. DBNPA is suitable for once-through cooling systems, because of its fast acting biocidal action (contact time often less than 1 h). DBNPA is not particularly effective against algae. The half-life of DBNPA decreases rapidly with increasing pH and temperature. This is not generally a problem because of the short contact time required, and may be a benefit when required to meet strict discharge regulations.
- *DTEA II.* Nonoxidizer. 2-(Decylthio)ethanamine. Alkylthioamine group. It is designed to operate effectively under a wide range of pH levels (pH 6 to10 or greater) as a biocideal cleaner. It was also designed as a specific sessile bactericide, biofilm remover, and biofilm growth control agent. DTEA or DTEA II functions by forming reversible chelant complexes with the salts and inorganic ions found in biofilm structures, and it severely weakens the biofilm and reduces its adhesiveness. DTEA or DTEA

II is highly surface active and can be thought of as a 'biocidal soap' to be used for cleanup programs (biofilm debris will quickly be in evidence and foaming may occur), as a biocide component with chlorine (although it is not recommended to be used at the same time as chlorine), and as a maintenance biostat. Application rates are typically 50–100 mg l^{-1}. It is consumed as it decays rapidly in heavily fouled systems (typically in 3–4 h); consequently, it is recommended to slowly add the complete dose over a four-hour period.

- *Glutaraldehyde.* Nonoxidizer. Pentane-1,5-dial. Aldehyde group. Glutaraldehyde is a good bactericide, especially with difficult and persistent organisms because of its good penetrating ability. It has limited effectiveness against algae and fungi. The kill mechanism is by cross-linking outer proteins of cell and preventing cell permeability. Glutaraldehyde is a fast-acting biocide (3–4 h, perhaps 4–6 h with difficult slimes), nonionic, nonfoaming, effective over a wide pH range (typically pH 6.5–9.0), and compatible with chlorine. It is also effective against SRBs and biofilms. The half-life tends to be short, depending upon the particular cooling system parameters, but typically 4–12 h. Careful evaluation is needed before application on some larger systems, especially as it may not be particularly cost effective. Glutaraldehyde is readily biodegradable. Typical use concentration is 100–125 mg l^{-1} at 45% active material, although heavily slimed cooling systems may need 200–300 mg l^{-1} as an initial, cleanup shock dose. It is an effective choice for biological control in air washers. Glutaraldehyde is probably a good biocide where the risk of *Legionella* sp. exists.
- *Isothiazolines.* Nonoxidizer. Alkyl isothiazolin-3-ones. Organosulfur group. Good, wide-spectrum bactericide and algaecide that is effective over a wide range of pH. Isothiazolines kill by inhibiting microbial respiration and food transport through the cell wall. It is recognized as an industry standard product for cooling systems but can be expensive. Isothiazolines are supplied to some markets as a 13.9% active concentrated blend (10.1% 5-chloro-2-methyl-4-isothiazolin-3-one and 3.8% 2-methyl-4-isothiazolin-3-one). It is always marketed to the end user, as a 1.5% active (1.11% + 0.39% to 1.15% + 0.35%) in-use blend. Isothiazolines are amber to yellow-green liquids that require very careful handling because of severe skin and eye irritant properties. They are effective against both general aerobic and spore-forming bacteria, over a pH range of 6.5–9.0. Isothiazolines are very effective algaecides and fungicides, but only at acid to slightly alkaline pH levels. Contact time is typically 5–6 h. Dose rate is typically 50–120 mg l^{-1}, for 1.5% active isothiazoline.

Table 9 Evaluation of control over bacterial growths

TAB result	*Evaluation*
0 to10^2 colonies per ml	Excellent control
10^2 to10^3 colonies per ml	Warning, but no serious fouling risk
10^4 to10^5 colonies per ml	10^4 is the maximum permitted for healthcare 10^5 is a typical maximum for commerce/industry
10^5 to10^6 colonies per ml	Unacceptable. Fouling anticipated. Also, a possible health risk
$>10^6$ colonies per ml	Serious risk of fouling and pathogens

Where waterside environments are modified by the use of biocides, various field and laboratory test methods are available to monitor the recirculating water to obtain a total bacteria count and predetermine the need for further addition or modification of the biocides. Field methods include test strips, dipslides, and ATP meters. Laboratory methods include plate counts. Tests made periodically during operation of the system will provide a history that will indicate if there is an increase in the bacteria count during any particular season, showing the possible need for a change in biocide program.

The biocide program performance should typically be evaluated on the basis of the total bacteria count (TAB) of microorganism in the recirculating cooling water, as indicated in Table 9.

4.27.20 Conclusion

It can be seen from the foregoing sections that the effective control of corrosion of water systems, by modification of waterside environments is part science, part art, and part experience, requiring a thorough understanding of the collective and often synergistic impact of a wide variety of risk factors that may cause other problems, including scaling and fouling. Additionally, in the primary heat-exchange and heat transfer applications for cooling and heating systems, any proposed environmental modification program must also take into account the economics, management and operational practicalities.

References

1. *Global Water Outlook to 2025.* International Food Policy Research Institute (www.ifpri.org).
2. Shiklomanov, I. A. Evolution of water withdrawals and consumption since 1900. Worldwide Council (www.worldwidecouncil.org), 1999.
3. *Vital Water Graphics.* United Nations Environmental Program (www.unep.org).
4. *Estimated Use of Water in the United States in 2000.* U.S. Geological Survey (www.usgs.com).
5. *Thermoelectric-power water use.* U.S. Geological Survey (www.usgs.com).
6. Koch, G. H.; Thompson, N. G.; Brongers, M. P. H.; Payer, J. H. *The United States Cost of Corrosion Study;* NACE International: Houston, TX, 2003.
7. U.S. DOD Corrosion Office. Global Cost of Corrosion Program Plan, Draft 2 Jan 2008.
8. National Oceanic and Atmospheric Administration (NOAA). http://www.esrl.noaa.gov/gmd/ccgg/trends/.
9. Stwertka, A. *Guide to the Elements,* rev. ed.; Oxford University Press, 1998.
10. UPAC. *Compendium of Chemical Terminology,* 2nd ed. (the ‘‘Gold Book’’), McNaught, A. D., Wilkinson, A., Eds.; Blackwell: Oxford, 1997.
11. Frayne, C. *Cooling Water Treatment Principles and Practice.* Chemical Publishing: New York, NY, 1999.
12. U.S. EPA. Drinking Water Contaminants and Quality Criteria for Water (Commonly known as the ‘‘Gold Book’’). Document No. EPA-440/5-86-001, Washington, DC, 1986.
13. Electric Power Research Institute. Recommendations for an Effective Flow-accelerated Corrosion Program (EPRI-NSAC-202L-R3), 1994.
14. Jeff, D. Update on Flow Accelerated Corrosion (FAC), Vogt Power International Inc. Technical Bulletin, 2004.
15. Reggiani, G. M. White Rust – An Industry Update and Guide Paper. Association of Water Technologies, 2002; www.awt.org.
16. Frayne, C. In Corrosion 2008 Conference; NACE International, 2008; Paper 083678.
17. Eble, K. S.; Feathers, J. Water Reuse within a Refinery Cooling Technology Institute, 1993; www.cti.org.
18. Sundstrom, G. Organoclay Aids Water Reuse at Canadian Refinery Industrial Water World, January 2006; www.pennet.com.
19. Cinna, L. Coalescer and Advanced Filter Designs for Removal of Oil and Solvents. *Pollution Equipment News,* August 2007; www.rimbach.com.
20. Frayne, C. *Boiler Water Treatment Principles and Practice;* Chemical Publishing: New York, NY, 2002; 2 vols.
21. Blake, R. T. *Water Treatment for HVAC and Potable Water Systems,* 8th ed.; McGraw-Hill: New York, 1980.
22. Boffardi, B. P.; Schweitzer, G. W. Cooling water system performance predicted by computer simulator; NACE Paper #80195, Material Performance, December1980; www.nace.org.
23. Vanderpool, D. Hidden assumptions in saturation calculations. ‘‘The Analyst’’, Association of Water Technologies, Laurel Functional Chemicals, Summer 2002; www.awt.org.
24. Ferguson Robert, J. In *52nd International Water Conference, Pittsburgh 1991;* IWC Paper #91-47; www.eswp.com.
25. Langelier, W. F. *J. Am. Water Works Ass.* **1936**, *28*(10), 1500–1521.
26. Larson, T. E.; Skold, R. V. Laboratory studies relating mineral quality of water to corrosion of steel and cast iron, Illinois State Water Survey, Champaign, IL, 1958; pp 43–46, ISWS C-71.
27. Cutler, P. Stainless steels and drinking water around the world. Nickel Institute UK. www.euro-inax.org/pdf/map/paper/Cutler_water_EN.pdf.
28. Frayne, C. The selection and application of non-oxidizing biocides for cooling water systems; ‘‘The Analyst,’’ Association of Water Technologies, Spring 2001; www.awt.org.

4.31 Economic Aspects of Corrosion

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Glossary

Discounted cash flow (DCF) A method of valuing a project or asset incorporating the time value of money in which all future cash flows are estimated and discounted to their present values using a discount rate that is generally the appropriate cost of capital that may be adjusted to incorporate uncertainties in future cash flows.

Net present value (NPV) The total present value of a time series of cash flows.

Life cycle cost (LCC) The total cost of ownership over the life of an asset.

Abbreviations

CRA Corrosion resistant alloy
CRF Capital recovery factor
GNP Gross national product
PVC Polyvinyl chloride
ROI Return on investment

Symbols

A Annualized cost (currency units)
EV Expected value (currency units)
FV Future value (currency units)
i Discount/interest rate (%)
n Number of time periods (normally years)
PV Present value (currency units)

4.31.1 Costs of Corrosion in Individual Organizations

4.31.1.1 Sources of Corrosion Costs

Corrosion is intrinsic to the procurement and operation of physical assets, and costs are inevitably incurred in its avoidance and/or its consequences. Corrosion costs can be disaggregated in several ways. The most obvious way is to differentiate the recognizable 'direct' costs of corrosion control expenditures, including any planned repair or replacement, from 'indirect' or 'consequential' costs that result from unexpected corrosion incidents. Accounting practices dictate that the costs of corrosion are recorded as 'capital' or 'operating' costs.

The direct, capital costs of corrosion arise from:

1. The process for selecting materials and associated protection technologies for the assets, including any materials testing and/or qualification.

2. The additional costs of the chosen materials over the cheaper materials from which the assets could be constructed in the absence of corrosion risks.
3. The provision of corrosion allowances.
4. The application of linings, claddings or coatings.
5. The purchase, installation and commissioning of equipment/systems for the injection of corrosion inhibitors, the application of cathodic or anodic protection, the monitoring or analysis for corrosion control purposes, and the maintenance of operation or containment of hazards in the event of corrosion-induced failures.
6. The prevention of any corrosion that may be anticipated during the procurement/construction phase.

The direct costs of corrosion that arise in service are:

1. Inspection and maintenance/servicing of linings, cladding and coatings, and corrosion control equipment/systems.
2. Consumable costs of chemicals and power used for corrosion control.
3. Planned repair and replacement of equipment/components damaged by corrosion.

Indirect, consequential operating expenditures arise from:

1. Failure analysis and corrosion problem solving processes.
2. Unplanned repair and replacement of equipment/components damaged by corrosion.
3. Revenue losses arising from unavailability of assets at any stage (delayed start up, unscheduled downtime, poor equipment performance) because of unforeseen corrosion damage.
4. Fines, compensation/remediation costs and the costs of lost goodwill and reputation arising from death, injury, or environmental damage because of unforeseen corrosion-induced failure.

Indirect, consequential costs are less obviously quantified but can be very large. Major incidents can result in bankruptcy, withdrawal of the organization's license to operate, and even custodial sentences for accountable individuals.

4.31.1.2 Investment Appraisal

Both commercial and public sector organizations use physical assets and labor to produce and deliver goods and services. Commercial sector organizations pursue profit whereas public sector organizations usually pursue social/economic benefits arising from the provision of utilities, infrastructures, transportation etc. Simplified, schematic flows of cash arising from investment in commercial organizations are shown in Figure 1 showing how the cash generated after tax is a source of investment capital for the future.

Any organization, commercial or public sector, must invest in the most profitable or beneficial projects available in order to survive and develop. At any particular time, there is inevitable competition among potential projects for limited capital funds, and organizations need appraisal processes to identify those potential projects that offer the best returns on investment. The simplest process is to favor projects that offer low first cost. However, in the cases of complex assets that are required to operate for many years, more sophisticated appraisal processes that balance the flows of revenues and costs over the whole life cycle, adjusted to allow for factors such as the cost of money and inflation/taxation rates, are required.[1,2]

A key to investment appraisal for the longer term is to recognize and incorporate the time value of money. The value or worth of a unit of money varies with time depending on the prevailing inflation and interest rates. Compounding uses the interest rate to provide a future value or worth of a present sum of money:

$$\mathrm{FV} = \mathrm{PV} \times (1 + i)^n$$

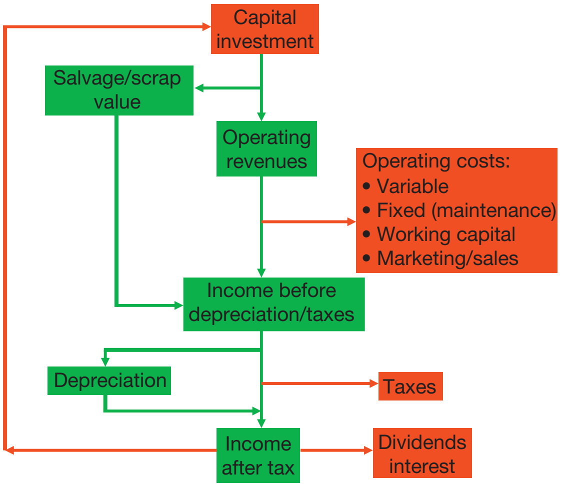


Figure 1 Simplified cash flows generated by investment in a commercial organization.

where PV is the present value, FV is the future value, i is the discount/interest rate (%); n is the number of time periods (normally years).

The term $(1 + i)^n$ is the so-called compound factor. Discounting is the reciprocal of the more familiar compounding, in which an interest rate is used to provide a present value or worth of a future sum of money:

$$\mathrm{PV} = \mathrm{FV} \times \frac{1}{(1 + i)^n}$$

The term $1/(1 + i)^n$ is the discount factor. Both compound and discount factors are available from tables in standard textbooks for different discount rates and times.[1,2] The effects of interest are incorporated into investment appraisal by the use of discounted cash flow (DCF) procedures in which all capital and operating costs and revenues associated with a particular investment throughout its life, adjusted to incorporate any anticipated effects of inflation, are discounted to their values in a base year. Summation of the discounted positive and negative cash flows at any stage of life produces a net present value (NPV) for the investment.

The patterns of cash flow and the effects of discounting are shown for a hypothetical example of a typical manufacturing investment in Table 1 and Figure 2, based on a major investment in capital assets of 200 currency units in the base year 0. In the two preceding years, −2 and −1, costs of 10 and 50 units, respectively, are incurred in activities such as market research and product and manufacturing process development. Over the following years 1–10, the assets operate to yield cash flow depending on the balances between sales revenues and the direct and indirect costs of sales and manufacture. In the case depicted in Figure 2, positive cash flows of 80, 90, and 100 units are delivered in years 1, 2, and each of 3–10, respectively, as a result of which net cash flow increases progressively over the operating life of the assets. The effects of discounting at different rates on the present worth of cash flows over time are shown in Table 1 and Figure 2.

Several criteria are available for comparing discounted cash flows for competing potential investments:

1. Money, expressed as the NPV after a given time period. In the case depicted in Table 1, the NPVs after 10 years are 321 and 119 currency units at discount rates of 20 and 10%, respectively, compared with an equivalent net cash flow of 710 currency units.
2. Time, expressed as the 'payback period' at which the cash flow for the project is equal to the original investment. The higher the discount rate, the longer the payback periods. In the case depicted in Figure 2, the undiscounted cash flow pays back at the end of year 2, but at discount rates of 10 and 20% the paybacks are during year 3 and at the end of year 4, respectively.

Table 1 Net cash flow (NCF) and net present value (NPV) as functions of time for a typical manufacturing investment at discount rates of 10 and 20%

Year	*Net cash flow currency units*	*NPV discount rate*	
		10% currency units	*20% currency units*
−2	−10	−12	−14.5
−1	−60	−67	−75
0	−260	−267	−275
1	−180	−194	−209
2	−90	−119	−147
3	10	−44	−89
4	110	24	−41
5	210	86	−1
6	310	142	33
7	410	193	61
8	510	240	84
9	610	282	103
10	710	321	119

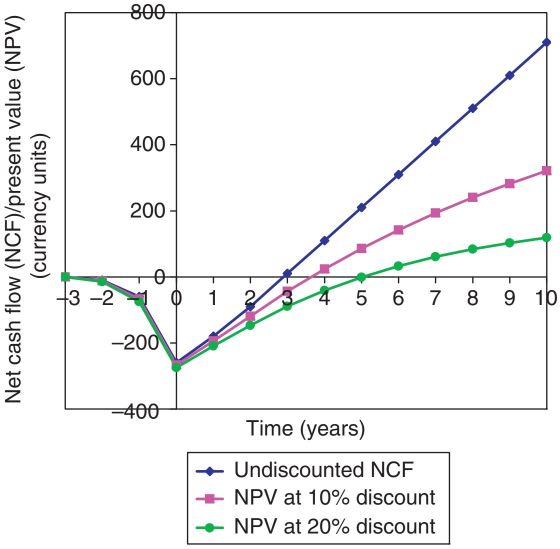


Figure 2 Net cash flow (NCF) and net present value (NPV) as functions of time for a typical manufacturing investment at discount rates of 10 and 20%.

3. Rate of return on investment (ROI), expressed usually as the average net income for a defined period (usually a year) over the life of the project as a percentage of the total investment. There are various methods for computing ROI. At its simplest, the undiscounted ROI for the case depicted in Table 1 is (97/260) × 100 = 37%

The most profitable or beneficial investment is that which yields the highest NPV over the design life of the investment and/or the shortest payback period, and/or the highest ROI.

An alternative basis for comparison is the annualized cost, A, which is calculated for each of the competing projects or options as follows:

$$\mathrm{A} = \frac{\mathrm{PV} \times i(1 \pm i)^n}{(1 + i)^n - 1}$$

The term $i(1 + i)^n/(1 + i)^n - 1$ is the capital recovery factor (CRF) that essentially allows the present worth of future expenditures to be converted into an equivalent annual cost that provides for the replacement of equipment to deliver the required operating life and, if appropriate, the decommissioning/scrapping of equipment at the end of the project life. On this basis, the most economic investment is that with the lowest annualized cost. Such evaluations must consider a sensible time period of the number of years for the project assessment to be realistic.

4.31.1.3 Identifying the Most Economic Corrosion Control Option

4.31.1.3.1 Life cycle costing

Corrosion control expenditures constitute negative cash flows, although the savings they provide arising from lower maintenance and downtime costs impact positively on NPV, particularly when they replace deficient or even nonexistent corrosion control practices.

In the cases of assets that are at risk of corrosion in service, choices have to be made at the investment stage as to how to mitigate the risks most effectively, not least the most economic deployment of capital expenditures across corrosion-resistant materials and/or operating expenditures on corrosion control. Essentially, these are alternative investment options that are best evaluated economically using DCF procedures to identify the option with the lowest life cycle cost (LCC). There are well-developed processes for predicting LCCs, including specific guidance on the life cycle costing of corrosion in specific contexts.[3,4] Life cycle costing is usually applied to new assets but is equally applicable to the evaluation of repair, rehabilitation or replacement options for the existing equipment. The use of LCC in both contexts is illustrated in the examples that follow.

4.31.1.3.2 Selecting the most economic material of construction

A decision that faces all car suppliers/owners is the choice of constructional material for the exhaust system. In practice, the three potential materials are unprotected mild steel, aluminized mild steel, and stainless steel that have lives of 2.5, 4, and 10 years at first costs of 60, 80, and 180 currency units, respectively. The simplest approach in identifying the most economic material is to calculate an undiscounted, average yearly cost for each material, as displayed in Table 2. On this basis, stainless steel appears to be the most economic material at an annual cost of 18 currency units per year, but this analysis takes no account of the time value of money.

Table 2 also displays annualized cost, *A*, for each of the materials that have been calculated on the basis that money to purchase the exhaust systems is borrowed at an interest rate of 10%, resulting in CRFs of 0.47, 0.32 and 0.16 for mild steel, aluminized steel, and stainless steel respectively. On this basis, aluminized mild steel emerges as the most, and stainless steel the least, economic material.

Table 3 demonstrates an alternative approach to incorporating the time value of money and displays NPV for the three materials on the basis that money to purchase the exhaust systems is borrowed at an

Table 2 Annualized costs (*A*) for three exhaust system options at a discount rate of 10%

System	*First cost currency units*	*Life years*	*Undiscounted annual cost currency units*	*CRF discount rate 10%*	*A discount rate 10% currency units*
Mild steel	60	2.5	24	$\frac{0.1(1.1)^{2.5}}{(1.1)^{2.5}-1} = 0.47$	28.20
Aluminized steel	80	4	20	$\frac{0.1(1.1)^{4}}{(1.1)^{4}-1} = 0.32$	25.60
Stainless steel	180	10	18	$\frac{0.1(1.1)^{10}}{(1.1)^{10}-1} = 0.16$	28.80

Table 3 Net present value (NPV) as a function of time for three exhaust system options at a discount rate of 10%

Year	*Cash flow currency units*	*PV discount rate 10% currency units*	*NPV discount rate 10% currency units*
Mild Steel			
0	60	60.00	60.00
2.5	60	47.28	107.28
5.0	60	37.26	144.54
7.5	60	29.34	173.88
10.0	60	23.10	196.98
12.5	60	18.24	215.22
15.0	60	14.34	229.56
17.5	60	11.32	240.88
Aluminized steel			
0	80	80.00	80.00
4	80	54.64	134.64
8	80	37.36	172.00
12	80	25.52	197.52
16	80	17.44	214.96
Stainless steel			
0	180	180.00	180.00
10	180	69.40	249.40

interest rate of 10% and an operating life for the car of 20 years is required. The outcome is the same as for the annualized cost analysis.

The interest/discount rate has a significant influence as to which material is the most economic. Lower rates favor stainless steel that becomes more economic than mild steel and aluminized steel at interest rates of ~4% and ~9%, respectively. In the 10–20% interest rate range, aluminized steel is the most economic material and only at very high interest rates, 35% and above, does mild steel become the most economic material.

The use of LCC for identifying the most economic materials of construction in a manufacturing context is depicted in Figure 3 that relates to the hypothetical manufacturing project defined in Table 1 and Figure 2. It is assumed that there are two alternative construction materials for the assets. Stainless steel corrodes at a very low rate and provides a 10-year life at an initial cost of 200 currency units. Mild steel costs only 100 currency units, but corrodes at rates that require extensive repair and refurbishment of assets during years 2–3, 5–6, and 8–9 at a cost of 100 currency units on each occasion. Figures 3(a) and 3(b) show discounted cash flows for the two alternative materials of construction at discount rates of 10 and 20%.

At a discount rate of 10%, mild steel pays back marginally earlier than the stainless steel option but, beyond the fifth year, the NPV for the stainless steel option is increasingly larger. In contrast, at a discount rate of 20%, the mild steel option pays back significantly earlier and, even after 10 years, the NPV advantage offered by the stainless steel option is marginal.

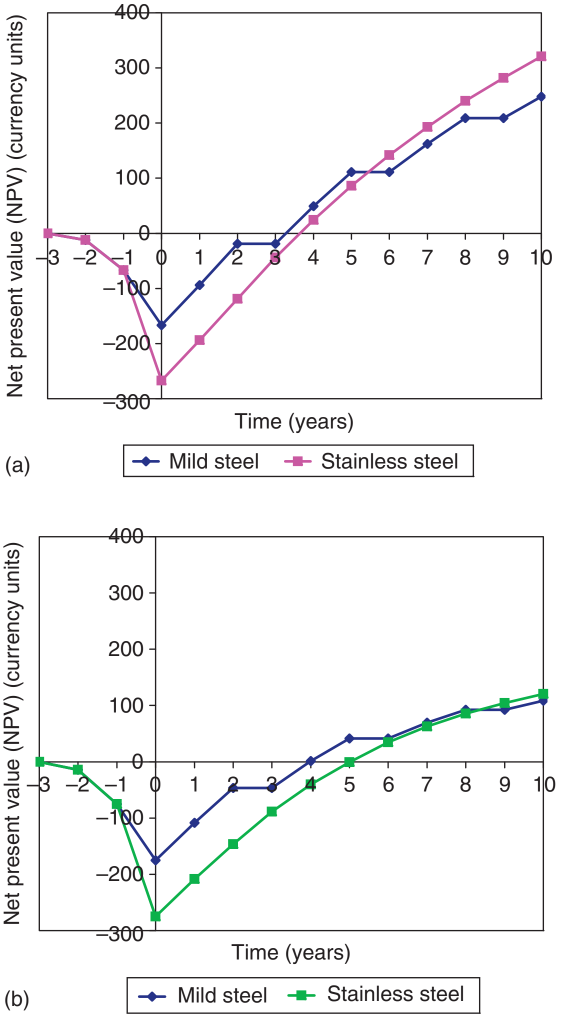


Figure 3 NPVs as functions of time for a typical manufacturing investment constructed in mild and stainless steels at a discount rate of (a) 10% and (b) 20%.

4.31.1.3.3 Deciding among repair, protection, and replacement options

This choice is illustrated by the case of a water main that has experienced a series of leaks because of external corrosion. The options for correction are:

1. ongoing repair of leaks,
2. install cathodic protection to the existing piping system, and
3. replace with a PVC piping system.

The basis for the assessment is that the main is required to operate for a further 40 years at a prevailing 12% interest/discount rate. The assessment is based on a 1-km length of pipe assuming a constant leakage rate of 3 per kilometer per year. Leaks cost an average of 18 currency units to repair.

Cathodic protection using magnesium anodes designed for a 20-year life is estimated to reduce repairs by 95%. The initial installed cost of a cathodic protection system is 180 currency units and the system does not require maintenance.

The installation cost of replacement with a PVC piping system is 1440 currency units per kilometer and a PVC main is expected to have a 40-year maintenance-free life.

Annualized costs for the three options are summarized in Table 4, from which it is clear that installing a cathodic protection system on the existing main is more cost effective than either of the alternative options. Even if the required life of the main was extended from 40 to 90 years, in which case the CRF for replacement would change from 0.121 at 40 years to 0.120 at 90 years, cathodic protection would remain the most economic option.

However, selection of the cathodic protection option assumes that the condition of the main remains sufficiently good for cathodic protection to sustain the ongoing failure rate at 5% of the existing level. If there are doubts about this, the choice reverts to ongoing repair or replacement of the existing main with PVC pipe. At a repair cost of 18 currency units per leak, a leakage rate of 9.7 leaks per kilometer would be required to equalize the annualized cost of 174 currency units for replacement with PVC. Although at face value, this is several times the current leak rate, the assumption that the leak rate will remain constant is probably optimistic. Studies of cumulative leak history curves suggests that leak rates are more likely to increase exponentially with time, in which case replacement is likely to prove a more economic option sooner rather than later. This illustrates that risks and uncertainties in the various cost inputs to economic evaluations must be recognized and incorporated into decision criteria.

4.31.1.3.4 Incorporating risks and uncertainties into economic evaluations

The previous economic evaluations in this chapter have all been deterministic. However, there are inevitable risks and uncertainties in the assumptions and data inputs and these can be allowed for in the evaluations by the use of probabilities. The importance of such analysis has been illustrated[5] for the case of a 10-mile, 6-in. diameter, offshore pipeline, for which the options for mitigating corrosion risks are:

1. carbon steel, protected by corrosion inhibitor addition;
2. carbon steel clad with a corrosion-resistant alloy (CRA).

In a deterministic analysis incorporating all relevant initial and operating costs, the NPV costs based on a discount rate of 10% and a cost escalation rate of 7% are $12 and $23 million for the inhibited carbon steel and clad carbon steel options, respectively. On this basis, the inhibited carbon steel option would be installed. However, this analysis does not consider the probability of failure or its economic consequences that are considerable in the case of offshore equipment.

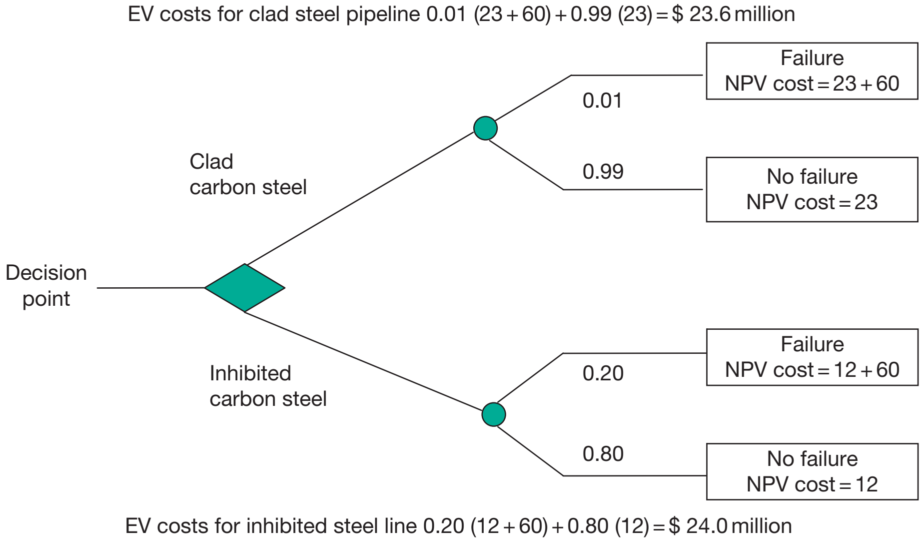
The expected value (EV) method can be used to compare options when there are multiple potential outcomes of a decision. The expected value of a decision is based on Bayesian logic and can be regarded as the ‘usual’ outcome of many instances of the decision. In the case of the pipeline, it can be used to incorporate the impact of failure as an additional NPV cost on the two base options arising from a single event or multiple events over the life of the pipeline. In the case of the clad pipeline, it is considered that there is a 1% probability of a single or multiple events having an NPV cost of $25 million. In the case of the inhibited

Table 4 Annualized costs (*A*) for pipe repair, protection, and replacement options at a discount rate of 12%

Option	*First cost currency units*	*Life years*	*Annual leakage cost currency units*	*CRF discount rate 12%*	*A discount rate 12% currency units*
Repair leaks			54	1	54
Cathodic protection	180	20	2.7	0.134	24.1 + 2.7 = 26.8
Replacement PVC pipe	1 440	40		0.121	174

pipeline, the equivalent corrosion risks and consequences are larger and are considered to amount to a 20% probability of an NPV cost of $75 million. The corresponding EV costs that result for the two options are shown in the decision tree in Figure 4 where it is apparent that the most economic option on this basis is the clad carbon steel pipeline.

In practice, it can be difficult to anticipate the probabilities, costs, and timings of specific possible failures. A more generalized approach to the EV method is provided by the so-called probability limit curves such as that depicted in Figure 5, based on the equivalence of failure scenarios that have the same NPV cost. In Figure 5, the probability and NPV cost of a clad pipeline failure are set at 1% and $25 million, respectively and the curve defines the locus of equal EVs for clad and inhibited carbon steel options that separates zones where one or the other option is the economic choice. This provides more flexibility in factoring risk into the decision process.



EV costs for clad steel pipeline 0.01 (23 + 60) + 0.99 (23) = $ 23.6 million

EV costs for inhibited steel line 0.20 (12 + 60) + 0.80 (12) = $ 24.0 million

Figure 4 Use of expected value (EV) calculations incorporating risk to decide amongst pipeline corrosion risk mitigation options. Adapted from Craig, B. D.; Thompson, R. S. *Corros. Mgmt.* **1995**, *7*, 14–17.

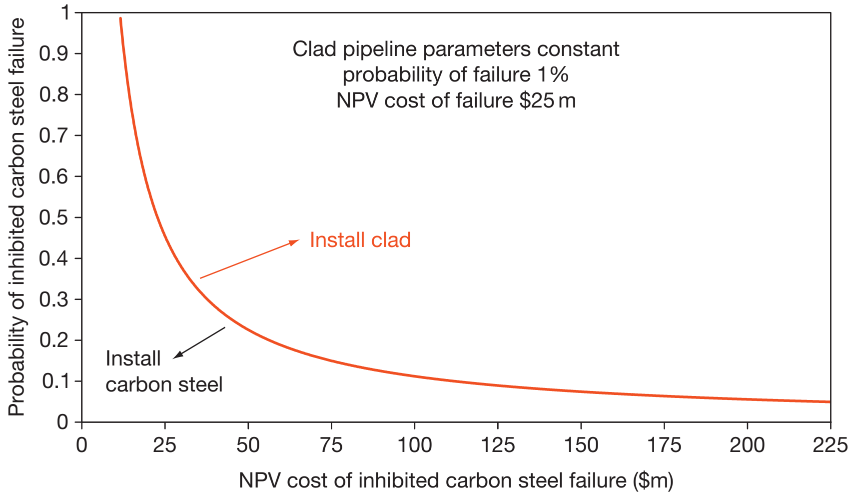


Figure 5 Probability limit curve incorporating risk to decide amongst pipeline corrosion risk mitigation options. Adapted from Craig, B. D.; Thompson, R. S. *Corros. Mgmt.* **1995**, *7*, 14–17.

4.31.1.3.5 General outcomes of LCC approaches

The examples above illustrate some general economic truths relating to the selection of corrosion control options:

1. Relatively low interest rates favor long-term economic planning and the cheapest may well not be the most economic option when LCCs are taken into consideration.
2. Alternatively, when the capital is very expensive, shorter-term considerations tend to dominate and large long-term investments have no merit over small frequently repeated investments. In these circumstances, the cheapest is also likely to be the most economic option.
3. It is essential that the risks and uncertainties attached to the inputs of a decision are understood and incorporated into the process of identifying the most economic option.

As to whether these truths are understood and practiced, a recent UK survey of the costs of corrosion in specific industrial sectors[6–10] revealed an increasing usage of LCC approaches in selecting corrosion control options, but a widespread lack of awareness of the total costs of corrosion in specific organizations. To some extent, this results from accounting practices that make it difficult to disaggregate corrosion costs from standard cost categories such as capital and maintenance costs. However, a detailed awareness of corrosion costs is essential to the development of optimal corrosion control management strategies, particularly, in those organizations where corrosion presents a significant threat to the reliability and availability of operating equipment.

4.31.2 Costs of Corrosion in Specific Sectors/Economies

4.31.2.1 Quantifying Corrosion Costs in Sectors/Economies

Over the past ~60 years, there have been numerous studies of the costs of corrosion to specific industrial sectors and/or national economies, including the United Kingdom,[6–11] United States,[12–15] Australia,[16–20] India,[21] Sweden,[22] Finland,[23] West Germany,[24] Japan,[25,26] China,[27] Kuwait,[28] and Canada.[29]

Early studies of corrosion costs tended to concentrate on direct expenditures. For example, Uhlig based his original USA study[12] on quantifying national expenditures on the direct costs of corrosion across the economy including corrosion-resistant materials, coatings, inhibitors, cathodic protection, and repair and replacement costs. Hoar's later UK study[11] focused on the estimates of recognized industry experts in specific industrial sectors in addition to the surveys of expenditure on corrosion protection measures. The application of the above approaches to the Japanese economy[25] resulted in a higher estimate of total cost using the Hoar rather than the Uhlig approach.

The USA economy has received the most frequent and detailed evaluation and the outputs of the key studies[13–15] are summarized in **Figure 6**. Following Uhlig's initial 1949 study,[12] NBS Battelle revisited the cost of corrosion to the national economy in 1978 in a much more rigorous study[13,14] that drew on the expertise of professional economists to evaluate sectorwise economic statistics. This approach introduced some top-down evaluation that was missing from Uhlig's earlier study and sought to trace expenditures on corrosion in different sectors of the economy through 'input' purchases of goods and services for corrosion control and their impact on 'outputs' including revenues. This input–output approach estimated a significantly higher cost than the original Uhlig study because it included the consequential costs of corrosion arising from the unavailability of assets and incidents with safety, health and environmental consequences. The 1978 study was updated in 1996 and a completely new study in 2002[15] confirmed a declining trend in total expenditures on corrosion in the 1978–2002 period.

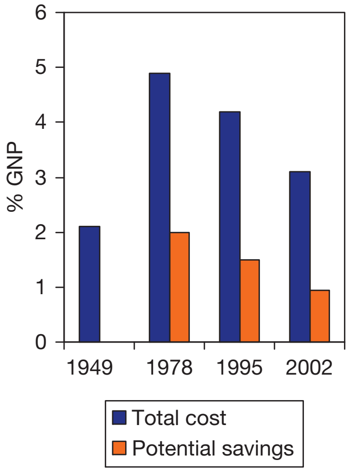


Figure 6 Total cost of corrosion and potential savings in the USA economy as percentages of GNP in 1949,[12] 1978/1995,[13,14] and 2002.[15]

A later study of the application of the input/output model to the Japanese economy[26,30] confirmed that it produces significantly higher estimates than earlier approaches and concluded that it is likely to estimate costs that are 2–4 times higher than the application of the Uhlig or Hoar approaches.

There is no recognized definitive approach towards estimating the cost of corrosion to industrial sectors and national economies. Some quite detailed models have been proposed[20,31] but all approaches involve degrees of judgment and approximation that reflect uncertainties in the contributions of corrosion to costs in individual organizations or sectors of an economy.

4.31.2.2 Corrosion Costs in Specific Sectors

In recent years, there have been numerous studies of the costs of corrosion in specific industrial sectors. The most recent USA study[15] examined corrosion costs in 26 individual sectors within the broader sectors of utilities, transportation, infrastructure, defense and production or manufacturing. The costs of the top 12 categories, shown in Figure 7 as percentages of the total USA cost of corrosion, provide an overview of the relative sizes of the various sectors in relation to the expenditures on corrosion control. Drinking water and sewerage systems comprise the most expensive individual sector, and together with electrical utilities and gas distribution they establish utilities as the largest broad sector. Corrosion control in motor vehicles dominates transportation, the second largest broad sector followed by infrastructure, including expenditures on highway bridges, hazardous materials storages, and gas and liquid pipelines. In the grand scheme of things, expenditures on production and manufacturing, including pulp and paper, petroleum refining, chemicals, and oil and gas are relatively small.

As important as the sizes of the various sectors depicted in Figure 7 is the relative efficacies of their expenditures on corrosion control *viz.* to what extent the expenditures represent money well spent as opposed to money wasted. The results of detailed studies of the total costs of corrosion and the potential savings in several sectors in the United Kingdom[6,7,9,10] and the United States[32] are shown in Figure 8 as percentages of turnover. Total expenditures vary from as high as 7% to as low as 1% of turnover in the cases of the USA electric power and UK food and drink manufacturing sectors, respectively. These broad differences are consistent with

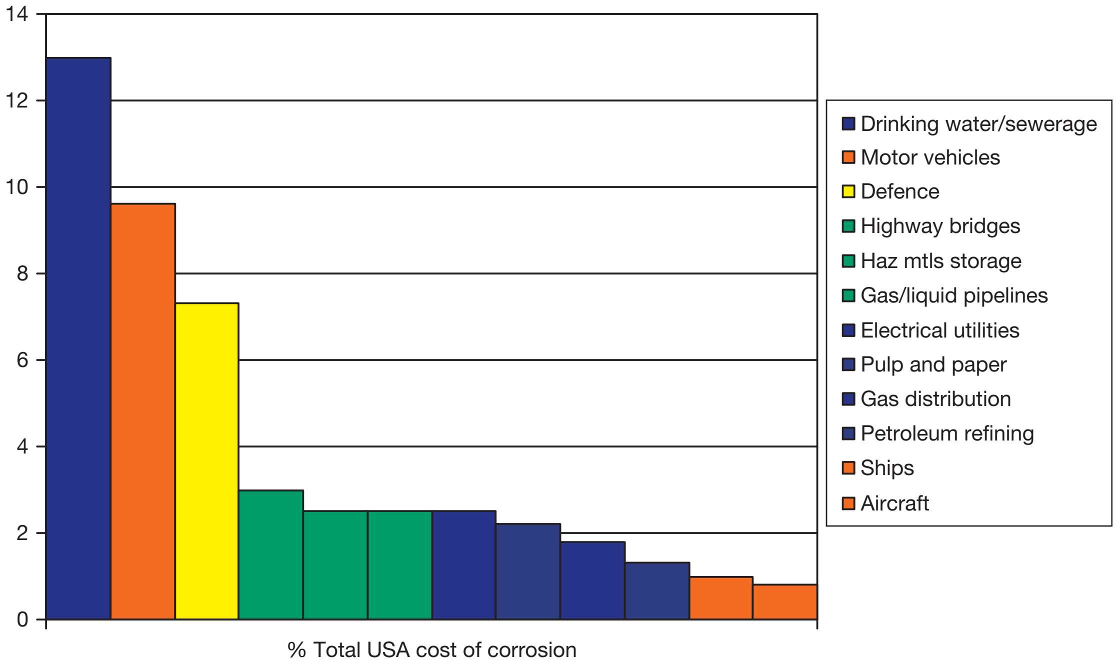


Figure 7 Costs of corrosion in top 12 sectors as percentages of the total cost of corrosion in the USA economy in 2002. Adapted from Koch, G. H.; Brongers, M. P. H.; Thompson, N. G.; Virmani, P.; Payer, J. H. *Corrosion Costs and Preventive Strategies in the USA*, Report FHWA-RD-01-156 to Federal Highways Administration; C. C. Technologies Laboratories, 2001.

the different types of processes and equipments in the different sectors. The USA electric power sector includes nuclear operations with significant corrosion risks to address using very stringent and expensive corrosion risk management procedures. The UK food and drink manufacturing sector is faced with much lower corrosion risks to its predominantly stainless steel equipment and its expenditures are correspondingly lower.

The total expenditures in Figure 8 are averages in each case based on the ranges of expenditures for individual organizations in the sectors that depend on the type, age and location of their equipment. Thus, in the UK petrochemical/chemical sector, total expenditures ranged from as little as 0.1% of turnover in the case of a small, contract manufacturing company with several glass-/tantalum-lined vessels in excellent condition that had been written off the books, to as high as 8.9% of turnover in the case of a large manufacturer with old assets with major external corrosion problems resulting in significant unscheduled downtime and heavy repair/replacement expenditures.

All the sectors examined made significant and increasing usages of risk-based methodologies in the management of their corrosion problems, including life cycle costing, reliability/availability/maintainability modeling and risk-based inspection. Despite this, all identified scope for further potential savings, ranging from 10% to 22% of the total expenditures in the UK food and drink manufacturing and USA electric power industries, respectively, by applying existing technology and best management practices. In only one sector in the UK study, automotive manufacturing (not shown in Figure 8), it was judged that corrosion expenditures were close to the economic optimum. This sector had been highlighted in Hoar's 1971 study[11] of the UK economy as a particular source of potential savings; since then technology and corrosion management practices have improved in the industry worldwide to the stage where the United States' second highest sector expenditure in Figure 7 can be classed as money well spent.

4.31.2.3 Corrosion Costs in National Economies

Studies of the costs of corrosion in different countries conclude generally that total corrosion expenditures comprise 3–5% GNP. Intuitively, the level would be expected to vary with the stage of development and mix of industrial sectors in any particular economy and to reduce with time as technology and management practices improve. There is some evidence for this from several studies[12–15] of the large and diverse USA economy over time, summarized in Figure 6, where total expenditures have reduced from 4.9 to 3.1% of GNP in the 1978–2002 period. Studies of the UK economy[6–11] widely separated in time suggest a similar trend, driven by improvements in:

1. Advances in corrosion-resistant materials and protection technologies.
2. Improved understanding and dimensioning of corrosion processes including the codification of knowledge in international/national standards, codes of practice and guidance documents in all sectors.
3. Improved corrosion management practices related to materials and protection selection and optimizing the availability and inspection of assets, including new and improved technologies for corrosion monitoring and inspection.

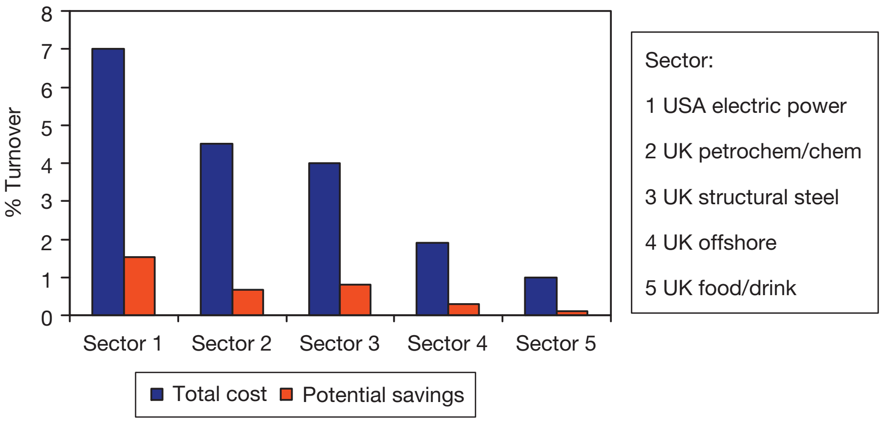


Figure 8 Total costs of corrosion and potential savings in various sectors of the United Kingdom[6–10] and United States[32] economies as percentages of sector turnover.

Over the same period, although the estimated scope for further potential savings in the USA and UK studies has reduced, it remains at 20–30% of prevailing expenditures as a result of:

1. Legacy issues – problems in ageing structures, designed, fabricated and protected to standards now recognized as inadequate, for example, external corrosion of 'baby boomer' process industry equipment, under thermal insulation and fireproofing.
2. Management issues – problems for which there are proven, economic, technical solutions, for example, corrosion in cooling water and steam-raising equipment or in CO_2/H_2S-containing produced water and seawater equipment.
3. Technology challenges – problems for which there are no proven economic solutions, for example, materials for chemical/petrochemical equipment that is vulnerable to metal dusting.

All studies recognize that there is scope for further significant reductions in corrosion expenditures by:

1. Promoting awareness and uptake of advanced design and good corrosion management practices.
2. Improving corrosion technology through research, development and implementation, including advanced life prediction and performance assessment methodologies.
3. Improving education and training of staff at all levels in corrosion control and safeguarding university training of future corrosion professionals.

In relation to the availability and deployment of corrosion professionals, the recent UK study[6–10] revealed concerns across all sectors about loss of expertise arising from a progressive decline in numbers employed in user organizations, resulting in a net migration of corrosion expertise to supplier and research/consulting organizations.

A further conclusion of several of the national studies is the potential benefits of changes in taxation policy to categorize operational corrosion control expenditures as capital investments rather than maintenance costs so that they attract tax allowances, thereby promoting front-end approaches towards corrosion control.

Extrapolating the evident trend in Figure 6 suggests that there is an optimum economic level of expenditure on corrosion for a large, diverse economy within the 2–2.5% GNP range. Although conventionally defined as the 'cost' of corrosion, this reinforces a rather negative image for corrosion as 'engineering's grim reaper' in relation to its impact on economic activity. In reality, corrosion control expenditures enable developed economies to sustain high levels of economic activity through the availability and reliability of their infrastructures and wealth-creating physical assets. In the process, they sustain profitable, high-technology businesses that provide employment and pay taxes. These constitute enormous 'benefits', as well as 'costs.'

In relation to the image of corrosion, the corrosion community might learn from the health sector. Human disease is a useful paradigm for corrosion. Developed economies spend 7–14% GNP on the health of their human assets and, although smaller, corrosion expenditure on physical assets, at a current 3–5% GNP, is of the same order of magnitude. Health expenditure is near the top of political agendas in all developed economies with increasing emphasis on predictive/preventative strategies. There is scope to raise the profile of corrosion and protection to achieve commensurate recognition and resources and deliver its full potential benefit to the national economies. This, however, relies on corrosion practitioners and educators being able to apply the basic economic tools of discounting/life cycle costing and to understand their relevance in the context of tactical and strategic decision making.

References

1. Lumby, S.; Jones, C. *Fundamentals of Investment Appraisal*; Thomson Learning, 2000.
2. Dayanada, D.; Irons, R.; Harrison, S.; Herbohn, J.; Rowland, P. *Capital Budgeting: Financial Appraisal of Investment Projects*; Cambridge University Press, 2002.
3. ISO 15663 *Petroleum and Natural Gas Industries – Life Cycle Costing, Parts 1–3*; 2001.
4. Jackman, P. *Working Party Report on the Life Cycle Costing of Corrosion in the Oil and Gas Industry: a Guideline (EFC 32)*; European Federation of Corrosion, 2003.
5. Craig, B. D.; Thompson, R. S. *Corros. Mgmt.* **1995**, *7*, 14–17.
6. McIntyre, P. *Corrosion and Associated Costs in the UK Chemicals and Petrochemicals Sector, Degradation of Materials in Aggressive Environments Programme (DME)*, Report NRW/PM/CORRO/D1; Paint Research Association, 2001.
7. McIntyre, P. *Corrosion and Associated Costs in the UK Offshore Sector, Degradation of Materials in Aggressive Environments Programme (DME)*, Report NRW/PM/CORRO/D2; Paint Research Association, 2001.
8. Jotischky, H. *Corrosion and Associated Costs in the UK Automotive OEM Sector, Degradation of Materials in Aggressive Environments Programme (DME)*, Report NRW/PM/CORRO/D1; Paint Research Association, 2001.

9. Whitehouse, N. *Corrosion and Associated Costs in the UK Food and Drink Sector, Degradation of Materials in Aggressive Environments Programme (DME)*, Report NRW/PM/CORRO/D1; Paint Research Association, 2001.
10. Whitehouse, N. *Corrosion and Associated Costs in the UK Constructional Steelwork Sector, Degradation of Materials in Aggressive Environments Programme (DME)*, Report NRW/PM/CORRO/D1; Paint Research Association, 2001.
11. Hoar, T. P. *Report of the Committee on Corrosion and Protection*; HMSO: London, 1971.
12. Uhlig, H. H. *Chem. Eng. News* **1949**, *27*, 27–64.
13. Payer, J. H.; Dippod, D. G.; Boyd, W. K.; Berry, W. E.; Brooman, N. *Economic Effects of Metallic Corrosion in USA*, Report 511-2 CCR 70-122; NBS Battelle: Houston, TX, 1978.
14. Bennett, L. H.; Kruger, J.; Parker, R. L.; Passaglia, E.; Reimann, C. *Economic Effects of Metallic Corrosion in the USA*, Report 511-1 GCR 78-122; NBS Battelle: Houston, TX, 1978.
15. Koch, G. H.; Brongers, M. P. H.; Thompson, N. G.; Virmani, P.; Payer, J. H. *Corrosion Costs and Preventive Strategies in the USA*, Report FHWA-RD-01-156 to Federal Highways Administration; C. C. Technologies Laboratories, 2001.
16. Worner, H. K. *Committee Report on the Symposium on Corrosion*; University of Melbourne, 1955.
17. Potter, E. C. *Aust. Corros. Eng.* **1972**, *16*, 21.
18. Revie, R. W.; Uhlig, H. H. *J. Inst. Eng. Aust.* **1974**, *46*, 3–5.
19. Cherry, B. W.; Skerry, B. S. *Corrosion in Australia, Report of the Australian National Centre of Corrosion Prevention and Control Feasability Study*; 1983.
20. Cherry, B. W. *Mater. Forum (Australia)* **1995**, *19*, 1–7.
21. Rajagopalan, K. S. *Report on Metallic Corrosion in India*; CSIR: India, 1962.
22. Tradgaidh, F. K. *Tekn. Tedskrift* **1965**, *95*, 1191.
23. Linderborg, S. *Kemiam Teollusius* **1967**, *24*, 234.
24. Behrens, D. *Br. Corros. J.* **1967**, *10*, 122.
25. Committee on Corrosion Loss in Japan. *Boshoku Gijutsu* **1977**, *26*, 401–512.
26. Committee on Corrosion Loss in Japan. *Zairyo-to-Kankyo* **2001**, *50*, 490–512.
27. Zhu, R. In Symposium on International Approaches to Reducing Corrosion Costs, Corrosion’86; National Association of Corrosion Engineers: Houston, TX, 1986.
28. Al-Kharafi, F.; Al-Hashem, A.; Matrouk, F. *Economic Effects of Metallic Corrosion in the State of Kuwait*; KISR, 1995.
29. Sastri, V. S.; Elboujdaini, M.; Perumareddi, J. R. In International Symposium on Environmental Degradation of Materials and Corrosion Control in Metals Proceedings of the 42nd Annual Conference of Metallurgists of CIM, Vancouver, Canada **2003**; pp 321–328.
30. Shibata, T. *Corros. Sci. Technol. (South Korea)* **2002**, *31*, 97–102.
31. Biezma, M. V.; San Cristobal, J. R. *Corros. Eng. Sci. Technol.* **2005**, *40*, 344–352.
32. Syrett, B. C.; Gorman, J. A. *Mater. Perform.* **2003**, *42*, 32–38.

4.30 Corrosion Management Overview

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Abbreviations

API American Petroleum Institute
APT Assessment performance tool
ASME American Society of Mechanical Engineers
CAD Computer aided design
CDF Cumulative distribution function
CIPS Close interval potential survey
COMAH Control of major accident hazard
CP Cathodic protection
CRA Corrosion resistant alloy
DCGV Direct current voltage gradient
DCS Distributed control system
DnV Det Norsk Veritas
EN European Normative (standard)
ER Electrical resistance
FMECA Failure mode effect and criticality analysis
FSM Field signature monitoring
GRP Glass reinforced plastic
HAZOP Hazard and operability
HSE Health and Safety Executive
ISO International Standards Organization
KPI Key performance indicator
MAT Minimum allowable thickness
MAWP Maximum allowable working pressure
mpy mils (0.001 in.) per year
NACE National Association of Corrosion Engineers
NDE/T Nondestructive examination/testing
NPV Net present value
PDF Probability density function
P&I Process & instrumentation
QA/C Quality assurance/control
RBI Risk-based inspection

RCM Reliability centered maintenance
SCADA Supervisory control and data acquisition
SHE Safety, health, and environment
SI Statutory instrument
TQM Total quality management
UT Ultrasonic testing

4.30.1 Background to Corrosion Management

4.30.1.1 Introduction

This chapter outlines some general concepts, techniques, methodologies, and interactive processes that together promote successful management of corrosion. A top-down, strategy-based introduction to the subject area is presented together with an introduction to the tactics used to mitigate the effects of corrosion. A holistic overview that accommodates economic aspects, corrosion control methods and corrosion inspection/monitoring practices, which are the subjects of separate chapters in this volume, is provided.

In this section, the background to corrosion management is outlined, including concepts, definitions, legislative drivers, and the need for a risk-based approach. Section 4.30.2 considers basic steps in corrosion management with emphasis on quality processes. In particular, the link between basic corrosion risk assessments (steps involving interactions between materials, environments, and engineering applications) and corrosion mitigation (control options, economics, and monitoring) is considered with the introduction of the requirements of a management system. In Section 4.30.3, the various methods (the tools) for the assessment of corrosion risks and development of corrosion strategies are reviewed. Management systems are addressed in Section 4.30.4 with considerations of further developments in Section 4.30.5. Many of the concepts outlined here will not be found in other chapters of this publication or in most standard corrosion texts and are therefore presented in sufficient detail to avoid the reader having to refer to other engineering/management texts.

4.30.1.2 The Need for Corrosion Management

To manage has been defined as "to succeed in one's aims (often with inadequate materials etc),"[1] an objective often wryly considered as appropriate by many corrosion engineers! Corrosion management is a process consisting of a series of steps to convert an input (corrosion risks) into an output (cost effective mitigation of those corrosion risks).

In principle, management of corrosion should be a simple process; the technologies are well established and most organizations understand the need for corrosion mitigation practices that are appropriate to their sector. However, the literature contains numerous reports of catastrophic events that have been caused by corrosion, the root causes of which are frequently poor management control, often identified as human errors:

1. "For many pipework failures, human error is identified as a dominant factor."[2]
2. ". . .analysis of the major accidents reported in the Community indicates that the majority of them are the result of managerial and/or organizational shortcomings. . .."[3]
3. "The cause of corrosion failures is human error/ poor management control."[4]

In practice, mistakes occur in the selection of corrosion control options, in application of mitigation technologies and in day-to-day activities needed to ensure that systems are monitored and corrective actions are carried out when necessary. In many instances, failures occur because basic lessons are not learned, particularly in organizations that cannot justify the services of a full time corrosion/materials specialist, and that, therefore, delegate corrosion control/monitoring activities to nonspecialist managers and engineers who may lack the required knowledge/experience. The effective implementation of mitigation practices from the design stage through the construction, commissioning, operation, and maintenance phases requires contributions from various teams of designers, constructors, commissioning staff, operations and maintenance personnel, and contractors and consultants/specialists. For such teams to be effective, they require clear objectives, transparent management systems, and appropriate reporting routes/procedures to ensure that appropriate decisions are made and implemented.

The author acted as a corrosion management expert witness in a case involving a major refinery incident resulting from inadequate control that exemplifies the need for good management practices.[5] An explosion and fire resulted from a rupture of a gas transfer line in a saturate gas plant because of local thinning by erosion–corrosion downstream of a water injection point after 13 years of operation.

The gas contained hydrogen sulfide, and water was periodically injected downstream of the overheads to control fouling of the condensers, a standard refinery practice for hydro-processing units. The heat exchangers had been replaced using corrosion resistant materials a few years previously, but the pipework was original and had been subjected to only one partial inspection. The failure was located on the surfaces downstream of the water injection point, as would be predicted by the injection point drawing in American Petroleum Institute (API) 570.[6] Subsequent discussions of the incident at the National Association of Corrosion Engineers (NACE) refinery work group[7] highlighted the requirement for inspections around any injection point, in intermittent or continuous use, at not more than three yearly intervals. There also appeared to be confusion at the refinery whether the injection point had been taken out of service following such a recommendation. A lack of management control over corrosion assessments/inspection/record keeping and procedures was identified as a major contributing factor to the failure during the subsequent trial. Following the incident, the refinery was shut down for 3 months, and a further 12 months was required to rebuild the gas plant, the company receiving a considerable fine as well.

In reality, the term ‘corrosion management’ is used in various contexts in many publications, but there is no body of knowledge/textbooks that adequately address this subject area, unlike asset management, safety management, and maintenance management. It therefore has different meanings to individuals and groups within the corrosion community. In order to clarify this issue during discussions on industrial short courses, the author developed a general definition in the mid-1990s, based on safety and environmental management definitions that was subsequently adopted in UK documentation for offshore oil and gas processing.[8] The definition also included the concept of a ‘corrosion policy.’ An organization’s policy is normally written by senior personnel, often at board/asset level, and is a statement of intent or an overall objective.

> *Corrosion management* is that part of the overall asset management system that is concerned with development, implementation, review, and maintenance of the corrosion policy.
>
> *A corrosion policy* includes establishment of organizational structures with defined responsibilities, reporting routes, practices, procedures, processes, and resources. This requires the demonstration of responsibility and accountability for corrosion performance, managing risks, decreasing costs, controlling compliance, and motivating personnel.

This definition of corrosion management has also been included by NACE International in their online resource library (management) but without defining the corrosion policy. Most large organizations have until recently not given serious consideration to corrosion policies even though they have as standard practice developed and implemented quality, safety, environmental and maintenance polices. This is in spite of the fact that they often have in place many of the necessary procedures, management structures, activities, and reporting routes required for implementing corrosion policies. It should also be noted that, since the mid-1990s, the UK HSE has also been asking organizations for copies of their corrosion policies but few have even considered such a concept. Such policies written by senior personnel, often at board/asset level, are statements of intent or overall objectives. The lack of a written corrosion policy may mean that the various interdisciplinary and multi-departmental contributions are inadequate to ensure appropriate corrosion mitigation; also the management of corrosion is poorly focused upon at both the senior management level and in the operational/day-to-day activities of an organization.

4.30.1.3 Legislative Drivers

In recent years, there has been an increased emphasis in commercial and public sector organizations on the identification and management of risks to safety, health and the environment (SHE) and to the economic viability that is driven by developments in SHE legislation across the world. A turning point in UK regulatory requirements was the 1990 Cullen Report[9] on the 1988 Piper Alpha offshore platform incident that ensured an increased emphasis on risk assessments and the use of appropriate safety management systems. This cultural shift from a rules-based regulatory system to a principles-based system with emphasis on defined objectives rather than the traditional prescriptive, rules-based practice, is summarized in **Table 1**.

The principles-based approach places a greater onus on organizations and individuals (the duty holders) to demonstrate a continuously improving safety culture with emphasis on regular assessment of risks, monitoring of performance and a proactive approach. Legislative enforcement, by the UK HSE with Statutory Instruments (SI), is the basis of the

Table 1 Legislative changes

Older legislation		*Principles-based legislation*
Detailed rules and regulations	⟶	Framework rules with guidelines
What must be done		How it must be managed
Prescriptive		Risk-based
Do it anyway		Identify hazards and risks first and prioritize actions accordingly

formal UK regulations that are typically based on European requirements as given in normative European standards (EN) and ISO standards.

The UK changes were first indicated in the 1991 publication of *Successful Health and Safety Management*[10] followed by requirements for the UK offshore oil and gas production in the *Safety Case Regulations*, in 1992[11] the *Design and Construction Regulations*[12] and the *Pipeline Standard*[13] in 1996. The general approach continued in *The Control of Major Accident Hazard Regulations* 1999 (COMAH)[14] for major hazard sites such as refineries and chemical plants and in the *Pressure Systems Safety Regulations* (SI 2000/128).[15]

The overall thrust of these approaches is illustrated as follows:

1. Reg. 8 of SI 1996/913:[12] The duty holder shall ensure that auditable arrangements are in place for maintaining the integrity of the installation, including suitable arrangements for: (1) periodic assessment of its integrity and (2) the carrying out of remedial work in the event of damage or deterioration which may prejudice its integrity.
2. Reg. 13 of SI 1996/825:[13] The operator shall ensure that the pipeline is maintained in an efficient state, in efficient working order and in good repair.
3. Reg. 12 of SI 2000/128:[15] The owner of an installed (pressure) system shall ensure that the system is properly maintained in good repair, so as to prevent danger.

In particular, written schemes of examination are required for pressure vessels and associated pipework.[15] Such documents have to be prepared by a competent person, either a named individual or a corporate inspection body within the organization. The accompanying Approved Code of Practice L122[16] provides further background information and it also notes that, "the contents may be highly toxic or the plant may form part of a major hazard site. These aspects are all subject to separate legislative requirements and duty holders will need to consider these other aspects (corrosion and erosion) when deciding on the level of precautions required," which requires organizations to be aware of all hazards, including corrosion, that can affect integrity.

Additional pressure on senior management in some sectors came with the introduction of legislation such as the UK Corporate Manslaughter and Corporate Homicide Act[17] that came into effect in 2008. A company, including senior personnel, may be guilty of this new offence if the manner in which its activities are managed or organized causes a death and amounts to a gross breach of a relevant duty of care owed to employees, the public or other individuals. If found guilty, unlimited fines and remedial orders may result, possibly affecting the viability of an organization. The challenge for industry arising from these legislative drivers is to demonstrate to the licensing authorities that the equipment is operating under safe conditions, while from a business perspective continuing to operate cost effectively, often under more aggressive conditions, and in some cases, to extend the life of aging facilities.

The impact of these drivers on engineering and safety procedures has been to focus them increasingly on failure modes likely to affect asset integrity, particularly those giving rise to catastrophic incidents such as corrosion related failures. Typical industry-centered documentation includes the American Society of Mechanical Engineers (ASME) Risk Based Inspection – Guideline Development,[18] the US Pipeline Safety Act,[19] which places emphasis on risk management and cost benefit, API 580 Risk-Based Inspection[20] plus the accompanying resource document API 581[21] and the DnV Risk Based Inspection of Offshore Topsides Static Mechanical Equipment.[22] The Australian/New Zealand Risk Management Standard[23] first published in 1995 provides an excellent basis for evaluation/management of business risk. In this context, New Zealand has also been at the forefront in total asset management, particularly public infrastructure legislation[24] and the publication of guidance.[25]

Risk management is only one of the tools employed to mitigate corrosion and, for example, risk-based inspection (RBI) must be backed up with management of change procedures and end of life strategies. Thus if the compositions of process fluids change or the operating conditions are modified then corrosion assessments must be carried out again for these new conditions. Ageing infrastructures and facilities need increased inspection frequencies and monitoring to ensure safe operation and this has implications for the allocation of resource for teams concerned with asset integrity and maintenance. Corrosion expertise is a relatively scarce commodity, particularly in management functions. Burdekin,[26] in a review of risk/integrity aspects of materials in 2000, noted that, although quantitative risk assessment for creep and corrosion is still in its infancy, RBI is becoming well established and engineers/materials scientists should have a basic grounding in risk assessment and the principles of reliability analysis since these will become a key basis for decisions.

The prevention of failures requires management systems that incorporate appropriate tools (procedures, risk assessments, and probabilistic methods) and teams (design, corrosion, inspection, maintenance, stakeholders) to develop and implement corrosion management strategies. This is achieved by the incorporation of best practices from Total Quality Management (TQM) as outlined in the ISO requirements for quality,[27,28] health and safety[10] and environmental[29] management systems. The major focus of this chapter is the development, implementation, and maintenance of risk-based management systems to ensure that corrosion mitigation strategies are in place and that mitigation practices are implemented in an effective manner. The chapter provides a framework that may be used to review, audit and continuously improve corrosion management systems. The framework highlights the need for organizations to develop performance standards or key performance indicators (KPIs) to monitor the effectiveness of day-to-day activities during the design, construction, and operation and maintenance phases of projects.

4.30.1.4 Basic Concepts

A corrosion control strategy is defined here as the management of available resources, including finance, materials, equipment and manpower, to provide the policies, procedures and organizational systems that are required to mitigate the effects of corrosion. Successful management strategies provide the means of achieving corrosion control objectives, such as optimal life-cycle costs, minimal leaks and the required life. It is in strategy development and/or in day-to-day implementation of policies that difficulties often appear in the field (essentially the control of who does what, where and when). Effective strategies are typically concerned with long-term objectives and encompass standard corrosion control procedures/established engineering practices that form the basis for written documentation appropriate for the project under consideration.

Corrosion control tactics can be summarized as the practice or implementation of planned procedures and courses of action necessary to achieve the required corrosion mitigation results. These require guideline documentation and background information for managers and engineers responsible for implementation of corrosion engineering procedures. The basic principles have been in place for decades and have been incorporated into industry practices by embedding them in design reviews and audits, hazard and operability (HAZOP) studies, integrity and operational practices. Fundamental requirements are that equipment is designed, constructed, operated, and maintained in an economic and safe condition.

Tactics involve specific solutions such as the use of corrosion control options and corrosion inspection/monitoring practices to solve particular problems and they are often delivered by specialists and/or contracting companies. The successful implementation of corrosion control options, either singly or in combination, requires not only the production of clear specifications and work instructions but also adequate management structures for the control and reporting of work. Regular reviews and audits are needed to maintain compliance with policies, standards, and company guidelines and also ensure continuing improvement to meet increasingly stringent SHE requirements. This is achieved by development and implementation of performance standards.

Performance standards or KPIs are the basis for planning and measuring achievement. In a practical sense, they are checks that are developed for all levels of the organization and used to ensure that appropriate actions are carried out as required. Setting the appropriate standard is crucial for effective implementation of policies. KPIs are agreed performance criteria that enable the performance of management systems, individuals and day-to-day actions to be judged against acceptable in-house standards and/or industry benchmarks. Failure to achieve the performance standard should trigger a review to identify reasons for under-performance, for example, inappropriate reporting methods, insufficient resources, slow response, and unrealistic KPI. Where appropriate, modifications should then be made to improve performance. The key questions are:

1. Who is responsible?
2. For what?
3. When?
4. With what expected results?

Management KPIs cover the monitoring and measurement of performance of the corrosion management system itself, and not the monitoring/measurement of corrosion which would be subject to separate KPIs. Improvements in corrosion management systems result from the constant reexamination and incorporation of learning from previous performance deficiencies.

4.30.2 Corrosion Management Processes

4.30.2.1 Introduction

In most organizations, capital investments and production activities are undertaken as projects with well defined boundaries and clear business objectives. Managers and teams are usually aware of corrosion as one of many potential threats to project viability but systematic evaluation with regular updates is required so that risks are formally identified and actively managed. Management is a process that should have clearly defined steps with appropriate means of ensuring adequate control of the process. Adoption of a risk-based approach to the corrosion management process can help to align corrosion mitigation practices with recognized good practices, worldwide, and corrosion management processes are likely to be more effective if based on recognized quality management processes.

4.30.2.2 Quality Management Processes

Any process, including a management process, is a series of steps that convert inputs into outputs. For example, a manufacturing process converts raw materials into products, whilst a corrosion process converts metallic items into corrosion products. This process approach, as summarized in the quality management system document ISO 9001:2008,[27] requires organizations to identify and manage numerous linked activities with the output from one process directly forming the input into the next if the functions are to be effective. The ISO standard focuses on an organization's ability to meet customer requirements of a product or service and also addresses both regulatory and the organization's own requirements in terms of quality management. It provides a benchmark for the development and application of corrosion management processes through which in-house or contractor corrosion teams can provide cost effective, corrosion mitigation products and services.

Adoption of basic 'quality' concepts is also important if a corrosion management system is to interface with an existing asset management system especially if it is to be provided by, and/or operated through, an external contractor. The linked standard ISO 9004:2000[28] has been designed to complement ISO 9001:2000[27] but here the emphasis is on senior management inputs in order to achieve continual improvement of performance. Managements inevitably change within organizations and the effectiveness of corrosion management processes will vary with time without the emphasis on 'continuous improvement' that is implicit in most quality management systems. Quality systems complement requirements in technical specifications and provide an auditable trail of documented quality measures and checks.

In general, the aim of a quality approach is to establish, document, implement and maintain a management system and continually improve its effectiveness. The organization needs to:

1. Identify the management processes.
2. Determine the sequence and interaction of these processes.
3. Determine the criteria and methods of operation and control.
4. Ensure availability of resources and information necessary to support the operation and to monitor these processes.
5. Monitor, measure, and analyze these processes.
6. Implement the actions required to achieve planned results.

The functional inputs and steps required in a successful management process are derived from inputs from teams (stakeholders), use of appropriate tools (risk assessments, monitoring methods, etc.) and well defined systems (organizational structures, reporting routes, etc).[30]

Corrosion management processes can therefore be envisaged as shown in **Figure 1**.

Teams involved in the corrosion management process during the various stages of a project may be drawn from a variety of functions. Team leaders will be selected on the basis of tasks to be undertaken, skills, and experience of the personnel and the specific stage of the project. Few organizations are large enough to justify the employment of a full time corrosion engineer. Many decisions related to corrosion issues have to be made by managers on the basis of reports and recommendations from design, production, inspection, and maintenance personnel and most operational/day-to-day corrosion mitigation

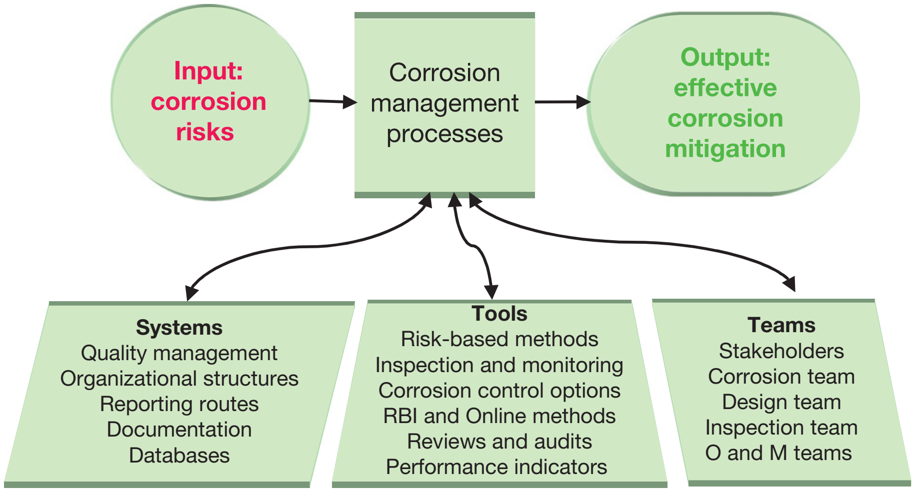

Figure 1 Corrosion management requirements.

activities are undertaken by members of the design, process/plant engineering or maintenance teams or contractors. For example, an electrical engineer often becomes responsible for cathodic protection (CP) systems, the site chemist or process engineer oversees the inhibition and biological control of cooling systems, chemical treatment programs, etc. Off-site specialists or consultants provide any required additional support. In general, during the operational phase, an on-site engineer or manager has to interpret field data to identify trends that are required to provide management information.

Tools used as part of corrosion management strategy development encompass corrosion risk assessments that may include risk matrices, and/or probabilistic analyses. Implementation of tactics involves use of corrosion control methods, employment of various corrosion inspection/monitoring techniques to obtain plant/field data, use of data storage, data analysis and trending to convert data into information for decision makers. The development and use of KPIs and risk control systems are tools for the control of operations and day-to-day activities.

Systems for corrosion management are used to implement corrosion mitigation strategies and tactics through well defined organizational structures. Such structures should be based on quality management principles and be clearly laid out on, for example, a flow sheet that highlights identifiable policies/objectives, notes the allocation of responsibilities, resources and the means of corrosion mitigation implementation through procedures that are regularly reviewed and audited. Systems may be paper- or computer-based.

4.30.2.3 Risk Management Processes

Corrosion is a risk to a project/operation and it is therefore appropriate to consider the benefits of well established risk management approaches especially as, for example, one source[31] identifies three levels of decision making in any project:

1. *Strategic decisions* include establishment and confirmation of goals, means, and constraints, identification of key risks and stakeholders plus setting these in context for tactical and operational decisions for each project/activity.
2. *Tactical decisions* involve choosing how to deploy the most appropriate means of achieving goals and managing tactical risks within the restraints set at the strategic level.
3. *Operational decisions* are concerned with implementing tactical choices and managing operational risks. A key element throughout is the development and implementation of written procedures.

Risk management is an iterative process of well-defined steps:

Risk identification → Risk analysis → Risk evaluation → Risk treatment.

When taken in sequence, these steps give rise to improved decision-making by providing greater insight into risks and their impacts on the operation. Two main outcomes from adoption of a risk management approach are:

1. Significant undesired or unexpected outcomes can be identified, and
2. Opportunities for improvement can be considered.

A useful framework is shown in the flow sheet in Figure 2 that identifies the main issues associated with a risk management process.[31] The specific approach adopted will vary depending on the type of project/industry/business requirements but a key element in all situations is the feedback required to maintain the system. The key features are:

1. *Risk assessment process* – identification, analysis, and evaluation of the risk, its likelihood and consequences, plus criteria used to quantify the risk and priorities to be set.
2. *Risk treatment* – selection of the mitigation options, planning of treatment measures and allocation of responsibilities/implementation of procedures.
3. *Secondary risk identification* – identification during the analysis, evaluation, and treatment process of such risks that are a key factor of any protocol and an important consideration when mitigation of corrosion risks is addressed.

Corrosion risk management must be integrated into the organization's philosophy, practices, and business plans and not viewed as a separate activity. In this context corrosion, management should be focused on the management of corrosion risk mitigation, that is, strategies and control of day-to-day activities rather than just specific tactics of corrosion control and corrosion inspection/monitoring that are merely the tools used in the mitigation process. Opportunities for improvement and benefits that are inherent in a risk management process are often neglected during the initial implementation of corrosion risk management because of an over-emphasis on risk mitigation. In addition, secondary risks relating to risk mitigation are often neglected, such as:

1. *Inspection risks* – criteria used to determine appropriate inspection methods and the selection of inspection frequencies appropriate for the type of corrosion damage must be understood and their applicability maintained. Loss of corrosion inhibition/chemical treating may result in a higher risk as it negates the basis used for inspection scheduling.
2. *Chemical treating risks* – caustic dosing/corrosion inhibition requires that the process fluids are monitored to ensure compliance to an agreed pH or inhibitor residual concentration. Injection equipment must therefore be maintained to an

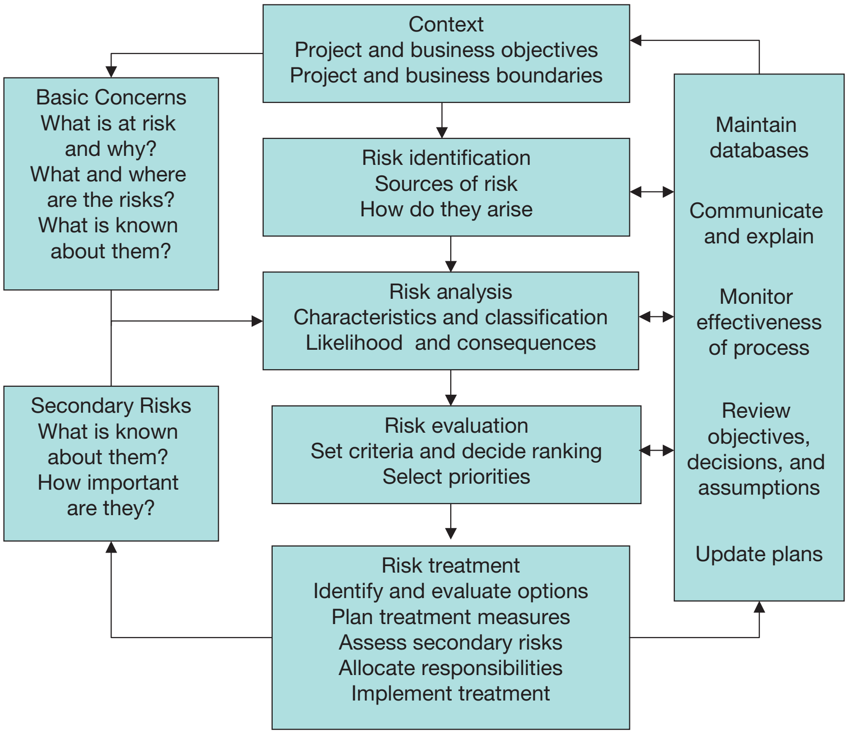

Figure 2 Risk management process, adapted from BS 6079–3:2000.

agreed level of reliability, otherwise the basis of the overall inhibition risk mitigation process and inhibitor availability criteria may be invalidated.

3. *Use of corrosion resistant alloys (CRAs)* – provides protection against general corrosion but will risks from pitting and cracking occur if process conditions change? Are fluid compositions and temperatures monitored to meet agreed upon criteria?
4. *Use of coatings/CP* – requires regular inspection/monitoring and maintenance. Are appropriate checks and regular audits made to ensure corrective actions are carried out?
5. *Design detailing aims* – to eliminate risks from local fluid chemistries/temperatures, equipment/component stresses, fluid flow/heat transfer characteristics, location/layout/geometry of equipment and components; requires reviews and audits.

Selection and application of any corrosion risk mitigation plan requires decisions to be made, responsibility allocated and reporting routes established. An audit of mitigation procedures is required before implementation is finalized. Feedback control from information derived from field data and involving comparison with agreed upon criteria and possibly information held in other company databases (production and maintenance) is needed. Also required is the effective monitoring of the management process, including regular reviews and update of plans. For example, every company standard and procedure should have a written agreed review date in a similar manner as is used in the maintenance of, for example, NACE and ISO standards.

An illustration of the complexity of the corrosion risk management challenge in a multidisciplinary activity can be seen in the flow sheet in Figure 3 that summarizes typical information flows, including feedback, that are required to mitigate corrosion risks within organizations in the oil industry.

There is already significant technical feedback information within the industry on corrosion issues, but as Milliams has noted,[32]

> The management of corrosion is a concern which extends beyond the responsibilities of corrosion and materials engineers. Whilst they should provide advice during both the design and operational phases, they are dependent upon the co-operation of other disciplines if an installation's projected design life is to be achieved. The model proposed provides a framework for that co-operation and for optimizing the contribution the corrosion and materials engineers make to an organization.

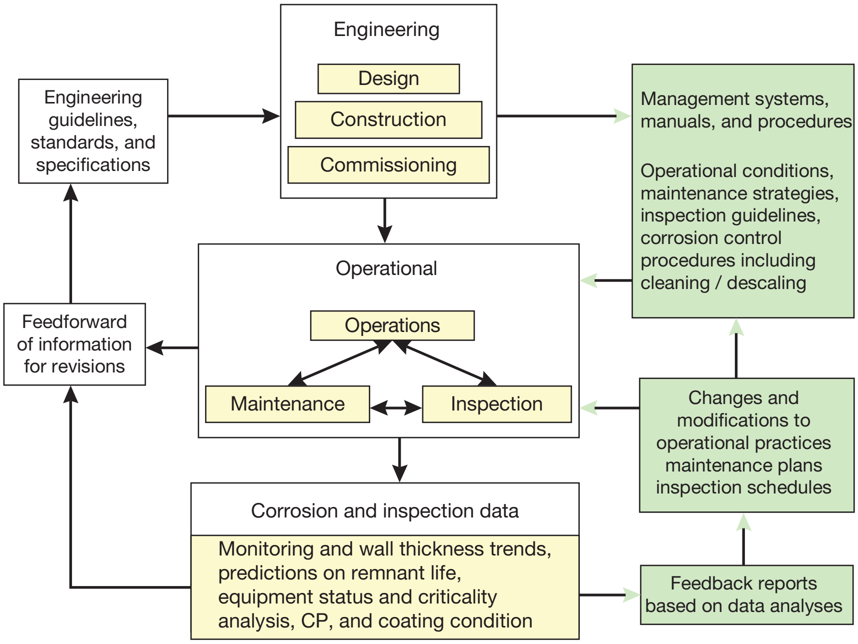

Figure 3 Information flows for the management of corrosion. Adapted from Milliams, D. In 12th International Corrosion Congress on Corrosion Control for Low Cost Reliability 19–24 September 1993; NACE International: Houston, TX, 1993; Vol. 4, pp 2420.

In general, corrosion risk assessment, the identification, analysis, and evaluation of corrosion risks, and corrosion risk treatment, the mitigation of the corrosion risk, are two separate steps in the corrosion management process. Both steps can involve the consideration of secondary risks incurred by the assessment or treatment processes but there must also be an acceptance that not all risks can be eliminated and contingency plans will be needed. For example, in RBI, a premise is that risk of failure can be assessed in relation to an acceptable level or probable annual frequency provided that the damage mechanism and process conditions are known. Eventually repair and/or replacement will be required (condition-based maintenance) but the consequences of a potential failure before that stage must be addressed. A third step is to use agreed upon procedures to monitor and modify the management process. These steps are shown in the summary flow sheet in Figure 4.

The success of corrosion management processes used to convert risk inputs into mitigation outputs are largely dependent on the management systems adopted (organizational structures, document systems, information flows, data management systems), the tools employed (risk assessment and mitigation procedures, field data collection, control tactics) and the composition of the corrosion teams.

4.30.3 Corrosion Management tools

4.30.3.1 Identification of Corrosion Risks

4.30.3.1.1 Corrosion damage and failure modes

The starting point of any assessment is the identification of the corrosion process or corrosion damage that may be sustained by structures/equipment and the impact that this damage may have on integrity and plant operation,[33] including side effects such as the fouling of equipment (sludge in lines/vessels, radioactive build-up in heavy water reactors, strontium scales in oil production) or on contamination of products (food and pharmaceutical chemicals). The various types of corrosion are described in detail in separate chapters in this volume. The more common examples of corrosion damage are:

1. *Uniform corrosion – metal loss due to general corrosion*, atmospheric corrosion/rusting, metal wastage in process streams/cooling water pipe work.
2. *Galvanic corrosion – accelerated localized corrosion* due to the effect of mixed metal combinations or compositional/metallurgical factors as in the corrosion of weldments.
3. *Localized attack – pitting and crevice corrosion*, often the result of a small area of damage in the

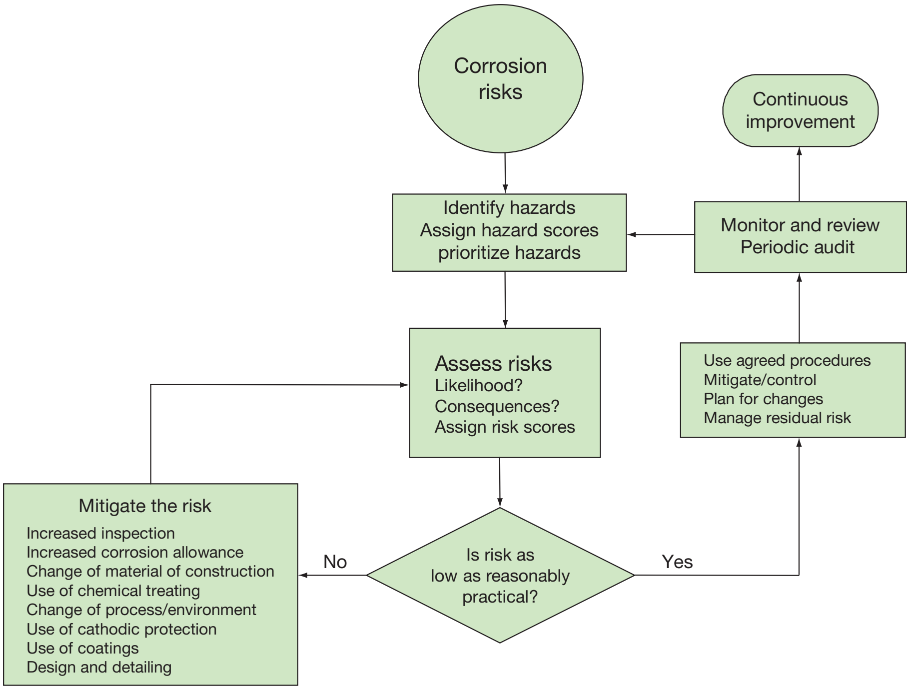

Figure 4 Overall corrosion risk analysis, mitigation, and control process.

protective/passive corrosion product film (small anode area and a large cathode area).

4. *Flow induced corrosion – erosion corrosion, cavitation, impingement attack*, the result of high fluid velocities/high wall to fluid shear stresses/high turbulence intensity, changes in fluid pressure and the presence of second phases such as bubbles and sand.
5. *Environmentally assisted cracking* – caused by the combined action of a mechanical load/tensile stress/residual stresses plus a specific corrosive environment/temperature on a susceptible alloy (essentially a brittle type failure in a normally ductile material).
6. *Corrosion fatigue* – combination of cyclic stresses and exposure of a susceptible metal to a corrosive environment.

Many reports and texts refer to corrosion damage or morphology, or the various forms of corrosion as corrosion failures but in the strict engineering sense, a failure occurs when an item, component, or unit does not meet the design/operational requirements. In this strict sense, corrosion *per se* is not a cause of failure but rather is a contributor to a failure mode that is the combination of the effect of damage on operational (and accidental) loads,[34] as summarized below:

Failure mode	Local leakage
	Rupture/severance
	Collapse or buckling
Corrosion damage	Uniform corrosion and isolated pitting
(corrosion morphology)	Flow induced corrosion & erosion
	Longitudinal and transverse cracking
Loads	Pressure (internal and external)
	Forces (tensional/hoop stresses, compressive, bending/torsional)
	Impacts (collisions, dropped objects)

Likely failure modes are key inputs into engineering risk, or criticality assessments. In most industrial situations the deteriorated condition that may lead to the undesirable leak or rupture, can usually be anticipated by a risk assessment for the specific damage mechanism. In the case of corrosion, this would be based on credible rates of deterioration obtained, for example, from internationally accepted and published values/mechanisms, and/or identified by on-site corrosion inspection.

Most assessments concentrate on corrosion that occurs to equipment during its operation but significant damage may also take place during construction and storage of items, start up/shut down periods (when conditions vary from the design basis) and maintenance activities. This requires an understanding of all the factors that may affect probable corrosion processes and cause equipment damage.

4.30.3.1.2 Sources of corrosion risk

Assessments of corrosion risks to either an existing or proposed new equipment start with the consideration of the corrosive environments, both internal and external, to which the equipment is likely to be exposed. The combination of the metal's environment and the influence of engineering factors, such as mechanical stresses, heat transfer and fluid flow, may play a crucial role in the corrosion processes, and will also have to be assessed. In a detailed study each item of equipment (vessel, reactor, heat exchanger, etc.), process stream compositions and temperatures (in and out) and connecting pipe work (including sections of the same pipe run of differing diameter) will have to be assessed.

Therefore, any corrosion risk assessment has to, at some point, consider a combination of three basic influences that control the physical/chemical processes that result in possible corrosion damage, as shown in **Figure 5**:

1. *Materials of construction*, in particular their compositions, fabrication, and required lives: There are many options, depending on the specific requirements. Along with resistance to corrosion and wear, the materials may have to withstand high temperatures, perhaps in the creep range of the material, or low temperatures where brittle fracture is a concern, as may occur during a high pressure gas leak.
2. *Corrosive environments* that vary widely depending on the application and may involve exposure to gaseous atmospheres, naturally occurring or treated waters, acids or alkalis: Some aqueous environments may contain bacteria that produce local highly corrosive conditions whilst some fluids may contain specific salts, for example chlorides and/or sulfates that cause pitting/stress corrosion cracking. Both internal and external and transient conditions, such as are associated with start up and shutdown of equipment, have to be considered.

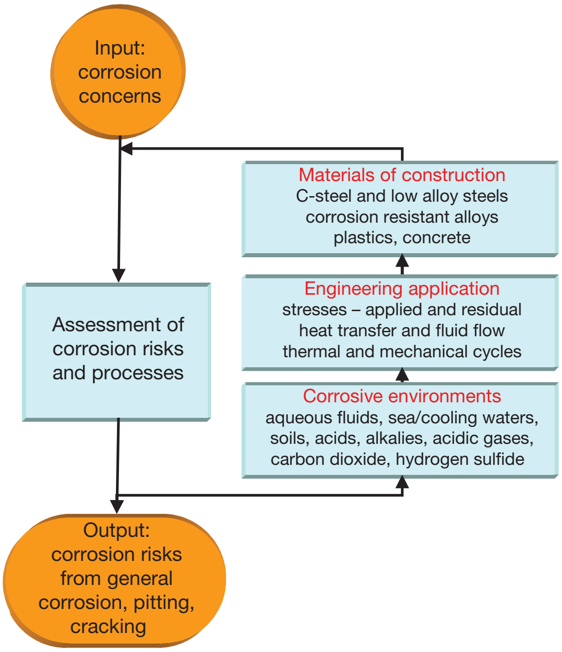

Figure 5 Basic corrosion risk assessment steps.

3. *Engineering application*, specifically the type of equipment, its functionality and associated influencing parameters such as exposure to various mechanical loads, fluid flow and heat transfer conditions that can have significant impacts on corrosion processes. Residual and applied stresses can introduce risks of corrosion fatigue and environmentally assisted cracking processes. Fluid flow conditions involving changes in direction, diameter, topography, etc., can cause areas of stagnation, stratified/slugging flow, or high turbulence intensity downstream of protrusions/restrictions/expansions that can introduce risks of erosion corrosion or even cavitation damage. Heat transfer rates and surface temperatures in equipment can result in problems associated with condensation, scaling, fouling/biofouling and high temperature corrosion.

Each of the above may contribute in varying degrees to the overall risk. A corrosion risk assessment of a conceptual design would probably concentrate on major specific risks as posed by the initial material selections, such as comparisons between low alloy steels and corrosion resistant alloys (CRAs). A detailed assessment, as employed for RBI scheduling would require each item of equipment to be itemized and evaluated for internal and external corrosion using a formal and audited approach.

4.30.3.2 Corrosion Risk Assessment Processes

4.30.3.2.1 Hazards and risks

Identification of hazards and assessment of risks are fundamental steps in corrosion mitigation and engineering studies. The relationship between hazards and risks emerges from their definitions:

1. *A hazard* has the potential to cause harm or damage; often defined as a physical condition or release of hazardous material as a result of component failure that can cause human injury or death, loss or damage, or environmental degradation.
2. *Risk* is the combination of the severity of the effect (the consequences) and the likelihood of it happening (damage mode and probable frequency).

The tools used to identify, analyze, and evaluate corrosion risks and then to treat or mitigate those risks vary considerably depending on the specific application. Identification and ranking of hazards and risks associated with corrosion lead to prioritization of actions, use of framework rules with guidelines/protocols and assessments of how corrosion and asset integrity systems are managed.

The assessment can be either paper-based or carried out using appropriate software on a PC-based system depending on the complexity of the facility. In its simplest form, it is a careful engineering examination of the items comprising a facility and the likely corrosive environments, the materials of construction and engineering application. For example, for a port or harbor facility a major concern would be the marine environment and ambient temperatures for specific items, for example the effects of anaerobic subsoil/mud, seawater, tidal/splash zones or saline atmospheres as appropriate on sheet steel piles and columns (possible ice flow abrasion?), reinforced concrete beams, pillars and mooring dolphins, storage sheds, cranes, lifting gear, etc. The effectiveness of existing or proposed corrosion control measures such as coatings, CP, and even chemical treating of vehicle cooling systems should be considered based on previous experience, existing maintenance, and published data records.

In general, the information needed for corrosion assessment includes a list of items of interest from the asset register (structures/vessels/pipework/storage tanks, etc.), historical data (inspection/monitoring/maintenance), theoretical analysis (new systems based on published data/models), informed opinions and concerns of stakeholders (individuals, groups, other areas of the organization) and field data where available. Such risk assessments are the tools that focus attention on critical areas and they are used to review a design, ensure asset integrity and improve corrosion control but do not by themselves provide management control. Outputs from risk assessments are recommendations that may include changes to the inspection/monitoring or use of/change of the corrosion control practices. The decision-making steps form a vital part of the management process.

At its simplest, the assessment is a common sense engineering approach that provides a means of checking on what is often a good existing practice. Decisions are based on questions such as:

What would be the worst case scenarios?

1. How likely are they to occur?
2. What would be the damage?
3. How many people could be injured or killed?
4. How will these events affect the business?

The three fundamental questions in corrosion risk analyses are:

1. Failure mode – what could go wrong?
2. Failure effect – how will it affect the project/plant integrity/operations?
3. Failure criticality – how likely is it?

Criticality analyses examine potential failures to assess the severity of each failure in terms of decreased performance, total loss of function, safety, and environmental hazards. Typical steps in such an assessment include:

1. Identify plant components (Tags) or process function.
2. List possible failure modes for each component (Tag number).
3. Identify likely effects of each failure mode.
4. List all possible causes of each failure mode.
5. Assess the failure modes numerically (e.g., on a scale of 1–10).
6. Evaluate a criticality index for each failure mode to assess priority of failure mitigation/prevention actions.
7. Indicate required corrective actions, expected completion date, and the departments/people with required responsibility.

The first step is therefore to consider potential hazards/escape of flammable gasses/liquids/toxic substances and the effect on people/the environment and the business. This focuses attention on the items at risk and the approach could be similar to the procedures that are used in the process industries to identify hazards and operability issues (HAZOP). In general, a corrosion risk assessment will incorporate appropriate findings from HAZOP/environmental studies for the evaluation of likely consequences as indicated below.

With hazardous or toxic fluids such as hydrocarbons and other chemicals the effect or consequences criteria of a failure depend on stored energy (E), pressure (P), volume (V), toxicity (T_x), flammability/explosive risk (F), and temperature (T). An overall hazard score H can be allocated:

$$H = E \times P \times V \times T_x \times F \times T$$

for each vessel, tank, piping system or other equipment items. Safety risks may be scored on the severity of the possible incident and number of people likely to be affected (<3, 3–9, >10). The effect of any failure is typically considered in an environmental impact study and the economics addressed by estimating the effects of shut down (partial/full) on the operations and time required to effect repairs. All risks are multiplied. A quantified (Level 3) assessment of an item depending on the numerical values chosen for the likelihood and consequences criteria, for example an oil/gas pipeline, could provide a total numerical score as follows (Table 2):

The criteria employed in any risk assessment are often based on judgment and agreed upon guidelines and are not absolute; therefore, a degree of skepticism is always helpful when the criteria adopted in the assessment are not specified.

4.30.3.2.2 Matrix analysis

In many engineering studies, the criticality of an item is presented as a table or matrix of the likelihood of failure against the effect of a failure:

$$\text{Criticality} = \text{Likelihood of failure} \times \text{Effect of failure}$$

Most corrosion risk assessments are qualitative using a judgment, based on descriptive ranking such as

Table 2 Risk score based on likelihood and consequences

Total score	*Criticality ranking*
<300	Low
301–1000	Moderate
1001–3000	High
3001–10 000	Very High
>10 000	Extreme

high, medium, or low that may be converted into a simple numerical description. For particularly critical equipment, for example in the nuclear industry, a rigorous quantitative analysis is adopted:

$$\text{Risk} = \text{Probability} \times \text{Consequences}$$

The outcome is a numerical value, with measured units, that may be simplified by assigning bands to the probability and consequences.

Corrosion risk assessments can be typically classified into three groups:

Level 1 – Qualitative risk analysis, a simple ranking of equipment

Level 2 – Semiquantitative risk analysis, a more accurate prioritization that retains vital inputs of a Level 3 analysis but simplifying assumptions

Level 3 – Quantitative risk analysis, an in-depth study including assessment of reliability, financial and limited environmental issues

Failure mode, effect, and criticality analysis (FMECA) is an example of an engineering risk evaluation process that has been used for over 40 years to evaluate systems, including those on commercial jet aircraft. The analysis considers the seriousness/consequences of a failure (*S*) and the probability (*P*) of the occurrence of each failure mode. The analysis may also include the difficulty of detection (*D*) of the failure mode/damage. Table 3 indicates that corrosion damage that may have a high rate of penetration such as stress corrosion cracking or corrosion fatigue which is the most difficult to detect by inspection, whilst the easiest damage to detect, general corrosion, is the simplest to manage by basic trending of inspection data, for example loss of corrosion allowance with time.

Table 3 Characteristics of corrosion damage

Damage	*Ease of detection*	*Rate of penetration*
Uniform	Very high 1	Low
Pitting	High 2	Medium
Erosion	Medium 3	Medium
Cracking	Low 4	High

In a simple corrosion or maintenance situation (i.e., using a common sense engineering assessment) a basic paper-based corrosion risk assessment (level 1) may be employed with the probability and consequences judged either high/unacceptable or low/acceptable. Alternatively a numerical value can be assigned (5 – low, 4 – medium, 3 – high, 2 – very high, 1 – unacceptable). The advantage of developing an agreed numerical ranking, as is employed with some visual inspections of equipment or paint deterioration based on the degree of rusting of coated surfaces,[32] is the ease of handling data input/output in computer systems.

Such a ranking is illustrated in the criticality index (*C*), shown in Table 4, which provides a numerical ranking ($C = P \times S \times D$) that enables a risk assessment team to focus on items of a plant, or processes, that have varying levels of corrosion risks. In this particular example, the following values have been arbitrarily assigned:

Probability and seriousness	between 1 and 5
Detection	between 1 and 4
Overall criticality rank of items	between 1 and 100

A more common approach to risk assessment is the use of risk matrices for evaluating various probabilities and consequences as illustrated in Figure 5 developed as a simple corrosion risk matrix for the assessment of corrosion mitigation options for reinforced concrete. Corrosion processes in reinforced concrete are described in a separate chapter in this book. Reinforced structures, including those constructed with good quality concrete, are susceptible to rebar corrosion damage resulting from carbonation and chloride ion ingress from marine/ground waters.

Table 4 Criticality index (FMECA)

Probability (*P*)	Rare 1	Unlikely 2	Moderate 3	Likely 4	Almost certain 5
Seriousness (*S*)	Not serious 1	Nuisance 2	Repair 3	Change 4	Shut down 5
Detection (*D*)	Easily detected 1	Medium 2	High 3	Detection unlikely 4	
Criticality (*C*) (Ranking value)	Low <20	Medium 20–60	High >60		

Chlorides in the presence of high levels of oxygen cause pitting of rebar and the corrosion spreads to give rise to high rates of general corrosion. The buildup of corrosion product causes the concrete cover to crack leading to increasing rates of attack. This is a particular problem in hot climates where the high temperature of cure increases concrete permeability and subsequent chloride penetration rates. Structures constructed in hot saline regions therefore have an increased risk of pitting/corrosion of rebar.

Practices that mitigate the effects of chloride ingress in concrete include:

1. use of coatings on the rebar;
2. use of sealant/coating on the concrete above grade;
3. use of waterproof membrane to prevent water ingress into foundations;
4. application of CP, retro-fitted to existing corroded concrete structures or designed into new structures.

The preferred choice depends on the particular situation and the life cycle costs for each option. Life cycle assessments should include the likely costs of future repairs and any associated downtime. The option of not including extra corrosion protection (reliance on concrete cover only plus probable maintenance/repair costs) should also be assessed as the base case.

The development of a simple risk or criticality ranking for reinforced concrete structures based on a 3 × 3 matrix analysis is shown in Table 5. The actual criteria used, Table 6, can be adjusted with experience. This approach essentially encompasses information in a number of international standards on concrete construction. However, these tend to underestimate corrosion risks in marine situations, particularly at high ambient temperatures and saline contents.

Table 6 illustrates the use of 'rules' or agreed-upon criteria to define the likelihood of corrosion, the effect of corrosion and the final ranking. A major risk factor is not only the technical and corrosion issues but the effect of future repairs and downtime on life-cycle costs as well. The results of the risk assessment could also form the basis of a mitigation strategy and development of agreed upon procedures as shown in Table 7, the success of which depends on the management of associated risks.

The above example illustrates the principle of matrix analysis but other risk assessment systems use 4 × 4, 5 × 5, or 4 × 5 matrices, with either linear or logarithmic scales with output as a numerical risk

Table 5 Example of a simple risk or criticality ranking for concrete structures based on a 3 × 3 matrix analysis

Criticality ranking, 1–5				
Effect of failure	Low	1	2	3
	Medium	2	3	4
	High	3	4	5
		Low	Medium	High
		Likelihood of failure		

Table 6 Typical guidance for reinforced concrete structures

Likelihood of corrosion	
High	Concrete contains chlorides. Average/low cover. Tidal marine zone, sabkha region ground waters, waste water pipes.
Medium	Atmospheric marine environments/wind-blown sabkha sand. Possibility of regular wetting from water spills.
Low	Office environments, aggregates and mix water had low chloride levels. Design mix and placement to standards.
Effect of corrosion	
High	Rapid corrosion/cracks/spalling in <10y which prevents facility use. Repairs are costly because of access.
Medium	Repairs in 10–25 years. Facility unavailability tolerable for repairs, Accessibility reasonable nor expensive
Low	No significant effect <25 years, availability not critical. Easy access/low scaffolding costs. Simple patch repairs OK
Risk/criticality ranking	
1	Use existing codes for concrete and cover thickness. Remedial works unlikely to include coatings/CP.
2	May consider sealant or anticarbonation barrier coating for new designs
3	May consider inhibition or coated rebar for new designs, Corrosion damaged structures consider realkalization/chloride removal
4	Additional corrosion protection is likely for new designs, Retain option to retro-fit CP. Repairs should consider realkalization/chloride removal followed by either sealant coatings or retro-fitting CP at later date.
5	Extra corrosion control should be mandatory with new designs. Repairs/refurbishment should consider CP option

Table 7 Selection of corrosion control options for concrete

Marine structures (chlorides, atmospheric oxygen)	Cathodic protection in tidal and splash zones Coatings for topsides
Foundations (chlorides, biological compositions)	Water proof membrane/tanking or cathodic protection in high salt content ground (especially sabkha regions)
Above grade structures (atmospheric exposure)	Sealants or coatings on the concrete. Fusion bonded epoxy coated bar where salt contamination is likely to be high
Inside buildings (controlled environment)	Combination of material selection and conventional design codes

factor. Some are based on the probability of the failure criteria as in the quantified or Level 3 assessment employed by API 580/581.[20,21] Weighted factors may be employed to develop the inputs for the likelihood of failure and consequences of failure.

The purpose of the matrix approach is to prioritize risks and to concentrate efforts on the most influential ones. The numbers on the diagram would typically correspond to threats and opportunities taken from a risk register. A drawback with this approach is that it is difficult to know when the optimum risk mitigation position has been reached unless it is also linked to further actions such as a probabilistic evaluation. However, it is relatively simple and time-efficient to implement. Some of the first practical applications of criticality/RBI methods were on UK North Sea platforms[35] from 1991, and refinery units since the mid-1990s. The approach has been adopted by many operators/service companies/vendors/software suppliers.

4.30.3.2.3 Risk-based inspection

RBI is the subject of a separate chapter in this volume. RBI of process equipment is arguably the most familiar example of how matrix analysis is used in the development of corrosion mitigation strategies at various levels of decision-making. An industry benchmark can be found in the API RBI approach[20,28] that uses a 5 × 5 matrix, Figure 6, to identify levels of risk in refinery/process equipment. The output from a quantified (level 3) assessment, as described previously in the determination of hazard scores, is used to determine the consequences category of the matrix.

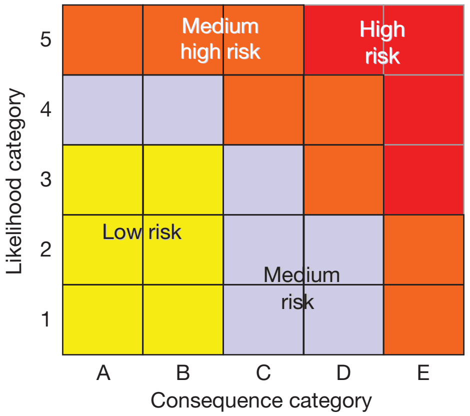

Figure 6 5 × 5 matrix used in the API 581 risk-based inspection procedure.

For example, equipment items at high risk (5*D*, 5*E*, 4*E*, 3*E*) are unacceptable, requiring a redesign in more corrosion resistant materials or alternative processing routes to be employed. Medium–high risk items could be assessed to see if increased inspection frequencies would allow continuing operation but obviously with a limited life (a predictive maintenance strategy) or if improved corrosion control measures would be effective at decreasing the likelihood of failure and moving the item into a medium risk level and also extending the life. Here a probabilistic analysis could also identify a cost effective option for such strategic decisions.

The resource document, API 581, and the accompanying software package assess consequences (leakage/rupture) for different areas of damage (size of holes in the pipe work and vessels) from general and localized corrosion and cracking. Various scenarios are then evaluated in terms of flammable/toxic effects together with environmental and business interruption effects. The resource document contains a number of technical modules that describe how the potential damage mechanisms are assessed for petrochemical process equipment (from recognized published data) in terms of a damage factor. Key elements of the API RBI approach are:

1. The use of a probabilistic approach for determining the rate of damage, metal loss or crack progression, also employed in the DNV G101[22] offshore inspection standard.
2. The effectiveness of inspection programs in finding and monitoring identified damage mechanisms by assessment of the inspection effectiveness, detection capability of the inspection methods employed and other factors in the inspection process.

Typical inspection methods are ranked, 1–5, in terms of their effectiveness for various forms of damage such as thinning, surface and subsurface cracking and blistering. For example, for general thinning:

1. *Highly effective (90%)* – complete internal visual examination plus ultrasonic thickness testing (UT).
2. *Usually effective (80%)* – partial internal visual examination plus UT.
3. *Fairly effective (50%)* – external spot UT.
4. *Poorly effective (40%)* – hammer testing/telltale holes.
5. *Ineffective (33%)* – external visual examination.

The underlying logic is based on expert opinion quantified using Bayes' Theorem by incorporating the information as a 'State of Damage,' with 1 = equipment damage is no worse than expected based on models/experience, 2 = damage somewhat worse than anticipated/as is sometimes seen in similar equipment, 3 = equipment is considerably worse than anticipated, that is, rarely seen but has been observed occasionally in industry. Combining the inspection ranking with the damage state enables the inspection effectiveness to be quantified to provide a probability ranking.

The software then determines the inspection frequency based on the thickness of the wall, probability of a failure, the damage factor for the type of corrosion (from recognized published data) and the extrapolation of the inspection data trend. When the damage factor increases to a value of 10 or higher after four or more 'highly' effective inspections then the equipment is at the end of its useful life. A value of 10 indicates that the probability of failure increases by an order of magnitude. The aim is to achieve or maintain a low damage subfactor at ideally 1 or less but in practice less than 10, by changing either the inspection frequency and/or the method of inspection (the effectiveness). As the number of effective inspections increase then confidence in the outcome also increases (the error band associated with the measured corrosion rates is decreased), that is, the trend becomes more reliable.

The protocol adopted is illustrated by the effect of progressive damage resulting from general thinning and localized thinning (pitting and erosion–corrosion) on the strength of an equipment item, as shown in Figure 7. The corrosion rate (wall thickness change with time) is determined from inspection data or may be initially obtained from published data and/or industry models and expert opinion. The default/baseline position is that the corrosion allowance is 25% of the original wall thickness but this is typically modified by use of the maximum allowable working pressure (MAWP) based on ductile overload calculations, operating conditions, diameter and the material properties, limit state function and the minimum allowable thickness (MAT).

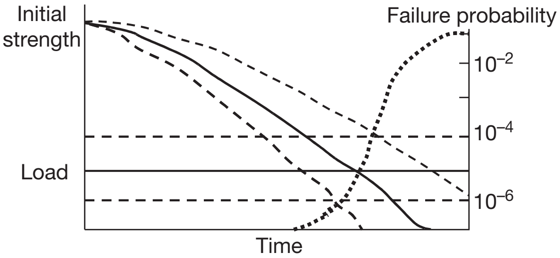

Figure 7 Probability of failure with time, adapted from API 581.

The equipment, for example, begins life with the initial strength exceeding the load by some factor of safety. The damage mechanism progressively weakens the structure but the damage rate is likely to be higher or lower than any deterministic mean value. There is therefore a distribution about the mean value of strength as shown by the dashed lines.

In practice, the applied load will also vary and hence the probability of failure will increase progressively as bounded by the intersection of the two sets of dashed lines. This failure probability is described by an *S*-curve which, for example, may follow a standard distribution, such as normal/lognormal/Weibull. The intersection of the two solid curves indicates the basis of the equipment design, the constructional material properties, equipment dimensions, etc. and a deterministic corrosion rate. This indicates there is a probability of failure of $\sim 10^{-5}$ at the required lifetime but also failure probabilities at lower and higher lifetimes. The probabilities of failure adopted for corrosion damage in process equipment are similar to risks in other engineering systems, for example, subsea pipeline as summarized in Table 8.

In summary, the API 581 approach and proprietary RBI software can produce reports for a particular plant item with consideration of the ranking, for example, of three levels of inspection activity:

1. A minimal inspection plan.
2. The current level of inspection.
3. An optimized level of inspection.

The first and obvious outcome is that the inspection frequency can be adjusted, but the methods and tools

Table 8 Example of an offshore risk category

Category	*Probable annual frequency*	*Description*
5 (Failure expected)	$>10^{-2}$	Event expected more than once in lifetime
4 (High)	10^{-2}–10^{-3}	Event expected to occur during pipeline life (100-year storm)
3 (Medium)	10^{-3}–10^{-4}	Event not expected but a once a year credibility with large number of lines
2 (Low)	10^{-4}–10^{-5}	Event rarely expected
1 (Negligible)	$<10^{-5}$	Considered negligible

Annual failure frequency for a pipeline/umbilical (based on DNV – RPF107, 2001).

used for the test and inspection (T&I) schedule can be changed. The scope, quality, and extent of the inspection and data collection/interpretation can also be modified. The benefits are that, the plant items at low risk can be inspected on a less frequent basis than by the more traditional procedures employed previously, resulting in lower inspection costs. There is, however, considerable resource needed to populate the database with the plant inventory, line diagram information and previous inspection history, plus the appointment of an experienced team leader/contractor.

At the tactical level, RBI identifies the specific levels of risk to various process units, vessels, tanks and pipe work or items of equipment and hence appropriate inspection frequencies can be scheduled, the level of resource predicted and maintenance action may be taken to mitigate the corrosion risk. At the operational level the day-to-day activities are determined by the agreed upon schedules and should be implemented by work instructions. At the strategic level, the analysis focuses management attention on corrosion of critical items and asset integrity issues but here the secondary risks resulting from, for example, failure of chemical treating systems or use of inadequate inspection methods must also be recognized by putting in place management-of-change procedures.

4.30.3.3 Probability Analysis – Dealing with Uncertainties

The probabilistic approach, which is similar to a reliability analysis, may be used to handle uncertainties in, for example, corrosion related design studies, the use of inhibition schemes or inspection strategies. This management tool assists the decision making process by presenting various scenarios that indicate possible futures. The input, that often includes imprecise data, can be varied to identify the sensitivity of the outcome to parameter changes. Incremental project funding is then only allocated on the basis that there are clear risk and uncertainty statements available at each investment decision point. The quantified output, typically expressed as a probability graph (*S*-curve), provides a clearer picture of risks and benefits derived from specific corrosion mitigation procedures. Thus although the overall results may be essentially similar to a qualitative judgment based on experience and/or traditional expert evaluation of a system, such subjective decisions are often taken without a full appreciation of the implications of uncertainty and risk.

Prediction of anticipated corrosion rates in a system is the first step in assessing corrosion risks and monitoring requirements. In most cases, information is obtained from published data and models. For example, in oil/gas production a number of predictive models are available for CO_2 corrosion of low alloy steels used in many vessel and pipeline fabrications. Most models are based on preliminary studies of de Waard and Milliams whose initial approach[36,37] was later modified to include the effect of fluid velocity.[38] The similar Norsok model[39] uses the fluid to wall shear stress rather than liquid velocity as the flow parameter. All models provide a single deterministic value of the corrosion rate (single value point data) but a probabilistic analysis shows that this statistical average can have higher anticipated values, for example, a corrosion rate of *c.* 1 mm year^{-1} could reach a maximum of 4.5 mm year^{-1}, depending on the distribution function employed, as shown in **Figure 8**.

A quantitative/probabilistic risk analysis uses random variables described by probability density functions (PDFs) or cumulative distribution functions (CDFs) to describe the various parameters that contribute to the overall process, such as the distribution of corrosion rates indicated above. Density functions describe probability using the area under the curve to the left of the associated value; distribution

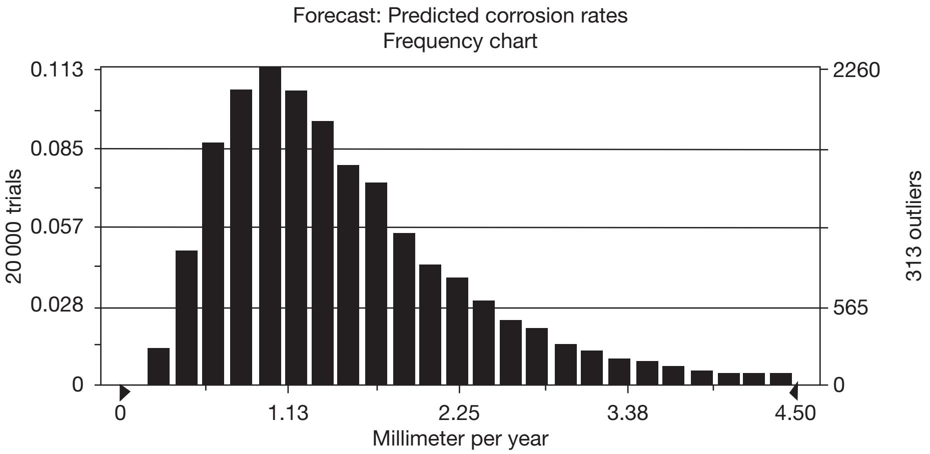

Figure 8 Typical outcome of a probabilistic approach for CO_2 corrosion rates. Reproduced from McMahon, A. J.; Paisley, D. M. E. *Corrosion Prediction Modelling*, BP Sunbury Report, ESR.96.ER.066, November 1997.[40]

functions compare value and probability directly. Various functions that describe the overall process (normal, lognormal, uniform/on/off, triangular, etc.) are then combined together to provide the output, for example survival probability or probable structure life, as shown in Figure 9. Importantly where any parameter is not known, a distribution is used to describe the (credible) range of values that are likely to occur. The outcome of the analysis, typically obtained using a Monte Carlo simulation, as illustrated in Figure 9, is recorded (for example on a histogram/*S*-curve) and the calculation repeated until sufficient information is generated in order to optimize the smoothness of the shape of the combined *S*-curve results. In practice, a network is developed to describe the overall process of interest, as indicated in the lower right hand part of the figure, and the variables/data are inserted as inputs with the outputs presented as a series of *S*-curves that describe various scenarios.

An illustrated example of the probabilistic method is shown in a pipeline pigging study to aid strategic decisions for inhibition and delivery of design life.[41] An off-shore oil pipeline had operated under stratified flow with a corrosion risk to the lower 70% wetted area due to dissolved carbon dioxide and hydrogen sulfide. The line condition after 3½ years of operation was unknown and the requirement was to identify the most cost effective means of achieving a maximum required life. Possible options were to inhibit and to clean by pigging either immediately or after 4 years' time as originally scheduled. The most effective option was determined using propriety decision analysis software developed for business risk modeling.[42]

The line had operated for 2.25 years with no corrosion inhibition (an industry procedure adopted for low water cut systems) followed by 1.25 years with corrosion inhibitor injection, although not always meeting target injection rates. The corrosion damage was likely to be a combination of general corrosion and pitting corrosion, with predicted corrosion rates between 0.05 mm year^{-1} due to general corrosion and 1 mm year^{-1} due to pitting corrosion with an average rate of 0.6 mm year^{-1}. Uncertainty was described for general and pitting corrosion rates by assuming a truncated normal and lognormal distribution curves respectively as given in DnV G101.[22] During inhibition the general corrosion rates would probably have decreased; however, any pits that formed prior to inhibition may not have been fully protected and could have continued to propagate. Minimum, peak (mode), and maximum values were estimated.

Limited UT thickness inspection data from topside pipework at three well heads provided a statistical distribution of corrosion rates that were compared to predicted values using industry corrosion models and a likely distribution of loss of metal obtained:

General corrosion rates	Pitting corrosion rates
Low = 0.15 mm year^{-1}	Low = 0.1 mm year^{-1}
Medium = 0.35 mm year^{-1}	Medium = 0.3 mm year^{-1}
High = 0.55 mm year^{-1}	High = 0.9 mm year^{-1}

Uncertainty in the corrosion inhibition efficiency was described using a triangular distribution as the variables had a limited range and a reasonably good best estimate was shown with some variance on either side as shown in Table 9:

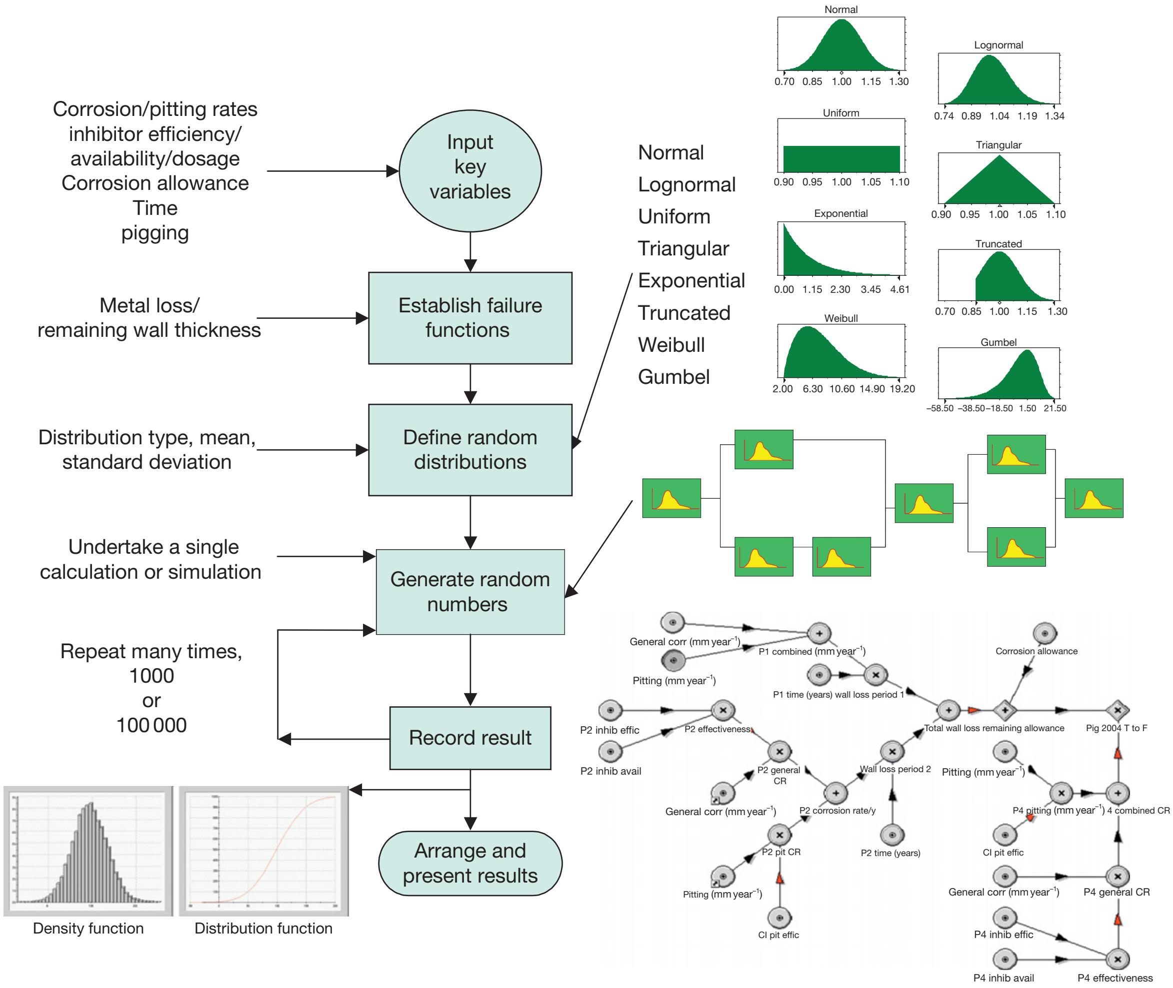

Figure 9 Probabilistic method as used in a quantitative corrosion risk analysis.

Table 9 Likely inhibitor performance

Inhibitor efficiency	*Inhibitor availability*	*Efficiency in pits*
Minimum = 0.7 Peak = 0.8 Maximum = 0.9	Minimum = 0.5 Peak = 0.7 Maximum = 0.95	Minimum = 0.1 Peak = 0.5 Maximum = 0.9

Table 10 Improved inhibition program

Improved efficiency	*Improved availability*
Minimum = 0.89 Peak = 0.9 Maximum = 0.95	Minimum = 0.94 Peak = 0.95 Maximum = 0.98

The following scenarios for the future lifetime of the pipeline with/without pigging and improved inhibition were evaluated:

Scenario 1: Continued operations with no pigging and current inhibitor regime – rate of degradation would continue as previous operational conditions.

Scenario 2: No pigging but implementation of an improved corrosion inhibitor program – Inhibitor efficiency and availability could be increased but inhibitor ingress into pits is retarded with little effect on protection of pits. The uncertainty in the improved inhibitor efficiency and availability are described in Table 10.

Scenario 3: Pigging in 4 years' time followed by an improved inhibition program – pigging reduces corrosion and corrosion inhibitor is more effective on a 'clean' surface, estimated pitting corrosion efficiency following pigging could reduce corrosion by 90%. This improved inhibitor efficiency in pits was described by a triangular distribution with the minimum = 0.87, peak = 0.90 and maximum = 0.93.

Scenario 4: Pigging now followed by an improved inhibition program.

The various options were determined using a Monte Carlo simulation and an appropriate network that describes the system with the probable range of outcomes expressed as a probability versus time plot (or *S*-curve), Figure 10. The integrity limit was assumed to be loss of corrosion allowance of 6 mm and a minimum allowable wall thickness (MAWT) based on the operational pressure.

The conclusion was that pigging should be carried out at the earliest opportunity to ensure a low level of risk over the next few years. Corrosion inhibition can be effective against pitting but some may perform better than others at inhibiting existing corrosion pits and a comparison of different inhibitors under simulated production conditions could be carried out to select the most appropriate inhibitor. This in combination with pigging should ensure a long operational life.

The above case study illustrates the main points of a quantified approach, that is, that the greater part of the value is realized in risk management by identification and implementation of the most appropriate risk treatment strategies. An expert opinion from a corrosion engineer would be that pigging is recommended when inhibition is employed to mitigate the effects of sludge/pitting corrosion but the graphs provide the justification for the recommendation and aid management decision-making processes.

The above provides a corrosion mitigation strategy but has to be followed up by development of tactics such as confirmation of the pipeline condition by in-line inspection, magnetic flux leakage detection for wall thickness and estimation of pitting, and tests to assess the effectiveness of inhibitor dosage to control pitting corrosion. A cost benefit analysis, using net present value (NPV) and a discount factor of 5%, of pigging and inhibition versus continuing to operate with the original regime indicated the financial incentive. A failure would be likely to cost $25 million, an improved inhibitor program $60k per year and regular (offshore) pigging $100k per year but these combined are ~21% that of the 'do nothing'/retain the current practice.

The statistical modeling/probabilistic method was extended using commercially available software (@Risk)[43] in a second case study of a sub-sea pipeline network but using an API 570 pipework data trending approach that had been described in a previous publication.[44] The aim was development of a written scheme of examination which provides an auditable trail for each pipeline that clearly identifies corrosion threats and mitigation measures. Remaining life is shown as an inverse *S*-curve that then forms the basis of an annual integrity approach based on available inspection and monitoring data that then defines a technical assessment of the asset condition.

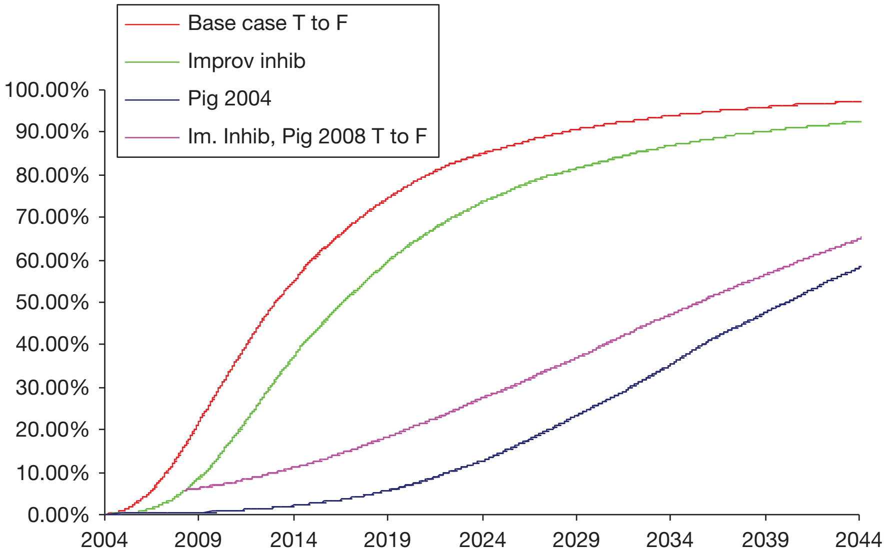

Figure 10 Probability of failure – loss of 6 mm corrosion allowance.

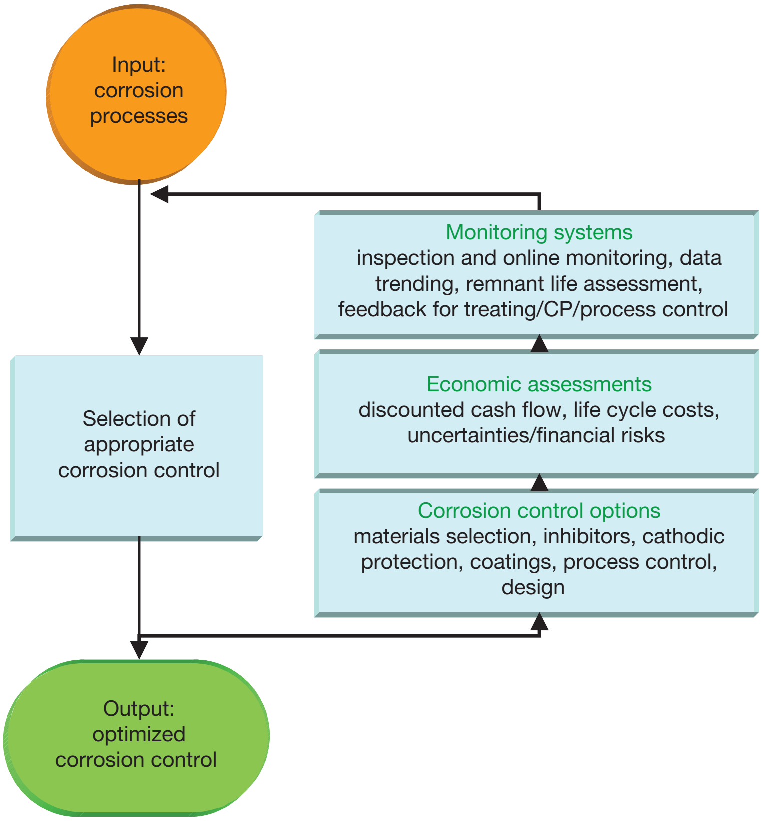

Figure 11 Basic corrosion risk mitigation steps.

4.30.3.4 Corrosion Mitigation Requirements

Identification, analysis, and evaluation of corrosion risks form the first steps in the corrosion management process. The next major step, as illustrated in Figure 11, is to provide cost effective solutions to mitigate corrosion risks by the selection of appropriate corrosion mitigation options.

The major tactics used to mitigate the effects of corrosion are embodied in many international/national standards, industry guidance documents, and in-house standards/procedures. These tactics are described in detail in the relevant chapters in this book but can be simplified into the following basic list:

1. *Materials selection* – metallic materials: carbon steels/low alloy steel (usual to include a corrosion allowance during design), CRAs (stainless steel, nickel alloys, titanium), nonmetallic materials (polymers, glass reinforced plastic (GRP), elastomers, ceramics).
2. *Chemical treatments* – typically inhibitors, biocides and scale control chemicals but packages also include surfactants, antifoaming chemicals. Inhibitors used in boiler and cooling waters, oil/gas production systems and in special concrete designs. Biocides are employed in cooling water systems and hydrotest fluids, water injection/waters systems, whilst scale control chemicals are used in cooling systems, boilers and oil/gas production and process plants.
3. *Use of coatings* – metallic, nonmetallic and organic/paints, used in external and internal environments, major factors are cost, availability, ease of surface preparation, application and life expectancy, important to ensure appropriate specifications, field application and inspection is carried out.
4. *Cathodic and anodic protection* – electrochemical methods of corrosion control. CP can be applied to immersed and buried structures, jetties, pipelines, tanks and concrete. CP is also used inside water containing vessels, tanks and the water boxes of heat exchangers. A low level of protection (cathodic prevention) is used in some concrete structure bridge designs that involve high-strength stressed steel. Anodic protection uses potentiostatic control of the internals of process equipment to ensure that electrochemical passivity is maintained.

5. *Process and environmental control* – modify moisture/humidity levels, lower oxygen concentrations. Change pH, throughput, decrease flow rate and/or heat transfer rate.
6. *Design* – use of codes/standards. At concept/front end engineering stage assess corrosion hazards and risks, evaluate life cycle costs. During engineering design phase use agreed codes and standards to produce specifications and drawings. Introduce QA/QC and inspection/testing procedures into specifications. During the detailing phase assess factors associated with stress, shape, compatibility, and surface condition, for example, eliminate stress raisers, crevices, and consider increased wall thickness on some bends. Use reviews/audits of concept, engineering, and detailing designs.
7. *Inspection and monitoring* – trending of deterioration rates, chemical dosages and changes in process chemistries

The first six options above are corrosion control methods and are used either singly or in combination, the choice depending on the specific application and the corrosivity of local environments. Many of these options are now covered by ISO/EN/NACE standards that are informative and contain guidance and recommendations for suitably trained, experienced, responsible personnel. However, such standards are not specifications or prescriptive and should not be used for certification purposes.

Key issues are reliability[45] and elimination of corrosion risks during the detailed design stage of the engineering design.[46] Design teams should be aware of likely damage as described in, for example, the compilation of photographs of corrosion damage to plant structures for oil/gas production[47] and the required mitigation procedures/audits.[48] The choice of the corrosion control method selected is highly dependent on materials cost, the discount factor/interest rate and life-cycle costs as described in the chapter on corrosion economics in this book and elsewhere.[49] However, as Turner noted in his life time observations on process engineers[50] "a fact of life is that the senior management is to fix the budget for a project as high as it could be to still provide a profit." The associated economic risk for a project is essentially the uncertainty that may lead to consequential/indirect costs of failures and shutdown/unavailability and the risk management aspect is illustrated in decision tree analysis of expected values for carbon steel and CRA pipeline[51] and probabilistic studies

Consideration has also to be taken of the need to monitor both equipment condition and changes in plant process fluids. Corrosion inspection and monitoring provide data on materials performance and the effectiveness of chemical treatments, such as corrosion inhibition, that form the basis of corrosion mitigation strategies in some industries. To be effective, any field data must be collected, analyzed, trended, and correlated with other relevant parameters in order to provide information for management to make appropriate decisions. Inadequate or poor field data means lack of information and may lead to inappropriate actions.

Corrosion inspection and monitoring are undertaken with one of two purposes:

1. To determine the condition of equipment and any consequent requirements for repair, and changes in wall thickness and/or rates of localized corrosion or cracking that have implications for future retirement that are prime concerns of asset integrity and maintenance teams.
2. To monitor changes in fluid corrosivity due to damaging excursions in environmental composition and/or to control chemical treatments, such as corrosion inhibitor/biocide dosage/oxygen scavenger injection that are prime concerns of operating teams that typically use probes and techniques that provide continuous rapid responses to changes in corrosion rate.

Inspection and monitoring technologies and techniques are described in a separate chapter in this book. In most cases use of inspection techniques (ultrasonics, gamma radiography, thermography, dye penetrant, magnetic particle and visual inspection) is a specialist area requiring employment of skilled technicians or appointment of contractors, particularly for applications such as intelligent pigging of pipelines (magnetic induction, ultrasonics) and downhole/wireline inspections (callipers, ultrasonics).

On-site inspection methods, traditionally based on handheld devices such as ultrasonic testing (UT) equipment, were primarily used for postfabrication tests. The advent of digital techniques has improved the sensitivity, ease of data collection, and data handling capabilities which allows for improved display, data storage and trending. For example, computed/'Filmless' Radiography systems can now collect and analyze all radiographic data, completely replacing conventional films and aiding storage, and retrieval needs. Some inspection techniques have now evolved into permanently installed surveillance tools such as UT mats,[52] piezoelectric sensors embedded in electronic circuit ribbon[53] and alternative transducers such as the GE cMUT cell[54] a Si flat-panel capacitive ultrasonic micromachined transducer (cmut).

The relatively clear distinction, both technically and managerially, between the traditional fixed-time inspections and on-line surveillance/monitoring is therefore now more diffuse.

Corrosion monitoring techniques range from simple coupons, electrical resistance (ER) probes, electrochemical measurements in aqueous fluids, hydrogen permeation for sour systems, to more specialist methods such as the field signature method (FSM) and sand probes in oil/gas production. In some oil field systems, sand production/erosion probes may also be employed to identify specific problems.

In many flammable and hazardous areas, such as oil/gas production systems and chemical plant, the risk of failure/seizure of the probe assembly during insertion and retrieval has led to the requirement of a double block system. There is therefore an increasing emphasis on nonintrusive monitoring methods that can be operated from remote locations. These include spool pieces for ER and electrochemical measurements, externally attached ultrasonic devices mentioned above and FSM which uses a spool piece to assess changes in uniform corrosion damage, pitting, and erosion in lines.

The sensitivity and response from monitoring systems is crucial, particularly for high risk systems where, for example, a high inhibitor availability and efficiency is required and Figure 12 illustrates the relative corrosion rates and the response times from various probes based on linear polarization resistance measurements (LPRM), traditional ER, Hall-effect monitors and FSM.

Field data held in personal PCs is not readily accessible by the rest of an organization, neither is it practical/effective to manage corrosion data systems from spread sheets. PC-based systems are increasingly employed, with either their own internal database or linked to the main asset database, but with the information readily available to other team members through an intranet link (transparent management approach). Input into electronic systems can be directly from hard wired monitoring instrumentation, from portable instrumentation/hand-held data loggers, and via keyboard entry as indicated in Figure 13. Data required for process control is usually retained in distributed control system (DCS) and supervisory control and data acquisition (SCADA) systems for a limited time period and therefore those data required as part of the corrosion management processing should be downloaded and retained in a separate database for correlation/trending.

Location of inspection/corrosion monitoring points need to be chosen carefully to ensure that they provide appropriate data for the specific application such as areas of high turbulence intensity, particularly where slugging-type flow or impingement of second phases occurs, or in areas of low flow or stagnation (dead legs) such as in the bottom of vessels and the 6 o'clock position in pipelines, in order to assess the aqueous phase/water dropout. Local variations of flow and temperature within processing equipment and pipework may have to be considered. In some cases, the highest/lowest temperature points that give rise to evaporation/condensation/concentration effects may be crucial. Such an assessment is typical of any corrosion risk evaluation where local variations can be significant.

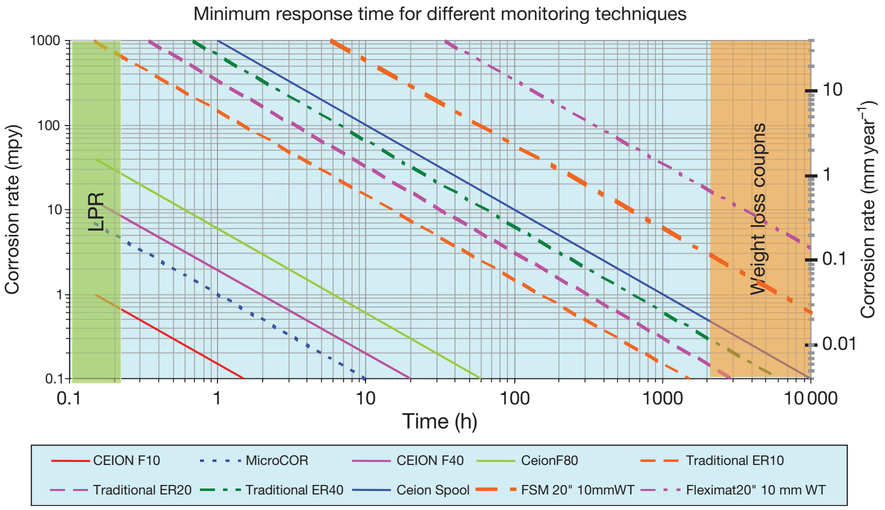

Figure 12 Comparison of responses from monitoring techniques. Courtesy of D.G. John, CAPCIS Ltd.

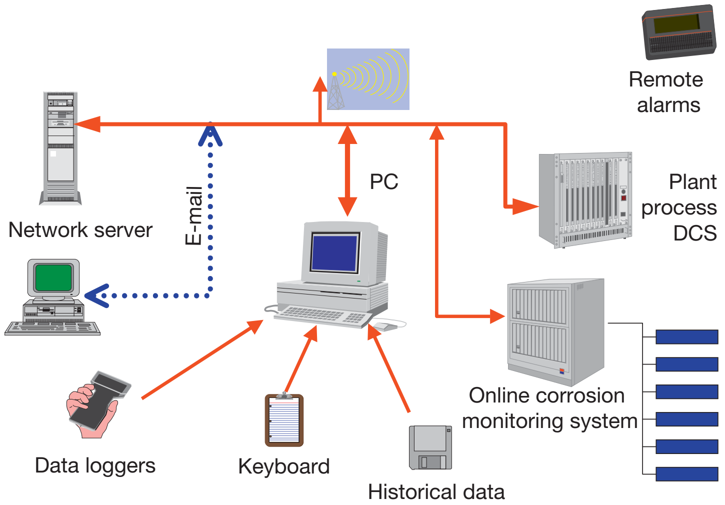

Figure 13 Inputs into a corrosion data system. Reproduced from John, D. G.; Attwood, P.; Rothwell, A. N. In *Corrosion'99*; NACE International: Houston, TX, 1999; Paper no. 249.[55]

The functions and roles of inspection and monitoring teams must be clearly defined and individual responsibilities for managing the systems, collecting and inputting field data, interpreting rate/correlating information and producing reports should be well understood. An overall management purpose is to devise strategies, tactics and systems that ensure that monitoring and inspection information contribute to safe and reliable operation irrespective of who obtains the field data. Those organizations that operate transparent data management systems are more likely to sustain the effectiveness of activities such as RBI, chemical treating, CP, the maintenance of coating systems, etc. that are so essential to successful asset management.

4.30.4 Corrosion Management Systems

4.30.4.1 Framework for Corrosion Management Systems

4.30.4.1.1 The corrosion risk mitigation system

Previous subsections outlined typical tools employed in corrosion risk assessment, mitigation and field monitoring steps but these must be placed in an overall context involving teams, such as the planning and implementation team and the team for decision-making and taking corrective action steps. An overview of a typical corrosion risk mitigation approach is illustrated in Figure 14, including feedback for control and the feed forward of information.

The inputs are corrosion concerns, life expectancy, life-cycle costs, project viability and SHE issues. The output is effective corrosion mitigation that is based on six distinct processing steps, including decision-making and actions:

1. Identification of individual corrosion team members, leaders/managers, and owners responsible for various procedures/processes/parts of the system.
2. Carrying out of the corrosion risk analysis.
3. Evaluation of the corrosion mitigation options.
4. Planning and implementation of the risk treatment process.
5. Development and maintenance of the required databases.
6. Regular use of informed decisions to instigate corrective actions.

Corrosion management requires that corrective actions be carried out as an outcome from the decision-making step. A structured approach with processes and procedures in place does not necessarily guarantee success without the key informed decision-making and action step. Team members must also undertake feedback from reviews, data monitoring, updating plans, and assessing secondary risks throughout the different project stages. Senior management/corrosion teams must allocate ownership of written corrosion risk assessment and mitigation procedures, planning and implementation processes and the decision-making step. Other inputs, for example, include the development and application of performance reviews and KPIs, and ensuring that management of change procedures

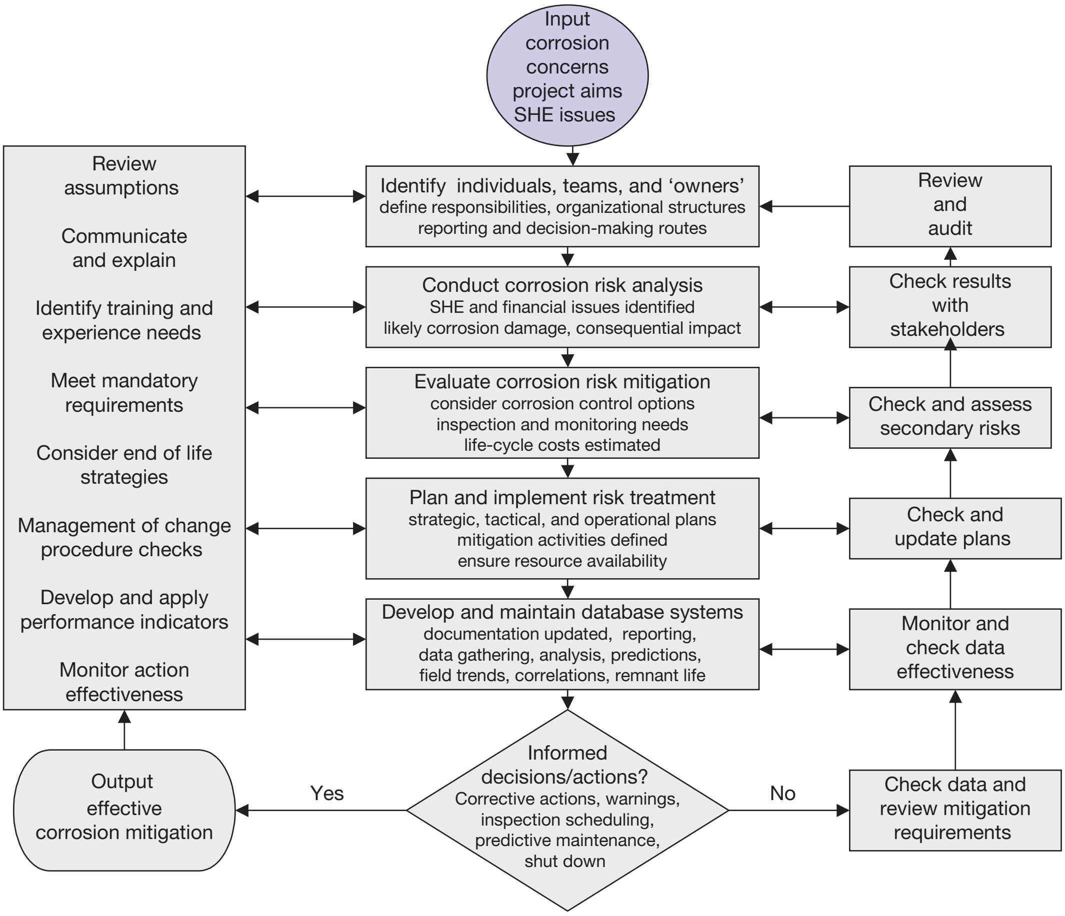

Figure 14 Outline of a corrosion risk mitigation system.

and monitoring of action effectiveness are in place. Some of these, such as KPIs, are also management control methods as will be described below in connection with Figure 15.

4.30.4.1.2 Corrosion management systems

Only in the past 10 years have formal corrosion management systems received attention in the literature, in contrast to voluminous publications on corrosion risk mitigation tactics. Formal systems for integrity management, including the use of competent persons, have been employed for over 50 years in industries where catastrophic failure prevention is crucial and SHE issues affect an organization's image. From a financial perspective, the prevention of engineering failures that affect up-time, throughput and process efficiency, and ensuring that corrosion risk mitigation in new projects and operations is cost effective, requires a responsive corrosion management system that integrates seamlessly into an organization's design and asset management systems. A corrosion management system should have many of the steps contained within a corrosion risk mitigation system but must also have feedback, reviews/audits and performance indicators to ensure that it operates effectively and is compatible with other management systems within the organization.

The original basis for the approach given in Figure 15 was the UK HSE *Successful Health and Safety Management* model.[10] The input and feedback loops were added by the author during the mid 1990s for industry-based corrosion training courses and was first reported as a generic corrosion management model in 1998.[56] It was developed further in 1999[4,8] in connection with continuing concerns by the UK HSE on hydrocarbon emissions from UK North Sea offshore processing facilities. A primary aim was to develop a template based on the UK regularity authority's

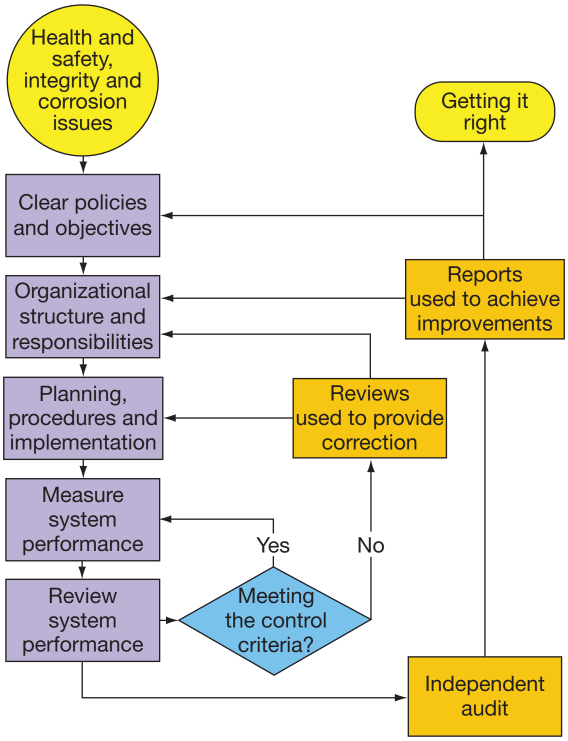

Figure 15 Basic management steps and feedback loops needed for control.[4,8]

approach to safety management and adoption of a common assessment of the corrosion management systems already in place.

The concern over hydrocarbon releases but also external corrosion damage of structures continued in *Guidance for Corrosion Management in Oil and Gas Production and Processing* published in 2008[48] and was first outlined in a workshop[57] in Aberdeen. The guidance focuses on the impact of internal and external corrosion, on integrity issues in existing facilities and is complemented by a *Corrosion Threats Handbook*,[47] the information presented is also instructive to designers of new facilities. The main text describes what would be appropriate for an oil/gas processing corrosion management system. The management system flow sheet differs slightly from Figure 15 in that the corrosion risk assessment/planning process and the implementation/analysis process are separated. Information on tasks and details and photographs of damage inspection are presented. Annex A provides *Guidance to Normative Requirements and Examples of Good Practice*, Annex B outlines the *Top Corrosion Threats and Corrosion Mitigation Methods* and Annex C provides a useful eight-page *Checklist for Assessment of Corrosion Management*. It is significant that this document considers that the corrosion management system requirements outlined should be considered normative for UK operators.

An illustration of the use of the corrosion management system to address external corrosion/coating issues[58] was presented in the Aberdeen workshop[57] where a risk-based assessment method was developed to enable work prioritization on structures, piping, handrails, walkways and gratings. Coatings condition/inspection was recorded in databases with the performance monitored on a visible KPI reporting system based on the ISO paint standard reference scale for coating breakdown.[59] Re5 and Re7, equating to 8% and more than 35% coating breakdown respectively, were judged to be the intervention levels for piping and structures, respectively, for the study. This then formed the basis for planning the work scope which included the ability to determine a cost effective long-term painting strategy allowing for scenario analysis and cost effective management. The importance of external corrosion mitigation/integrity of walkways from the regulator's viewpoint can be seen from their external corrosion project[60] that aims to reduce risks by a combination of improvements to both the physical condition of installations and the management systems in place.

A more general approach for corrosion management systems in a range of applications and project stages but based on the risk management approach described previously[31] as shown in Figure 16. Major factors for any corrosion management system are a series of logical steps and an ability to review and audit those steps. The flow sheet in Figure 16 indicates typical processing steps required in a system that incorporates both a risk-based mitigation process and control of the management process. The inputs are corrosion concerns in the context of the project and SHE issues, etc. The main processing steps are risk-based and auditable with effective corrosion mitigation and continuous improvement as the outputs of the management system.

Figure 16 should be read in conjunction with the mitigation detail provided previously in Figure 14 and the outline of the system review and audit shown in Figure 15. The inclusion of the concept of continuous improvement is a quality management system criterion output, as discussed previously, whilst the crucial step in any management process must be informed decision-making, based on reliable data. Procedures and protocols form the basis of a management system but without responsible and informed decision making the overall process will fail. Any management

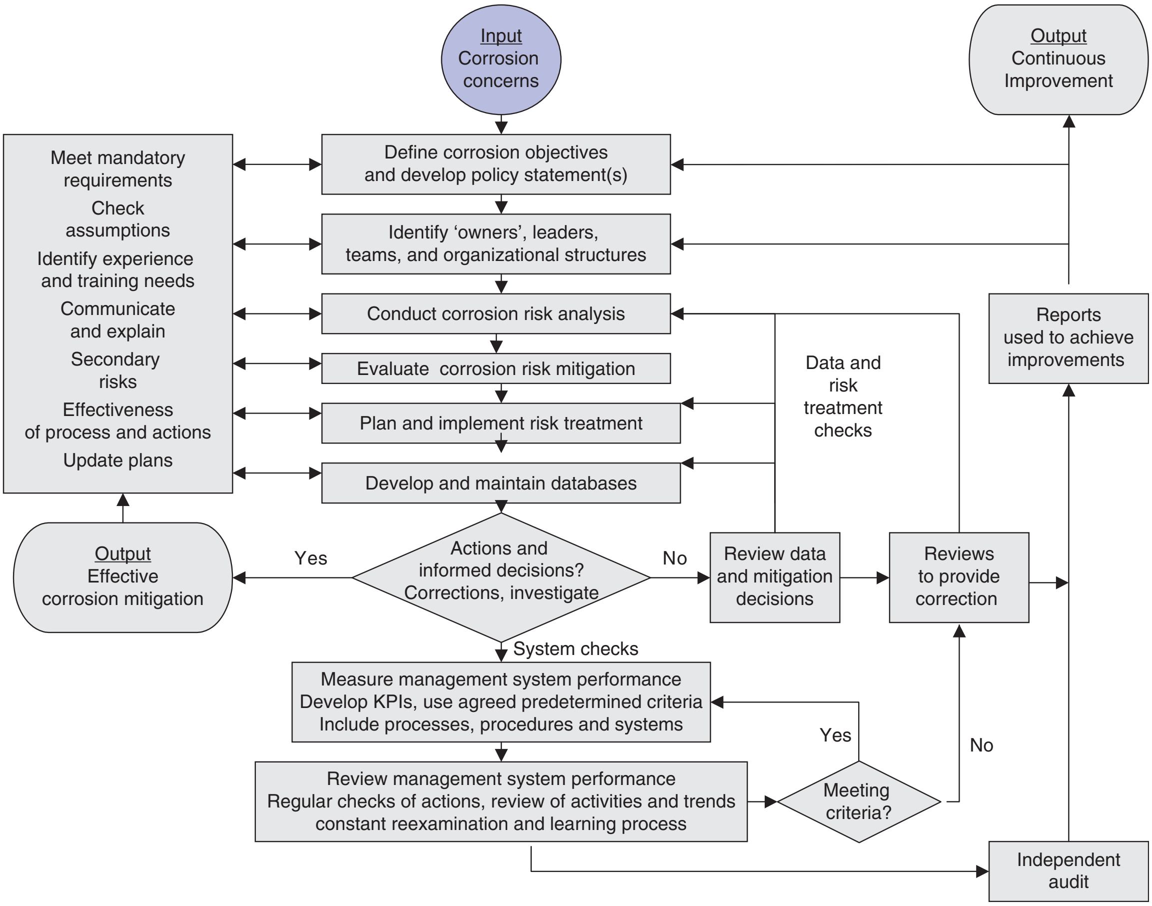

Figure 16 Requirements of a corrosion management system.

system has also to be regularly reviewed to ensure that the various steps continue to meet predetermined criteria as addressed by the development and use of performance standards such as KPIs.

In practice, many corrosion management systems will combine two or more steps/tasks/actions in some processing steps but the overriding requirement is to ensure that the different tasks and associated overall management actions are completed. In many ways Figures 15 and 16 provide a template or idealized corrosion management system, without attempting to prescribe exact arrangements within established organizational systems. For example, a basic documentation and data control system will be needed at the start of a project but will not appear in its fully operational state until later. Details of the key steps for both mitigation and management are given below:

1. *Aims/objectives/policies.* An initial step in developing a corrosion management system is to define the aims and objectives of the corrosion input to a project. These then form the basis of the corrosion policy, in principle, a permanent directive with authority from senior site management. The policy specifies overall/longer term objectives such as lowest life cycle costs during design, no leaks or emissions during the operational phase or with life enhancement meeting the required life, etc. The policy may incorporate elements of an organization's safety or environmental policy or even simple day-to-day guidance, such as that general corrosion rates should be less than 10 mpy. Guidance on the series of steps was outlined in the corrosion policy definition given in the chapter introduction. This includes establishment of organizational structures with defined responsibilities, reporting routes, practices, procedures, processes, and resources. It also requires the demonstration of responsibility and accountability for corrosion performance, managing risks, decreasing costs, controlling compliance, and motivating personnel.

2. *Individuals/teams/organizations.* Identification of individuals and teams with ownership of corrosion management processes also helps to define roles, responsibilities and accountabilities of managers, staff and contracted bodies concerned with corrosion issues. Appointment of corrosion team members with appropriate skills, an experienced team leader and an asset/project manager would be typical with the team comprised of representatives from the design team, engineering, inspection, production/operations, coatings/chemistry/biological laboratories, specialist contractors/consultants and even vendors/suppliers. Project boundaries with related/associated activities such as asset integrity (inspection teams), maintenance (engineering department teams) and production (process engineering teams) must be defined. Technical competence of personnel is normally a given but for nonspecialists/managers appropriate training may be required. Communication routes should be clearly identified and cooperation between team members and other groups encouraged ensuring that corrosion implications for other areas of activity are understood. The use of transparent data bases/trend information is helpful and often crucial.
3. *Corrosion risk evaluations and assessment of mitigation options.* These are fundamental steps conducted throughout the project life as conditions and facility operational requirements/procedures change. At some stages, such as design or plant upgrades/life extension, these activities form the largest single part of any corrosion management process and can have the largest impact on life-cycle costs and reliability. Issues arising from consideration of secondary risks or failure of a specific corrosion mitigation procedure must also be addressed. The basis of the designs/decisions must be clearly documented with materials/process limitations highlighted in the corrosion/operating manual for each unit. This should link through to management-of-change documentation, etc. The development of corrosion risk mitigation procedures includes the development and the methodology for documentation the implementation of various corrosion risk assessments and corrosion mitigation measures.
4. *Corrosion risk treatment planning and implementation.* These are vital to ensure that strategic, tactical, and operational/day-to-day activities designed to mitigate corrosion are employed effectively. Strategic activities address longer term issues such as best practices to ensure optimal life-cycle costs, SHE/mandatory requirements, corporate corrosion practice/integrity requirements and business concerns including the development of condition-based maintenance/equipment reliability/uptime needs. Such issues should have been considered as part of corrosion risk/mitigation analyses with the outcome requirements specified to provide for detailed plans to be developed. Planning involves the production of methods and/or procedures for all activities including specification/procurement of materials, testing, fabrication/welding, coatings/CP equipment applications, corrosion monitoring/inspection instrumentation, field data collection/analysis, required databases and their population, specification of reporting by appropriate routes and development of corrective action procedures to be carried out when necessary. Corrosion management plans should be formally recorded in the system documentation as part of a facility design and construction record, including consideration of facility start-up, operating, emergency/shutdown procedures where conditions impact on corrosion mitigation. Planning also includes assessment/development of chemical treating, inspection, and maintenance procedures. In many cases, these in-house company standards/protocols are typically based on international standards such as ISO, NACE, API, DnV, etc.
5. *Database development and maintenance.* Suitable databases for storage of system documentation, facility design/as-constructed diagrams, commissioning information and field data during operation/inspection/maintenance is a given. Specification, development, and maintenance of databases must be carried out in conjunction with stakeholders who will operate the system. It is not recommended that a design contractor/central authority specifies the system without adequate consultation. Consideration must be given to how previous experience/design/construction data is transferred through to the operational phase database. Examples of what may be required include: changes from the basis of design, testing requirements, modifications, that is, how will the incorporation of likely changes noted as part of the basis of design be built into the operating and maintenance/inspection plans? Also postfabrication inspection data provides the initial field data point for trending as in RBI and should be linked with specific locations on P&I/line/isometric diagrams. The means by which field data such as

visual inspections/coating surveys, hand-held/permanently wired instrumentation, DCS/SCADA downloads is to be collected, is analyzed and used for trending/correlations must be agreed and specified.

6. *Informed decisions and actions.* These are key processes; many management systems fail because of a lack of a clear decision-making step even though adequate protocols and procedures are in place. Corrective actions are an outcome from the decision-making step and these include investigative studies, the issuing and following-up of warnings or even instigating shutdown actions when required. Operational/day-to-day actions include rescheduling of inspections, change of chemical treating and predictive maintenance work that involve other teams. Any recommendations made must either be followed up or rejected in a positive manner due to other factors but not by default.
7. *Performance measurement of the management system.* Regular checks on the operating system should be conducted against agreed-upon predetermined criteria – the performance standards or KPIs. Responsibility for overseeing this process should lie with suitably competent individuals who are, ideally, appropriately free of production pressures. Performance measurement covers all aspects of the processes, procedures, and management systems using different levels of measurement at appropriate frequencies. Some may require immediate review/measurement on completion of a task. Measurement systems may be either proactive (to ensure agreed criteria are being met or identification of an inadequate system) or reactive (a postfailure activity to evaluate repair incidents or near misses and identify improvements).
8. *Regular reviews.* These are normal in-house checks of overall corrosion management system performance. They ensure that management procedures and processes are consistent with any changing business plans, changing production requirements and changing legislation. The aim is to improve performance and reduce incidents, improving conformance to schedules and improving procedures. It is the constant reexamination and incorporation of lessons learned that lead to continuous improvement of the corrosion management system.
9. *Periodic audits.* Management and monitoring system audits provide evidence that the corrosion management system is efficient, effective and reliable, and that processes and procedures are being implemented in accordance with agreed upon procedures. Regulations typically require owners to ensure that adequate arrangements are established for audit report-making.

Figure 16 was developed from a risk-based approach for corrosion mitigation that also provides a structured framework for control of the management system by use of reviews/audits/performance indicators. It is able to integrate statutory SHE goals and delivery of cost benefits to a project. In practice, contributory factors such as identification of training needs, management of change and end of life strategies will also have to be addressed where required. Delivery of a working system will depend on the use of performance indicators for both the management system, Figure 16, and the mitigation system, Figure 14.

4.30.4.2 Setting Performance Measures

Use of performance measurement/KPIs is a normal practice in most quality and safety systems. For example, the UK pressure system regulations require asset owners to record/inform the regulatory authorities of any delay to a scheduled inspection. The delay may be justified in order to either fit in with a scheduled maintenance shutdown or due to other valid operational reasons. However, a second, further delay beyond the next scheduled inspection is not permitted, the aim being to ensure that the plant is not operated in an unsafe condition; an illustrative proactive use of a KPI. A significant record of inspection delays is likely to be symptomatic of significant management problems.

Typical objectives of performance measurement/KPIs for corrosion management are:

1. Ensure that corporate corrosion objectives are met with respect to SHE and financial issues, usually by reactive/lagging indicators.
2. Ensure that strategic/tactical/operational strategies are implemented effectively by checking the success of corrosion management activities, often by checking on the success of plans by proactive/leading indicators.

These might be translated into specific indicators for various project stages and organizational levels as follows:

1. *Corporate level*
   - Provide written policy statements.
2. *Strategic level* (design/proponent/asset manager/owner)
   - Ensure that corporate/SHE/local legislative/long term objectives are addressed.

  - Ensure that corrosion rates provide the agreed upon equipment life and that cost effective corrosion mitigation is employed.
  - Ensure that individuals have delegated responsibility/ownership of corrosion issues and identify who is accountable for various components of the corrosion mitigation program.
  - Ensure that corrosion risk assessments and sensitivity studies are conducted as a regular feature of project/design/inspection/operations/maintenance activities.
  - Ensure that decision makers are suitably trained/competent/responsible to action necessary changes/modifications/issue work instructions for the improvement of corrosion mitigation processes.
  - Ensure that various aspects of the program remain effective with stated time frames when they will be updated/reviewed/audited and that management-of-change procedures are in place.
  - Ensure that the performance indicators are acceptable/measurable/achievable/realistic.
3. *Tactical level* (design/proponent/asset manager/owner, plus supervisors from design, engineering, production, maintenance, inspection, corrosion).
   - Ensure that a corrosion team/team leader/team members are allocated/named as part of the design/construction/O & M/project teams.
   - Ensure agreed-upon codes/standards/in-house guidance/procedures/work practices are authorized/reviewed/audited at set intervals and placed in a central quality controlled documentation database.
   - Ensure that corrosion mitigation methods employed are appropriate/cost effective/suitably managed/monitored/subject to regular review/audit.
   - Ensure that annual review of corrosion/inspection/chemical treating/CP/coating systems are carried out.
   - Ensure that audit of corrosion/inspection/chemical treating/CP/coating systems are carried out every 2–5 years.
   - Carry out an internal audit of the corrosion management system (6 months after implementation and thereafter on an annual basis).
4. *Operational/corrosion team level* (Responsibilities reside with specific individuals depending on the size of the operation and organizational arrangements; these could include managers, supervisors, corrosion team members).
   - Specify and cost materials ($ per mm) as part of life-cycle studies including any testing required.
   - Ensure that cost effective corrosion mitigation is employed such that corrosion rates are consistent with the corrosion allowance/required integrity/agreed upon life of equipment.
   - Optimize chemical treatments.
   - Report any corrosion related failures identified during routine inspections or data acquisition.
   - Undertake urgent field activities within 24 h of the request.
   - Enter all planned field data into the appropriate database within 1 week of taking the measurements for low and medium risk items.
   - Collect corrosion monitoring data and download data to asset management database within 1 week of due date.
   - Issue a written report about out-of-compliance findings within an agreed-upon time period of taking measurements.
5. *Corrosion team leader*
   - Review records to assess conformance and report out of compliance when necessary.
   - Track specific procedures and processes to ensure compliance including competency of responsible individuals, departments, and organizations and correct implementation, reporting and reaction.
   - Check if appropriate investigations were undertaken in accordance with procedures.
   - Check if the investigations were effective and that necessary changes to procedures/processes are developed to prevent recurrence.
   - Have the changes implemented/incorporated into procedures/processes.
   - Review the corrosion related documentation.

Examples of measurement of corrosion management performance can be found in oil/gas production,[8,48] chemical treatment of systems,[61] coatings maintenance[58] and management of CP systems where much of the practical requirements are covered in the EN on CP and Cathodic Protection Measurements.[62] For example, following successful commissioning of a CP system and establishment of a steady state CP level, the following checks would be typical for the basis of development of KPIs and data review by an experienced CP specialist:

1. On a monthly basis check for satisfactory operation of transformer-rectifier and record output voltage and current.

2. On a six-monthly basis record polarized pipe-to-soil potentials at each test station, especially those located furthest from the CP drain point. Visually check all test facilities and transformer-rectifiers for serviceability and damage and carry out maintenance and repairs as necessary.
3. On a 12-monthly basis repeat the six-monthly tests and also test for possible stray current interference effects where other facilities are located close by.
4. At intervals of 5–8 years carry out a close interval potential survey (CIPS) and a direct current voltage gradient (DCVG) survey to assess changes in performance of both CP and coating in order to accurately determine the status of the CP on the entire length of the pipeline.

Recommendations/conclusions by the specialist should be acted upon without unreasonable delay to ensure the continued satisfactory CP of the pipeline. Many organizations fail to respond to reports submitted by their own teams and specialist contractors because of a lack of appropriate KPIs used to ensure that the required actions are carried out as scheduled and appropriate decisions are made when required.

4.30.4.3 Data Management Systems

Documentation, both paper-based and/or electronic, form part of any management or quality management system. The choice will depend on the size of the project/operation. In many facilities such as refineries, oil/gas production fields and chemical plants the complexity of the various plant items/infrastructure plus the various corrosive environments can make the recording, trending, and correlation of data a difficult task. A number of PC-based software systems are commercially available that focus on specific aspects such as the recording of inspection or CP data. There are many common features[53] amongst the various integrated asset management systems employed to manage corrosion/inspection/CP systems/chemical treating. To be fully effective for corrosion management they should not only link to the maintenance/production systems but also output control instructions for activities such as planning, work control, stock control, materials handling, project management, procurement, contracts and finance. The requirements include:

1. *An asset register* – which is user configurable, holds design information, line diagrams and as built drawings, etc., that is, usually an electronic system that accurately reflects the physical facilities. These are set up in a logical/hierarchical manner to identify individual equipment (Tags) that is, physical items that perform a function, such as vessels, units, etc., some of which may be interchangeable for maintenance, their components or segments for example, pipe work/the position/measurement locations. A typical asset register/facility list may include: plant code, area (plants, storage facilities and utilities), station (downhole, flowlines/manifolds, sub-sea facilities, gas compression systems and pipelines), position (vessel internals and equipment component) and line list (pipework database).
2. *A documentation system* that contains supplementary information and data on the above such as environmental conditions, pipe classification and constructional materials. These are usually held in separate listings on user-configurable records in a standardized format and include additional information and data such as that which has been scanned electronically from photographs, images and hand-drawn sketches, CAD drawings, and text files.
3. *Data collection input and interfaces* – these include keyboard entry, an ability to collect selected process data and download data from hand-held, portable or hard-wired instrumentation, plus the ability to operate on standard PCs/servers and especially have compatibility with other IT platforms.
4. *Data analysis capability* – ability to retrieve/trend data, cross correlate/determine equipment condition/process history/identify common corrosion circuits/predict future life. Data-trend displays, with alert/warning indicators, are needed to determine when deterioration is at a level necessary for corrective/maintenance action.
5. *Planning/work control* – ability to schedule activities and check on progress.
6. *Reporting* – identify safe/unsafe conditions (alert and alarm warnings), produce audit trails, generate recommendations and create action lists.
7. *Functionality enhancement* – capable of extension to encompass/interface with maintenance systems/materials procurement systems/contract/project control systems/finance systems/executive information systems.

Corrosion management and inspection management databases need a functionality that combines data storage from monitoring and inspection records, analysis of trends and predictions of remaining life, evaluation of corrosion circuits (process streams with similar corrosion from analysis of process stream changes) and generation of management reports for decision making. The ability to compare data from various sources to produce reports/conduct financial evaluations/just-in-time inhibitor deliveries, etc. is a key requirement of a corrosion management system. For example, although field data is a key input into the management of operational plant and facilities, the acquisition and disposition of field information does not necessarily mean that adequate knowledge of equipment/plant condition is available or that the performance of the asset/facility process is provided in a lucid or easily understood manner. The system should bring the corrosion language in line with that of asset managers/the boardroom.

Effective corrosion management requires, for example, that the inspection frequency and information must be combined with online data from corrosion monitoring, which is used to control chemical treatments, such as corrosion inhibitor/biocide dosage or oxygen scavenger injection, plus the retrieval of appropriate process data such as flow rates, temperatures, and fluid compositions from SCADA systems. This flexibility of software is typically found in an IT benchmark product such as *Amulet*[63] which is used in a wide range of industries ranging from water companies, supermarkets, waste disposal, mobile phone stations for maintenance/operational control of various activities; it has also been employed for the management of corrosion data from various offshore and onshore production facilities including refining/oil field treating chemicals/management of corrosion monitoring/inspection/CP. Inputs are from probes, laboratory analysis, third party/historical/archive databases, as described previously in **Figure 13** with outputs including alarms/anomalies, mitigation schedules, reports leading to key performance checks, actions for inspection/maintenance.

Typical reports to the corrosion team/decision-makers from a data management system would include: wall thickness calculations, remaining life analysis and prediction, inhibitor treatment and usage, corrosion coupon and retrieval reports, advice on type, location, frequency of corrosion monitoring, corrosion prediction, pipeline inspection, periodic status reporting, deviation reporting, traceable records of installation corrosion history, CP data-trending, CP on/off test reports, anomalies for CP test posts, corrosion damage/failure analysis, defects categorization, leakage and spillage reports, downhole log reports, and changes to operations/maintenance/inspection activities and scheduling. **Figure 17** illustrates the typical data flow and outputs that form the basic reporting to the corrosion management system/team.

The type of management questions asked of such systems[55] are about the:

1. Distribution of corrosion rate in various parts of the system <0.05 mm year^{-1} (<2 mpy), 0.05–0.25 mm year^{-1} (2–10 mpy), >0.25 mm year^{-1} (>10 mpy).
2. Present distribution of remaining life, Items requiring replacement in: <1.5 years, 1.5–3 years, 3–10 years, >10 years.
3. Cost of the current corrosion control program.
4. Costs of chemical treatment.
5. Costs of CP.
6. Repair/maintenance/replacement costs.
7. Downtime (lost production) costs.
8. Inspection/monitoring costs.
9. Business drivers/criteria which have been meet.
10. Average corrosion rates.
11. Allowable outage (offline) time.

Figure 18 shows data from oil field chemical treating that correlates chemical usage with production rates to provide financial information on the treating program. This illustrates the point that data management is not just providing trends of corrosion rate, metal loss, chemical use, etc. for reports but that useful management information is abstracted by suitable correlations/analysis to enable appropriate decisions to be made regarding operational, integrity and strategic/tactical issues. Further information on monitoring and data handling, including case studies can be found in *The Corrosion Monitoring Handbook.*[64]

The above section has highlighted how systems for the control of project documentation, including standards, guidance, specifications, design, construction, and operating/maintenance procedures and protocols typically form part of a quality assurance system and provide a key input to any corrosion management process. Equally important is the functionality of the data management system used to store field data that has then to be converted into information for the decision makers. Both form discernable parts of the corrosion management system, as do the organizational arrangements and reporting routes. All have to be subject to regular reviews and audits to ensure that they, together with the various project teams, deliver effective corrosion mitigation. Successful data management systems are those that are used on an everyday basis as a live system, often through a web based/transparency methodology, to actively control all aspects of the mitigation processes including costs and actions. Some are specified to indicate on a traffic light basis the corrosion conditions of

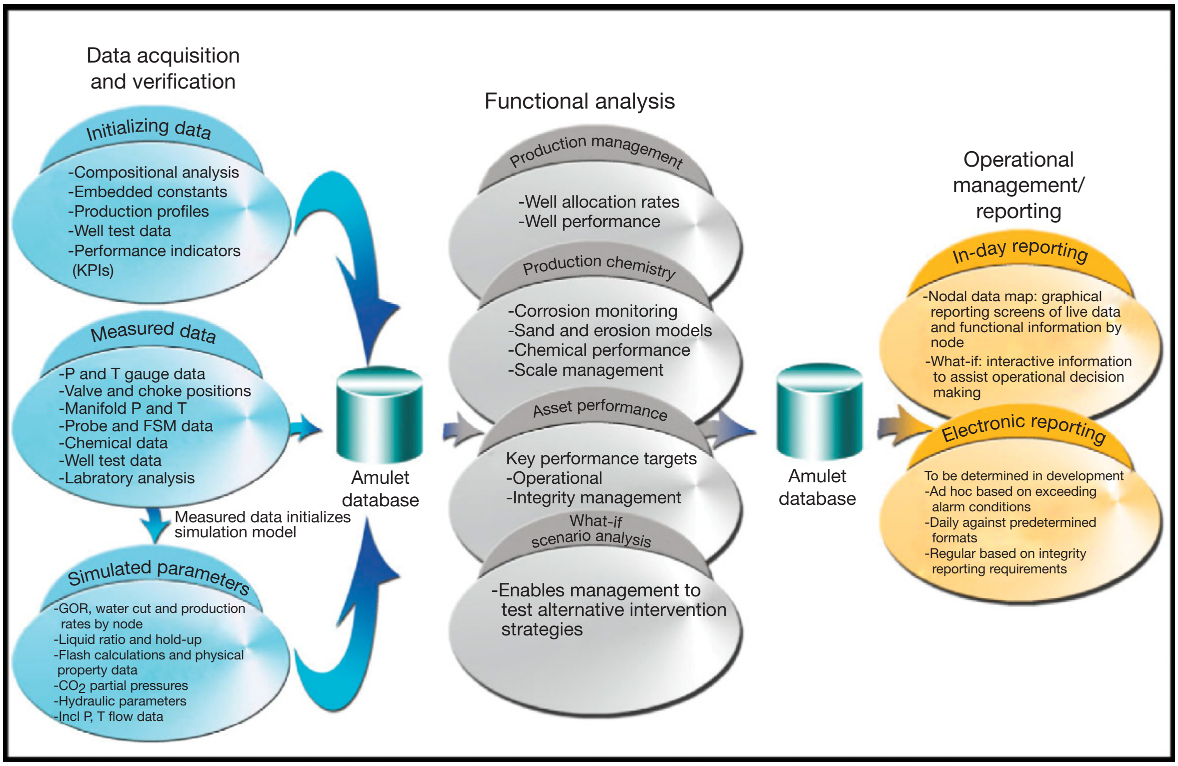

Figure 17 Schematic of data management. Courtesy of A. N. Rothwell. Reproduced from Amulet, C^3 Ltd., Dingwall Business Park, Dingwall, UK.

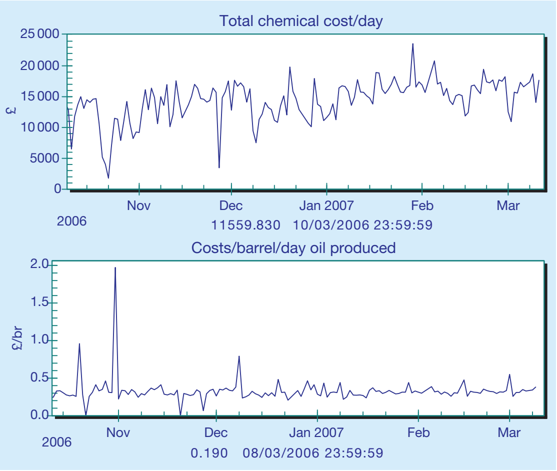

Figure 18 Correlation of cost of chemical treating with production. Courtesy of A. N. Rothwell. Reproduced from Amulet, C^3 Ltd., Dingwall Business Park, Dingwall, UK.

units throughout the asset. In practice, many systems provide regular reports but essentially prepare data for storage/long-term burial rather than playing a key part in the decision process.

4.30.5 Conclusions

There are many ways to organize and operate successful corrosion management systems, each of which is asset specific and dependent on factors such as design, the life-cycle stage, process conditions, operational history and organizational culture. Key issues from the project/asset manager perspective are corrosion risks that threaten structural integrity, economic viability and SHE performance. Most organizations rely on nonspecialist managers, designers and plant engineers to manage the facility corrosion specification, operational aspects and day-to-day activities required to mitigate corrosion whilst specialist corrosion/materials engineers are normally employed in an advisory capacity only. This is a pragmatic and appropriate use of a limited resource provided that corrosion issues do not become every employee's concern but no person's responsibility.

A primary aim should be to make corrosion risk management an integral part of both good management practice and the training/educational process within organizations. All risk management processes comprise a series of iterative steps that promote continuous improvement in decision-making. Effective corrosion management depends on the experience and judgment of corrosion team members/leaders to provide guidance to design, construction and asset managers but such teams may also have to learn new management skills to be more effective. Incidents, failures and poor equipment performance will occur if reliance is placed solely on a routine of following steps outlined in procedures, guidelines and standards. Individuals must be aware of competence limitations and recognize when to call on more experienced members of staff/third parties. Senior management support is also needed to define clear strategies and corrosion policies that are promoted by the adoption of workable corrosion management systems using correct technological tools operated by trained people who have the motivation and commitment with adequate supervision.

Management system failings and human errors pose as big a risk to corrosion mitigation as do physical and chemical hazards. Serious corrosion related incidents occasionally make the front page such as the 1988 Aloha Airlines loss of a cabin roof during flight due to adhesive failure, crevice corrosion and fatigue cracks,[65] the Humberside refinery fire[5] referred to previously and the recent Alaska pipeline leak due to a lack of cleaning and inspection by pigging.[66] These are the tip of an iceberg and, with hindsight, preventable, but they beg the question whether lessons are learned from the minor leakages, poor equipment performance and shorter-than-expected lives that are an everyday occurrence in industry at large.

Catastrophic incidents from other engineering sectors, particularly investigations of process plant failure, provide insights how established process/safety engineering methods could deliver continuous improvement of corrosion mitigation practice. For example, control of safety hazards to prevent incidents can be visualized as a series of barriers. Some are hard/physical, others are soft/procedures/systems, but each will have weaknesses. This 'Swiss cheese' hazard management model,[67] depicted in Figure 19, illustrates that as long as the holes in the

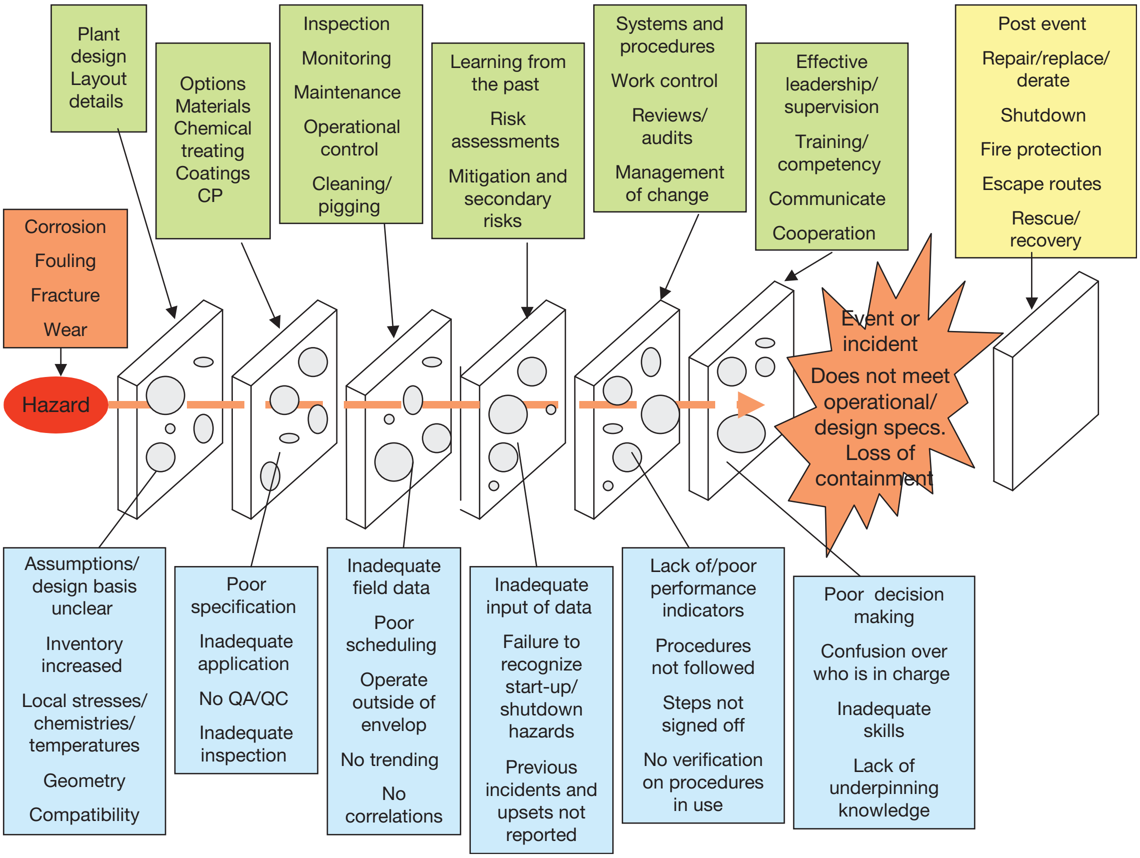

Figure 19 Example of a degradation hazard management concept.

various protective barriers/layers do not align then a hazard can be controlled but that a series of human errors/unmanaged circumstances can give rise to porosity in the hazard control barriers resulting in incidents and catastrophic accidents. This hazard management model was used recently to analyze the March 2005 Texas City refinery incident.[68] The study emphasized the extent to which hazard prevention depends on three layers of protection:

1. *Plant* – engineering hardware, control systems, and layouts to eliminate, control and mitigate potential hazards to people, and improve productivity.
2. *Processes* – management systems to identify, control and mitigate risks, and drive continuous operational improvement.
3. *People* – capability of our people in terms of leadership skills, relevant knowledge and experience, and the organizational culture they create in layers of protection, 'hard barriers' are more reliable than 'soft barriers,' but all rely on people.

A list of typical problem areas at the refinery included:

1. Incidents and upsets not reported.
2. Hierarchy of control not applied.
3. Previous start-up review not performed.
4. Procedural compliance not checked.
5. No interventions.
6. Inadequate KPIs.
7. Lack of underpinning knowledge.
8. Failure to follow procedures.
9. Confusion over who was in charge.
10. No verification on procedures in use.
11. Procedures not followed.
12. Steps not signed off.
13. Use of local practices.

Learning from the Texas City incident would be relevant to most corrosion related incidents where equipment fails to meet design/operational requirements due to deficiencies in the inputs from corrosion risk mitigation tools, systems and teams. As indicated in **Figure 19**, hazards to performance/structural integrity arise from a combination of one or more of the generic degradation processes, corrosion, fouling, fracture and wear. The hard barriers for mitigation of corrosion related hazards that include fit-for-purpose materials, coatings, chemical treatment, CP, etc. are more physical and robust than the soft barriers that include generic management systems for control of mitigation processes. The robustness of all barriers depends on effective functioning of individuals and teams who must respond to continuing changes. Holes in various barriers introduced by individual/team action or inaction are indicated in the lower boxes.

Corrosion technology is not new; corrosion mechanisms are understood and documentation/standards/knowledge on corrosion mitigation tactics are widely known and available. The difficult part is in translating this corrosion background information into reliable solutions for the real world. Important aspects are not only technical solutions but also involvement/acceptance of key personnel, particularly in organizations where management of change involves different ways of doing things, as demonstrated in a study of a long-term problem with hot potassium carbonate acid gas removal plants.[69] Organizational aspects were identified as critical and the *Six Sigma* methodology,[70,71] traditionally employed to solve problems in manufacturing and continuous process industries, was used as a tool. The principle is that improvements occur when people doing the job are involved, guided by an individual experienced in the implementation methodology. Mature organizations with workforces that are highly experienced and knowledgeable may be less adaptable to change as, for example, is sometimes found when RBI is proposed/introduced. In the above site corrosion study, a team approach encompassing integrity, process and process control engineers and chemists provides a broader input to define the problem, identify the likely root cause and then deliver the required change by enabling the management decision to release the funds necessary for improvement.

Delivery of services such as corrosion mitigation in an era of increasing demand, in more difficult environments, and often with squeezed budgets, requires development of strategic models that may well include input from both in-house and third-party specialists. What counts is the provision of improved quality and value rather than whether the service provider is in-house or a contractor. Asset-centered organizations based on multidisciplined teams tasked with improvement of the asset management processes of optimizing costs, risks and performance, are increasingly replacing traditional activity-centered organizations based on functions such as design/engineering, production/operations, maintenance and materials/purchasing with individual budgets. The new focus is on inputs with responsibility for investment/expenditure and outputs of performance/accountability. The asset manager and team have budget decision-making responsibility for resources and services. The client 'assets' provide funds for technology specialists, designers, information technology, human resources, SHE and finance, obtained from both in-house, central, shared sources and external providers. The challenge for an operating company/asset is to choose those services required to achieve defined objectives that realize longer term savings/benefits.

Such developments in asset management cannot be ignored in the delivery of corrosion management services and may even continue to drive the changes instigated in the 1990s by SHE issues. Corrosion management, defined previously in Section 4.30.1, is also part of asset management, which is in turn now defined[72] as "Systematic and coordinated activities and practices through which an organization optimally and sustainably manages its physical assets and their associated performance, risks and expenditures over their life cycles for the purpose of achieving its organizational plan." An organizational strategic plan, based on stakeholder aims/expectations and legal requirements, is translated into local asset business goals with intentions converted into actions as depicted in Figure 20.

Best practices and development of risk-based methods for management of physical assets formed the basis of MACRO, a multiindustry collaboration project, which was a UK government supported joint venture and a European 'Eureka' Project, EU1488.[73] The aim was to promote a change in approach that incorporates guidelines, education and decision-support tools (Asset Performance Tools (APTs))[74] that comprise a set of methods to quantify and optimize over 40 different types of asset management decisions in target areas such as asset life-cycle costing, inspection and condition monitoring, maintenance optimization, work grouping and shutdown strategy. An outline is provided in '*Risk-based Decision-making in Maintenance, Inspection, Spares and Asset Renewal*' by John Woodhouse.[75] This highlights some of the limitations of tactical/bottom-up/individual task tools such as FMECA, RBI, reliability centered maintenance (RCM), Six Sigma, and TQM that focus on one risk at a time, whereas the APT suite is designed to address multiple interacting risks and performance.

For example, APT-Inspection can help in deciding optimum asset inspection intervals as illustrated by Smith[76] who compared the total impact on items comprising a continuous chemical processing unit by optimizing inspection costs, outside limit risks and operational failure risks. FMECA was used to determine maintenance strategy and RBI showed most items had an optimal 4-year inspection/shutdown frequency, but some a 3-year and, a particular HCl stripper, a 2-year frequency. Changing some materials of construction for the stripper and pipework and also assessing a small column containing sacrificial iron packing by APT-Maintenance for loss of efficiency showed that an in-line spare column was a cost effective approach. Although there were some relatively small costs associated with the implementation,

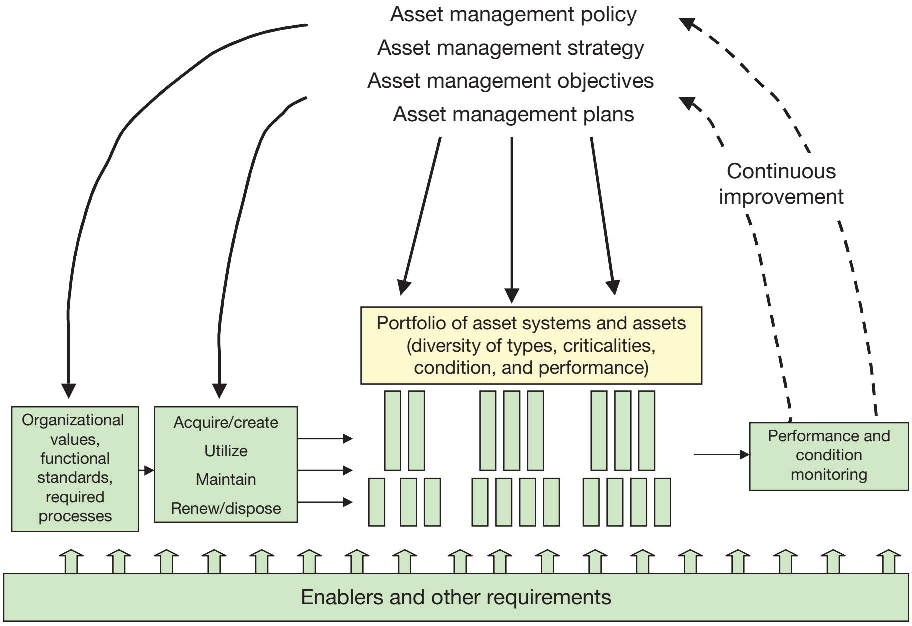

Figure 20 Asset Management System. Adapted from BS PAS 55.

the benefits amounted to a NPV of £2.5 million over 12 years.

The need to meet increasingly challenging SHE and financial demands will need a cultural shift in corrosion thinking within both industrial organizations and educational establishments that will require a wider appreciation of risk-based approaches and exposure to mainstream engineering concepts found within safety management, asset management, project/process management and maintenance management. A shift in the management model for corrosion services based on different approaches to the management of corrosion risk mitigation requires new standards to be set if the design/planning and operational delivery phases are to improve. This will include increased information sharing, system transparency and merging of services, including partnerships with specific contractors in order to benefit from shared experiences and additional/different resources. Cross fertilization of approaches, tools and procedures is occurring as in the cases of functionality analysis, criticality assessments and RBI in the petrochemical industries, total productive maintenance in the manufacturing sector, and reliability centered maintenance that is crucial in complex, down-time critical plant, and that differentiates failure response/prevention strategies into preventative, predictive, design-out and breakdown (operate-to-failure).

The previous sections of this chapter provide sufficient background information on tools, systems, and teams to address the inadequacies of many corrosion management processes but emphasis is still lacking on the regular auditing of corrosion management systems, the development of effective corrosion mitigation strategies and the control of operational, day to day activities. Successful organizations combine a strategic and tactical culture with daily operations conducted within a responsive, principles-based corrosion management system by competent personnel. As a result, they are enabled to practice cost-effective, predictive/condition based maintenance strategies that incorporate risk-based approaches to inspection. Weaker organizations tend towards an emphasis on tactical issues and less transparent management systems, resulting in a high reliance on expensive, breakdown/repair maintenance strategies.

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References

1. The Concise Oxford Dictionary, 5th ed.; Oxford University Press: Oxford, 1964; p 739.
2. Blything, K. W.; Parry, S. T. *Pipework Failures. A Review of Historical Incidents,* SRD 441, UKAEA, 1988.
3. *The Control of Major Accident Hazards Involving Dangerous Substances*; Seveso II Directive 96/82/EC, Council of the European Union, 1996.
4. Dawson, J. L.; Bruce, K.; John, D. G. Corrosion Risk Assessment and Safety Management for Offshore Processing Facilities, Offshore Technology Report 1999/064 UK Health and Safety Executive, 1999.
5. Public Report of the Fire and Explosion at the ConocoPhillips Humber Refinery on 16 April 2001, UK Health and Safety Executive. hse.gov.uk/comah/conocophillips.pdf.
6. API Document 570 Inspection, Repair, Alteration, and Rerating of In-service Piping Systems, American Petroleum Institute, 1998.
7. Minutes, NACE STG 34 2004 Committee Meeting. NACE International: Houston, TX, 2004.
8. Review of Corrosion Management for Offshore Oil and Gas Processing. Offshore Technology Report 2001/044, UK Health and Safety Executive, 2001. www.hse.gov.uk/research/otopdf/2001/oto01044.pdf.
9. *The Public Inquiry into the Piper Alpha Disaster*, Report by the Hon. Lord Cullen; HMSO: London, Nov. 1990. ISBN 0 10 113102.
10. *Successful Health and Safety Management*, UK HSE HS (G) 65 1991. ISBN 0-11-882055-9.
11. *The Offshore Installations (Safety Case) Regulations,* SI 1992/2885; The Stationery Office Limited: London, 1992. ISBN 011025869X.
12. *The Offshore Installations and Wells (Design and Construction, etc.) Regulations*, 1996 SI 1996/913; The Stationery Office Limited: London, 1996. ISBN 011054451X.
13. *The Pipelines Safety Regulations*, SI 1996/825; The Stationery Office Limited: London. ISBN 0110543734.
14. *The Control of Major Accident Hazard Regulations*, SI 1999/743; The Stationery Office Limited: London. ISBN 0 11 082192 0.
15. Pressure Systems Safety Regulations, SI 2000/128; The Stationery Office Limited: London. ISBN 0 11 085836 0.
16. Approved Code of Practice (ACOP) L122. *Safety of Pressure Systems and Guidance on the Pressure Systems Safety Regulations* 2000, UK Health and Safety Executive, 2000.
17. *The Corporate Manslaughter and Corporate Homicide Act, 2007*; Office of Public Sector Information, 2007.
18. *Risk Based Inspection – Development of Guidelines: General Document*; American Society of Mechanical Engineers, 1991; Vol. 1.
19. US Pipeline Safety Act. 1995.
20. API Recommended Practice RP580, Risk Based Inspection; American Petroleum Institute, 2000.
21. API Publication 581, Risk Based Inspection Resource Document; American Petroleum Institute, 2002.
22. DnV RP G101 Risk Based Inspection of Offshore Topsides Static Mechanical Equipment; DnV, 2002.
23. AS/NZS 4360:1999 Risk Management Standard; Australian and New Zealand Standards, 1999.

24. New Zealand Local Government Amendment Act, No 3, 1996.
25. *International Infrastructure Management Manual*; 2006 ed., nams.org.nz
26. Burdekin, F. M. *Interdiscipl. Sci. Rev.* **2000**, *25*, 141–151.
27. ISO 9001:2008 *Quality Management Systems – Requirements*; International Organisation for Standardisation, 2008.
28. ISO 9004:2000 *Quality Managements Systems – Guidelines for Quality Improvements*; International Organisation for Standardisation, 2000.
29. ISO 14001:2004 *Environmental Management Systems – Specification with Guidance for Use*; International Organisation for Standardisation, 2004.
30. Oakland, J. S. *Total Quality Management*; Butterworth-Heinemann: Oxford, 1995.
31. BS 6079–3: 2000 *Project Management – Part 3: Guide to the Management of Business Related Project Risk*; BSI Standards, 2000.
32. Milliams, D. In Corrosion Management, 12th International Corrosion Congress on Corrosion Control for Low Cost Reliability 19–24 September 1993; NACE International, 1993; Vol. 4, p 2420.
33. John, D. G.; Dawson, J. L.; Feng, A. C. In *Corrosion Risk Assessment as a Critical Part of Integrated Asset Integrity Management*, Proceedings of the Conference on Engineering Management for Utilities, Industry and Commerce, Oct 1997, London, ERA report 97-0847, 1997.
34. Edwards, J. D.; Sydberger, T.; Mork, K. J. *Corrosion'96*; NACE International, 1996; Paper no. 29.
35. Jones, J. S. *Application of Risk-Based Inspection Systems to the British Gas Rough Field*; Institute of Marine Engineering: London, 1996.
36. de Waard, C.; Lotz, U.; Milliams, D. *Corrosion* **1991**, *47*, 976.
37. de Waard, C.; Lotz, U. *In Corrosion '93*; NACE International, 1993; Paper no. 69.
38. de Waard, C.; Lotz, U.; Lugstad, A. *In Corrosion'95*; NACE International, 1995; Paper no. 128.
39. NORSOK M-506 Rev. 2, June 2005, *CO_2 Corrosion Rate Calculation Model*; Norwegian Technology Standards Institution; www.standard.no.petroleum.
40. McMahon, A. J.; Paisley, D. M. E. *Corrosion Prediction Modelling*, BP Sunbury Report, ESR.96.ER.066, November 1997.
41. Oliver, K. E.; John, D. G. *In Corrosion'07*; NACE International: Houston, 2007; Paper no. 124.
42. *iDECIDE software*; Decisive Tool, LLC. www.decisivetools.com
43. @Risk is the trade mark of Palisade Corporation, Ithica, NY. www.palisade.com
44. John, D. J.; Stokes, P.; McIntosh, P. *In Corrosion'03*; NACE International: Houston, 2003; Paper no. 163.
45. Edwards, J. D.; Sydberger, T.; Mork, K. J. *In Corrosion'96*; NACE International, 1996; Paper no. 29.
46. Pludek, V. R. *Design and Corrosion Control*; Wiley, 1976.
47. *Corrosion Threats Handbook – Upstream Oil & Gas Production*; Energy Institute & Oil and Gas UK: London, 2008.
48. *Guidance for Corrosion Management in Oil and Gas Production and Processing*; Energy Institute: London, May 2008.
49. Potthoff, W.; Fitzer, E.; Faessler, K.; Spaehn, H. A study of alternative cooling water circuits in a large petrochemical plant, Economics of Corrosion Control, Institution of Metallurgists Autumn Review Course, November 1974.
50. Turner, M. E. D. The Chemical Engineer, 9 August, 1990, Institution of Chemical Engineers: Rugby, UK.
51. Craig, B. D.; Thompson, R. S. *Corros. Mgmt.* **1995**, *7*, 14–17.
52. RIGHTRAX Systems Limited, Ashpoole House, Sandy Lane, Lowton, Warrington, WA3 1BG, UK.
53. SMART Layer@, Acellent Technologies Inc., Sunnyvale CA, USA.
54. GE cMUT cell, GE Global Research Center, Niskayuna, NY, USA.
55. John, D. G.; Attwood, P.; Rothwell, A. N. *In Corrosion'99*; NACE International: Houston, TX, 1999; Paper no. 249.
56. Brouwer, R. C. In 8th Middle East Corrosion Conference Bahrain; Bahrain, Society of Engineers & NACE International, 1998.
57. *Effective Corrosion Management*; UK Oil & Gas and Energy Institute Workshop, Aberdeen, 18 June 2008.
58. Paterson, S. *External Corrosion Management in Shell;* UK Oil & Gas and Energy Institute Workshop, Aberdeen, 18 June 2008.
59. ISO 4628 Part 3/BS 3900-H3:2003 *Assessment of Degree of Rusting*; BSI Standards, 2003.
60. www/:hse.gov.uk/2007/08/02/offshore-external-corrosion-project
61. Palmer, J. W.; Hedges, W.; Dawson, J. L. The use of corrosion inhibitors in oil and gas production, European Federation of Corrosion Document Number 39; Institute of Materials: London, 2004.
62. PrEN 13509:1999, Cathodic Protection Measurement Techniques; EN 12954:2001, Cathodic Protection of Buried or immersed Structure; EN 12696, Cathodic Protection of Steel in Concrete.
63. Amulet, C^3 Ltd., Dingwall Business Park, Dingwall, UK.
64. Rothwell, N.; Tullmin, M. *The Corrosion Monitoring Handbook*; Coxmoor: Kingham, Oxford, 2008. ISBN 1 90189 203 4.
65. Excerpts from Aircraft Accident Report – Aloha Airlines, Flight 243, Boeing 737–200 – N73711, near Maui, Hawaii, 28 April 1988; National Transportation Safety Board, 1989. http://www.aloha.net/~icarus/index.htm.
66. Congressional Report Services, Library of Congress, *BP* Alaska North Slope Pipeline Shutdowns, Regularity Policy Issues, October 2006, www.cnie.org/NLE/CRSreports/06Oct/RL33629.pdf.
67. Reason, J. T *Managing the Risks of Organizational Accidents;* Ashgate Publishing Ltd: England, 1997.
68. Broardribb, M., In 23rd Center for Chemical Process Safety International Conference, Curran Associates Inc, 7 – 9 April 2008. www.hse.gov.uk/aboutus/meetings/iacs/oiac/murrayfield0508/texas.pdf.
69. Harjac, S.; Atrens, A.; Moss, H. *In Corrosion'07*; NACE International: Houston, 2007; Paper no. 401.
70. Pande, P.; Nueman, R.; Cavanagh, R. *The Six Sigma Way: How GE, Motorola and Other Companies are Honing Their Performance*; McGraw-Hill: USA, 2000.
71. Eckes, G. *Six Sigma Team Dynamics: The Elusive Key to Project Success;* John Wiley, 2003.
72. BSI PAS 55–2: 2008, *Asset management: Guidelines for the application of PA 55–1*, and BSI PAS 55–1: 2003, *Asset management, Specification for the optimised management of physical infrastructure assets*; British Standards Institute.
73. www.aptools.co.uk/Macro%20Project.
74. decisionsupporttools.com.
75. www.macroproject.org/casestudies/MACRO%20LAUNCH%20-20%risk-based%20decisions.pdf
76. www.macroproject.org/casestudies/MACRO%20LAUNCH%20Eutech.pdf

4.32 Materials Selection for Corrosion Resistance

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Abbreviations

AISI American Iron and Steel Institute
API American Petroleum Institute
ASTM American Society for Testing and Materials
DCF Discounted cash flow
EFC European Federation of Corrosion
LCC Life cycle costing
MSD Materials selection diagram
NACE National Association of Corrosion Engineers
NPV Net present value
PREN Pitting resistance equivalent number
SAE Society of Automotive Engineers
SHE Safety, health, and environment
UNS Unified numbering system

Symbols

K_{IC} Fracture toughness (MPa m$^{1/2}$)
σ_f Strength (MPa) (metals, 0.2% offset yield; polymers, 1% yield; ceramics/ glasses, compressive crushing; composites, tensile; elastomers, tear)

4.32.1 Materials Selection in the Design Process

4.32.1.1 Overview

The selection of materials, including the processes by which they are shaped, joined, and finished, is integral to the design process through its various stages. In the early, conceptual stages of design, selection of materials is focused primarily on identifying the classes of materials (metals, polymers/elastomers, ceramics/glasses, composites, etc.) that will be used to construct the product. As the process progresses through detailed design, procurement and fabrication/construction, materials selection converges in line with the design process, through subclasses of materials (stainless steel, polypropylene, alumina, glass-reinforced polyester resin, etc. to specific grades of material (SA-516 grade 70 steel, EN 1.4404 equivalent to AISI 316L stainless steel, etc.) and the specific processes that are to be employed in their shaping, joining, and finishing.

Successful selection of materials is based upon identifying and delivering the key materials property and performance requirements of the product that is being designed with regard to:

1. *Functionality* – appropriate combinations of physical, thermal, mechanical, electrical, and/or magnetic properties in combination with appropriate formability and ease of fabrication.
2. *Appearance* – appropriate formability and ease of fabrication with surfaces amenable to appropriate finishing that might include processes such as coloring, patterning, and texturing.
3. *Durability* – predictable resistance to fracture, wear, corrosion, or other deterioration processes throughout the design life of the product.
4. *Economy* – acceptable cost and availability.

The progressive convergence into details, as the design process proceeds, requires increasing precision in the data on which the final materials selection is based and, when the final selection is made, it is vital that the grade of material specified should ensure the delivery of the required combination of properties and performance.

4.32.1.2 Grades of Engineering Materials

The process for identification of specific grades of materials varies with the class of the material. Materials usually have a common name such as stainless steel, brass, bronze, polypropylene, alumina, etc. For example, brasses and bronzes are alloys of copper with zinc and tin respectively. Apart from the fact that different grades of brass and bronze have different properties, this method of identification is inconsistent. For example, manganese bronze contains no tin at all. Clearly, more precise methods of identification beyond common names are required for specific grades of materials.

In the case of metallic materials, there is a long history of identifying specific grades of material by national standardizing societies, trade associations and individual users and producers of metals and alloys, usually by some form of alphanumeric designation. For example, the numbering system for stainless steels based on composition ranges, typified by the 300 (e.g., 304 or 316) and 400 (e.g., 430) series, was introduced originally by the American Iron and Steel Institute (AISI) and is widely adopted internationally by stainless steel specifiers and users. These grades are not specifications in themselves but have been widely used by standardizing bodies such as the American Society for Testing and Materials (ASTM) to identify grades of stainless steel products such as sheets and plates, bars, tubes, etc. More recently, ASTM in collaboration with the Society of Automotive Engineers (SAE) introduced a unified numbering system (UNS)[2] for metals and alloys that have a 'commercial standing' which correlates the various national designations into a single system. The UNS numbers attempt to incorporate widely adopted, historical designations. Thus, the UNS numbers for the AISI grades 304, 316, and 430 stainless steel are S30400, S31600, and S43000 respectively. Most, but not all, metals and alloys have a UNS number but new or developing alloys take time to acquire a number and producers may have proprietary alloy grades that they prefer to identify by a trademarked name.

The identification of nonmetallic classes of materials is much less standardized than in the case of metals and alloys. Thus, there are no recognized designations based on composition or other properties for materials such as polypropylene or alumina. Instead there are many grades of polypropylene and alumina that are specific to commercial suppliers, the compositions and properties of which might vary significantly. Thus, the selection of nonmetallic materials converges to the consideration of specific grades earlier in the design process than is necessary for metallic materials.

4.32.1.3 Materials Selection in Mechanical Design

In the specific area of mechanical design, Ashby and his coworkers[3] have developed systematic approaches to the selection of materials based upon 'material selection charts' in which one key property of the material is plotted against another. Materials are represented as elliptical areas that define ranges of values for the properties in question. Performance indices that define quantitative selection criteria can be plotted on the charts, allowing identification of those materials that comply with the selection criteria.

An example of a materials selection chart for safe design against fracture, such as would apply in the case of pressure vessel design, is shown in Figure 1, in which fracture toughness is plotted against strength. Two performance indices have been applied to the chart based on the selection criteria, yield before break ($M_1 = K_{1C}/\sigma_f = 0.6\,\mathrm{m}^{1/2}$) and minimum strength ($\sigma_f = 100\,\mathrm{MPa}$) and as a result a 'search region' for candidate materials has been defined. It is clear from the chart that the combinations of fracture toughness and strength that are required for pressure vessels to operate safely are confined mostly to metallic and a few composite materials. Despite

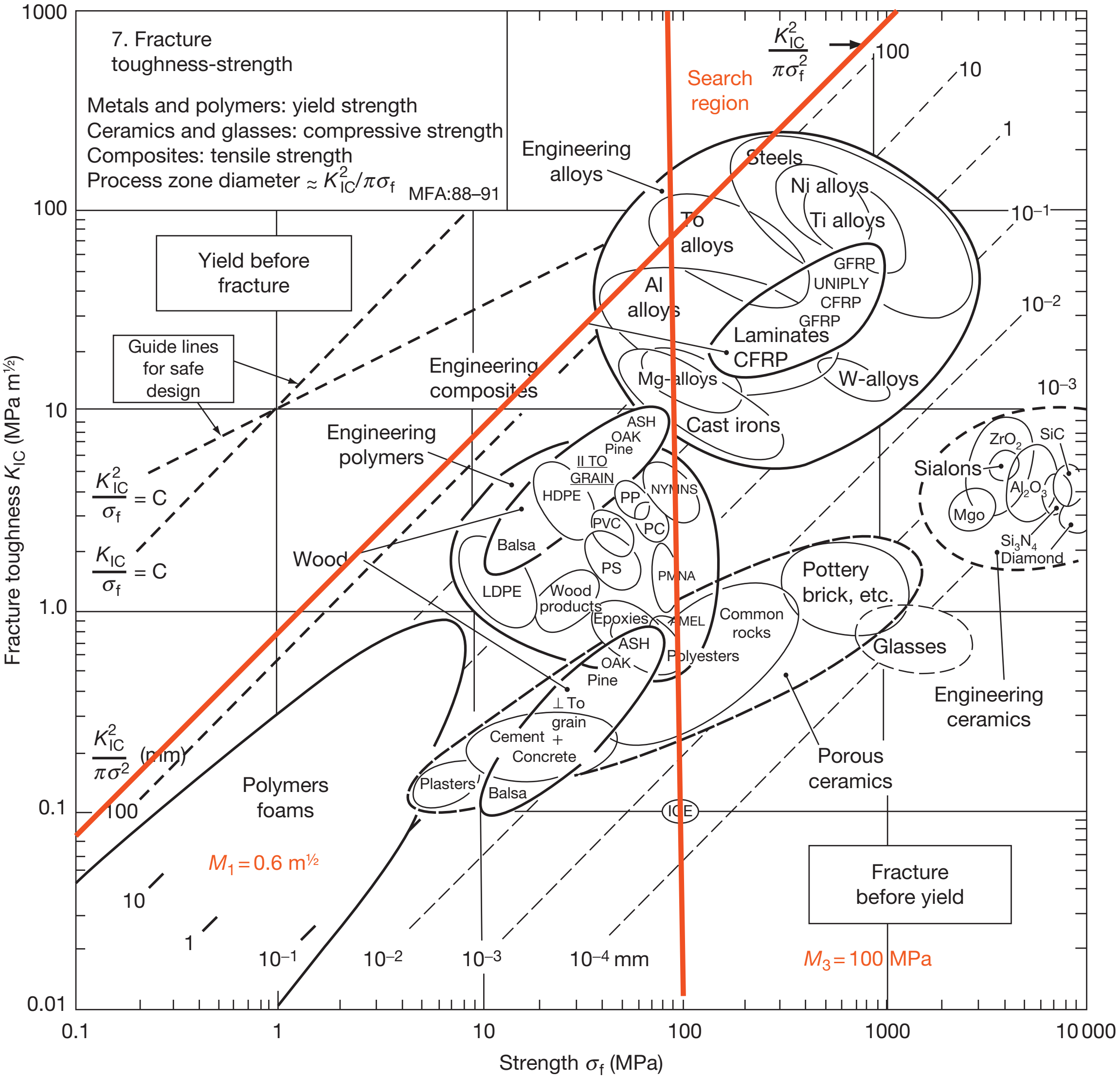

Figure 1 Materials selection chart for safe design of pressure vessels to avoid fracture. Adapted from Ashby, M. F. *Materials Selection in Mechanical Design*; Butterworth Heinemann, 2005.

their generally excellent corrosion resistances, polymers and elastomers lack the strength and ceramics and glass the ductility to qualify as materials for pressurized systems, although both classes of materials find use as coating and/or lining materials on tougher, steel substrates.

This approach is extremely powerful for the selection of materials in the designing of engineering applications where the key material properties fall into either of the following categories:

1. Invariant properties such as density, stiffness, heat capacity, etc. that do not change as a function of the material's condition, for example, in the case of an alloy whether the material is annealed, work-hardened, quenched, etc.
2. Deterministic properties such as yield strength, hardness, fracture toughness, electrical conductivity, etc. that vary significantly as a function of the material's condition, but for a given condition of heat treatment, mechanical deformation, etc. are invariant.

However, the approach is less powerful in engineering design applications where the key property of the material is nondeterministic and the property depends on some other parameter that is external to the material or its condition, such as the environment in the case of corrosion performance. In that case, the Ashby approach at its current stage of development is confined usually to assigning only broad performance categories against broad classes of corrodents and is thus of rather limited use for applications relating to specific environmental conditions.

4.32.1.4 Contribution of Design Codes to Materials Selection

The design of infrastructural or industrial structures/components that present significant safety, health, or environmental (SHE) risks in the event of failure is governed generally by international or national design codes. These codes have mandatory status in most countries and provide rules and guidance on detailed design, including aspects of materials selection, based on experience and technical analysis. Design codes are updated periodically to incorporate learning from accumulating experience and technology advances. The codes are approved and updated by standing committees of the various stakeholders in the design and operation of the equipment governed by the design code, and specific equipment designers, purchasers/operators, suppliers/fabricators, and inspection/regulatory authorities.

Design codes focus on the functionality and safety of the equipment that goes into service. For example, in relation to mechanical design, codes provide rules to reduce to acceptable levels, the risks of failure by brittle fracture or ductile overload as the equipment enters service or by fatigue or creep during its design life. In relation to materials, this is achieved by specifying limiting allowable values of relevant properties, for example, design stresses based on maximum proportions of yield or ultimate strength, toughness based on minimum impact energy or fracture toughness and fatigue/creep lives, based on relevant cyclic stressing and stress rupture properties. Design codes also provide rules and guidance on the fabrication of materials.

A historical example of the successful application of a design code is shown in Figure 2 that shows the aftermath of a hydraulic pressure test applied to a pressure vessel as the final proof of its suitability for service. In the event, the steel vessel failed catastrophically by brittle fracture that initiated as fabrication defects in the heat affected zones of welds that had been inadequately heat treated, resulting in low toughness of the material in the presence of high residual stresses. Although a disaster from the commercial standpoint, the event was a victory for the relevant design code, because a potentially unsafe vessel was prevented from entering service.

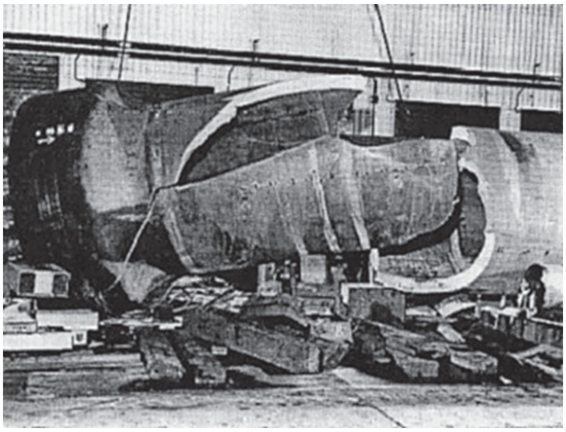

Figure 2 Catastrophic failure of a pressure vessel during final hydraulic test – an example of a commercial disaster, but a successful application of a design code preventing a potentially unsafe piece of equipment from entering service.

Design codes rarely provide rules or significant guidance for the selection of materials to avoid failure by wear or corrosion processes in service. Their treatment of these matters is normally confined to cautionary advice to consider these potential deterioration processes, and provide appropriate thickness allowances and protection measures to reduce the risk of failure to acceptable levels if necessary. It follows that the mitigation of corrosion risks by materials selection has to be based on knowledge and data from other sources.

4.32.2 Mitigating Corrosion Risks by Materials Selection

4.32.2.1 The Process

A corrosion risk can be defined as the product of the probability and consequences of a specific corrosion outcome. An overall process for mitigating corrosion risks by the selection of materials and associated corrosion protection measures is shown schematically in Figure 3.

At the design stage, the selection of materials and corrosion protection measures in specific applications can be divided into four stages:

1. The first stage is to define fully the environment. In most applications, the important contributors are the thermal, mechanical, and chemical conditions that the equipment has to withstand for

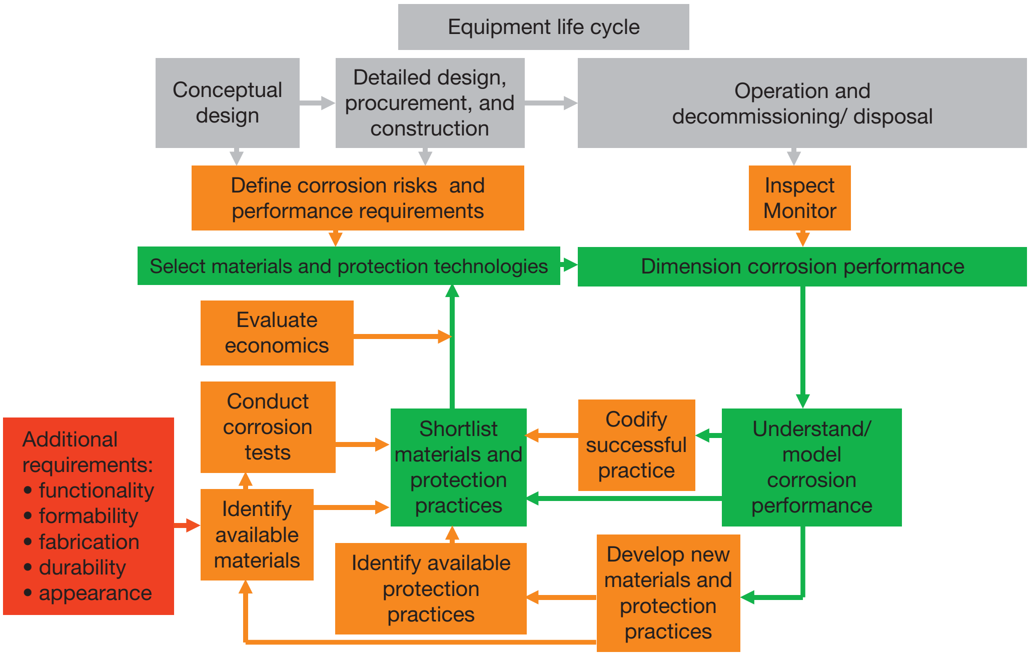

Figure 3 Outline process for managing corrosion risks by materials selection.

design purposes and during operation. In some situations, for example, in the process industries, there can be uncertainties in defining environments in terms of their phase and full chemical compositions, particularly during start up, shut down, and transient conditions. Other environmental factors may also contribute. For example, the microbiology of the environment may be important and radiation fields can have important effects on the performance of the materials such as the potential effects of solar radiation on the deterioration of polymeric materials.

2. The second stage is to define performance criteria for candidate materials. The basis for this is the design life, but criteria will vary depending on the application. For example, in applications where appearance or purity is a dominating requirement, corrosion rates that are very small may still be unacceptable. In other applications, higher corrosion rates may be acceptable as long as they do not jeopardize functionality during the design life.
3. In the third stage, credible corrosion risks are identified and evaluated and the corrosion performances of materials that satisfy other critical requirements, such as thermal and mechanical properties, are predicted based on data obtained from experience and testing. Protection measures that are required to control or prevent specific corrosion outcomes are identified. A shortlist of candidate materials and their required corrosion protection measures is identified.
4. In the final stage, cost and availability data are factored into the decision process to identify the most economic combination of material and corrosion protection measures.

4.32.2.2 Predicting Corrosion Performance

4.32.2.2.1 Identifying credible corrosion risks

The starting point in the prediction of corrosion performance is the identification of credible corrosion risks to the equipment under consideration. This is achieved by considering and evaluating the vulnerability of the equipment to deterioration or failure by the various types of corrosion that can be classified as follows:

1. Uniform corrosion resulting in general thinning or loss of strength.
2. Localized corrosion of passive or oxidized materials resulting in damage mechanisms such as pitting or intergranular corrosion or 'breakaway' oxidation, possibly initiating after an induction period.
3. Stress-induced corrosion promoted by static fabrication stresses and/or static or cyclic operating loads resulting in environmentally assisted damage

mechanisms such as stress corrosion cracking or corrosion fatigue.

4. Flow-induced corrosion promoted by velocities beyond 'critical' levels and the presence of second phase particles such as bubbles, droplets, or solids and the presence of flow disturbers, resulting in damage mechanisms such as erosion–corrosion or cavitation.
5. Galvanic corrosion promoted by the coupling of dissimilar materials including the breakdown/transpassivation or activation of passive metals due to coupling with more noble or active materials respectively.
6. Corrosion processes to which wear is a contributory factor.

Initial assessment of possible corrosion outcomes is based on the basic design characteristics of the equipment under consideration in relation to its design and operating environment, thermomechanical loadings, etc. However, corrosion risks can be influenced significantly by local thermomechanical and process conditions that may be less obvious at the design stage. For example, corrosion processes can be initiated by the development of microenvironments with compositions very different to the bulk fluid at locations such as heat transfer surfaces or in crevices and beneath deposits. The importance of detail in designing, in the recognition and mitigation of corrosion risks is described in a separate chapter and it is important that such considerations are factored into the assessment of possible corrosion outcomes for equipment.

4.32.2.2.2 Performance prediction based on experience

The most reliable predictor of a material's performance is previous experience of the material in an identical or similar application. The capture and dimensioning of the materials performance in operating equipment by appropriate inspection and monitoring, as illustrated in Figure 3, contributes significantly to the understanding and modeling of corrosion behavior. Feedback of the acquired knowledge results in a more reliable selection of materials in the design process and contributes to the development of new and improved materials and protection procedures.

In risk-aware organizations, corporate corrosion experience and knowledge is embedded in the databases that underpin the procurement and maintenance of assets that capture history and learning. This focuses attention on specific materials/corrosion vulnerabilities, resulting in increasingly reliable design, and corresponding reductions in maintenance costs. This data is usually captured in a what-works-where format related to specific types of equipment or sometimes more generally related to specific environments as exemplified in Figure 4 that summarizes a particular organization's view of the areas of usefulness of various materials in sulfuric acid.

In the cases of generic corrosion risks in specific applications/industries, industrial knowledge and experience and best practices for mitigation have been extensively codified in industry guides and recommended practices published under the auspices of bodies such as the National Association of Corrosion Engineers (NACE),[4] the European Federation of Corrosion (EFC),[5] and numerous, industry-specific bodies. Many of these sources relate to materials selection, including materials condition requirements, for specific environments. For example, the recommendations of NACE relating to the avoidance of stress corrosion cracking in the use of carbon steels for caustic soda service are summarized in Figure 5.

Informal industry networks are a further source of experiential knowledge on corrosion risks. Conferences can be as useful for networking as for the formal sessions and the email addresses and telephone numbers of other professionals in the field are particularly valuable potential sources of corrosion experience.

4.32.2.2.3 Performance prediction based on corrosion testing

In the absence of relevant experience, recourse must be had to the results of tests of the performances of materials. There are several published compilations of corrosion test data[6–12] and all materials suppliers provide performance data based on tests for a wide range of corrosive environments. Such data are usually presented as tables or maps of corrosion performance.

Data tabulations usually provide only an indication of the corrosion rate, or of a corrosion performance grading, over a range of corrosion rates. An example of corrosion data tabulation for mixtures of acetic acid + sodium chloride ($CH_3COOH + NaCl$) is shown in Table 1.

More detailed materials performance guides are usually based on mapping approaches, where the corrosion property of interest such as corrosion rate or resistance to a specific form of corrosion, such as crevice corrosion or stress corrosion cracking, is mapped on a field or in a space defined by key environmental parameters. Two- or more dimensional,

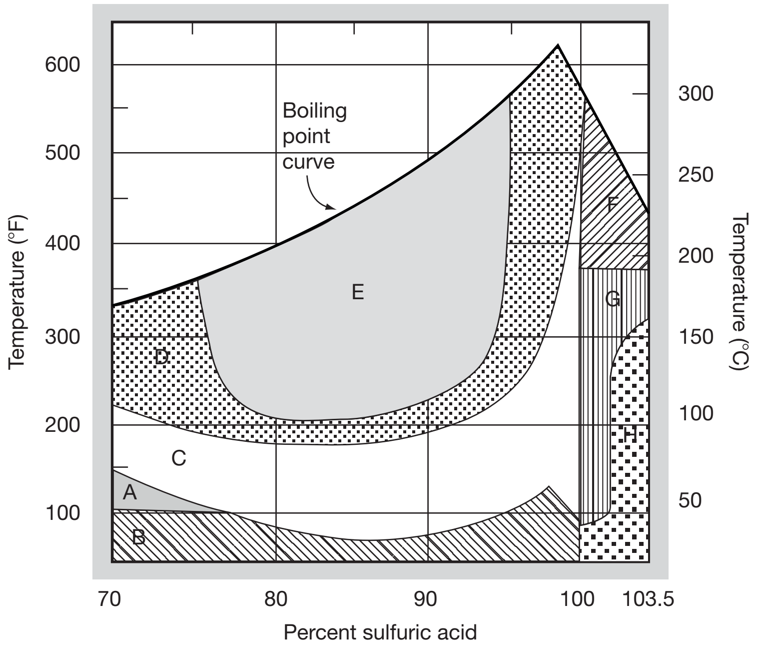

Figure 4 Areas of usefulness of various materials in concentrated sulfuric acid. A – Alloy B-2, lead, silicon cast iron, tantalum, cast alloy C, impervious graphite, glass. B – Alloy B-2, silicon cast iron, carbon steel, tantalum, impervious graphite and lead <96%, 316 SS >80%, glass, Worthite. C – Alloy B-2, silicon cast iron, tantalum, impervious graphite, and lead <175 °F and <96%, alloy 20Cb-3 < 150 °F, glass. D – Silicon cast iron, tantalum, alloy B-2, glass. E – Silicon cast iron, tantalum, glass. F – Glass. G – Alloy 20Cb-3, 304 SS, glass, Worthite. H – Alloy 20Cb-3, alloy C-276, 304 SS, carbon steel, Ilium G, glass. Adapted from Bulletin E-86405 *Sulphuric Acid Storage and Handling*; DuPont Company, Wilmington, DE, 1986.

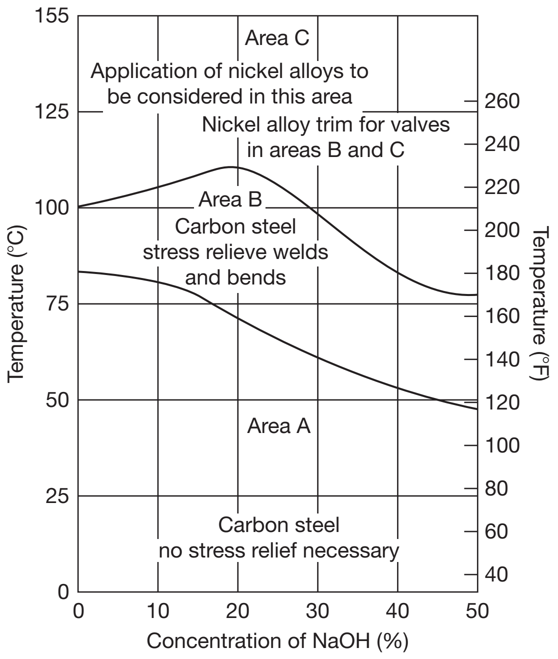

Figure 5 Temperature and concentration limits for stress corrosion cracking susceptibility of carbon steels in caustic soda. Adapted from *Corrosion Data Survey – Metals Section*, 6th ed.; National Association of Corrosion Engineers, 1985.

isocorrosion maps in which lines of constant corrosion rate are plotted as functions of the temperature and concentration of a corrodent are the commonest forms, a typical example of which is shown in Figure 6 that presents isocorrosion curves for various stainless steels at a rate of 0.1 mm year^{-1} in formic acid.

Corrosion tables and maps can be useful guides to performance but, in the absence of detailed information regarding the test conditions relating to the data, are no more than that. A corrosion rate from a table or map is unlikely to define fully the corrosion performance of a component in an environment unless the test procedure that generated the result replicates all of the potential contributing influences on corrosion performance in the specific application such as material condition, stress, flow, and heat transfer.

Corrosion testing is the subject of a separate chapter in this book. There are two broad approaches to testing:

1. Laboratory tests that attempt to quantify the performances of candidate materials in simulated or sampled service environments.
2. Tests/trials in prototype or operating equipment.

Table 1 Corrosion performances of various materials in mixtures of acetic acid and sodium chloride

CH_3COOH (wt%)	*NaCl (wt%)*	*Temp. (°C)*	*Carbon steel*	*410*	*18-2*	*304L*	*316L*	*904L*	*Sanicro28*	*254SMO*	*SAF2304*	*2205*	*SAF2507*	*Titanium*
1%	1%	70	2	2	0p	0ps	0ps	0ps	0	0	0	0	0	0
1%	5%	50					0p	0p	0	0	0	0	0	0
3%	4%	BP					0ps	0ps	0	0	0	0	0	0
4%	1%	70-BP				0ps	0ps	0ps	0	0	0p	0	0	0
7%	5%	70				1ps	0ps	0ps	0	0	0	0	0	0
7–10%	8.50%	80				1ps	0ps	0ps	0	0	0	0	0	0
10%	5%	BP				1ps	0ps	0ps	0	0	0	0	0	0
10%	26%	BP					1ps	1ps	0p	0	2	1p	0	0
25%	26%	BP					1ps	1ps	0p	0			0	0

0: corrosion rate less than 0.1 mm $year^{-1}$ – material may be considered for use (NB: This is still an unacceptably high corrosion rate in many situations); 1: corrosion rate 0.1–1.0 mm $year^{-1}$ – material may be used only in special cases; 2: corrosion rate over 1.0 mm $year^{-1}$ – serious corrosion, material is not usable. p, P: risk (severe risk) of pitting and crevice corrosion; s, S: risk (severe risk) of stress corrosion cracking; c, C: risk (severe risk) of crevice corrosion; ig: risk of intergranular corrosion; BP: boiling point.

Adapted from *Steel Professional Tool – Corrosion Handbook*; Outokumpu, www.outokumpu.com.

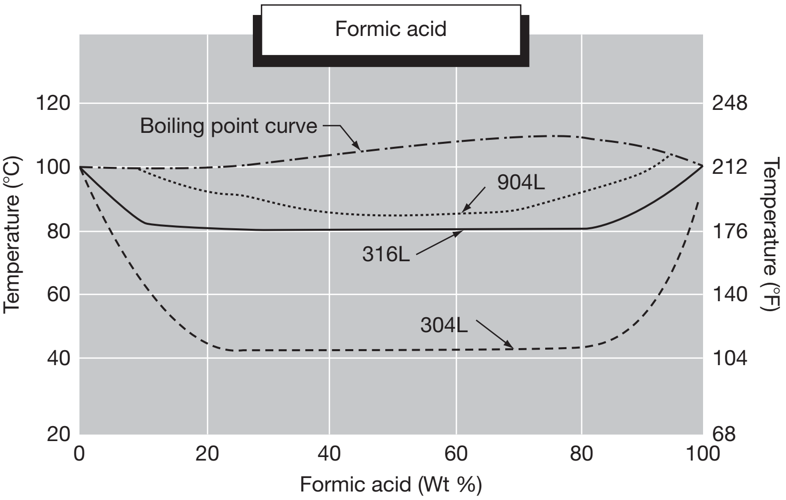

Figure 6 Isocorrosion diagram of 0.1 mm year^{-1} for various grades of stainless steels in formic acid. Adapted from MTI Publication MS-2 *Materials Selector for Hazardous Chemicals Vol. 2: Formic, Acetic and Other Organic Acids*; Materials Technology Institute of the Chemical Process Industries Inc., St Louis, 1997.

Laboratory tests have inevitable limitations for predicting corrosion performance. The commonest, simplest tests[13] involve exposure of small coupons of material, possibly preloaded, to fluids in heated glassware at atmospheric pressure, with only intermittent fluid refreshment. The maximum test temperature is the fluid boiling point, and the scope for simulation of the effects of factors such as flow, the presence of crevices, or the effects of heat transfer is very limited. More complex experimental arrangements involving the uses of autoclaves, heated and/or rotating test pieces, flowing fluids, etc. have been developed to address such limitations, but practicality and cost considerations usually dictate that such tests focus on a particular subset of contributory factors at the expense of others.

Where the lead times for corrosion testing are short, or in an attempt to increase the credibility of performance prediction, accelerated corrosion tests may be considered in which tests are conducted using intensified variables such as increased temperatures, stresses, concentrations of corrosive species, etc. to accelerate corrosion processes. It is vital in such testing that the possible deterioration and failure modes that are being evaluated should not be altered by the intensified test conditions. Staehle[14] has reviewed the advantages and potential pitfalls of accelerated testing for evaluating nuclear industry corrosion processes.

It is obvious that the inherent limitations of laboratory testing dictate that a degree of judgment is necessary in their use for the prediction of long term performance. However, this can also apply to performance data obtained from operating experience. This is illustrated in Figure 7, which compares the measured stress corrosion cracking resistances of austenitic stainless steels in neutral solutions in laboratory tests[15] with the incidences of stress corrosion cracking in stainless steel shell and tube heat exchangers in water cooling systems for periods up to >10 years.[16] The laboratory tests were relatively simple, involving exposure of types 304/304L/316/316L stainless steels under constant loads equivalent to yield strength to oxygenated, chloride solutions at various concentrations and temperatures for 1000 h. The data set for the >700 heat exchangers included all the basic austenitic grades operating in a wide range of water compositions and configurations for extended periods and, *per se*, incorporated the accelerating effects of heat transfer, crevices, etc.

In the event, the two performance curves in Figure 7 are relatively close, the major difference being in the predicted minimum temperatures for cracking of ~50 and ~30 °C for the laboratory test solutions and operating heat exchanger surfaces (skin temperatures) respectively. On the basis of the data in Figure 7, the laboratory tests might be construed as insufficiently conservative in relation to maximum skin temperature to avoid stress corrosion cracking. However, the operating experience data set also contains some inherent uncertainties and conservatism. For example, the skin temperatures are calculated, rather

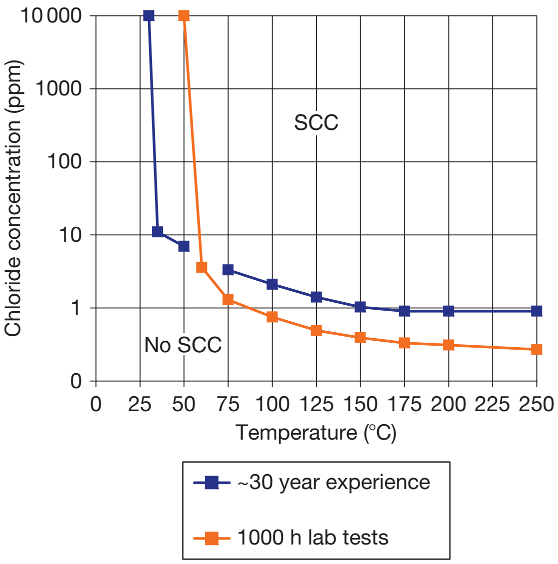

Figure 7 Resistances of austenitic stainless steels to stress corrosion cracking in neutral solutions in 1000 h lab tests[17] and in heat exchangers in recirculating cooling systems for periods up to >10 years.[18]

than measured, and the water compositions cover a wide range, short of brines and seawater. In practice, a maximum skin temperature of ~50 °C is widely considered as acceptable in the process industries for the avoidance of stress corrosion cracking of austenitic stainless steels in waters of potable quality over a 10-year design life and this is closer to the laboratory tests than the experience data set.

Notwithstanding the latter point, tests or trials in prototype or operating equipment allow for the mitigation of most of the inherent deficiencies associated with laboratory tests. Test coupons can be installed in racks that are bolted or welded onto appropriate components or onto retractable coupon holders. Their exposure to the service environments eliminates the risks relating to the environment in laboratory tests such as failing to include undefined constituents or time dependent chemistry changes in nonrefreshed liquors. However, the use of coupons does not eliminate simulation deficiencies relating to fluid flow characteristics, component geometry/stress, heat transfer effects, etc.

The most reliable option for testing materials is the use of trial components in prototype or operating equipment such as spool pieces in piping, impellers in pumps, tubes in heat exchangers, paddles on agitators, etc. Clearly, full scale trial components provide perfect simulation of all the contributory factors to corrosion. However, their use introduces risks of premature component failure, resulting in possible equipment damage and downtime, the consequences of which have to be evaluated and accepted.

4.32.2.2.4 Performance prediction based on material composition

Research studies of the performances of metallic materials in specific corrosion environments often generate correlations between materials resistance and alloy composition. Probably the most widely recognized correlation is the pitting resistance equivalent number (PREN), first introduced in 1969 by Lorenz and Medawar[17] and updated and refined by many authors since then, that relates the pitting resistances of stainless steels and nickel alloys to their compositions using linear formulas of the general form:

$$\mathrm{PREN} = \%\mathrm{Cr} + m\%\mathrm{Mo} + n\%\mathrm{N}$$

The most commonly used values of m and n are 3.3 and 16, respectively, although some versions give more weighting to nitrogen for specific grades and for superduplex stainless steels and nickel alloys the concentrations of tungsten and niobium are also weighted.

Correlations of this type are completely empirical and, although very useful for ranking and comparing candidate alloys, they are not a reliable basis for predicting the materials performance in specific applications where the corrosion outcome for which they were developed is a risk.[18]

4.32.2.2.5 Performance prediction based on quantitative modeling

Performance predictions, based on experience and corrosion testing, are essentially empirical. In industries where the consequences of unpredicted failure have unacceptable SHE and/or financial consequences, such as power generation, aerospace and oil and gas recovery, major expenditures on corrosion research into generic industry corrosion processes can be justified. Such research results in a sufficiently detailed understanding and dimensioning of corrosion processes to allow the development of quantitative models of corrosion mechanisms and such models can be used to predict corrosion performances as functions of relevant contributing variables.[19] Reviewing of the various approaches to modeling is beyond the scope of this chapter and the reader is referred to other chapters in this book that are concerned specifically with corrosion modeling, specific corrosion processes and the management of corrosion in specific industries.

4.32.2.3 Evaluating Corrosion Risks in Materials Selection

One of the more important requirements of the materials selection process is that the level of risk inherent in a materials recommendation is understood and aligned to the overall philosophy for managing the SHE and commercial risks in specific applications. The extent to which such risks need to be quantified rigorously depends upon the application and in particular the SHE consequences of corrosion failure.

For example, in the process industries, the SHE risk aspects of materials and protection selection are embedded in the hazard study methodologies[20] that evaluate hazards throughout the process and equipment design at its various stages. Such methodologies attempt to ensure that the safety and health risks presented to employees and the public and the contamination risks presented to the environment are contained within are acceptable defined limit values. Risks, including those arising from the materials selection, are evaluated and mitigated by teams of functional professionals, including materials/corrosion engineers.

In the process industries, the semiquantitative evaluation of corrosion risks is normally regarded as sufficient, based on the essentially empirical corrosion data that is used to predict corrosion performance, the reliability of which is normally classified as of high, medium or low reliability, depending on the source. For example, the American Petroleum Institute classifies the reliability of corrosion data as follows[21]:

1. *High reliability sources* – extensive field data through inspection, test coupon data from >5 years exposure in operating equipment.
2. *Moderate reliability sources* – laboratory testing with simulated process conditions, limited operating plant corrosion coupon testing.
3. *Low reliability sources* – published data, corrosion rate tables.

In contrast, in the nuclear industry, quantitative corrosion risk assessment is required, consistent with the greater consequences of equipment failure and more demanding acceptable limit values for risk. For example, Staehle[14] has described a 'corrosion based design approach' (CBDA) process for the prediction of materials performance consisting essentially of the same stages described above, but evaluated to a much greater level of detail using statistical methodologies. This allows a total probability of equipment failure to be calculated as a function of the probabilities of failure, by specific corrosion processes at specific locations in the equipment.

4.32.3 Economic Evaluation in Materials Selection

The costs of materials vary widely and their relative costs vary with time, depending not the least on the cyclical nature of the costs of metals and other raw materials. The cheapest constructional material is usually steel but its limited thermal and corrosion capabilities require consideration of alternative materials in many applications. In highly corrosive applications, expensive materials such as nickel, titanium, zirconium and tantalum alloys may have to be employed. Nonmetallic materials can provide excellent corrosion resistance at a modest cost but have mechanical property limitations that may require them to be used as protective coatings/linings on stronger substrates such as steel.

The procedures that are used to incorporate costs into the materials selection process are described in a separate chapter in this book concerned with the economic aspects of corrosion.

Whatever the application, the scarcity and cost of capital favor selection of the cheapest of the shortlisted materials of construction at the design stage. In some applications this is a valid approach. However, in the cases of complex assets it is recognized that the so-called life cycle costing (LCC) procedures are required that factor in the costs of maintenance and potential unreliability associated with the performances of alternative materials of construction throughout the operating life of the assets in the prevailing economic environment.

This is achieved by the use of discounted cash flow (DCF) procedures that provide an appropriate balance between capital and operating costs by factoring in variations in the value of money with time and the requirement for organizations to obtain an appropriate return on their investment. In the DCF process, all capital and operating costs and revenues associated with the assets are discounted to their values in the base year of the investment appraisal and summed to produce a net present value (NPV) for each materials option. On this basis, the most economic material of construction is that which yields the highest NPV and this is not necessarily the cheapest material of construction.

Application of such procedures produces some general economic truths relating to the selection of materials and corrosion control options:

1. Relatively low interest rates favor long-term economic planning and the cheapest may well not be the most economic option when life cycle costs are taken into consideration.
2. Alternatively, when capital is very expensive, shorter term considerations tend to dominate and large, long-term investments have no merit over small, frequently repeated investments. In these circumstances, the cheapest is also likely to be the most economic option.
3. It is essential that the risks and uncertainties attached to the inputs to a decision are understood and incorporated into the process of identifying the most economic option.

4.32.4 Outputs/Records of Materials Selection Processes

The output of a materials selection process should be much more than one or more proposed grades of materials. A materials selection process should produce and record, as a minimum, the following elements:

1. Materials recommendations, citing relevant specifications and trade names, including alternatives that may be used on the basis of price and availability.
2. Relevant limitations arising from the materials selected and their potential for deterioration such as limiting materials properties, required corrosion allowances, equipment operation limitations and inspection or future repair/replacement requirements.
3. Relevant tests, fabrication, erection, or other requirements to ensure quality and condition and correct use of the materials selected.
4. Defined sources of corrosion and other data, including tests, used in assessing the suitability of materials

In the cases of complex assets consisting of numerous subcomponents such as an airplane or a chemical process plant, it is vital that selections of materials are documented to capture the know-how that they embody, record any changes that are required and render the information accessible to the wider community of engineers and managers concerned with the design and operation of the assets. For example, in the process industries, the use of materials selection diagrams (MSDs) has been adopted for these purposes[22] that comprise simplified process flow diagrams showing relevant operating conditions together with materials selection information and any associated corrosion protection practices. These diagrams capture the information needed to ensure that decisions for the selection of materials for the many specific items of equipment that comprise the final plant (vessels, piping, machines, instrumentation) incorporate the outcomes of corrosion risk identification and evaluation, together with any necessary mitigation practices, for the relevant operating conditions. This is particularly important when materials selection decisions are spread across several supplier organizations to mitigate the risks of deficient information transfer across organizational boundaries.

4.32.5 Characteristics of Successful Materials Selection for Corrosion Resistance

Materials selection is a complex process of which the predictable resistance to corrosion is but one element. However, there are some general features that differentiate successful from less successful materials selection for corrosion resistance. Success is characterized by:

1. Early, sustained involvement from initial definition of the corrosion environment and performance requirements through design iterations during the conceptual and detailed design stages. In industries such as the process industries, materials selection issues may well influence process development.
2. Incorporation of learning from similar designs/processes.
3. Integration of materials evaluation into laboratory simulations and the development of pilot scale equipment and prototypes.
4. In the case of complex assets, a management process to ensure that materials selection for all subcomponents is informed as to the prevailing corrosion risks and required mitigation practices.

In contrast, less successful materials selection for corrosion resistance is often characterized by:

1. Involvement after the conceptual and even some of the detailed design stages are complete, when

the degrees of freedom for materials selection are much more limited.

2. Failure to incorporate learning from similar designs/processes.
3. Deficient corrosion environment definition, particularly in relation to transient or upset conditions.
4. Deficient corrosion testing/evaluation due to the failure to simulate real operating conditions.
5. Failure to inform the materials selection process for subcomponents of complex assets about the prevailing corrosion risks and required mitigation practices.

References

1. Ashby, M. F. *Materials Selection in Mechanical Design;* Butterworth Heinemann: London, 2005.
2. ASTM E527-07. Standard Practice for Numbering Metals and Alloys in the Unified Numbering System (UNS); ASTM International: Philadelphia, PA, 2007.
3. Granta Design: Materials Selection Tools for Industry and Education Available at http://www.grantadesign.com.
4. NACE International; http://www.nace.org.
5. European Federation of Corrosion; http://www.efcweb.org.
6. Craig, B. D.; Anderson, D. S. Eds. *Handbook of Corrosion Data*, 2nd ed.; ASM International: Materials Park, OH, 1995.
7. Schweitzer, P. A. Ed. *Corrosion Resistance Tables*, 5th ed.; Marcel Dekker: New York, NY, 2004.
8. Graver, D. L. Ed. *Corrosion Data Survey – Metals Section*, 6th ed.; National Association of Corrosion Engineers: Houston, TX, 1985.
9. Hamner, N. E. Ed. *Corrosion Data Survey – Nonmetals Section*, 5th ed.; National Association of Corrosion Engineers: Houston, TX, 1975.
10. Pruett, K. M. Ed. *Corrosion Resistance Guide for Metals and Alloys*; Compass Publications: La Jolla, CA, 1995.
11. Pruett, K. M. Ed. *Corrosion Resistance Guide for Plastics*; Compass Publications: La Jolla, CA, 1999.
12. Pruett, K. M. Ed. *Corrosion Resistance Guide for Elastomers*; Compass Publications: La Jolla, CA, 2005, Vol. III.
13. ASTM G31-72(2004): Standard Practice for Laboratory Immersion Corrosion Testing of Metals; ASTM International: Philadelphia, PA, 2004.
14. Staehle, R. W. In *Uhlig's Corrosion Handbook*, 2nd ed.; Wiley: New York, NY, 2000.
15. Sandvik Materials Technology Corrosion Handbook; AB Sandvik Materials Technology, 2004.
16. Haruyama, S. *Mater. Perform.* **1982**, 14–19.
17. Lorenz, K.; Medawar, G. *Thyssenforschung* **1969**, *1*, 97–108.
18. Cleland, J. *Eng. Failure Anal.* **1996**, *3*, 65–69.
19. Parkins, R. N. Ed. *Life Prediction of Corrodible Structures*, Proceedings of the Conferences, Cambridge, UK, 23–26 Sept. 1991 and Kauai, Hawaii, 5–8 Nov. 1991; National Association of Corrosion Engineers: Houston, TX, 1991.
20. Kletz, T. A. *HAZOP* and *HAZAN*: *Identifying and Assessing Process Industry Hazards*, 4th ed.; Institution of Chemical Engineers: UK, 1999.
21. API Publication 581 *Base Resource Document on Risk Based Inspection*; American Petroleum Institute, 2000.
22. NACE Standard SP0407-2007 *Format, Content and Guidelines for Developing a Materials Selection Diagram*; National Association of Corrosion Engineers: Houston, TX, 2007.

4.33 Mitigation of Corrosion Risks by Design

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Abbreviations

ASME American Society of Mechanical Engineers
barg Gauge pressure relative to atmospheric pressure (bar)
CR Corrosion rate
EAC Environmentally assisted cracking
EPC Engineering, procurement and construction
FEED Front end engineering design
KPI Key performance indicator
OOE Opex operating expenditure

Symbols

f Fluid to wall friction factor
h_n Film heat transfer coefficient ($\mathrm{W\,m^{-2}\,K^{-1}}$)
k Thermal conductivity ($\mathrm{W\,m^{-1}\,K^{-1}}$)
K_{Idesign} Maximum design stress intensity factor ($\mathrm{MPa\,m^{1/2}}$)
K_{ISCC} Threshold stress intensity factor for stress corrosion cracking ($\mathrm{MPa\,m^{1/2}}$)
q Heat flux ($\mathrm{W\,m^{-2}}$)
T Temperature (K)
V Pipe average velocity ($\mathrm{m\,s^{-1}}$)
V_e Erosional velocity (according to API RP 14E) ($\mathrm{m\,s^{-1}}$)
x Wall thickness (m)
ρ Fluid density ($\mathrm{kg\,m^{-3}}$)
τ_W Shear stress (Pa)

4.33.1 The Design Process

Design is the process that translates needs or aspirations into products. The need is satisfied or the aspiration realized in some appropriate combination of functionality, appearance, durability, and cost of the designed product that can range from a simple, individual component, such as a fastener or a wedding ring, to a complex system assembled from many individual components, such as an aeroplane or a nuclear power station.

Ashby[1] has differentiated three types of design.

1. Original design that is based on a new working principle(s).
2. Adaptive/developmental design seeking incremental advances in performance through refinements to working principle(s).
3. Variant design involving changes in scale or dimensions without changes in function or methods of achieving it.

The design process is usually undertaken at the front end of a project life-cycle which then progresses through construction to operation and maintenance and finally to decommissioning, dismantling, and removal of plant and equipment. Depending on the size and complexity of the project, the design process may be broken down into distinct stages of conceptual design, engineering design, and detailing. In practice, there can be considerable overlap of these stages due to the need to meet specific milestones within the project engineering phase and the iterative nature of the design process. During this process, sometimes referred to as the design loop, the design brief requirements are translated into options which, after detailed, critical appraisal and possible modification/recycling, are reduced to a preferred option that can be subjected to a final engineering review/audit that verifies its viability.

A common objective of the design process is to minimize life-cycle costs. In practice, these are determined early in the design process when major decisions, including the selection of materials and possible corrosion control options, are made. Studies of reliability and maintainability data from various types of projects[2] indicate that 10–25%, 25–60%, and 95% of the life cycle costs are predetermined by the concept design review, preliminary design audit, and final critical design review respectively, the timings of which are shown schematically in Figure 1. However, the early design stages account, typically, for less than 20% of the total project budget, and thus, a slight increase in spending on corrosion risk mitigation at the concept and design development stages can pay off handsomely in large cost savings during operation and even savings during the detailed design and construction stages.

Regardless of the particular application, the early stages of original and adaptive/developmental design processes are divergent in character. Alternative options are explored and evaluated and, where the product is large and complex, a structured process is used, the output of which is commonly described as a front end engineering design (FEED) or similar. A FEED evaluates the feasibility of a potential project and defines its business and technical scope. Thus, a FEED provides an economic justification for the project and a cost/benefit estimate that usually seeks to be accurate to within ±10% or thereabouts. In relation to the technical scope, a FEED identifies the technology that is to be adopted and the basis for the ensuing detailed engineering design. Regarding corrosion risk mitigation at the FEED stage, it is usually sufficient to identify the likely classes of material that are to be used for products/equipment together with any attendant significant corrosion risks and corresponding mitigation strategies such as the use of protective coatings, anodic or cathodic protection, or process/environmental modification to inhibit corrosion. These evaluations are commonly desktop studies based on published data and computer based models.

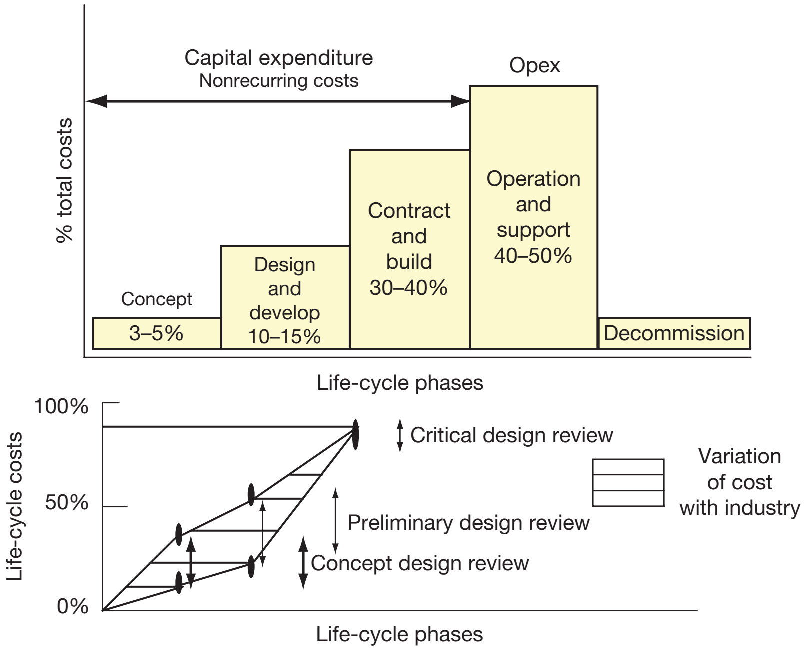

Figure 1 Effect of project phase expenditure on life-cycle costs. Adapted from Kennedy, I. Design and specification for reliability and maintanability; Presented at National Tribology Course on Reducing Plant and Equipment Life-cycle Costs; 24 November 1994.

Projects that are approved to proceed beyond the business feasibility/FEED stage move into the detailed engineering design, procurement, and construction (EPC) phase. At this stage, the design process converges into increasing detail as the functionality, appearance, durability, and cost of the final product or equipment are specified to facilitate manufacture. The detailed design of infrastructural or industrial structures/components that present significant safety, health, or environmental (SHE) risks in the event of failure is governed generally by international or national design codes. For example, much of the world's process and power equipment is designed in accordance with design codes produced by the American Society of Mechanical Engineers (ASME). The codes have mandatory status in most countries and provide rules and guidance on detailed design, including aspects of materials selection, based on experience and technical analysis. Design codes are updated periodically to incorporate learning from accumulating experience and technology advances. The codes are approved and updated by standing committees of the various stakeholders in the design and operation of the relevant equipment, specifically designers, purchasers/operators, suppliers/fabricators, and inspection/regulatory authorities.

In the case of a large, complex project, the detailed engineering may well be undertaken by a specialist contractor who also undertakes procurement and construction – a so-called EPC contractor. During this stage, drawings and data sheets are produced for products or individual equipment items that finalize the detailed thermomechanical and process design in compliance with the relevant code. Design codes focus on the functionality and safety of equipment that goes into service. For example, in relation to mechanical design, codes provide rules to reduce to acceptable levels the risks of failure by brittle fracture or ductile overload as the equipment enters service or by fatigue or creep during its design life. Design codes also provide rules and guidance on the fabrication of materials. However, design codes usually offer little more than general guidance on the mitigation of corrosion risks that also requires detailed consideration at this stage. The specific grades of materials need to be specified along with the procedures and practices that are to be used to fabricate them and protect them from corrosion.

Arguably the most important input to this detailed design stage is feedback of learning from previous operating experience within an organization or an industrial sector relating to causes of equipment or component failure and the success or otherwise of engineering practices that have been deployed to mitigate the risks of failure. Some of this learning may have been codified in corporate and national/international engineering guides, standards, and specifications. In relation to corrosion risk mitigation, these documents are concerned mostly with the selection of appropriate materials and practices that are available for corrosion protection in specific applications. The selection of materials and protection practices is considered in a separate chapter in this volume.

However, localized thermomechanical effects and process design practices themselves can also have a significant influence on corrosion risk and its mitigation. This is not widely appreciated amongst design engineers and a lack of assessment of these parameters can result in avoidable corrosion problems in service. A significant challenge facing design teams is how to ensure that operating experience of good and bad design practices is fed back into the design stages of new projects through effective communications amongst operating and maintenance staff, design teams, and corrosion specialists.

The activities and information flows that are essential to the successful mitigation of corrosion risks in the design process are summarized in **Figure 2**, which confirms the crucial significances of the FEED documents and the detailed drawings/data sheets that form the inputs and outputs of the engineering design and detailing stages.

Major corrosion concerns and risk mitigation issues are usually identified and addressed in the reviews and audits of the FEED documents which result from the conceptual and early design stages and are essentially driven by likely life-cycle cost benefits. Good design practices relating to the various thermomechanical and process factors summarized in **Figure 2** come into play in the engineering design and detailing stages. They are less codified than is the case for the selection of materials and corrosion protection practices and, crucially, designers often have limited experience of the service performance of equipment that would provide insights into good practices in these areas. Unless such risks are controlled they can have considerable financial implications that are many times those of the budgeted direct cost of corrosion control. In the following sections of this chapter, potential corrosion risks that can arise from poor design are reviewed along with general approaches to the mitigation of such risks by good thermomechanical and process design practices. There are sources that overview the subject,[3,4] the most comprehensive of which is Pludek's book[3]

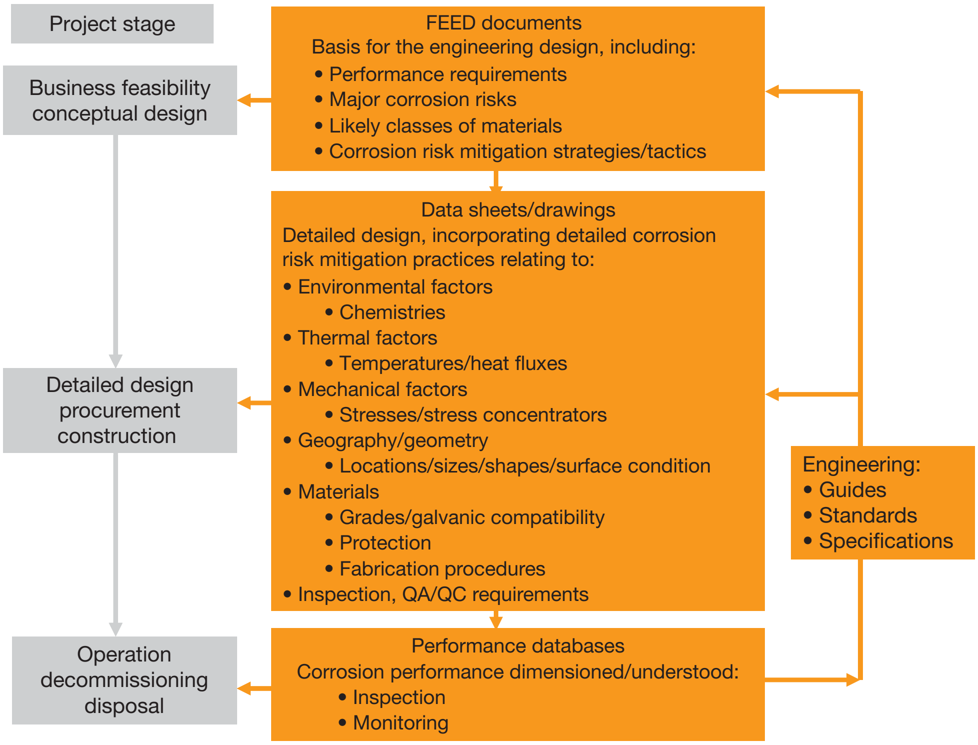

Figure 2 Activities and information flows for mitigating corrosion risks by design.

that provides many examples of design practices that exacerbate corrosion risks and corresponding good practices for the mitigation of such risks by detailed design. However, awareness of the need for good thermomechanical and process design practices throughout the design process is not sufficient to deliver effective corrosion risk mitigation unless corrosion issues are managed effectively within the project design process and this is addressed in the final section of the chapter.

4.33.2 Corrosion Risks Arising from Microenvironments

In any particular application, materials are selected relative to a defined corrosion environment, the key contributory factors to which are:

1. fluid chemistries;
2. fluid temperatures;
3. equipment/component stresses;
4. fluid flow characteristics;
5. heat transfer characteristics;
6. location/layout/shape of equipment and components.

These factors that define the macrocorrosion environment are interactive. Thus, fluid flow characteristics are dependent on shape, heat transfer characteristics on fluid temperatures, etc. The performance of a specific material in a particular application will be determined by clusters of the various factors that will vary with the application. For example, fluid flow and heat transfer are particularly relevant to the process and power generation industries. Clearly, if a piece of equipment is to be fabricated from several different materials, then there are additional corrosion risks arising from potential galvanic interactions that have also to be evaluated and mitigated.

All of the contributory factors are, in theory, degrees of freedom in the design of a component or a piece of equipment for a particular application. In practice, fluid chemistries and temperatures are predetermined in many applications, but the dimensions and characteristics of the other factors can all be influenced by the detailed thermomechanical and process design of equipment and components. Materials selection *per se* is rarely sufficient. It needs to be overlaid with good design practices if corrosion risks are to be mitigated in subsequent operation.

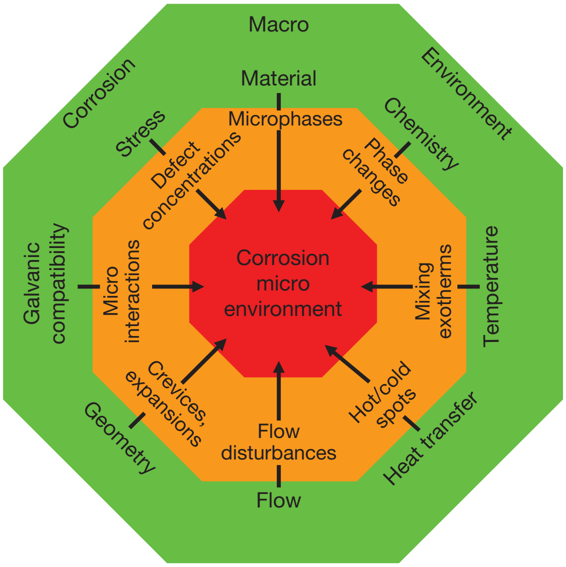

Figure 3 Contributors to the corrosion macroenvironment can intensify locally, individually or in clusters, to create a corrosion microenvironment in a specific application.

The recognition of corrosion risks relating to the macroenvironment at the design stage is relatively straightforward. However, as illustrated in Figure 3, all of the contributory factors can intensify and interact locally in equipment and components. Thus, fluids may condense locally at cold spots to produce chemistries that are much more corrosive than the bulk chemistry of the fluid. Stresses may be concentrated significantly by fabrication and other defects in equipment and components that may increase the risks of initiation of environmentally assisted cracking. Local shape features may disturb fluid flows with significant outcomes regarding the vulnerability of components to erosion–corrosion. In practice, these intensified local factors can also cluster to define local microenvironments that present much larger corrosion risks than clusters of the equivalent bulk factors. Such microenvironments can be much more difficult to predict at the design stage and are a common source of unscheduled failure of equipment due to corrosion.

4.33.3 Mitigation of Risks Arising from Chemistry Definition/Control

The commonest cause of unpredicted corrosion problems is the failure to define accurately the chemistries of environments or to anticipate changes in chemistry that are caused by other prevailing factors at specific locations in equipment. The major components of environments are normally identified and dimensioned with sufficient accuracy to allow prediction of corrosion performance, even for equipment that is designed to alter bulk chemistry such as in the cases of process industry reaction and separation equipment. However, uncertainties in environment chemistry can arise, usually from one or more of three sources that may not be recognized or dimensioned at the design stage.

1. Variations in bulk chemistry may occur with time, under climatic influences, or during start-up, shutdown, or upset conditions in operation. For example, in the process industries, the lives of carbon steel reactors that are used for the manufacture of ethylene dichloride are determined almost exclusively by the incidence or otherwise of condensation of hydrochloric acid during start-up, in sharp contrast to the steady state operating environment, where corrosion rates are low.[5] It is important that potential changes in bulk chemistry with time are defined, quantified, and evaluated at the design stage.
2. The presences and concentrations of minor components may dominate corrosion performance. For example, the performances of passive alloys in reducing acid solutions are influenced strongly by the presences or otherwise of oxidizing metal ions (favorably) or chloride ions (unfavorably) at relatively low levels in the tens to hundreds ppm range.[6] It is important that minor components are defined, quantified, and evaluated at the design stage, including their possible local concentration such as in distillation and separation equipment.
3. Local shape and/or heat transfer may promote the development of local chemistries that are very different from and much more corrosive than the bulk fluid chemistry, in particular where phase changes may occur. Early condensates from acid gas/vapor streams can be very concentrated and corrosive relative to bulk condensates as in the cases of combustion flue gases,[7] and refinery overhead streams.[8] Initially benign condensates or cooling fluids can concentrate due to intermittent contact with surfaces hot enough to promote concentration or dry-out, as in the chloride-induced, external stress corrosion cracking of austenitic stainless steels under thermal insulation.[9] Extremely high concentration factors are possible under boiling heat transfer in crevices or under deposits, or under film boiling conditions at high heat flux regions, as in water side, on-load corrosion in process and utility boilers.[10]

A typical example of potential microenvironment development under the combined influences of shape and heat transfer is the shell and tube heat exchanger that is widely used for cooling and heating applications in the process and power industries.

The critical design feature of these exchangers is the tube/tube-plate joint that separates the two working fluids and which almost inevitably contains a crevice, unless it is eliminated by employing expensive fabrication procedures. Sections of a typical shell and tube cooler fabricated with welded tube/tube-plate joints using shell-side water as the cooling medium are shown schematically in Figure 4 in a vertical configuration, characterized by the existence of a vapor space between the water exit and the upper, hot tube-plate.

The chloride contents of waters vary over many orders of magnitude, depending on the source. Demineralized waters and condensates generally contain <1 ppm chloride. Lake waters commonly contain low levels of chloride in the range 1–10 ppm, potable waters in the range 10–100 ppm, rivers in the range 100–1000, and estuarine and seawaters in the range 1000–10 000 ppm. During operation, cooling water splashes onto the underside of the hot tube-plate, where it evaporates to dryness. Successive events result in the accumulation of scale/salt deposits, in which the concentration of chloride is many orders of magnitude greater than in the bulk cooling water. The crevices between the tubes and the tube-plate provide for retention and further concentration of aqueous fluid.

The thin tubes contain residual stresses equivalent at the yield strength of the material, arising from tube expansion and welding of the joint during fabrication. It follows that if, as is commonly the case, the heat exchanger is constructed in austenitic stainless steel, the microenvironment that develops in and around the tube/tube-plate joint introduces significant risks of chloride-induced stress corrosion cracking, particularly within the crevice, as illustrated in Figure 4.

There are several approaches to mitigating these risks, the most direct of which is the selection of ferritic or duplex austenitic–ferritic grades of stainless steel that are more resistant or even immune to chloride-induced stress corrosion cracking. However, there are also practical design measures that can be used to mitigate the risks for austenitic stainless steels. As confirmed in Figure 5, risks are significantly lowered in horizontal relative to vertical heat exchangers because the vapor space that is the essential cause of microenvironment development is removed.

Risks are further lowered if the cooling water is transferred to the tube-side, because the tube/tube-plate crevice that contributes to microenvironment development is eliminated. If the exchanger, for other reasons, has to be vertical with shell-side cooling, risks can be lowered by venting the hot tube-sheet, thereby eliminating the vapor space, as shown schematically in Figure 6.

4.33.4 Mitigation of Risks Arising from Thermal Design

The bulk temperature of an environment can usually be predicted accurately, notwithstanding the need to incorporate, if appropriate, the influences of

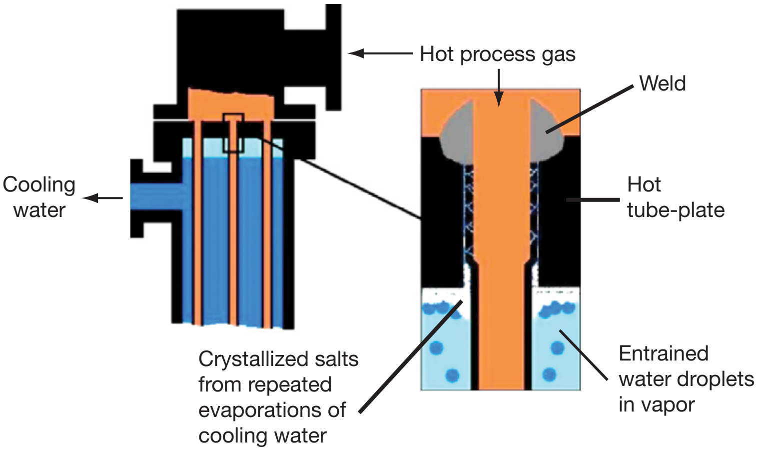

Figure 4 Creation of microenvironments that promotes stress corrosion cracking by repeated wetting/drying events in the tube/tube-plate regions of vertical, austenitic stainless steel heat exchangers with shell-side water.

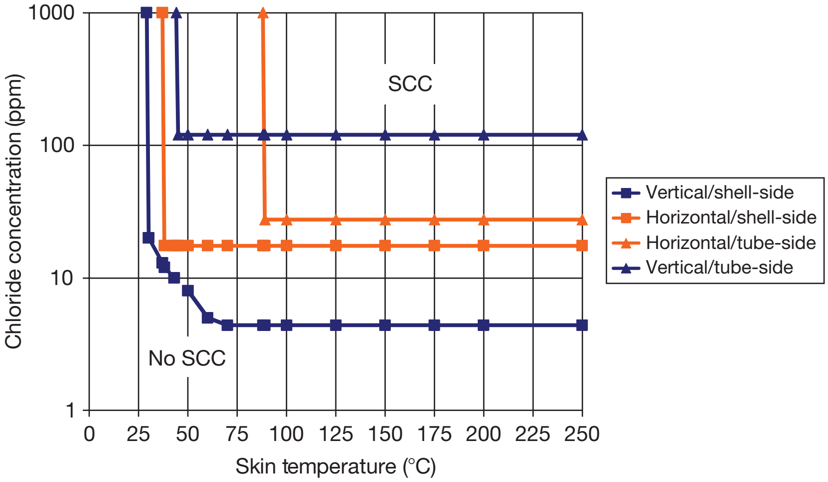

Figure 5 Resistances of austenitic stainless steel heat exchangers to chloride induced stress corrosion cracking in open, recirculating cooling systems for periods up to >10 years. Adapted from Haruyama, S. *Mater. Perform.* **1982**, *21*, 14–19.

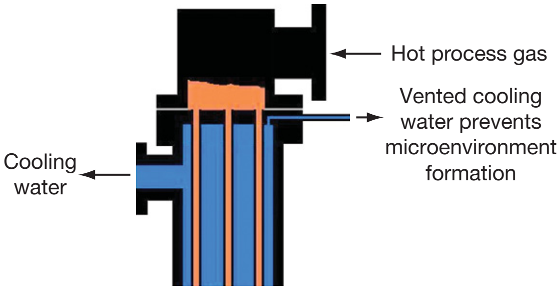

Figure 6 Prevention of microenvironments that promote stress corrosion cracking in the tube/tube-plate regions of the shell-sides of vertical shell and tube heat exchangers by venting the top tube-sheet.

time-dependent factors such as climatic conditions, or start-up, shut-down, or upset conditions during operation. The possible effects on local temperatures of fluid mixing need to be recognized. For example, the addition of acids to process streams may be characterized by significant dilution exotherms that produce a much hotter, local microenvironment with additional corrosion risks which may have to be mitigated by a local materials upgrade at the design stage.

Heat transfer introduces additional factors that need to be evaluated. The case of heat transfer from a fluid to a solid wall controlled by convective/turbulent flow with fluid eddies, and through the solid wall by conduction, is shown schematically in Figure 7. The local heat flux is given by:

$$q = h_1(T_1 - T_2) = k_w/x_w(T_2 - T_3) = h_2(T_3 - T_4)$$

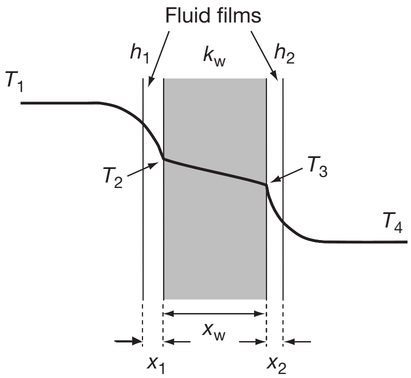

Figure 7 Temperature profile for the case of heat transfer between fluids and a solid wall controlled by turbulent flow/convection (h_n), through the solid wall by conduction (k_w/x_w). T = temperature (K); k = thermal conductivity (W m^{-1} K^{-1}); x = wall/film thickness (m); h_n = fluid to wall heat transfer coefficient (W m^{-1} K^{-1}).

where q is the heat flux (W m^{-2}); h_n, the film heat transfer coefficient (W m^{-2} K^{-1}); T, the temperature (K); k, the thermal conductivity (W m^{-1} K^{-1}); x is the wall thickness (m).

From the design standpoint, heat transfer is promoted by low thickness and high thermal conductivity of the solid wall, high values of ΔT ($T_1 - T_4$) and turbulence that generates high values of h_n. One of the more important features of heat transfer in relation to its corrosion effects is the difference between metal surface, or skin temperatures, T_2 and T_3, and the bulk fluid temperatures, T_1 and T_4, as depicted schematically in Figure 7.

There are additional potential corrosion risks arising from the effects of heat transfer. Heat exchangers typically operate under relatively high flow rates to promote turbulent flow conditions, resulting in reduced boundary layer thickness. The supply of reactants, or the removal of intermediates or products, is dominated by flow-induced mass transfer. In single phase fluids, the overriding additional effect of heat transfer is the influence of wall temperature on diffusion coefficients and viscosity. These influence boundary layer thicknesses and concentration profiles and the stabilities, solubilities, and compositions of the relatively thick diffusion barrier layers which are continuously penetrated by turbulent eddies and localized areas of high turbulence intensity at tube inlets, downstream of protrusions and other changes of shape. These not only increase heat transfer rates but have controlling effects on the corrosion and erosion–corrosion of metals such as steels and copper alloys in specific applications.[11]

For example, heat transfer to a liquid makes it more difficult to transfer oxygen from the bulk solution to a hot wall surface because of the reduced solubility of oxygen as temperature increases. In cases where the solubility product increases with temperature, heat and momentum transfer at the wall–liquid interface may tend to undermine and detach protective barrier layers, whilst encouraging thickening of scales by diffusion and precipitation at the outer face. Conversely, where the solubility product decreases with temperature, heat transfer to a liquid may promote the formation of adherent, thin scales, the classic case of which is the formation of calcium carbonate and sulphate scales on heat transfer surfaces in cooling waters.

Wall conditions can also be influenced by whether the heat exchanger design is co-current or counter current as local wall temperatures may be higher than indicated by average design figures. The design will allow for a fouling factor to account for lower overall heat transfer rates during operational life. These apparently minor differences on the process design flow sheet can result, in practice, in significant changes to local microenvironments that give rise to corrosion.

Heat transfer is also promoted by phase changes such as boiling or condensation and these can, as noted previously, promote the formation of local environments with significant additional corrosion risks. For example, modern high pressure boilers are designed utilizing high heat fluxes, typically 1000 kW m^{-2} that can promote film boiling conditions that result in fouling/corrosion processes during operation (on-load), depending on the efficacy of the prevailing boiler water treatment. Process plant boilers are commonly designed with particularly high heat fluxes to reduce capital costs, and can therefore be particularly vulnerable to on-load corrosion, as illustrated schematically in Figure 8 for a typical, horizontal, fire-tube boiler constructed in carbon

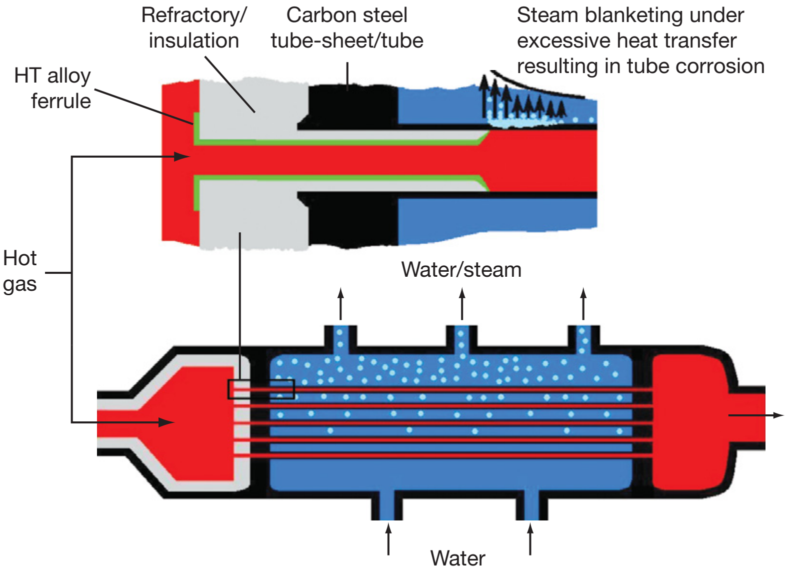

Figure 8 Creation of corrosion-promoting microenvironments at high heat flux regions of horizontal, fire tube boilers resulting in on-load corrosion.

steel that uses a hot process gas, typically entering at ~1000 °C, to raise steam from water on the shell-side at a typical pressure of ~100 barg.

The boiler depicted in Figure 8 would typically be designed with average heat fluxes of ~3000 kW m^{-2}, increasing to ~6000 kW m^{-2} locally, and would operate on fully demineralized water. The hot channel end and tube-plate would be refractory clad to maintain the carbon steel temperatures within the code design range, with the tube temperatures determined largely by the boiling water temperature, ~310 °C. A typical tube entry construction detail is illustrated in Figure 8, consisting of high temperature alloy ferrules set into the tube-sheet refractory and extending some distance into the tubes, separated from them by an insulating material. The ferrules are required to protect the tube inlet regions from excessive heat flux by providing a transition region to reduce the inevitable region of enhanced heat transfer just beyond the ferrule to within the design requirement.

The corrosion rate of carbon steel in boiler waters at ~310 °C depends on the solubility of magnetite, and therefore pH. It is known that concentrated acidic or alkaline solutions can form at local sites where convection/mixing are restricted, such as crevices at tube/tube-plate joints, on horizontal or inclined surfaces, or at flow disturbances such as tube bends or weld protrusions. Steam blanketing under film boiling conditions can result in intermittent wetting/drying and solute concentration by several orders of magnitude, exacerbated by porous deposits such as oxides of iron or copper that promote so-called wick boiling. Concentrated alkaline solutions usually arise from concentration of alkaline corrosion inhibition species from which free sodium hydroxide can be liberated, particularly sodium phosphate treatments. Concentrated acid solutions arise when bulk contamination of the boiler water with dissolved oxygen and chloride, typically by sea or river water ingress, occurs. The boiler depicted in Figure 8 is at risk of such local microenvironments developing on tube surfaces in the regions of maximum heat transfer beyond the ferrules, resulting in pitting and ultimately tube perforation.

In practice, the risks depicted in Figure 8 can be mitigated by tight control of water chemistry during operation to prevent the formation of highly alkaline or acid environments in the event that film boiling conditions occur. However, the risks can also be mitigated by the attenuation of excessive heat fluxes with an improved design, as depicted in Figure 9, which shows an extended, profiled ferrule for that purpose.

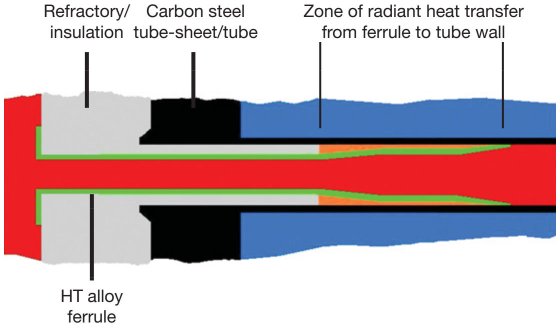

Figure 9 Tube ferrule design to mitigate risks of on-load corrosion due to excessive heat fluxes in horizontal, fire-tube boilers.

4.33.5 Mitigation of Risks Arising from Mechanical Design

Engineering structures are exposed to a range of operating stress regimes, depending on the application. Static structural loadings are usually limited to maximum proportions of yield or ultimate strength of the material at lower temperatures, or stress rupture properties of the material if operating at temperatures within its creep range, as dictated by the relevant equipment design codes. In practice, design codes usually permit higher stresses in local regions of equipment than the maximum allowable specified for the majority of the structure, for example at penetrations through the vessel wall in the case of pressure vessels. Fabrication processes such as cold working and welding can introduce local, static, residual stresses at levels up to and beyond the yield strength of the material.

Equipment may also be required to withstand dynamic loadings. These cyclic loadings may be associated with equipment start-up and shut-down conditions, or may be intrinsic to the application itself, as for example in the cases of marine structures that have to withstand tidal and/or wave loadings, or pressure vessels for processes based on pressure cycling. They may arise indirectly from thermal cycling/transients, particularly under conditions of restricted expansion and contraction. Higher frequency, vibration loadings may be wind excited, or arise from pressure pulsations, or be transmitted from adjacent reciprocating or rotating machinery. In some applications, loading regimes are complex combinations of static and dynamic loadings, as for example in the case of turbine blades that may have to withstand static centrifugal loads at temperatures within the material's creep range that are overlaid with relatively high frequency, low stress range loadings arising from varying fluid pressures as the blades rotate. As in the case of static loads, equipment design codes provide guidance on the confinement of dynamic loadings to within the appropriate fatigue strength capabilities of the relevant materials.

Where thinning of structural components due to corrosion and/or wear is anticipated in service, appropriate thickness allowances or sacrificial shielding components such as impingement plates may be specified at critical locations at the design stage to ensure that components retain sufficient thickness throughout their service lives to maintain membrane stresses below the design maximum allowable levels. This approach to corrosion risk mitigation is applicable only to relatively thick section components where some loss of section thickness can be tolerated such as major structural members, pressure vessel or pipe walls, etc. It is impractical for thin section components such as heat exchanger tubes/plates, or where dimensional clearances must be maintained throughout service life such as in seals, or where environmental contamination by corrosion products is unacceptable such as in the food and pharmaceutical industries.

The potential risks of environmentally assisted cracking (EAC) have also to be evaluated and mitigated at the design stage. Regions of relatively high static stress, in particular associated with residual fabrication stresses, are preferred sites for the initiation of the various forms of EAC that are described in separate chapters in this book. Corrosion has significant potential influences on the risks of initiation and rates of propagation of fatigue cracks in materials, and both static and dynamic stresses can be concentrated by defects in materials or welds. In the cases of equipment for critical duties such as offshore structures and nuclear pressure vessels, these factors are incorporated formally into relevant design codes. However, for most equipment, the additional risks they promote have to be evaluated and mitigated on the basis of more general engineering good practice.

The general approaches to the mitigation of EAC risks by the control of stress and its concentration are as follows:

1. Design stresses and the sizes of fabrication defects are controlled to levels where the maximum stress intensity for the equipment, K_{Idesign}, is below the critical stress intensity for EAC, K_{IEAC}. Given that design codes commonly allow membrane stresses that are significant proportions of the yield strength of a material, this approach offers limited scope to mitigate risks in many practical situations. An example of its successful use would be the case of steel gas cylinders that are usually hot forged to final shape in one operation in thicknesses well above the minimum required to sustain maximum operating pressures. As a result, they operate with very low applied stresses and contain very small residual stresses and are therefore effectively immune to EAC even when containing environments such as anhydrous ammonia or HCN that are known to present risks of EAC to steels.
2. Stress concentrations are controlled by appropriate control of shape and by confining defect sizes below specified limiting values, for example by the use of transitional radii at changes in cross section such as at notches and key ways, the control of surface finish etc. Welds are the commonest sources of defects in fabricated structures and therefore require appropriate inspection and possible repair to eliminate potentially critical fabrication defects. For particularly critical applications, practices such as the machining/grinding of weld toes to eliminate small defects are specified.
3. Residual/fabrication stresses are controlled by specifying thermal or mechanical stress relief procedures. Thermal procedures have been employed routinely for the relief of fabrication stresses in carbon and low alloy steels using procedures that are detailed in relevant design codes. Typically, structures are heated to temperatures within the range 550–650 °C for short time periods that depend on component thickness. Rules exist that govern rates of heating and cooling, allowable temperature gradients, etc. Ideally, completed structures are heat treated in furnaces, but large structures may have to be furnace treated in sections, and the final welds heat treated locally using electric heating elements. Local heat treatments may not achieve the degrees of stress relief that are achieved with furnace heat treatment. So-called temper bead welding is a special case of local heat treatment in which successive weld beads impart a degree of stress relief to earlier deposits and a final, temper bead heat treats the last of the deposits required for strength purposes. Where thermal stress relief is impractical, or cannot be applied because the material's properties are likely to be altered unacceptably during the process, mechanical procedures can be employed such as

vibratory stress relief or peening. Vibratory stress relief[12] uses high amplitude, resonant vibrations to attenuate and redistribute residual stresses. Peening uses shot or beads,[13] or laser energy,[14] to produce compressive layers over regions of residual tensile stress to prevent the initiation of environmental cracks.

4. Vibrations can be transmitted from one item to another through connecting pipe work and/or supports and may promote high cycle corrosion fatigue and related damage mechanisms. One such example is where standby pumps are attached to the same plinth as the working pump, leading to failure to start on switch over, due to fretting of the bearings. Vibrations are controlled by specifying additional stiffening or support and/or by damping local resonant vibrations.

4.33.6 Mitigation of Risks Arising from Geography/Shape

There are limits to the degrees of freedom governing the geographic location of sites and/or equipment, but geography does exert some significant influences on corrosion risks and their mitigation. For example, marine corrosion is a well documented phenomenon, but the transference of designs from one global region to another requires that many items have to be reappraised for higher ambient temperatures and salinities in order, for example, to avoid crevice and pitting corrosion of stainless materials. Also, given the dependence of atmospheric corrosion upon temperature, relative humidity, rainfall and the presence or otherwise of pollutants, the location of equipment to avoid particularly damaging microclimates can provide significant mitigation of atmospheric corrosion risks. Of particular significance in this respect are the directions of prevailing winds and/or river/sea currents in relation to potential sources of pollutants. For example, in coastal locations, off-shore winds are preferable to on-shore winds and at any location it is preferable to be up-wind/stream rather than down-wind/stream of emissions from cooling towers, stacks and outflows.

Much more control is potentially exercisable at the design stage over the shape of equipment and this can provide significant mitigation of specific corrosion risks, particularly those that arise from poor drainage, the creation of crevices, the disturbance of flow in fluid transport and the condition of surfaces prior to coating:

1. The entrapment of fluids in equipment that is unable to drain completely results in corrosion risks that are usually mitigated readily by simple changes in shape, in some cases by the simple introduction of drainage holes. Some examples of good and bad design relating to the fabrication of steel sections and the drainage of tanks are shown schematically in Figure 10.
2. Crevices and their associated corrosion risks are to some extent inherent in components of complex shape but it is possible to control their severity or even eliminate them altogether by appropriate design and fabrication practices. Some examples of good and bad practices relating to flanged joints in piping systems are shown schematically in Figure 11. Evidently, crevices are inherent to the uses of threaded, or so-called socket-weld, flanges that present open crevices to the process fluid. In principle, the crevice can be removed in the case of the slip-on flange by seal welding the bore as depicted in Figure 11, but the best design is the so-called weld neck flange in which the flange is attached to the pipe with a butt weld, thereby eliminating the crevice. Figure 11 also illustrates how the use of undersized gaskets can create crevices in flanged joints that are eliminated by specifying gaskets of the correct size. Another classic source of crevices in process equipment is the ubiquitous tube/tube-plate joint in the shell and tube heat exchanger. Joints are conventionally fabricated by seal welding the tube into the tube-plate as depicted in Figure 12, followed by expansion of the tube onto the walls of the drilled hole in the tube-plate to reduce the severity of the crevice between them. However, as Figure 12 illustrates, it is virtually impossible to eliminate the crevice, and there remains a residual risk in fluids that are inherently prone to promote crevice corrosion, or where high heat fluxes into the crevice can create such fluids by superheating and concentrating the crevice liquor relative to the benign bulk fluid. In such cases, consideration might be given in design to locating fluids that might promote crevice corrosion on the tube-side of the exchanger. If this is impractical, the crevice can be eliminated, in principle, by back face bore welding of the tube/tube-plate joint, as depicted in Figure 12. However, this is an expensive, difficult procedure and residual risks are more usually mitigated by upgrading the tube and tube-plate materials. In compact heat exchangers in which thin plates or ligaments are

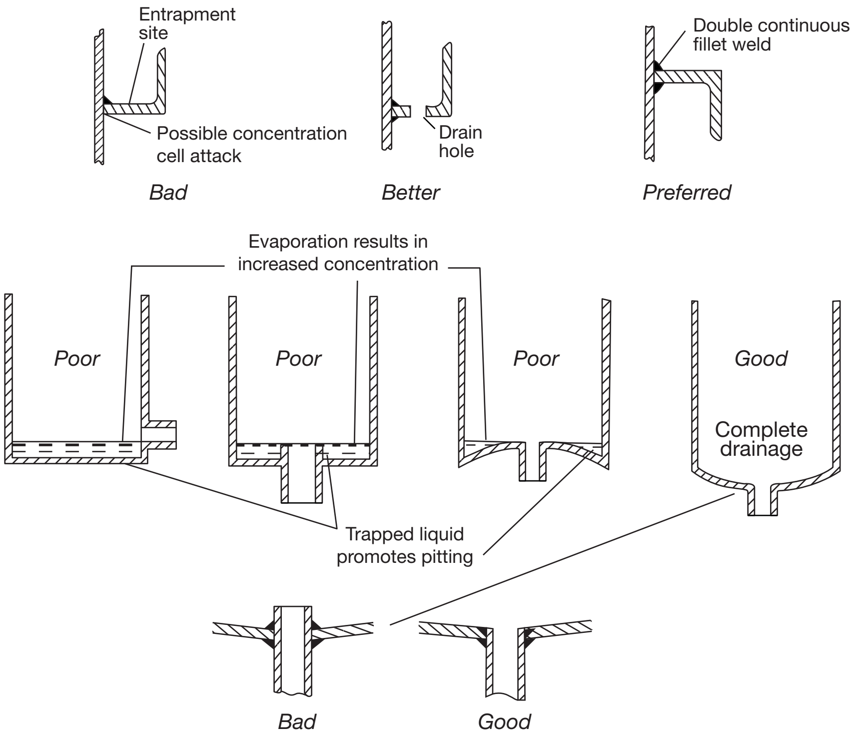

Figure 10 Examples of bad and good practices in avoiding the entrapment of fluids in structural steelwork and tanks. Adapted from Pludek, V. R. *Design and Corrosion Control*; Wiley: New York, 1976.

separated with very large areas of compression or welded joints, upgrading the material provides the only practical mitigation of crevice corrosion risks. Crevice corrosion risks can also arise at welds where lack of sidewall fusion or root penetration creates a crevice, and appropriate fabrication and inspection procedures must be implemented to prevent such defects.

3. Flow disturbance is a common source of local erosion–corrosion problems and it is avoidable by the appropriate design and fabrication of fluid transport systems. In many cases, the basis for designing against erosion–corrosion is the specification of limiting velocities for fluids that have been established by testing and/or experience as in the cases, for example, of cupronickel alloys in seawater[15] and carbon/stainless steels in concentrated sulfuric acid.[16]

However, geometric features of fluid systems can disturb and introduce local turbulences into flows as depicted in Figure 13 that illustrates schematically how protuberances, cavities, and abrupt changes in direction and cross section can all disturb streamline flows to introduce local turbulences and associated erosion–corrosion risks. Hydrodynamic considerations show that under typical attached turbulent flow conditions:

$$\tau_w = f/2\rho V^2$$

τ_w is the shear stress (Pa); f, the fluid to wall friction factor; ρ, the fluid density (kg m^{-3}); and V is the pipe average velocity (m s^{-1}).

The corrosion rate (CR) can be shown to be proportional to $\tau^{1/2}$ and it thus follows that:

$$\mathrm{CR} \propto (f/2)^{1/2}\rho^{1/2}V$$

An erosional velocity, V_e, may be defined:

$$V_e = C\rho^{1/2}$$

The constant C is a combination of fluid corrosivity, fluid to wall friction factor, material properties/chemistry (film strength), and pipe wall surface roughness. This is the basis for the arbitrary erosional velocity in API RP 14E[17] for multiphase fluids in oil/gas production, where C values of 100 indicate a shear stress range of 75–90 Pa. Once the flow becomes detached/separated as with multiphase slugging flow or down stream of flow disturbances, typified by those shown in Figure 13, the corrosion rate is

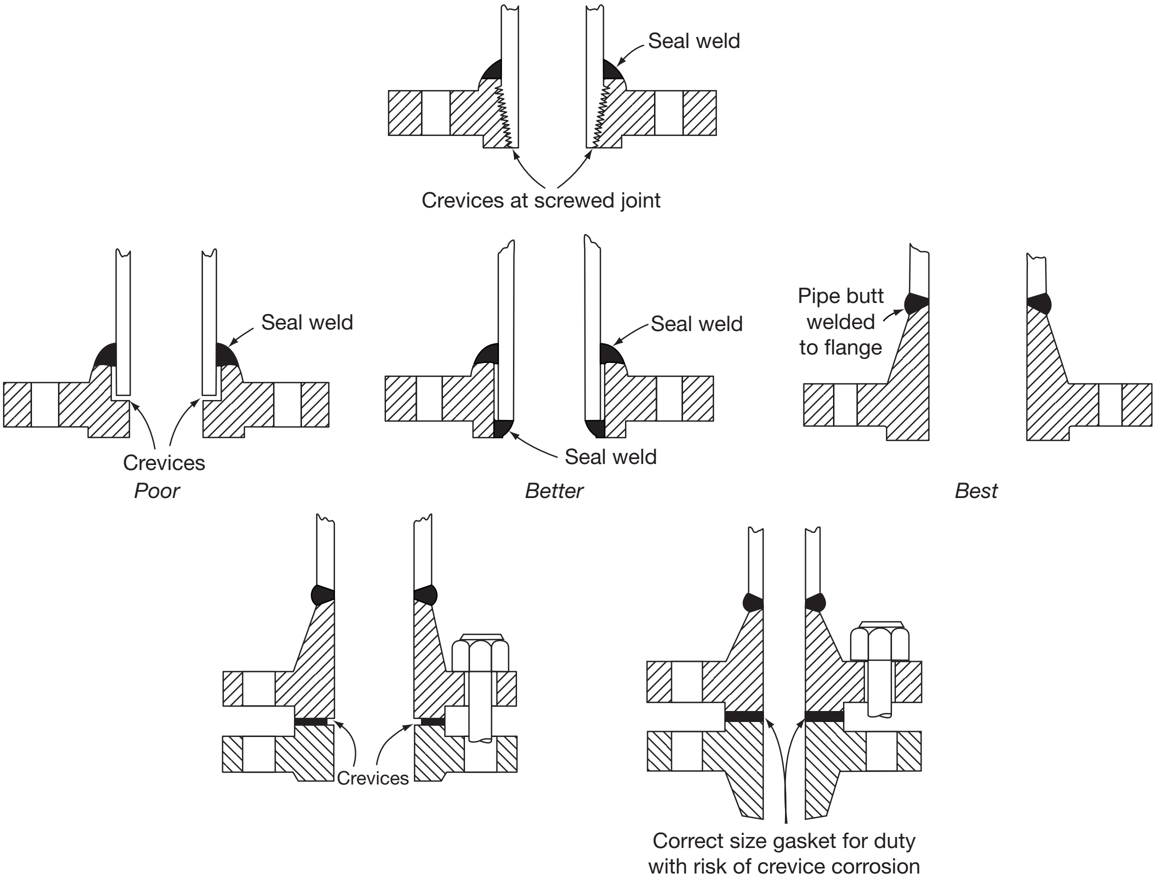

Figure 11 Examples of good and bad practices relating to the avoidance of crevices in flanged joints in piping systems.

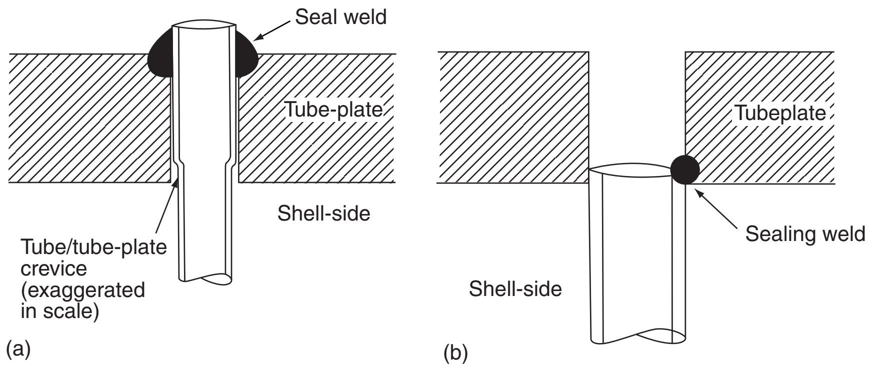

Figure 12 Fabrication practices that (a) reduce and (b) eliminate crevices in tube/tube-plate joints in tubular heat exchangers.

controlled by the turbulence intensity and is then proportional to the root mean square value of the shear stress, τ_{rms}. Many of these risks can be mitigated by good design and fabrication practices. Thus, it may be important in specific material/fluid combinations to use long radius bends/elbows and gradual changes in cross section in piping systems. Correct alignment of joints is important and gaskets or welds should be neither recessed nor protruding into the flow, either of which can introduce damaging flow disturbance.

Components that inevitably disturb flows, such as probes, valves, and orifice plates should be selected, sized, and located to minimize local and downstream turbulence. Thus, straight-through types of valve such as gate, butterfly, or plug valves disturb flows less than throttling, globe, and angle valves, and venturi tubes are preferable to orifice plates, as shown schematically in Figure 14. It is also good design practice to separate individual flow disturbers to prevent synergistic effects. For example, it is bad practice to locate an orifice plate or a control valve immediately upstream of a bend and much better practice to locate it at a significant distance upstream or even downstream of the bend as shown schematically in Figure 15.

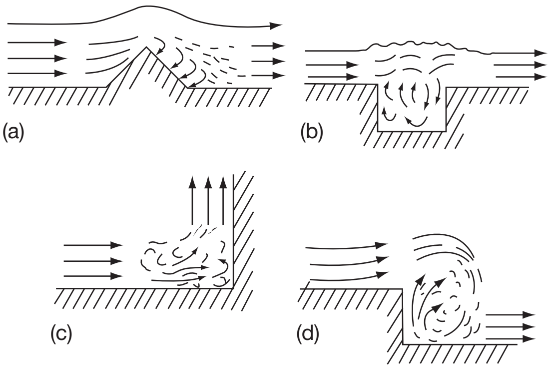

Figure 13 Effects of (a) protuberances, (b) cavities and abrupt changes in (c) direction and (d) cross section in disturbing streamline flows to introduce local turbulences and associated erosion–corrosion risks. Adapted from Pludek, V. R. *Design and Corrosion Control*; Wiley: New York, 1976.

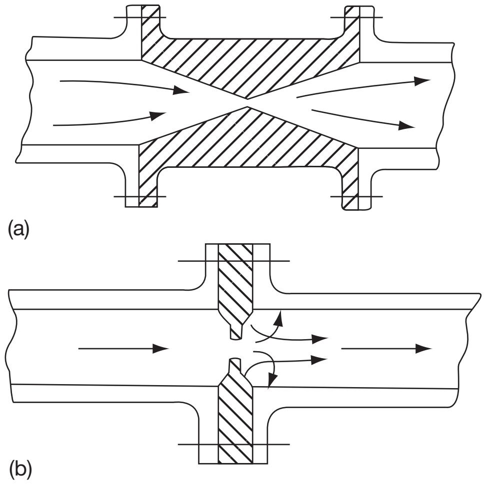

Figure 14 Flows are disturbed less by (a) venturi tubes than (b) orifice plates. Adapted from Pludek, V. R. *Design and Corrosion Control*; Wiley: New York, 1976.

4. Surface condition can influence vulnerability to some forms of localized corrosion. It is particularly significant in relation to the effectiveness coatings that may be used to mitigate corrosion risk for which cleanliness and surface profile are typically specified using internationally recognized standards[18] for blast cleaning to white metal (SA3) and near white metal (SA 2½,) as described in more detail in the chapters relating to coatings in this volume. Also important are good shapes and contours and removal of weld spatter, as illustrated in Figure 16, all of which should be specified for components that are to be coated.

4.33.7 Mitigation of Galvanic Compatibility Risks

Inevitably, equipment and components are constructed in a variety of materials, and the potential for galvanic interactions needs to be addressed in the design. Although the risk of galvanic corrosion is confined mostly to mixed metal systems, specific ceramic materials such as carbon, graphite and silicon carbide that are used, for example, in heat exchange and jointing systems, have electrical conductivities that are high enough for their potential contributions to galvanic corrosion to require evaluation. Corrosion risk evaluations should address components exposed to external and internal environments, including where moisture films can arise from leaks, splashes or condensation such as at fastenings and welds and electrical earth bonding straps that are bolted, brazed, or welded to structural elements since lack of electrical continuity can have significant safety/instrumentation implications.

The various, published galvanic series of materials have been obtained in specific environments, mostly seawater, and are of limited use in assessing galvanic corrosion risks in other fluids that may have very different conductivities, tendencies to promote passivity on specific materials, etc. However, as a general rule, it is good design practice to avoid material combinations that are widely separated in such series, and in particular to avoid unfavorable area ratios involving small areas of active, anodic material such as fasteners or weld filler metals coupled to larger areas of noble, cathodic material.

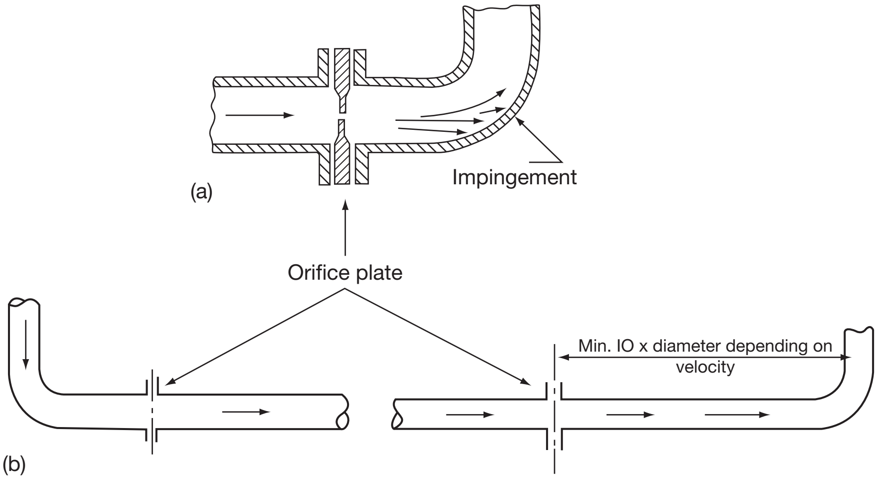

Figure 15 Locating orifice plates and other flow disturbers too close to bends, as in (a), introduces additional risks that are mitigated by (b) downstream, or distant upstream locations. Adapted from Pludek, V. R. *Design and Corrosion Control*; Wiley: New York, 1976.

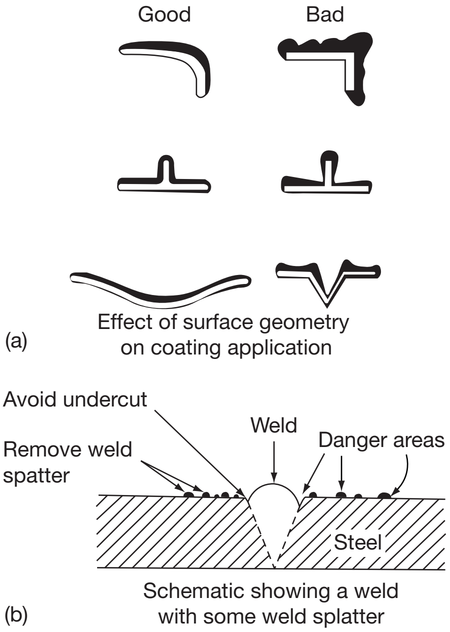

Figure 16 Effective coating requires (a) smooth shapes and contours and (b) removal of weld spatter. Adapted from Pludek, V. R. *Design and Corrosion Control*; Wiley: New York, 1976.

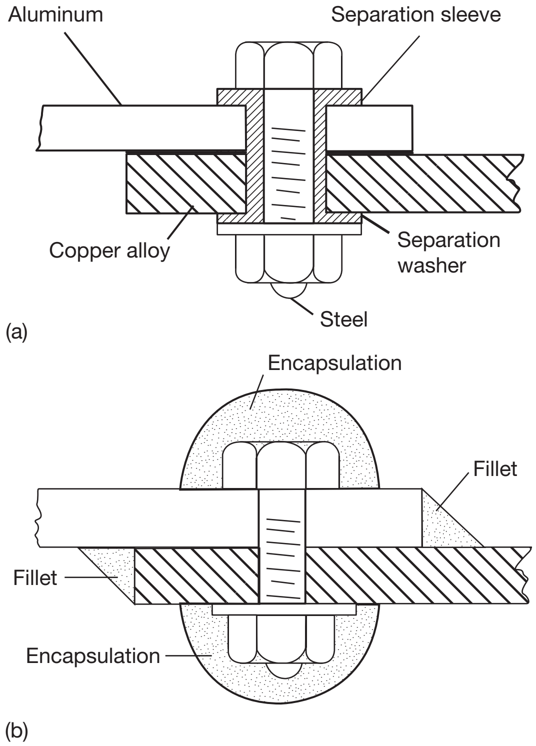

Figure 17 Elimination of galvanic interactions in fasteners by (a) electrical isolation and (b) encapsulation. Adapted from Pludek, V. R. *Design and Corrosion Control*; Wiley: New York, 1976.

Where combinations of materials that present galvanic corrosion risks are unavoidable, mitigation is provided by:

1. Isolation with dielectric sleeves and washers, as shown schematically in Figure 17. Where mitigation is dependent on electrical isolation, this may be frustrated by remote earthing through steel supports, pipe hangers, etc.
2. Encapsulation to exclude the environment, as shown schematically in Figure 17.
3. Coating, preferably of both couple members. If only one can be coated, it should be the noble, cathodic member.

4. Physical separation of couple members to attenuate galvanic interactions, such as at material breaks in piping systems where risks can be mitigated by using insulated spool pieces of appropriate length made from fiber reinforced plastic, or a coated, more noble couple member, as illustrated in Figure 18.
5. Cathodic protection, application of which overrides the spontaneous couple interactions providing protection to both, as in the protection by sacrificial anodes of the steel water boxes of seawater coolers that would otherwise corrode rapidly due to galvanic coupling with the more noble tube materials.

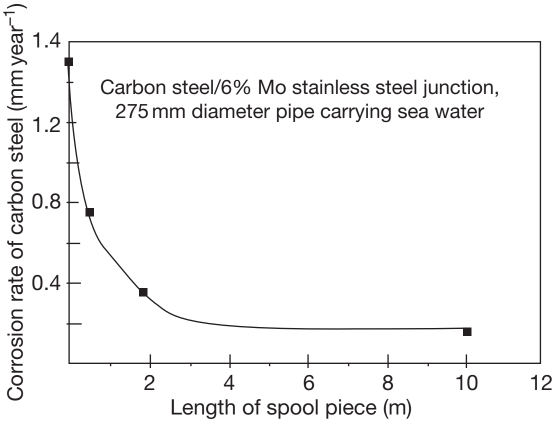

Figure 18 Corrosion rate of carbon steel in seawater at a pipe junction with 6% Mo stainless steel as a function of the length of an intervening, insulating spool piece, adapted from Francis, R. *Galvanic Corrosion: A Practical Guide for Engineers*; NACE International: Houston, TX, 2000.

Francis's book is an excellent source of guidance on good practice for the mitigation of galvanic compatibility risks.[19]

4.33.8 Management of Corrosion Risks within the Design Process

The previous sections have reviewed the major inputs/outputs needed to mitigate corrosion risks through attention to detailed thermomechanical and process design issues that may otherwise introduce uncertainty and consequential costs to a project. However, further risks arise from poor control of the management of the design process itself, in particular the effectiveness with which corrosion risks are addressed and appropriate mitigation procedures are implemented within the project design team.

Corrosion management processes and systems are reviewed in a separate chapter in this volume. In keeping with any management process, corrosion management relies on a series of steps using suitable systems, tools and teams, based on standard, international systems for quality, risk, and safety management, as summarized in Figure 19. Various tools are available for specific project stages, such as corrosion risk assessments, corrosion mitigation tactics, and regular formal reviews/audits of corrosion mitigation and management systems. Appropriately staffed, multidisciplinary corrosion teams need to be established and performance indicators adopted that have been developed to ensure that actions are carried out as recommended.

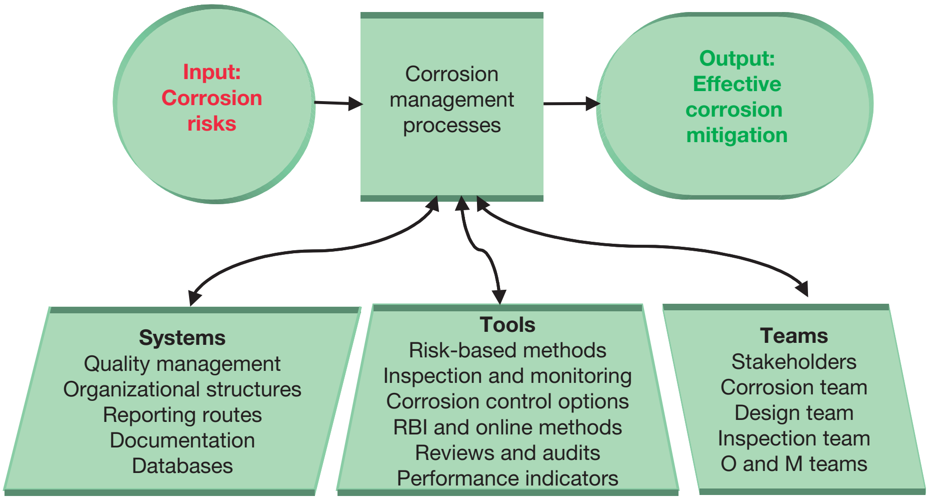

Figure 19 The corrosion management process.

A corrosion management system should operate simultaneously at various levels, and include:

1. An overall management structure, process, and policy to deal with corrosion issues.
2. Procedures and documentation for engineers and managers with responsibility for corrosion as part of the corrosion strategy or plan.
3. Specification and use of clearly defined tactics based on proven corrosion mitigation practices.
4. Provision of means for the collection and assessment of equipment inspection and monitoring data as part of the operating, maintenance and safety procedures.
5. A system to audit corrosion related activities on a regular basis.

The management of corrosion risk mitigation during the design, procurement, and construction phases of a project requires a formal system that includes measurement and monitoring of the performance of the corrosion management aspects of the overall design system by defining:

1. The objectives of the corrosion control program, be it to reduce risks and/or costs, to promote life enhancement, to define end-of-life strategies, or whatever.
2. Nominated responsibility and accountability for the various components of the program.
3. External sources of acceptable corrosion data, its interpretation to provide trends, and the location and format of a corrosion database.
4. When corrective actions should be implemented, and who is responsible for actions on a day-to-day basis.
5. The duration of the program and when it will be updated.
6. A management-of-change procedure.

This leads to an obvious need for suitable organizational and reporting systems, operating through appropriate documentation and database systems, which provide evidence, for example, that:

1. design engineers are aware of potential corrosion risks associated with the proposed design;
2. advice has been obtained from qualified corrosion specialists where appropriate;
3. suitable corrosion control procedures have been introduced at an early stage in the design;
4. corrosion appraisals have taken place throughout the design process;
5. two or more of the appraisals during design are formal corrosion audits, the first to be undertaken towards the end of the conceptual/early design stage and the second towards the end of the engineering design/detailing stage;
6. hold points for corrosion audits are introduced into quality plans at critical stages of design, manufacture, construction, installation, or application;
7. guidelines, specifications, and QA/QC procedures are available for the construction, operation, and maintenance phases;
8. plant and equipment items, including units and components, supplied by subcontractors have been subjected to appraisals and audits similar to those carried out for the major plant and equipment items.

In order to ensure that such systems perform effectively, they need to be reviewed and formally audited on a regular basis.[20,21] Performance should be assessed against agreed key performance indicators (KPIs), which for the corrosion team leader during the design process, might typically include:

1. ensuring that cost effective corrosion control is employed;
2. ensuring that appropriate corrosion risk assessments and sensitivity studies are conducted;
3. reviewing all corrosion related documentation;
4. reviewing corrosion related records to assess conformance and reporting out of compliance when necessary;
5. tracking specific procedures and processes to ensure compliance include competency of responsible individuals, departments and organizations and correct implementation, reporting and reaction;
6. ensuring that changes are implemented and incorporated into corrosion-relevant procedures and processes;
7. ensuring that new materials and corrosion control methods are evaluated.

The development and use of performance measurement/KPIs together with the use of regular reviews and audits of the corrosion management system using a formal and transparent framework should ensure that the management of corrosion risk mitigation becomes an integral and effective part of the overall design process.

In the conceptual and early design stages of a project the role of the design team involves:

1. assessment of the technical brief and initial engineering concept;
2. control of costs/budgets within overall economic constraints;

3. production of a technical solution for the project;
4. control of safety, health and environmental (SHE) risks within acceptable limit boundaries;
5. incorporation of corrosion mitigation to deliver the required equipment life.

Risk-based methods are now used routinely to evaluate financial and engineering uncertainties at this stage and are also applied to the evaluation of corrosion risks. They are iterative processes using well-defined steps to support decision-making by providing greater insight into risks and their consequences. They can be used not only to identify undesired and/or unexpected outcomes but also to assess opportunities provided by novel or modified designs. In the conceptual and early design stages, corrosion appraisals would typically include:

1. proposed design and type of construction of equipment items;
2. environments – internal and external, transient and steady state;
3. likely materials;
4. significant corrosion risks and associated SHE and/or financial consequences;
5. proposed corrosion risk mitigation strategies such as protective coatings, corrosion inhibition and anodic or cathodic protection.

The assessment of environments and selection of likely materials are described in the separate chapter on materials selection for corrosion resistance in this volume. Corrosion risks to equipment items would normally be assessed using a qualitative risk analysis (Level 1) that provides a simple ranking of equipment or, in the case of items at higher risk from corrosion, a more rigorous evaluation using a semiquantitative risk analysis (Level 2), a more accurate prioritization that retains vital inputs of a Level 3 analysis but with simplifying assumptions. Only at a later design stage or with highly critical items would a quantitative corrosion risk analysis (Level 3) be employed, which is an in-depth study including assessment of reliability, financial and limited environmental issues. Level 2/3 corrosion risk assessments often employ a risk matrix approach where the likelihood of corrosion is compared against the consequences. In the case of complex installations such as chemical and petrochemical plant, where risk-based inspection is to be employed in service, the assessment of equipment at this stage provides the basis for the initial specification of inspection intervals for equipment.

One of the tools used routinely and effectively in design projects is a series of hold points where key risks and their mitigation are addressed and reviewed/audited by appropriate procedures, as in the case of HAZOP studies of SHE issues in the process industries, or in third-party reviews of major civil engineering designs. The aim is to manage not only technical issues and ensure compliance with codes and standards but also to manage human responses and actions such as ensuring that any changes are checked and approved by suitably experienced specialists as part of a management of change procedure. These overarching risk management procedures are very effective vehicles for the management of corrosion risks and their mitigation.

At the engineering design/detailing stages, corrosion risks rarely arise from inadequate basic design or initial materials selection, but from deficiencies in the detailed design or poor provision of information for certain aspects of the construction, operation and maintenance of the equipment. These are essentially quality control issues that should also be addressed by appropriate reviews/audits of the design. Data sheets and drawings are best addressed with checklists that cover the detailed issues summarized in **Figure 2**. The compilation of such lists will depend on the industry and the type of project. For example, API 570[22] is a qualitative risk analysis approach used in the petroleum industry for guidance on areas/locations subject to corrosion damage and the need for inspection. It also identifies specific features that are susceptible to high rates of corrosion attack or cracking which require attention during design such as injection points, deadlegs, surfaces beneath insulation, linings and deposits, etc. Another publication[21] compiled by the UK offshore oil/gas industry addresses the impact of corrosion on integrity issues in existing facilities, in particular the management of external marine corrosion on support structures, walkways, cable trays, etc. and it provides many illustrations of typical damage which are instructive to designers of new facilities.

Sufficient information must be provided in the final specifications and drawings to enable the development of plans for construction, fabrication and manufacture of all items and components. The final reviews/audits of the detailed engineering design may require modifications or revisions and should anticipate that corrosion control in completed facilities can be adversely affected by poor workmanship and site damage. These effects can be minimized by correct supervision and inspection based on frequent QA/QC reviews of all aspects of construction and commissioning as part of the design. These checks and inspections should be specified in the final design as to be carried out on a regular basis as part of organized appraisals and must include agreed reporting procedures and means of implementing corrective actions to minimize future problems.

It is important that recommendations and specifications with regard to corrosion mitigation should not be negated during the construction phase of a project. The contractor typically undertakes procurement of construction materials and equipment, vendor assessment and commissioning of associated plants. The detailed design stage corrosion audit should have already addressed those aspects associated with required reliability, maintainability and ease of construction as prescribed in detail in the contract documents and specifications. The aim should be to ensure that procedures used during manufacture and construction do not jeopardize the longer term corrosion control requirements of the design. The overall priority must be with the project life cycle and associated SHE issues and not with minimizing construction time or costs. Some typical examples of such issues are as follows:

1. The shape of items should not be changed in a manner that might reintroduce corrosion risks.
2. Installed pipework should be self-cleansing to prevent deposit build-up (minimum velocity) and self draining to prevent pooling during shutdown.
3. Bend radii, changes of section, etc. should be as per design to mitigate erosion corrosion risks.
4. Specified impingement/wear plates should be installed.
5. Adequate access for inspection and maintenance should be provided.
6. Chemical cleaning and passivation procedures should be undertaken in strict compliance with specification.
7. Shapes, contours, surface preparation, and cleaning should be as per specification on surfaces that are to be coated.
8. Weld spatter should be removed and weld protrusions ground to specification.

In conclusion, problems often occur in operation because of failure to apply good management practices during the design process to the deployment of good technical practices, many of which have been codified in industry standards, recommended practices and guidelines. The corrosion management practices described in this section should do much to improve the deployment of resources to achieve project design objectives and the implementation of specific solutions to maximize the effectiveness of corrosion mitigation tactics.

References

1. Ashby, M. F. *Materials Selection in Mechanical Design*; Butterworth Heinemann: Oxford, 2005.
2. Kennedy, I. Design and specification for reliability and maintanability; Presented at National Tribology Course on Reducing Plant and Equipment Life Cycle Costs; 24 November 1994.
3. Pludek, V. R. *Design and Corrosion Control*; Wiley: New York, 1976.
4. Landrum, R. J. *Fundamentals of Designing for Corrosion Control*; National Association of Corrosion Engineers: Houston, Texas, 1989.
5. Ohtsu, T.; Miyazawa, M. Corrosion 2007; NACE International: Houston, Texas, 2007; Paper 07266.
6. Brubaker, S. K. In *ASM Handbook Vol. 13C Corrosion: Environments and Industries*; ASM International: Materials Park, Ohio, 2006; pp 659–667.
7. Cox, W.; Huijbregts, W.; Leferink, R. *ASM Handbook Vol. 13C Corrosion: Environments and Industries*; ASM International: Materials Park, Ohio, 2006; pp 491–496.
8. Crude Unit Overhead Corrosion Control; Refining Industry Corrosion Information Compilation Series; NACE International: Houston, Texas, 2001.
9. Ahluwalia, H. *ASM Handbook Vol. 13C Corrosion: Environments and Industries*; ASM International: Materials Park, Ohio, 2006; pp 654–658.
10. Mann, G. M. W. *Br. Corros. J.* **1977**, *12*, 6–14.
11. Ross, T. K. *Br. Corros. J.* **1967**, *2*, 131–142.
12. Claxton, R. A.; Lupton, A. *Weld. Metal Fabricat. (UK)* **1991**, *59*, 541–544.
13. Ni, H.; Ling, X.; Peng, W. *J. Chin. Soc. Corros. Prot.* **2005**, *25*, 152–156.
14. Hammersley, G.; Hackel, L. A.; Harris, F. *Optics Lasers Eng.* **2000**, *34*, 327–337.
15. Copper Nickel Fabrication; Publication 139; Copper Development Association, 1999.
16. *Materials Selector for Hazardous Chemicals Vol. 1: Concentrated Sulphuric Acid and Oleum*, 2nd edn.; MTI Publication MS-1, Materials Technology Institute of the Process Industries Inc.: St. Louis, Missouri, 2005.
17. *API Recommended Practice RP14E: Design and Installation of Offshore Production Platform Piping Systems*; American Petroleum Institute: Washington, 1991.
18. SS-EN ISO 8501–1:2007: Preparation of steel substrates before application of paints and related products – Visual assessment of surface cleanliness; Swedish Standards Institute: Stockholm, 2007.
19. Francis, R. *Galvanic Corrosion: A Practical Guide for Engineers*; NACE International: Houston, Texas, 2000.
20. Guidance for Corrosion Management in Oil and Gas Production and Processing; Energy Institute: London, May 2008.
21. OTO 2001/44: Review of corrosion management for offshore oil and gas processing; Health and Safety Executive, 2001.
22. API Document 570: Inspection, repair, alteration, and rerating of in-service piping systems; American Petroleum Institute: Washington, 1998.

4.34 Risk Based Inspection

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Abbreviations

AIM	Asset integrity management
ALARP	As low as reasonably practicable
HAZOP	Hazard and operability study
RBI	Risk-based inspection
TML	Thickness measurement location
UK HSE	United Kingdom Health & Safety Executive
UTW	Ultrasonic wall thickness measurement

4.34.1 Introduction

Until fairly recently, the structural integrity of most engineered structures has been assured by two factors:

- Design in accordance with codes or rules incorporating empirical safety factors.
- In-service inspection to provide assurance that no accidental or unanticipated damage has occurred.

However, it is only prudent to accept that operational loads may vary beyond design levels, and material degradation may be greater than anticipated. The safety factors used at the design stage may not, therefore, guarantee through-life structural integrity. Hence, periodic inspection is also carried out to determine the actual levels of damage, and to check the adequacy of the design loads and resistance values.

There is a widely held view that prior to the emergence of risk-based inspection (RBI) as a process for planning inspections, specifically of pressure containing equipment, all inspection activity was conducted on a time basis, that is, at regular set intervals. These intervals would vary according to the type of equipment, its service, and any specific national regulations that applied. This, of course, is generally not entirely true!

RBI has been practiced by engineers responsible for integrity management since the very first time an inspection budget, or the time allowed for inspection, did not cover the entire plant. Engineers were forced into a position where they had to decide between inspecting one thing or another. In almost all cases, that decision would be made on the basis of a perceived risk. In this case, the specific risk of concern is that of loss of integrity due to structural failure. RBI as we know it today is a means of formalizing that decision process such that it becomes consistent, transparent, and fully auditable.

Both design and inspection strategies must take account of the risk of structural failure: that is, both the probability of failure and its consequences need to be considered. Using traditional approaches to inspection planning, risk tends only to be considered implicitly and is not quantified in an auditable manner. There is thus real concern that high-risk and low-risk areas will not be clearly identified. This may then mean that low-risk areas are inspected to an excessively high level (leading to needlessly high inspection costs), while high-risk areas may not all be afforded sufficient attention and priority. Without the explicit and rigorous consideration of risk, it may not therefore be possible to demonstrate that the structural integrity of the plant has been satisfactorily characterized.

An inspection strategy based on risk avoids the inadequacies of the traditional approach. The concept of risk takes into account, not only the probability, but also the consequences of structural failure. These may encompass consequences in terms of lost profits, repair and compliance costs, human casualties, and environmental clean up costs. Such a strategy ensures that inspection effort is targeted appropriately to optimize costs and benefits, and provides an auditable demonstration that this has been done with due diligence.

With such an emergent technology, there are many ways in which the objectives can be achieved. The methods available vary in cost, quality, and detail and operators can experience difficulty in selecting a methodology which is fit-for-purpose. This review aims to summarize the concepts, technology, and currently available approaches and the advantages and disadvantages of each.

4.34.1.1 What is Risk?

In order to be clear about what RBI really is, it is first necessary to gain an understanding about what ‘risk’ is in this context. The term is used in common parlance to describe a range of features of a real or postulated event. For example, ‘risk’ may be used to indicate the likelihood of an event or perhaps even to describe the consequences of the same event. If used correctly the term should describe both. The situation is further complicated by the use of the term ‘hazard’ as applied in hazard and operability studies (HAZOPs). ‘Hazard’ and ‘risk’ are used interchangeably in everyday vocabulary.

The UK Health & Safety Executive has sought to make a conceptual distinction between a ‘hazard’ and a ‘risk’ by describing a ‘hazard’ as[1]

> the potential for harm arising from an intrinsic property or disposition of something to cause detriment

and ‘risk’ as

> the chance that someone or something that is valued will be adversely affected in a stipulated way by the hazard.

Accepting this distinction it follows that risk in the context of RBI is the product of the chances and consequences of a structural failure. It also follows that the management of risk in this context has three components:

- hazards must be identified;
- risks they give rise to should be assessed;
- appropriate control measures should be introduced to address the risks.

Additionally, and because of the way in which we define risk, it is both convenient and commonplace to divide risk into three categories:

- safety risk, that is, risks to people's lives and health;
- environmental risk, that is, risk to the environment, for example, pollution, effects on marine life, etc.;
- business or economic risk, that is, risk of lost production/revenue.

These are all the things that we value and could be affected adversely if structural failure occurred.

4.34.1.2 Who is Responsible for the Management of Risk?

The public accepts that we need to continue to operate hazardous plant and equipment in order to manufacture products which are a vital part of modern life, for example, gasoline, diesel, plastics, pharmaceuticals, etc. However, as part of their review of this subject within the United Kingdom,[1] the Health & Safety Executive observed that this acceptance is moderated by expectations that:

- those responsible for the hazards should ensure that adequate measures are taken to protect people from the harmful consequences that may arise from such hazards; and
- the State should be proactive in ensuring that its arrangements for securing the protection of people from risks are adequate and up to date as distinct from reacting to events; and that those arrangements should address, as necessary, the concerns to which the hazards give rise.

This clearly puts responsibility for management of risks into the hands of organizations who own and operate hazardous installations. It is this line of thinking that has led many parts of the world to the conclusion that regulations need to reflect responsibility for risk management. As such, there has been a move away from prescriptive time-based inspection (inspection being a risk management activity) to inspections based on an understanding of the level of risk represented by each part of any hazardous installation.

4.34.1.3 The Structure of a Risk Management Program

The UK Health & Safety Executive's report on how it comes to decisions on risks[1] outlines six stages in the decision-making process:

- deciding whether the issue is primarily one that can impact safety and health;
- defining and characterizing the issue;
- examining options available for addressing the issue, and their merits;
- adopting a particular course of action for addressing the issue efficiently and in good time, informed by the findings of the second and third points above and in the expectation that as far as possible it will be supported by stakeholders;
- implementing the decisions;
- evaluating effectiveness of actions taken and revisiting decisions and their implementation if necessary.

Figure 1[2] illustrates the process of RBI.

It is clear from Figure 1 that an RBI process encompasses all the aspects of a risk management program as defined above. The focus of risk management is also clear, that is, asset integrity.

4.34.1.4 The Role of RBI in Asset Integrity Management

Hazard management of large industrial facilities is a complex process which is active at each of the six key stages in the asset life-cycle (i.e., design, construction and hook-up, commissioning, operation, modification, and decommissioning).[3] The primary process in hazard management is considered to be asset integrity assurance.

Asset integrity management (AIM) of a large industrial facility encompasses three essential elements, as shown in Figure 2.

These elements may be defined as follows:

> *Mechanical integrity* is the ability of the asset to withstand the design loadings (i.e., design pressure/stress, design temperature, etc.). It is primarily concerned with structural integrity, pressure containment, and leak tightness, and focuses on pressurized equipment, piping systems, and major structures.
>
> *Functional integrity* is the ability of the asset to perform its required function effectively and safely. It is primarily concerned with the reliability of safety critical elements such as emergency shutdown systems, critical process control systems, and hazard mitigation systems (e.g., gas/fire detection systems, fire fighting systems, etc.).
>
> *Operational integrity* is the ability of the asset personnel to operate the facility safely and effectively. It is primarily concerned with human factors such as competency, management systems, reporting systems, anomaly management, etc.

Several risk-based methods are employed in hazard management of large complex plants. RBI is the use of risk assessment to formulate and prioritize inspections

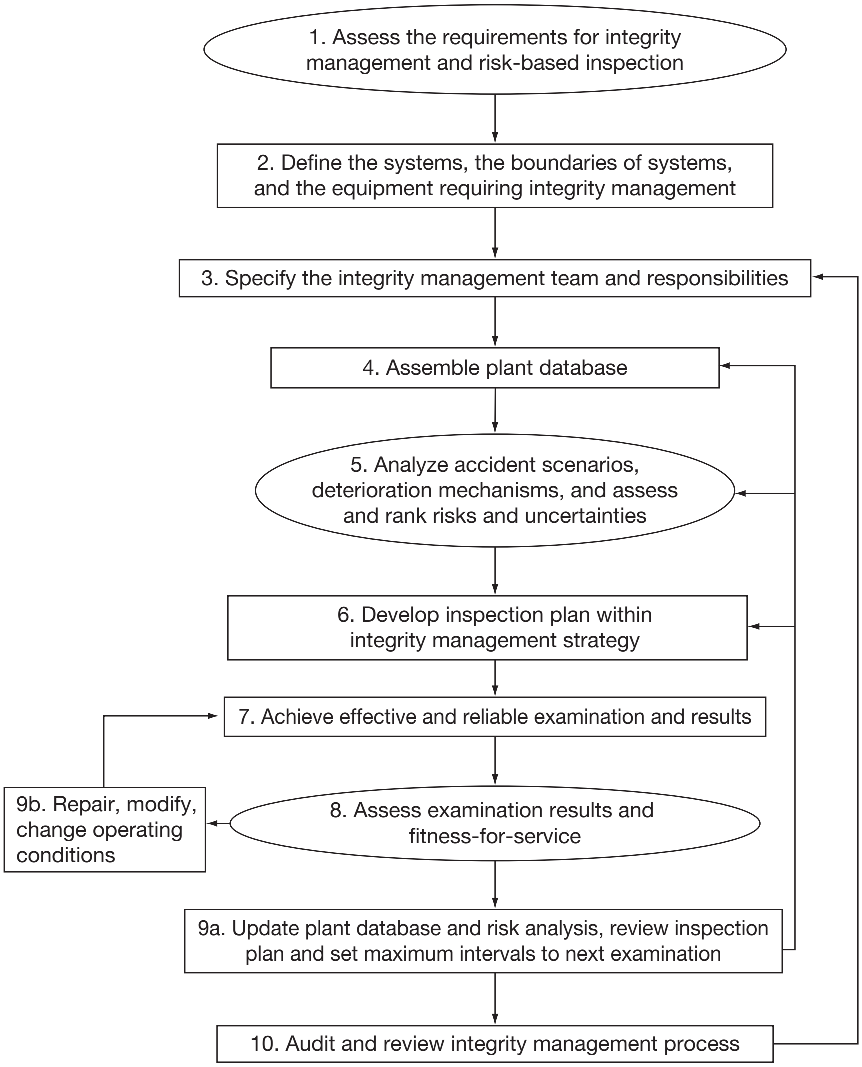


Figure 1 Risk-based inspection (RBI) process.

of pressure vessels, piping systems, and pressure safety valves. Its primary concern is mechanical integrity. Figure 3 shows the role of RBI within a typical AIM system for an oil and gas production facility.

4.34.1.5 Types of Risk Assessment

Risk assessment methodologies may be defined in terms of the nature of the assessment performed. Three terms in common usage are qualitative, semi-quantitative, and quantitative risk assessment.

These three assessment techniques are broadly aligned with three different strategies in the performance of risk evaluation, which include expert judgment, rule-based analysis, and quantitative calculation.

4.34.1.5.1 Qualitative RBI

Qualitative RBI is based on the results from a qualitative risk assessment, which is usually executed through expert judgment. Normally this would employ an expert, multidisciplined team, with representatives from all relevant engineering disciplines, including materials/corrosion, mechanical, process, operations, maintenance, and safety engineering. Risk assessment would be performed through discussion, with the team agreeing on the likelihood of failure and the resulting consequence.

Expert judgment can be the result of informal or formal processes.[4] It is necessary to distinguish between formal, expert judgment and informal expert judgment processes – the latter being the way expert judgment has traditionally been used during RBI assessments. Expert judgment has been used in analysis and assessments in informal ways, through the expert's implicit and undocumented reasoning, inferences, and scientific knowledge.

The advantages of this risk assessment technique are that it is relatively easy to perform and can incorporate lessons from the plant experience gained by experts present on the team.

More recent formal uses of expert judgment exist that are explicit, structured, and well documented. They aim to bring out assumptions and reasoning that are at the base of a judgment, to quantify and document it so that others can appraise it. Although formal judgment can be resource consuming (in terms of cost and time) and appear less flexible and creative than informal judgment, it brings out a deeper understanding of the issues, drawing out diverse opinions. This can reveal areas of disagreement or agreement with increased possibility of a solution. Furthermore, formal judgment gives access to all aspects of the analysis (assumptions, models, data, expert's thinking) and provides the possibility for others to review the process of judgment.[4] One UK HSE study that examined RBI in practice[5] found a lack of transparency in parts of the RBI decision making process indicative of informal expert judgment. It seems therefore that the natural development of qualitative RBI assessment will be to move to a formalized expert judgment method in the future.

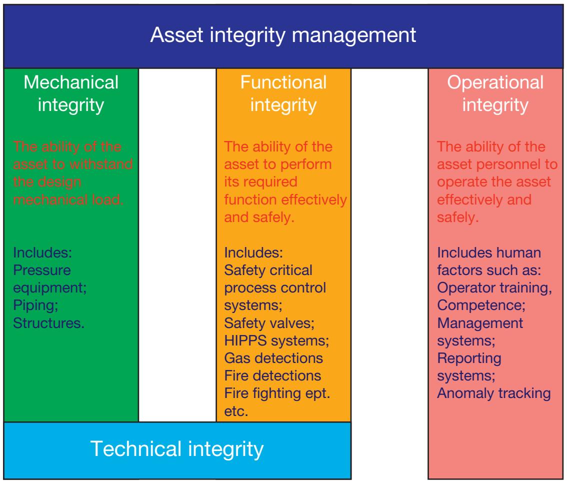


Figure 2 Essential elements in AIM.

The main disadvantages of the technique in both its informal and formal modes are inconsistency (less so for formal expert judgment), cost, and speed. As each item needs to be discussed in detail, assessments are never rapid and this has the effect of pushing up costs simply because of the consumption of large volumes of expert's time. It should also be noted that the next time the RBI team is assembled in order to conduct the review process, any change to the team line-up introduces another element of variability that can affect the outcome of the assessment.

4.34.1.5.2 Quantitative RBI

Quantitative RBI is based upon a quantitative risk assessment. It results in fully quantified absolute failure probabilities and consequences specific to the

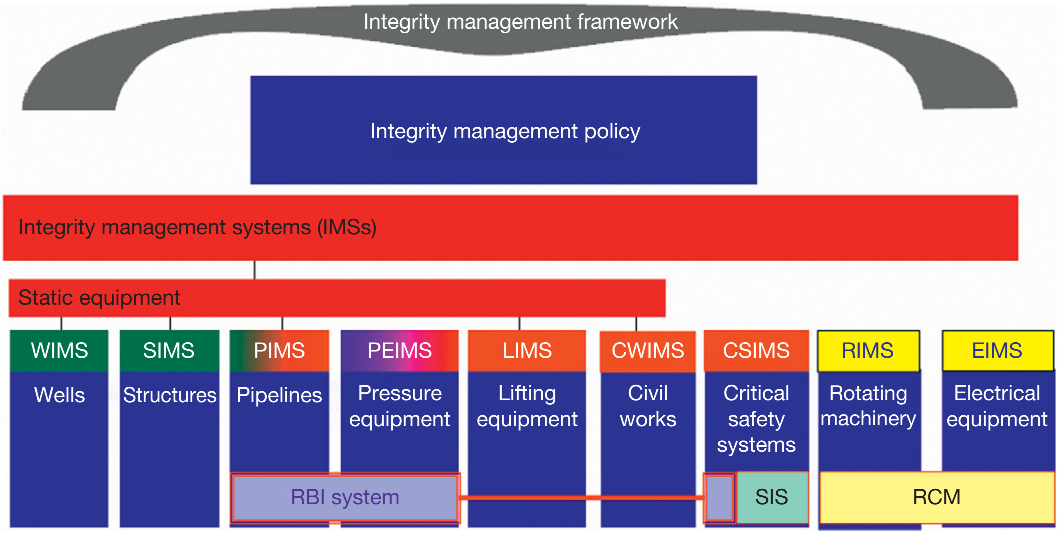


Figure 3 The RBI in the asset integrity framework.

item under consideration and using only the attributes of that specific item.

Robust consequence of failure calculations should consider the influence of each chemical constituent of each process fluid. The assessment should model the dispersion of each chemical constituent, and assess its contribution to failure scenarios such as explosion, flash fire, pool fire, toxic release, overpressurization, pollution, etc.

Robust likelihood of failure calculations should include accurate predictive, often probabilistic modeling of all damage mechanisms, regardless of their 'perceived' likelihood.

The advantage of the quantitative method of risk assessment is accuracy; the major disadvantage is that the process is extremely slow and has extremely challenging data requirements.

There are a number of reportedly 'quantitative' methodologies available, including the API level III assessment.[6] However, all these techniques fall short of a truly fully quantitative assessment. First, they normally rationalize the process fluid into a 'representative fluid' which, necessarily, does not represent all chemical constituents present. For instance, API 581 allows for 17 different representative fluids,[7] which includes C_9–C_{12}, C_{13}–C_{16}, C_{17}–C_{25}, H_2, and H_2S as separate 'representative fluids', but never considers combinations of the same. Clearly, this could be a significant limitation. For example, in a refinery hydroprocessor plant, where the process stream consists of 50% H_2, with the balance being hydrocarbons and H_2S, the calculations would only quantify 50% of the actual release.

Secondly, many 'fully quantitative' techniques only quantify damage mechanisms that are selected for assessment in a preassessment phase, which is normally qualitative in nature. Thus, the assessment is selectively quantitative, rather than fully quantitative, and is reliant upon the expert correctly identifying appropriate damage mechanisms to assess.

4.34.1.5.3 Semiquantitative RBI

Semiquantitative RBI employs simplified quantitative assessment models to derive pragmatic risk ranking for components within a pressure system. It should be noted that the term 'semiquantitative' refers to an assessment methodology that seeks to quantify all deterioration mechanisms and consequence scenarios, albeit in a simplified manner that requires less data than a fully quantitative methodology. Semiquantitative RBI does not include systems which quantify some aspects and usequalitative judgment for other aspects.

4.34.1.6 The Matrix

At this point in the review, having just discussed the qualitative, semiquantitative, and quantitative methods of assessment, it is appropriate to examine the means by which the results of the risk assessment phase of an RBI study are presented, that is, the risk matrix.

The matrix has been the cause of much debate since RBI was first used. Questions of what size it should be, that is, 3 × 3, 4 × 4, 4 × 5, 5 × 5, and whether or not it should be 'skewed' are often the subject of discussion.

The answers to these questions are intrinsically linked to two features of RBI:

- which methodology you choose;
- the data with which you have to work.

First, consider fully quantitative RBI. Figure 4 presents the type of results you might expect to generate.

Each red dot represents an individual assessment for a uniquely identifiable item of equipment or piping. Three regions are clearly marked.

- *Acceptable*: The evaluated risks are acceptable.
- *ALARP*: The identified risks should be maintained as low as reasonably practicable. These risks need active risk management, for example, inspections, monitoring, maintenance, etc.
- *Unacceptable*: These risks cannot be tolerated. The owner of the risk should either introduce engineered mitigations or redesign the equipment to mitigate the risk.

Failure probability is expressed as a number between zero and one and is often the result of very detailed probabilistic assessment taking into account details of the various potential failure modes and the

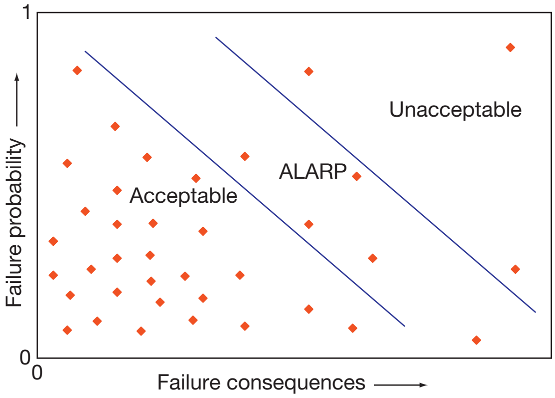


Figure 4 Illustration of results from a quantitative RBI study.

material/structural response at every stage of the degradation process. Failure consequences are often expressed in currency terms but may also include expected number of fatalities or injuries caused by a failure. Full dispersion, blast and fire modeling are required, together with financial modeling and environmental impact assessment for every postulated failure.

The amount and quality of data required to conduct this type of assessment is prohibitive in terms of normal budgets available. The solution to this problem is to apply an approximation to the fully quantitative methodology. The approximation is the matrix approach. **Figure 5** illustrates the concept of a matrix superimposed on fully quantitative results. In this case, a simple 3 × 3 matrix is shown.

It is immediately apparent that the matrix approach seeks to define broad bands of failure probability and consequences into which individual risks can be assigned. This can be done qualitatively by expert judgment as discussed above, by simply assigning a high, medium, or low score to each identified risk. Alternatively, rules can be used to assign the categories in a semiquantitative manner.

The 3 × 3 matrix has a couple of significant disadvantages.

- The resolution is not sufficient to deliver improvements in inspection planning that can be achieved by using narrower bands, that is, the bands are too wide to distinguish between equipment that may need inspection every 10 years and that which requires it every 5 years. This, for a large inventory of equipment, can have a major impact on inspection costs.
- It is difficult to justify ‘skewing’ a 3 × 3 matrix. Often, these matrices are skewed to reflect the understandable desire to inspect equipment with high consequences of failure even if the probability is low.

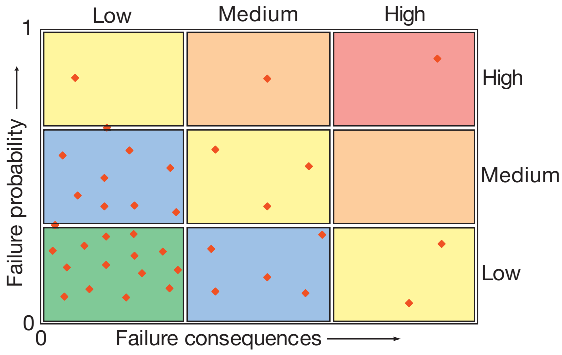


Figure 5 3 × 3 risk matrix.

Since the publication of API 580 and 581 it has been normal to consider the use of a 5 × 5 matrix as shown in **Figure 6**.

This dimension of matrix has a number of advantages.

- The resolution is as high as reasonably possible for the use of expert judgment allowing qualitative RBI to be chosen if appropriate.
- The number of bands is sufficient, but not too many, to allow sensible construction of rules for semiquantitative analysis using commonly available data, that is, that from process flow diagrams, piping and instrument diagrams, material selection reports, heat and material balance data, and equipment drawings.
- It is relatively easy to justify a degree of skewing to this matrix. The highest risk level extends to lower failure probabilities to place emphasis on failure consequences. This skewing process also goes some way to mitigating uncertainty inherent in the RBI analysis (qualitative and semiquantitative), particularly in the degree of knowledge or modeling assumptions used to predict failure modes.

There are other variants to the matrix size, for example, 4 × 5 (four levels of failure probability and five of failure consequences), but all are essentially approximations to the fully quantitative approach designed to reach a useful conclusion without prohibitive data requirements. In choosing an approach and/or a matrix size, practitioners should consider the following:

- *Resolution*: will the resolution I am using deliver distinctions that I can use in planning inspections to better target risks within the inspection budget? Can the resolution I want be justified given the data/information I have to do the assessment?
- *Auditability*: can my approach be fully audited, that is, can I justify the decisions made in the process?
- *Uncertainty*: what are the uncertainties in my assessments and where are they? How do I mitigate these uncertainties? Importantly, do any of the uncertainties introduce optimism into the risk assessment?
- *Practicality*: can I conduct the level of assessment I want to with the resources I have?
- *Reproducibility*: if I did the analysis again next week, would I get the same result? If not, why and how can I reduce the effects of this variation?
- *Cost*: what are the real costs of doing this assessment and what benefits can it achieve?
- *Time*: can I complete this assessment in a reasonable timeframe?

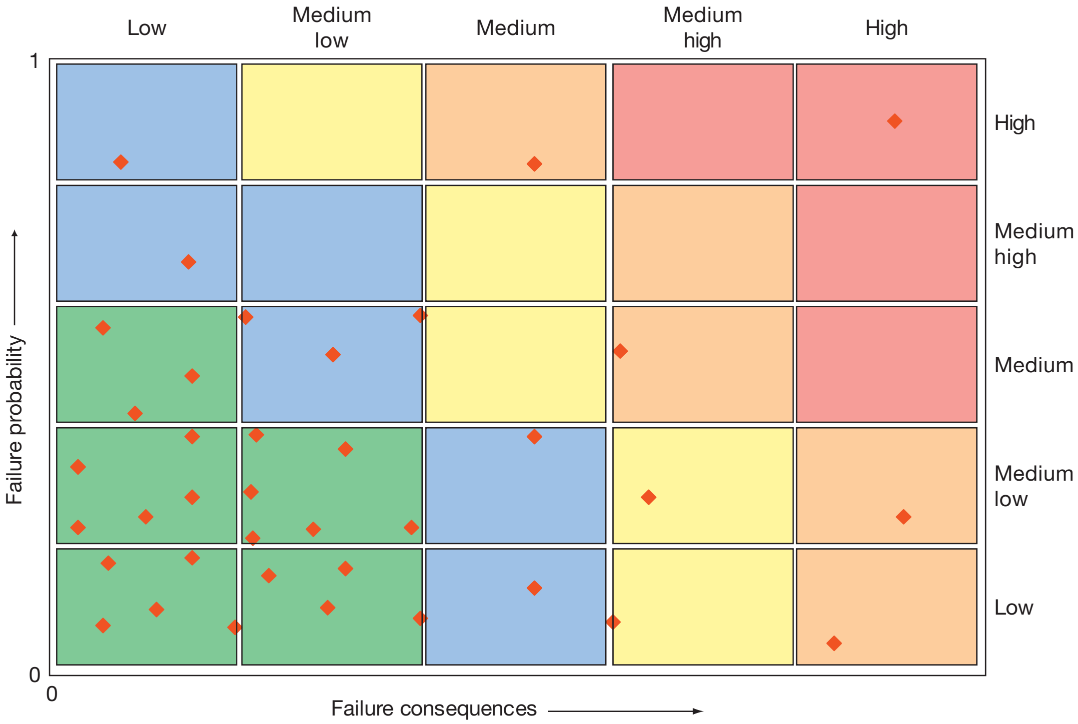


Figure 6 5 × 5 RBI matrix.

4.34.1.7 Current International Practice

The first point to note when considering international practice of RBI is that there are presently no national or international standards that cover the technology of planning inspections on the basis of risk. There are various standards that cover implementation of inspections on plant, but none of these address the manner in which RBI should be carried out.

Two publications that have gained prominence in RBI are API publication 581[6] and API recommended practice 580.[8] In essence, API RP 580 describes the necessary features of an RBI procedure, providing guidance on development of an RBI program for static equipment and piping in oil and gas industry service. API 581 is somewhat different in that it builds on API RP 580 to produce a methodology which may be followed by anyone wishing to conduct RBI on such equipment. It is not however, a standard that requires 'compliance' in a legal sense.

4.34.1.7.1 API 580 and 581

API 580 was initially developed over 5 years by a group of more than 22 international refining, chemical, and exploration companies.[9] The group comprised mechanical engineers, materials/corrosion engineers, NDE specialists, and individuals responsible for mechanical integrity and inspection programming on operating plant.

The document is very clear that it is a guidance document and not intended to:

- supplant other practices that have proven satisfactory;
- discourage innovation and originality in inspection;
- be a substitute for the judgment of a responsible, qualified inspector, or engineer; and
- be construed as a code of rules, regulations, or minimum safe practices.

The document is a supplement to other API publications, codes, and standards on plant inspection. It requires RBI assessment to systematically evaluate both failure probability and consequences based on all forms of deterioration that could reasonably be expected to affect equipment in its particular service.

One particularly important element of API 580 is that it sets out what RBI will not do, that is, it will not compensate for:

- inaccurate or missing information required in assessments;

- inadequate design or faults in equipment fabrication or installation;
- operation of equipment outside the acceptable design envelope;
- not effectively executing the inspection plans;
- a lack of qualified personnel or the absence of required disciplines in the assessment process; and
- a lack of sound engineering or operational judgment.

API 580 also requires that RBI assessment should be documented in such a way that it allows recreation and updating of the assessments by people not involved in the original assessment. In other words, the assessments should be fully auditable and justifications are required for all decisions and judgments made.

API 581 is a development of API 580 insofar as it provides a recommended practice for the practical application of the principles described in API 580. It should be noted, however, that API 581 is a 'recommended' practice and does not claim to be the only approach that can satisfactorily achieve the aims set out in API 580. This distinction has given rise to a number of subtly different approaches in common use, many of which are housed in software applications. Virtually all RBI software claims API 580 compliance.[10] Only software produced by API itself is compliant with API 581 in every respect.[10]

4.34.1.7.2 *Common practice*

Besides API 581, there are many RBI approaches in common use. Many larger companies have chosen to develop 'in-house' approaches and associated software to achieve consistency across their total assets worldwide. Beyond the larger operators, there are many independent RBI applications available. These vary in cost and quality but all can reasonably claim to be compliant with API 580 as can the company specific approaches.

4.34.1.8 Creating the Inspection Plan – Assigning Inspections from Risk Assessment

4.34.1.8.1 *Selection of appropriate inspection techniques*

RBI is ultimately concerned with optimizing inspection activity. Part of this process is the selection of appropriate inspection techniques. In the modern world, there are many new and innovative inspection techniques available, and this complicates the inspection method selection process.

The overriding principle in selection of an inspection technique is that the technique should be able to detect the type of damage identified by the RBI assessment. This should be a matter of record, that is, the technique should be documented to the extent that it can be shown to be capable of relevant damage detection in a robust and reliable manner when applied in the field under plant conditions.

A second, but essential principle in technique selection is the degree to which the results of the inspection can be quantified. The feedback loop in the RBI process is dependent on information trends to justify increasing or decreasing inspection intervals to match the actual risk. Techniques should be capable of directly capturing trends in data, for example, wall thicknesses or crack dimensions, or be recordable in a systematic manner that allows trends to be inferred, for example, percentage of surface affected by general corrosion. Phrases like 'some corroded areas' or 'OK' are of no use in management of the RBI feedback loop.

4.34.1.8.2 *Selecting the interval*

Inspection intervals are related to the risk of failure and their assignment requires full documented justification within the RBI documents for a plant. In many cases 'risk' at this stage is referred to as 'criticality.' Returning to Figure 6 as an example, the various locations on the matrix represent different levels of risk, but the colors of the 'boxes' represent criticality or 'risk rank.' In this case red represents criticality 1 (high), orange is criticality 2 (medium high), yellow is criticality 3 (medium), blue represents criticality 4 (medium low), and green is criticality 5 (low).

For the purposes of inspection, scheduling it is good practice to plan on the basis of damage specific criticality, that is, combination of each identified failure probability (per damage mechanism) with the overall failure consequences for the equipment. This makes sense because individual damage types require different techniques to detect them and will occur at different rates, thereby requiring different intervals. Some rationalization of inspections is possible in most inspection planning exercises but this is normally best handled by detailed planning that also encompasses logistical considerations such as the availability of scaffolding and portable power supplies, etc. These latter considerations are not a part of RBI assessment.

An example of an inspection interval specification is provided in Table 1.

In this example, confidence grade is a measure of the degree of confidence that exists in the predictability of future integrity performance based on known information. The definition of each grade is broadly based on the definitions given for inspection grades by the Institute of Petroleum.[11,12] These grades reflect confidence in inspection data and anticipated future condition.

- Grade 0 – no relevant inspection history, or rapid confirmed/anticipated degradation, or uncertain process conditions, that is, uncertain present and future condition.
- Grade 1 – at least one recorded relevant inspection but with potential significant degradation, that is, certain present condition, uncertain future condition.
- Grade 2 – at least one satisfactory inspection, that is, certain present and future conditions.
- Grade 3 – more than one satisfactory inspection over a prolonged period of time.

An alternative and in some cases complimentary approach is to schedule inspection based on calculated remnant life for the equipment, adjusted according to the assessed consequences of a failure. Table 2 provides an example of how this can be achieved.

In the example, it is clear that an item of equipment with high consequences of failure and low confidence grade would be inspected on a much shorter timescale (in terms of remnant life) than another item with low failure consequences and high confidence.

Table 1 Example of inspection interval specification based on damage specific criticality

Damage specific criticality	*Confidence grade*			
	0	*1*	*2*	*3*
1	12	36	36	36
2	24	36	72	72
3	24	48	72	96
4	36	48	84	120
5	36	48	84	144

Table 2 Example of fractions of remnant life used to schedule inspections

Consequence level	*Confidence grade*			
	0	*1*	*2*	*3*
1	0.1	0.13	0.16	0.2
2	0.175	0.23	0.29	0.35
3	0.25	0.33	0.42	0.5
4	0.375	0.5	0.625	0.75
5	0.5	0.67	0.83	1

Most RBI systems, which are in operation utilize concepts such as those above in order to form working RBI plans. The terminology changes, as do the precise values for intervals and life fractions used, but the basic process remains the same.

By combining the risk assessment, the assigned confidence grade, and the selection of a suitable inspection technique, the inspection plan is formed. It is important that the logic for creating the plan is documented because this constitutes a critical part of the audit trail for the whole RBI program.

4.34.1.9 Key Success Factors for RBI

Three distinct parties have an interest in the effectiveness of a RBI program. These may include the RBI practitioner (whether this be an individual or a team within the operating company, or an external consultant), the operating company, and the regulation authority. Each of these parties has a different interest, and hence, each judges successful RBI by different criteria.

4.34.1.9.1 RBI practitioner

The practitioner judges RBI by the ease and speed of application. This requires minimal data and simplified assessment methodologies. Restricting data requirements to that available in common engineering documentation such as process flow diagrams, piping and instrumentation diagrams, piping line lists, and heat and mass balance data normally provides sufficient data for RBI assessments, and is frequently available in electronic format, making data capture very efficient.

Additionally, as the RBI system needs continual feedback from completed inspections, changes in operating parameters and feedstock, the RBI practitioner needs an RBI system that is readily managed. The capture of changes and updating of results need to be simple and efficient.

4.34.1.9.2 Operator

Key success factors for an operating company include an optimized inspection program, with minimal plant down time for scheduled inspections. The inspection regime should maximize plant reliability and eliminate surprise failures or unplanned shutdowns.

In order to achieve this, the RBI system needs robust likelihood of failure models that accurately predict plant behavior. Optimistic likelihood models and assessment techniques, which are liable to overlook pertinent deterioration models would clearly lead to unpredicted failures, and damage the credibility of the RBI methodology.

On the other hand, overly conservative likelihood models also harm confidence in the RBI system by continuously overestimating the rate of deterioration, leading to unnecessarily onerous and frequent inspections which can overload the operator's resources. In one plant, a simple, qualitative RBI approach to creep damage resulted in the scheduling of frequent inspections for creep damage in 400 pipes in one process unit. After several inspection campaigns, early stage creep was found in only five pipes.[13] Using a more accurate, quantitative likelihood model reduced the number of pipes for which creep damage was credible to 30, which included all five pipes which had experienced early stage creep damage.[11]

Accurate prediction of plant condition allows optimization of inspection driven shutdowns, maximizing the operating period between inspections and optimizing the workload in each shutdown. These models need to be readily and efficiently adaptable to process and feedstock changes, capturing any significant changes, and revising the plant inspection program accordingly.

4.34.1.9.3 Regulating authority

A study performed on behalf of the UK Health & Safety Executive compared RBI assessments performed by a number of different RBI assessment teams for a specific set of case studies. Results showed inconsistencies between the findings from the various RBI assessment teams,[5] including:

- variation in the damage mechanisms selected for likelihood assessment;
- significant variation in the assessed likelihood of failure between the assessment methodologies;
- significant variation in the type and frequency of inspection; and
- a lack of speculative inspections aimed at confirming the absence of deterioration through damage mechanisms considered unlikely or inactive.

These findings demonstrate the primary concerns of regulatory bodies. Essentially, safety and environmental impact are the primary and secondary concerns, while business impact is of no concern. Consequently, key success factors for RBI include a robust, comprehensive assessment methodology that addresses all safety threats adequately and consistently.

The regulatory authority is often concerned that RBI scheduling may elevate business risks above safety risks. A robust RBI system should therefore ensure that safety consequences are not diluted in their significance to the overall consequence of failure result by use of an average consequence of failure from individual assessment results that consider safety, business, and environmental impact.

4.34.1.9.4 Summary

In summary, therefore, the key factors for a successful RBI program that meets the needs and expectations of all parties may be defined as:

- accurate likelihood modeling;
- application of confidence criteria;
- realistic consequence modeling;
- selection of appropriate inspection techniques;
- robust authoritative reviews;
- intelligent interpretation of inspection findings;
- efficient capture of process or hardware modifications;
- speed of application; and
- consistency of results.

4.34.1.9.5 Accurate likelihood modeling

Accuracy in likelihood modeling includes correct identification of all active deterioration mechanisms, and accurate prediction of the rate of this deterioration.

The identification of all active deterioration mechanisms presents a significant challenge to the RBI assessment. Deterioration may occur under normal operating conditions, which include normal operating fluids, pressures, temperatures, and flow rates. In qualitative RBI systems, and those which employ a qualitative preselection of pertinent damage mechanisms, the selection of likelihood assessment models is critically dependent upon the competence and expertise of the RBI practitioner or expert review team. In other words, the weakness of these systems is that they rely upon human expertise to correctly identify which damage mechanisms are actually assessed. A more robust system is one that considers a comprehensive range of deterioration mechanisms and requires each damage mechanism to be ruled out based on quantitative or semiquantitative calculations.

Following identification of pertinent damage mechanisms, the likelihood assessment requires accurate modeling of the likelihood of failure. For time dependent deterioration mechanisms, such as corrosion, creep, or fatigue, the likelihood assessment should be able to predict a deterioration rate (in the case of corrosion) or an anticipated life (in the cases of creep and fatigue). For non-time-dependent mechanisms, such as stress corrosion cracking, brittle fracture, etc., calculation of a susceptibility rank is probably the best option.

In either case, accurate modeling of deterioration mechanisms is essential for two reasons. First, an accurate understanding of the likelihood and rate of deterioration is essential for optimization of inspection plan. Overly conservative assessments will lead to specification of an onerous inspection plan both in the number of inspection tasks specified and their frequency. An optimistic assessment will specify too few inspections, with too long an interval between inspections.

Secondly, accurate likelihood modeling is essential to demonstrate the credibility of the RBI system. Confidence in the RBI assessment is gained when the RBI prediction and the actual observed experience are in agreement. Any significant difference between the prediction and the experience demonstrates that susceptibility to failure is not well understood. Accurate prediction of deterioration, rather than a simple reliance on the past measured rate of deterioration, provides better confidence in the integrity of the asset because the prediction can be modified to account for process or operating changes as they occur.

In a simple practical example, an oil and gas terminal experienced failure of a tube bundle after 11 years of operation. The corrosion engineer used the measured corrosion rate from the original bundle to predict the expected life for a like-for-like replacement, concluding that it would give a similar life, which was acceptable. Accurate RBI likelihood assessment (performed by an external consultant after ordering the replacement bundle), told a different story. The terminal had recently brought a new field online. Following the addition of the new field, the exchanger started to operate under wet conditions and the corrosion rate was high. The replacement tube bundle failed within a few months of installation.

4.34.1.9.6 Application of confidence criteria

A robust RBI system should account for the degree of confidence that can be assumed in any assessment. Confidence should consider the accuracy of the assessment technique, predictability of operating conditions, effectiveness of the inspection technique, and the integrity of the item under consideration.

Some form of confidence index is necessary to address the degree of accuracy of the models used to assess the deterioration rate. Factors to consider are the inherent accuracy of the deterioration model, its degree of conservatism (e.g., creep calculations and fracture assessments often use very conservative material property data), and the comparison of predicted deterioration rates with actual measured rates.

First, when the deterioration rates experienced in service agree with thepredicted deterioration rates, there is good confidence in the assessment technique. However, when the predicted rates differ from the measured deterioration rates it must be concluded that likelihood of failure is not well understood

Second, deterioration frequently occurs due to process upset conditions, process degradation products, or rogue elements, such as catalyst fines or particulates. As many of these conditions are abnormal or unexpected operating scenarios, they are difficult to anticipate and are readily overlooked. Additionally, failures may occur due to design errors or undetected manufacturing defects. Even the most robust RBI system would be challenged to identify all of these possibilities.

Third, the confidence index should consider the effectiveness of previous inspections. Inspection effectiveness has two aspects; first, the ability of the inspection technique to actually identify and correctly characterize a defect or deterioration rate, and second, the coverage of the technique.

Finally, the confidence index should reflect the confidence in the integrity of the item under consideration. For example, in the case of an item known to be susceptible to high rates of deterioration, with robust inspections showing that the item has suffered significant damage and is close to failure, confidence in the RBI assessment is very high, but confidence in the integrity of the item is very low.

Failures often approximate a 'bath tub' curve (see Figure 7), where early in the plant life several failures occur due to design errors, undetected manufacturing defects, etc. Following this initial operating period, failures decline to a minimum level, but then increase once again toward the end of the plant design life.

As a result, confidence is never a constant, but changes with time. For new facilities, a confidence index should be employed to promote early inspections to identify any active deterioration mechanism not identified through the RBI assessment. These inspections should include a general type of inspection (e.g., a thorough internal visual examination), which has the capability of detecting unexpected deterioration such as previously undetected manufacturing defects.

In the middle of the plant life when deterioration rates are confirmed by several inspections, inspection interval may be extended, provided in-service inspections have confirmed the rate of deterioration is both reasonable and predictable. Toward the end of the plant life, when the equipment is approaching the end of its serviceable life, confidence in the integrity of the item is necessarily reduced and inspections performed more frequently.

4.34.1.9.7 Realistic consequence modeling

Consequence modeling needs to be realistic for RBI to deliver a sensible inspection plan. Figure 8 shows a comparison of consequence of failure results for a steam reformer plant using two different proprietary RBI software packages. As can be seen, the results are not at all comparable. Both RBI assessments are described as 'semiquantitative,' although the assessment methodologies are radically different.

The methodology employed in Figure 8(a) was a very simple consequence assessment using nine simple assessment criteria, which are answered with "yes," "no," or a simple number (size, temperature, pressure, etc.). Because of the simplicity of the methodology, the results are necessarily very conservative,

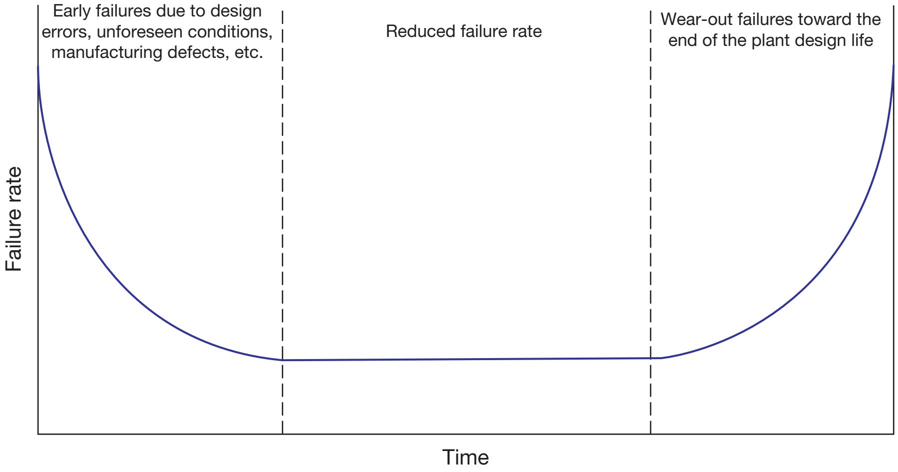
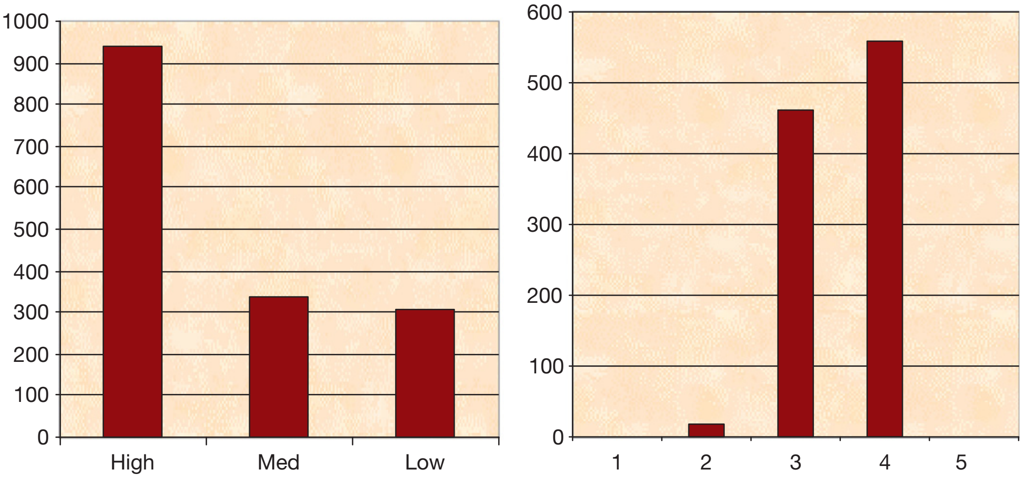


Figure 7 'Bath tub' curve of hypothetical failure rate versus time.



(a) Consequence of failure results from a proprietary RBI software package.

(b) Consequence of failure results from an alternative proprietary RBI software package.

Figure 8 Comparison of RBI consequence of failure assessments from two proprietary RBI software packages. Assessments cover the same piping from a refinery steam reformer plant. (a) Consequence of failure results from a proprietary RBI software package. (b) Consequence of failure results from an alternative proprietary RBI software package.

with 60% of items being given the highest possible rank for consequence of failure.

The second methodology is more complex, employing quantitative methods to calculate hazard areas for several failure scenarios. The technique is semiquantitative because it simplifies the dispersion modeling of any release into three specific phases (gas, dense gas, and liquid), and makes broad assumptions on repair times and mitigation systems. This technique is much less conservative, with only 2% of items being assigned the highest two consequence categories.

Clearly, the consequence of failure assessment methodology has a significant impact on the risk ranking results. A more conservative assessment will result in more items being considered critical, and this will drive more frequent inspections. However, overly conservative assessments do not give sufficient separation in risk ranking, and thus fail to focus inspection on those items that actually constitute the highest risk.

4.34.1.9.8 Intelligent interpretation of inspection findings

A key factor in the success of any RBI program is feedback of inspection findings to the risk assessment. This sounds very simple, and yet in practice information gained from inspection activities is frequently not interpreted intelligently, leading to inappropriate use of inspection findings to revise the RBI assessment and consequently the revised inspection plan.

Intelligent use of inspection data is best illustrated through specific examples.

4.34.1.10 Case Study 1: Corrosion Rate Trending

Corrosion rate trending is one of the most common plant inspection techniques, and is commonly performed using ultrasonic wall thickness (UTW) gauging. However, the UTW measurement technique has a practical accuracy of ~±0.5 mm, partly due to accuracy of the instrument itself, and partly due to repeatability of the probe placement in precisely the same location on a pipe for subsequent readings, and the fact that corrosion is frequently not uniform. Consequently, wall loss trends can be misleading.

Figure 9 shows different forms of corrosion, including general corrosion, bottom of the line corrosion, and top of the line corrosion, all of which are commonly found in process plant piping systems. Other common nonuniform forms of corrosion are pitting, preferential weld corrosion, and mesa attack. Measurements are typically taken at four coordinal points (normally 3, 6, 9, and 12 o'clock positions).

While a simple average of differences between two sets of wall thickness measurements in a system experiencing general corrosion may yield a sensible corrosion rate (assuming minimal errors from instrument calibration, probe placement, and thermal influences), in all instances where corrosion is nonuniform, the measured average corrosion rate will always be very optimistic. For instance, a straight average corrosion rate calculated for pipes in Figure 9 showing bottom of the line corrosion and top of the line corrosion would return a corrosion rate which is ~25% of the actual worst case corrosion rate.

Use of proprietary software tools for trending UTW measurements is worldwide standard practice. These tools calculate corrosion rates for each thickness measurement location (TML) as well as an average corrosion rate for an entire corrosion loop. Two corrosion rates are normally reported; a short term corrosion rate (difference between the last and the previous reading), and a long term corrosion rate (difference between the first and last readings). These terms are illustrated in Figure 10, which shows actual wall thickness readings for a pipe in service.

Table 3 shows results from trending of the wall thickness data from the above and other TMLs from

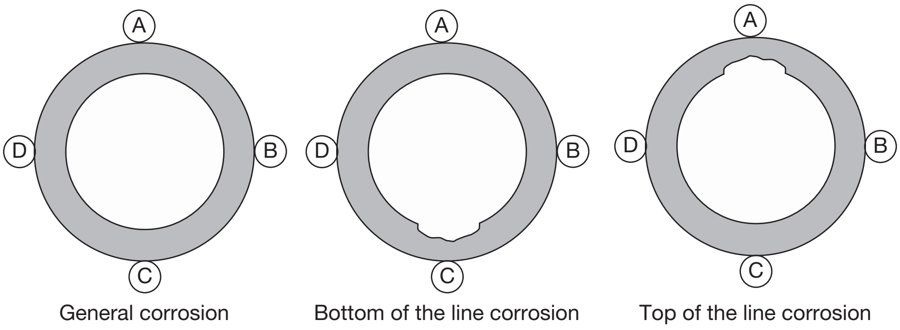


Figure 9 Different forms of corrosion.

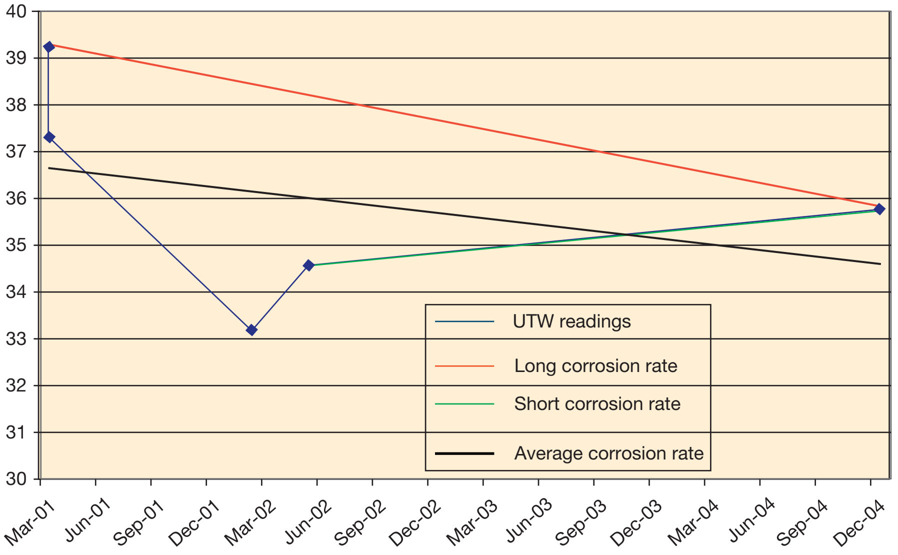


Figure 10 Historical ultrasonic wall thickness readings for a pipe in service.

the same pipe. Trends using a proprietary software package, as well as standard statistical analysis are shown. The latter evaluates thickness measurements from the entire pipe, and seeks to eliminate inaccuracies arising from the measurement methodology and localized corrosion. Normally a reasonable evaluation of corrosion rate is obtained using a mean value plus one standard deviation.

Results displayed in **Table 3** demonstrate that it is possible to obtain very good agreement between the predicted corrosion rate and the experienced rate. Moreover, it demonstrates potential shortcomings with accepted methods of wall thickness trending.

4.34.1.11 Case Study 2: Use of Robust RBI to Enhance Understanding of Inspection Data

Robust RBI likelihood modeling should provide insight into deterioration mechanisms that may be anticipated in service. This case study concerns linear indications discovered in a pipe to branch weld during a routine inspection, **Figure 11**.

Areas of the process system in question were known to be susceptible to stress corrosion cracking due to CO and CO_2. The initial assumption of the inspector, therefore, was that the pipe had suffered SCC, and a recommended repair was issued. The recommended repair was to coat the weld with a coating system that has proven capability in mitigating this form of SCC.

Prior to approving the recommended repair, the RBI database was reviewed. This indicated that thesusceptibility to SCC in this line was very low, as the pipe was a compressor discharge line which operates at warm and dry conditions.

The RBI analysis, however, did identify a potential susceptibility to mechanical fatigue, both due to vibrations from the compressor and the high velocity gas flow (calculations performed were simple screening calculations for flow induced vibration in accordance with the recommendations of the MTD guidelines).[14]

In the light of the RBI assessment, the recommended repair was altered, with the defect being removed by blend grinding.

4.34.1.12 Case Study 3: Use of Robust RBI to Understand Plant Wide Integrity from Restricted Inspection Data

Inspections are generally task driven. A job card is raised to perform a specific inspection task on a specific item of equipment. In the event that the inspection identifies a degree of damage, the inspector may raise a recommendation for reparations to the item inspected. Once the reparations have been completed, the task is closed out. The weakness in this system is that information gained from any single inspection is rarely captured in order to infer the

Table 3 UTW trends for using proprietary software and statistical analysis

	TML	*Pipe*
Trended long rate (UTW software product)	0.89	−0.63
Trended short rate (UTW software product)	−0.46	0.65
Statistical valuation (average + one standard deviation)	–	0.23
Prediction from proprietary RBI software package	–	0.23
Prediction from competitor RBI software package	–	0.62

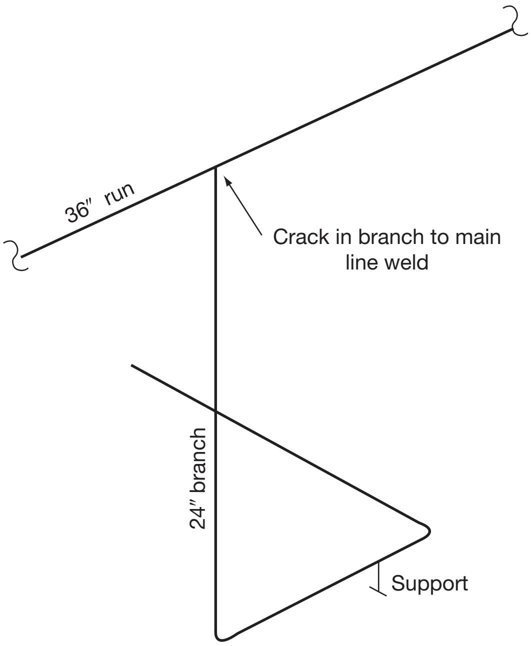


Figure 11 In-service cracking of a branch to header weld.

condition of areas of the process system that have not been inspected (e.g., upstream or downstream piping and equipment in similar service).

Use of robust RBI deterioration models facilitates a better understanding of inspection data. This case study concerns a refinery process unit which is similar in layout to a hydrotreater, Figure 12.

The RBI assessment predicted a susceptibility to hydrochloric acid (HCl) corrosion in the reactor effluent heat exchangers. Prediction of HCl corrosion is difficult as corrosion rate is a function of chloride concentration (a few ppm), reactor temperature, and the stream water content, all of which are variable. However, RBI assessments predicted low levels of corrosion in ES-101B/C and D, moderate corrosion in ES-101A, and severe corrosion in EA-101 and ES-102.

Inspections performed included visual examinations and UTW readings. The tube bundle in exchanger ES-102 suffered significant corrosion, and needed retubing within 2 years of commissioning. All other inspections reported superficial corrosion.

Authoritative review of inspection data included intelligent use of the wall thickness data, which confirmed no corrosion loss in the first heat exchanger (ES-101D), but noted that corrosion rate increased in each subsequent heat exchanger through to ES-102.

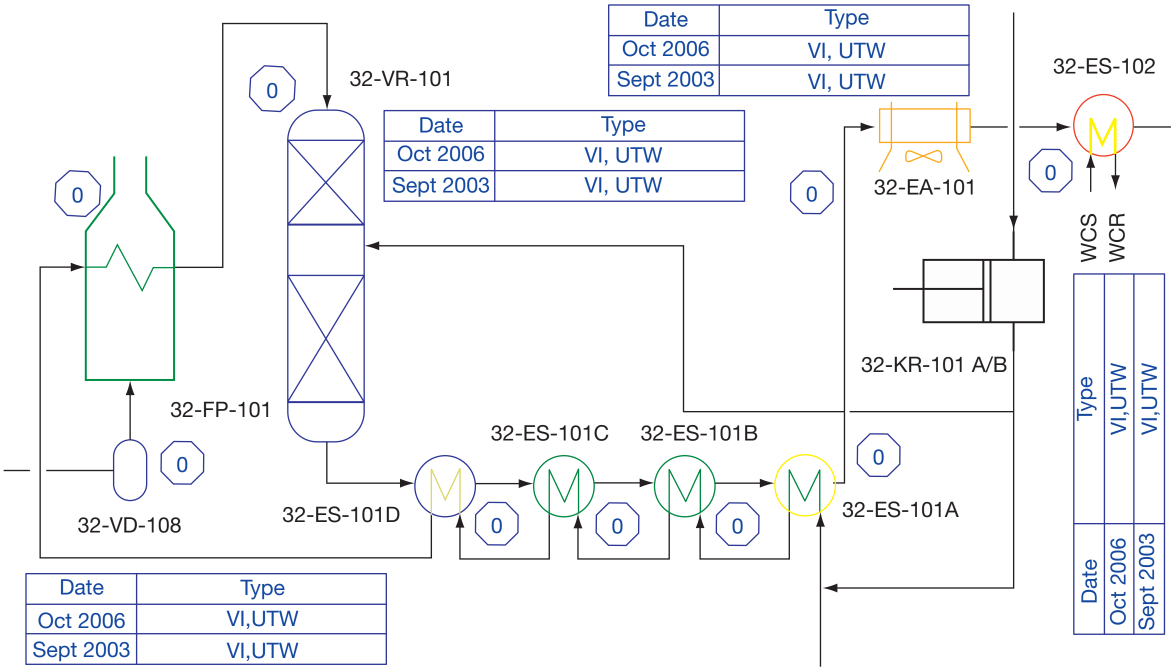
Interpretation of the inspection data in the light of RBI assessment confirmed the RBI predicted corrosion mechanism, and gave insight to the condition of the air cooled heat exchanger tubes, which had not been inspected directly. As the interpretation of corrosion threat was applied to the pressure system, rather than to just the items inspected, the air cooler was identified as a location for potentially significant deterioration, allowing the scheduling of Eddy current and IRIS inspections of the tubes to establish their condition.

4.34.1.12.1 Efficient capture of process or hardware modifications

A common definition of madness is to keep doing the same thing and yet expect a different outcome. The opposite is also a true definition of madness; namely, to keep changing what you do and yet expect the same outcome.

In the modern, real world of process plant operations, process conditions are frequently changed. Oil and gas production facilities often experience changes in feedstock and pressure profile over the field life, for example, increasing water content, declining well pressure, increased H_2S production, periodic reflux of well stimulation or work over fluids, etc. Petroleum refineries often source crude from various sources, introducing frequent feedstock changes; and plants are frequently run to optimize production to latest market needs.

These changes in feedstock or operating parameters may have a major impact on both likelihood and consequence of any failure, and need to be captured within the RBI system. Many RBI systems, however, are very time consuming to set up, and are inflexible to process changes. For instance, qualitative RBI assessments can rarely readily accommodate frequent changes as each change would require reconvening of the expert review team to assess significance of changes.



Date	Type
Oct 2006	VI, UTW
Sept 2003	VI, UTW

Date	Type
Oct 2006	VI, UTW
Sept 2003	VI, UTW

Date	Type
Oct 2006	VI,UTW
Sept 2003	VI,UTW

Date	Type
Oct 2006	VI,UTW
Sept 2003	VI,UTW

Figure 12 Schematic of unit layout.

What is apparent is that the RBI process applied on a plant needs to be directly linked into the management-of-change (MoC) procedure as part of the overall AIM scheme. A properly applied MoC should encompass risks associated with all process and hardware changes. RBI can be used to assist this assessment and the MoC procedure should ensure that the RBI system is updated following each change.

4.34.1.13 Major Challenges for RBI

There are a number of major challenges for RBI application development. These include:

- Abnormal operations and upset conditions: these are not currently modeled well in any RBI system because of the large uncertainties on the value and range of important parameters that might change during a process upset. The duration of any upset is also a very important parameter. At present, best practice is to review the RBI scheme following each process upset to either formally confirm that the specific upset had no effect on the existing risk level or specify actions to reassess the risk following the upset.
- Possible degradation products: no current RBI approach predicts with any great certainty the precise form and properties of degradation products. Material-process fluid interactions are capable of producing solids, liquids, and gases that may or may not initiate or contribute to further degradation. This is an issue of extending current RBI assessment practice to include secondary and tertiary effects of materials degradation within a process stream.
- Batch operations: current RBI approaches were designed for continuous operations. Risk can be accounted for by weighting anticipated corrosion rates with their respective service times. Complex batch operations, where several different chemicals are processed at different times, or where chemical cleaning cycles etc. may be included, are frequently covered inadequately.
- Flexible operations (changing pressure, temperature, throughput, etc.): as with batch operations, flexible operations often result in varying risk characteristics for each operating scenario. Consequently, careful thought needs to be afforded to the RBI assessment.
- Changing feedstocks: feedstock changes, which are often very subtle, are common and yet are frequently not adequately addressed in current RBI approaches. Consideration of the current and future process fluid chemistry and/or operating parameters at the start of an RBI planning project can assist in minimizing the risk of using inappropriate assumptions in the assessment. Sensitivity studies should be used to estimate the influence of changing parameters. Moreover, a robust RBI program should identify

key process parameters (e.g., pressure, temperature, chemical restrictions, operating mode, etc.) beyond which the RBI assessment is invalid.

- Areas where basic data may not be appropriate (e.g., deadlegs): conditions in deadlegs, piping, or equipment which are used infrequently and low flow areas which are not the same as those in the main process streams. Many RBI schemes fail to recognize these differences, and hence may significantly under estimate the risk in these locations. A sensible approach is to employ corrosion circuit assessments, which would require evaluation of the main flow, lines under intermittent flow, and deadlegs.

As RBI approaches develop, some challenges will be met and other new ones will appear. Many answers will come from improvements in plant operational software and developments in process modeling. As data becomes fully integrated, the opportunities to conduct rapid and accurate RBI assessment will become more common.

4.34.1.14 Future Developments

Many consider that the goal of RBI must be to achieve the ability of the system to interrogate live process and operating data (e.g., digital control systems, corrosion monitoring, and direct inspection data) in order to give a real time integrity assessment, assessing the impact of actual operating conditions on plant integrity as they occur. Moreover, the risk and integrity status could be displayed on intelligent plant drawings (P and IDs, isometrics, equipment drawings, etc).

When RBI was first applied in the oil and gas industry this was something of a dream, but all the elements required to achieve it now exist and it is seemingly only a matter of time before it becomes reality.

References

1. Reducing Risks, Protecting People – The HSE's Decision Making Process, Her Majesty's Stationary Office, 2001.
2. Best Practice for Risk Based Inspection as a Part of Plant Integrity Management, HSE Contract Research Report 363/2001, HSE.
3. UKOOAH, Asset Integrity Toolkit, UK Offshore Operators Association, 2006.
4. Formal Expert Judgement An Overview, K. Simola, A. Mengolini, and R. Bolado-Lavin, EUR 21772 EN, 2005.
5. Risk Based Inspection – A Case Study Evaluation of Onshore Process Plant, HSL/2002/20, W Geary, 2002.
6. API 581, RBI Base Resource Document.
7. API 581, Table 7-2.
8. API Recommended Practice 580, Risk-Based Inspection.
9. Risk Based Inspection, Beyond Implementation to Integration, Lynne Kaley, The Equity Engineering Group Inc.
10. Sitton, R. Integration of RBI with an Inspection Data Management System, 3rd MENDT, Middle East Nondestructive Testing Conference & Exhibition, November 2005, Bahrain.
11. Pressure Systems Examination. Model Code of Safe Practice, Part 13. Pressure Piping Systems Examination, 2nd ed. Institute of Petroleum.
12. Pressure Systems Examination. Model Code of Safe Practice, Part 12. Pressure Vessel Examination, 2nd ed. Institute of Petroleum.
13. Amphlett, G. Audit Report: Validation of Changes to RBI Strategy for Onshore Facilities and Pipelines, Allianz Cornhill Engineering, 2005.
14. MTD 99/100, Guidelines for the Avoidance of Vibration Induced Fatigue in Process Pipework, ISBN 1 870553 37 3, 1999.

4.35 Assessment of Fitness for Service

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Glossary

Defect A metallurgical imperfection.

Degradation A detrimental change in the material by a metallurgical, electrochemical, or mechanical process, for example, precipitation, stress corrosion cracking, or fatigue.

Failure An event that results in a loss of structural integrity of a component containing a flaw.

Failure assessment diagram A graphical approach to quantify the structural integrity of a component containing a flaw in terms of failure by fracture or plastic collapse.

Fitness for service assessment Quantitative evaluation of the structural integrity of a component containing a flaw carried out to a published procedure.

Flaw Any macroscopic metallurgical imperfection involving a discontinuity, such as a crack, solid inclusion, gas pore, etc.

Limit load The load applied to a structure at plastic collapse.

Plastic collapse The failure of a structure by the development of plastic strain across the net section.

Abbreviations

ASME American Society of Mechanical Engineers
FAD Failure assessment diagram

FFS Fitness for service
HAZ Heat affected zone
SCC Stress corrosion cracking

Symbols

a Crack Length
c Half surface-breaking length of surface defect
G_0 to G_5 Geometry coefficients
g Geometry parameter in calculation of reference stress
K_r Ordinate of the failure assessment diagram providing a measure of the proximity of a component to failure by brittle fracture
K_{mat} Material fracture toughness
K_I Mode I stress intensity factor
K_{ISCC} Threshold stress intensity factor for stress corrosion cracking
L_r Abscissa of the failure assessment diagram providing a measure of the proximity of a component to failure by plastic collapse
$L_{r(max)}$ Maximum extent of the failure assessment curve on the L_r axis
M_b Bending correction factor
M_m Membrane correction factor
M_s Surface correction factor for a surface crack
p Pressure
P Load
P_b Through-wall primary bending stress
P_L Limit load
P_m Through-wall primary membrane stress
Q Geometry parameter in calculation of stress intensity factor
R_i Inner radius of cylinder
R_o Outer radius of cylinder
t Wall thickness of cylinder
W Half-width of flat plate
Y Geometry parameter
α Geometry parameter in calculation of reference stress
σ Applied stress
$\sigma_{0.2}$ Proof stress at 0.2% plastic true strain
σ_b Bending stress
σ_f Flow stress (average of yield and ultimate tensile stress)
σ_m Membrane stress
σ^P Primary stress
σ_{ref} Reference stress
σ^S Secondary stress
σ_m Membrane stress
σ_y Yield stress

4.35.1 Introduction

The safe design and reliable operation of engineering plant is critical to all industries. Design codes, such as those published by the American Society of Mechanical Engineers (ASME) for the process and power industries, provide clear rules for the design, fabrication, inspection, and proof testing of new plant prior to going into service.[1] However, as such codes are developed for engineering design (rather than operation), they do not fully consider that materials degrade in service by a range of mechanisms, including:

- metallurgical degradation (including graphitization, temper embrittlement, sigma phase embrittlement, strain ageing, and irradiation damage);
- mechanical degradation (including creep cavitation, erosion, mechanical and thermal fatigue, ductile tearing, and brittle fracture);
- chemical/electrochemical degradation (including oxidation, sulfidation, carburization and metal dusting, general and localized corrosion, corrosion–fatigue, stress-corrosion cracking, and erosion–corrosion).

Examples of material degradation by fatigue and stress-corrosion cracking are illustrated in Figure 1.

(a) Fatigue crack in 2024-T351 high strength aluminum alloy containing a tensile residual stress
(b) Transgranular stress corrosion cracking in sensitized 304 stainless steel due to chloride contamination
(c) Intergranular stress corrosion crack in sensitized 304 stainless steel exposed to high temperature oxygenated water

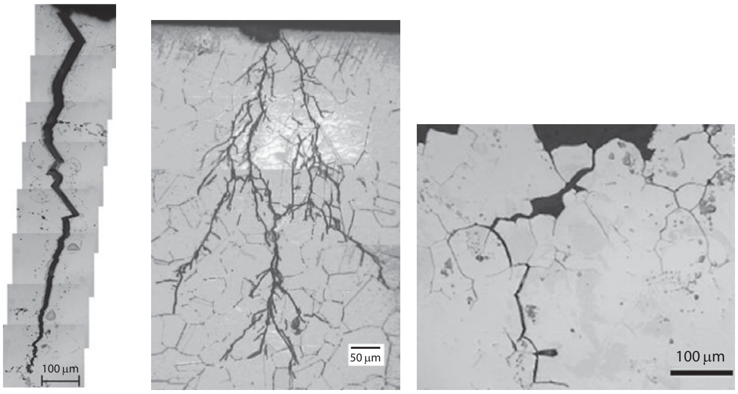
Since materials degrade and defects can initiate and propagate in engineering components during plant operation, there is an ongoing need to demonstrate the structural integrity of engineering components during service life, thus ensuring the continued safe and reliable operation of the plant. While nondestructive examination (NDE) methods provide information regarding the presence and development of crack-like flaws, fitness-for-service (FFS) assessment methodologies provide the means for judging the severity of such flaws and the consequence for component integrity. Such FFS methodologies have been developed to provide the engineer with clear guidance regarding: (i) the information required to undertake FFS assessment, (ii) the steps required to perform FFS assessment, and (iii) the information to be presented with respect to the results of FFS assessment. The results from such assessments provide the plant operator with valuable information that may be used to inform decisions regarding component operation, component repair, and (or) component replacement. These results also form part of the development of safety cases to support the continued operation of plant components.

There are a number of FFS assessment methodologies used within the process and power industries world-wide, including:

- BS 7910:2005, 'Guide to methods for assessing the acceptability of flaws in metallic structures', British Standards Institution, 2005;
- R6 Revision 4, 'Assessment of the integrity of structures containing defects', British Energy Generation Ltd, 2006;
- API 579, 'Fitness for Service', American Petroleum Institute Recommended Practice, 2000;
- FITNET MK7, 'Fitness-for-service procedure' European Fitness for Service Thematic Network (FITNET TN), 2006.

Common to each of these procedures is the failure assessment diagram (FAD) approach for assessing the significance of crack-like flaws which may be present at the start of a component's life (e.g., lack of fusion weld defect) or which may form during service (e.g., by one or more of the degradation mechanisms outlined above). A typical FAD is illustrated in Figure 2.

This chapter describes the FAD approach to structural integrity assessment. Section 4.35.2 provides a brief overview of the different components of the FAD. Section 4.35.3 describes the L_r parameter while Section 4.35.4 provides a description of the K_r parameter. Finally, Section 4.35.5 presents a working example of the use of the FAD approach to assess a component containing a flaw. This chapter



(a) (b) (c)

Figure 1 Examples of crack-like flaws in engineering materials.

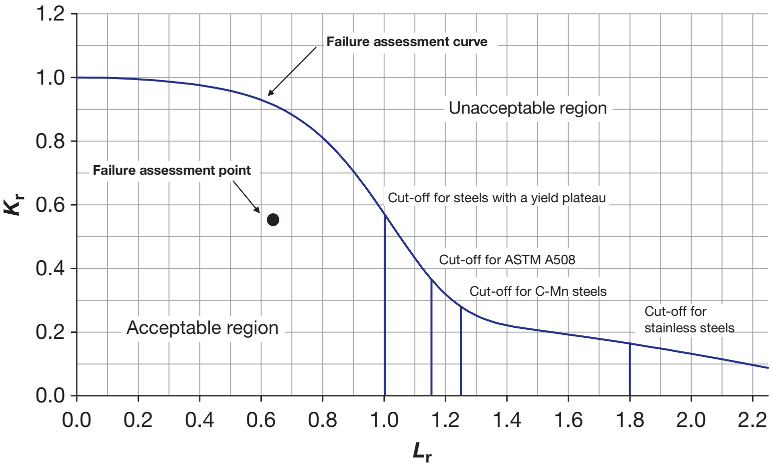


Figure 2 Failure assessment diagram.

should be read alongside the chapter on the mechanical and fracture properties of materials in this book, which provides important background material.

4.35.2 Overview of the Failure Assessment Diagram

The FAD is a graphical representation of the acceptability or unacceptability of a crack-like flaw in a given component under particular operating conditions. As shown in Figure 2, the FAD includes a 'failure assessment curve' and 'failure assessment point'.

The FAD provides the means for judging the proximity of a component to failure by either plastic collapse ('bending') or fracture ('breaking'). The FAD is plotted with an abscissa L_r, which defines the proximity of the component to plastic collapse, and an ordinate K_r, which defines the proximity of the component to unstable fracture. Plastic collapse usually controls component failure when the flaw is large relative to the thickness of the component and the material has high fracture toughness and low yield stress. Unstable fracture usually controls component failure when the defect is small relative to the thickness of the component and when the material has low fracture toughness (e.g., brittle materials) with high yield strength.

The failure assessment curve defines the boundary between acceptable (or safe) and unacceptable (or unsafe) regions with respect to component failure by unstable fracture or plastic collapse. The curve may be defined in a general manner (as shown in Figure 2) by the following equation:

$$K_r = (1 - 0.14L_r^3)(0.3 + 0.7\exp[-0.65L_r^6])\ \text{for}\ L_r \le L_{r(\max)} \qquad [1]$$

The maximum extent or 'cut-off' of the failure assessment curve on the L_r axis is determined by the ratio of the material flow stress σ_f (the average of the yield and ultimate tensile stress) and material yield stress σ_y at the temperature of interest, that is,

$$L_{r(\max)} = \frac{\sigma_f}{\sigma_y} \qquad [2]$$

The yield stress is conventionally defined by the 0.2% proof stress $\sigma_{0.2}$ of the material. Typical cut-off values are shown in Figure 2, and are due to the significant differences of work hardening behavior. They include:

- $L_{r(\max)} = 1.00$ for materials with a yield plateau
- $L_{r(\max)} = 1.25$ for carbon–manganese steels
- $L_{r(\max)} = 1.80$ for austenitic stainless steel

The failure assessment point defines the position of a specific flaw in a specific component under specific operating conditions with respect to the failure assessment curve. If the point lies below the failure assessment curve, the flaw is deemed to be acceptable (the component is safe) and the flaw may be left in service with no impact on the operational safety or the structural integrity of the component. However, if the failure assessment point lies outside the failure assessment curve, the flaw is deemed to be unacceptable (the component *may be* unsafe) and corrective action may be necessary, for example, the repair or replacement of the component. The assessment used commonly has significant conservatisms due to simplifications in the analysis. In some cases, a more sophisticated reassessment of the flaw, with reduced conservatisms, may be sufficient to demonstrate that the component is, in fact, safe.

To define the location of the failure assessment point, the parameters L_r and K_r need to be calculated for the component containing a given flaw under the operating conditions of interest.

The parameter L_r is defined by the ratio of the reference stress σ_{ref} to the materials yield stress σ_y at the temperature of interest, that is,

$$L_r = \frac{\sigma_{ref}}{\sigma_y} \qquad [3]$$

Where σ_{ref} is defined from the knowledge of the dimensions of the flaw and the stress acting on the flaw under the operating conditions of interest. The yield stress, σ_y, is usually defined from a standard tensile test using the 0.2% proof stress $\sigma_{0.2}$. An equivalent definition of L_r is as follows:

$$L_r = \frac{P}{P_L} \qquad [4]$$

where P is the load applied to the structure and P_L is the limit load. The parameter L_r is discussed in greater detail in Section 4.35.3.

The parameter K_r is defined under *primary* loading (see Section 4.35.3) by the ratio of the linear elastic stress intensity factor K_I to the material fracture toughness K_{mat} at the temperature of interest, that is,

$$K_r = \frac{K_I}{K_{mat}} \qquad [5]$$

where K_I is defined from the knowledge of the component geometry, the dimensions of the flaw, and the stress acting on the component under the operating conditions of interest. The material fracture toughness is defined by fracture toughness testing of the component material at the temperature of interest. The parameter K_r is described in further detail in Section 4.35.4.

4.35.3 The L_r Parameter

The calculation of the L_r parameter in FFS assessment not only requires the definition of the material yield stress σ_y (conventionally defined by $\sigma_{0.2}$)[1] but also an understanding of the stress condition of the component being assessed. In FFS assessment, this understanding must take full account of all the stresses acting on the component. There are broadly three types of stress that can act on an engineering component:

1. applied stresses such as those due to internal pressure,
2. thermal stresses such as those due to thermal transients, and
3. internal (residual) stresses such as those due to welding.

For the definition of the L_r parameter, only the applied stresses are considered. Such stresses are necessary to satisfy equilibrium conditions with externally imposed loading and are defined as '*primary*' stresses σ^P. These contribute to the plastic collapse of a structure (e.g., as pressure is increased within a pressure vessel or pipe). Thermal and internal stresses are necessary to satisfy continuity conditions within the structure (e.g., weld residual stress) or with an external constraint (e.g., pipe fit-up stress). Such stresses are defined as 'secondary' stresses σ^s. Secondary stresses do not significantly contribute to plastic collapse as these stresses will, in most cases, be self-equilibrating, that is, the net force and bending moment will be zero, and their effect will be effectively 'washed out' as plasticity extends across the ligament. The following definition of stresses is given within the R6 defect assessment procedure[2]:

- Primary stresses σ^p arise from loads that contribute to plastic collapse.
- Secondary stresses σ^s arise from loads that do not contribute to plastic collapse.

A more complete discussion of primary and secondary stresses is given in Lu *et al.*[3].

The application of a primary stress lower than the yield stress to an uncracked component will result in elastic deformation of the component, as defined by Young's modulus and Poisson's ratio. However, for components containing crack-like flaws, the stress concentrating effect of the flaw can lead to local yielding of the material at the tip of the flaw. A zone of plastically deformed material surrounded by elastic material will develop at the tip of the flaw. Increasing the applied stress will expand this plastic zone until plasticity first extends across the uncracked ligament to the wall of the component. This condition is defined as the 'local collapse condition.' Further increases in applied stress lead to the uncracked ligament becoming fully plastic. This condition is defined as the 'net section collapse' condition. Finally, when the additional increases in applied stress cause the component to become fully plastic, 'gross collapse' of the component has occurred. It is important to note that under some circumstances the flaw will extend under an increasing primary load, for example, by ductile tearing. Crack growth will reduce the dimension of the uncracked ligament and increase the likelihood of plastic collapse.

These three limiting conditions are illustrated schematically in Figure 3 for an axially cracked pipe under an internal pressure p:

- *Local collapse* occurs when the plasticity first extends across the uncracked ligament ahead of the flaw.
- *Net section collapse* occurs when the uncracked ligament becomes fully plastic.

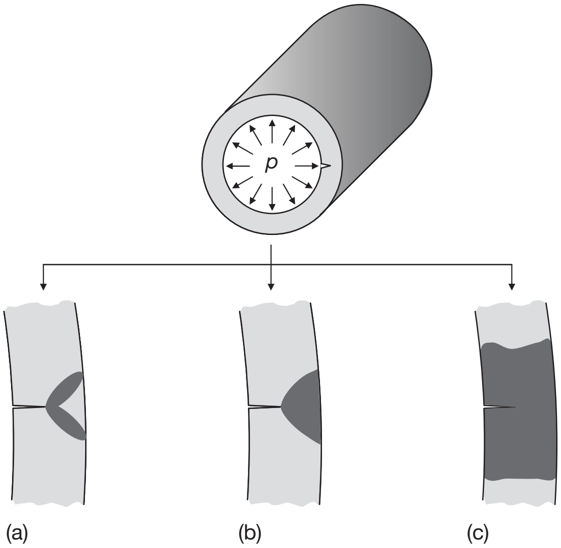


Figure 3 Schematic illustration of plastic collapse solutions for a pressurized cylinder containing an axial flaw. The dark shaded regions indicate the region of plasticity. (a) Local collapse, (b) net section collapse, and (c) gross collapse.

- *Gross collapse* occurs when plasticity extends across the full component thickness.

The 'failure' of a component by plastic collapse may be defined at each of these conditions.

The reference stress σ_{ref} defines the effective primary ligament stress (for local collapse) or the effective net section stress (for net section collapse) within the component containing a defect under an applied primary stress. Compendia of standard equations defining σ_{ref} for a wide range of cracked geometries are available within FFS procedures such as in R6 Revision 4[2] and API 579.[4]

Equation [4] shows that L_{r} can be defined with reference to the applied load on a structure normalized by the limit load for the structure.

For example, the following equation defines the reference stress with respect to the net section collapse of the cracked cylinder shown in **Figure 3**[4]

$$\sigma_{\mathrm{ref}} = \frac{\sigma_{\mathrm{b}} + \left[\sigma_{\mathrm{b}}^2 + 9\{M_{\mathrm{s}}\sigma_{\mathrm{m}}\}^2\right]^{0.5}}{3} \qquad [6]$$

where σ_{b} is the through wall primary bending stress, σ_{m} is the primary membrane stress intensity, and M_{s} is a surface correction factor for a surface crack. The membrane stress is defined as the average stress across the thickness of a section. The bending stress is the bending component of the stress acting across the same section. The surface correction factor is required to take into account the local effect of the crack on the membrane and bending and stresses on the cracked plane. The primary bending and membrane stresses are dependent on the internal pressure and thickness of the diameter and wall of the cylinder. The parameter M_{s} is dependent on the ratio of crack depth to the cylinder wall thickness.

4.35.3.1 Example Calculation of L_r

This example calculation is based on the axially cracked cylinder geometry illustrated in **Figure 3** with the following parameters:

Material	AISI Type 304L stainless steel
Temperature	20°C
Internal radius (R_{i})	120 mm
Outer radius (R_{o})	132 mm
Wall thickness (t)	12 mm
Crack depth (a)	4.8 mm
Internal pressure (p)	10 MPa

Step 1. Define the yield stress σ_{y} of the material at the temperature of interest.

The yield stress of AISI 304L stainless steel at 20 °C is given as 210 MPa using the Matweb database.[5]

Step 2. Define the reference stress σ_{ref} for the cracked component of interest.

Using eqn [6] along with the stress solutions given in API 579,[4] the parameters P_{m}, P_{b}, and M_{s} are given as follows:

$$P_{\mathrm{m}} = \frac{pR_{\mathrm{i}}}{t} \qquad [7]$$

$$P_{\mathrm{b}} = \frac{pR_{\mathrm{o}}^2}{R_{\mathrm{o}}^2 - R_{\mathrm{i}}^2}\left[\frac{t}{R_{\mathrm{i}}} - \frac{3}{2}\left(\frac{t}{R_{\mathrm{i}}}\right)^2 + \frac{9}{5}\left(\frac{t}{R_{\mathrm{i}}}\right)^3\right] \qquad [8]$$

$$M_{\mathrm{s}} = \frac{1}{1 - a/t} \qquad [9]$$

Inserting the parameters of interest into these equations gives $P_{\mathrm{m}} = 100$ MPa, $P_{\mathrm{b}} = 5$ MPa, and $M_{\mathrm{s}} = 1.67$. Inserting these parameters into eqn [6] gives the reference stress for this component and internal pressure of $\sigma_{\mathrm{ref}} = 168$ MPa.

Step 3. Calculate L_{r}.

L_{r} is defined as $\sigma_{\mathrm{ref}}/\sigma_{\mathrm{y}}$. Therefore, for this component geometry, defect size and internal pressure, $L_{\mathrm{r}} = 168/210 = 0.80$.

4.35.4 The K_r Parameter

The K_{r} parameter quantifies the proximity of the component to failure by fracture in the elastic or small-scale yielding regime of the FAD when L_{r} is small. Under these circumstances, if the failure assessment point lies outside the failure assessment curve (the unacceptable region); the component would be assessed to fail by fracture with very limited plastic deformation, that is, the plastic zone is typically less than one-twentieth the size of the uncracked ligament. This condition is illustrated schematically in **Figure 4(a)**, where the crack-tip plastic zone size is small compared with the dimensions of the uncracked ligament just prior to fracture. Failure at intermediate levels of L_{r} is shown in **Figure 4(b)**. Within this region, failure occurs with more extensive plasticity emanating from the tip of the crack, such that just prior to the fracture, the plastic zone size is a significant proportion of the uncracked ligament. In contrast to this, and as discussed in the previous Section, failure by plastic-collapse occurs due to the development of plasticity across the full uncracked ligament, **Figure 4(c)**.

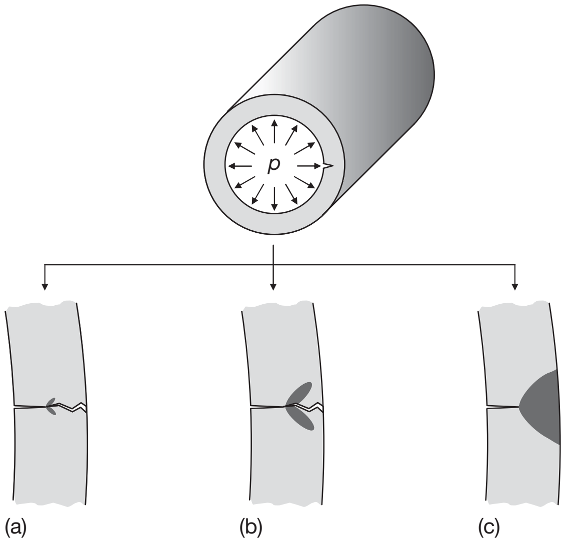


Figure 4 Schematic illustration of failure by (a) fracture in the elastic or small-scale yielding regime, (b) failure in the elastic–plastic regime, and (c) failure by net section plastic collapse. The dark shaded regions indicate the region of plasticity.

Fracture under linear-elastic or small-scale yielding conditions usually controls component failure when the flaw is small relative to the thickness of the component and when the material has low fracture toughness and high yield stress.

Only under primary loading, the parameter K_r is defined by the ratio of the linear elastic stress intensity factor K_I to the fracture toughness K_{mat} of the material at the temperature of interest. The fracture toughness is defined with respect to the failure mode of interest, that is, cleavage fracture toughness for ferritic materials operating at temperatures within the cleavage fracture regime, or ductile fracture toughness for austenitic stainless steels. For FFS assessment of ductile materials in normal operating conditions, the ductile fracture toughness normally relates to the initiation of ductile tearing, or the fracture toughness at 0.2 mm of stable ductile tearing as measured in a standard fracture mechanics test at the temperature of interest. For ductile materials under particularly infrequent loading scenarios (e.g., postulated accident conditions) some benefit may be taken from the enhanced level of fracture toughness associated with up to 2 mm ductile tearing. However, such FFS assessments would normally be judged on a case-by-case basis.

The fracture failure condition is defined when $K_I = K_{mat}$, or equivalently when $K_r = 1$. The reader is referred to **Chapter 1.04, Mechanical Properties and Fracture of Materials** for a full description of the stress intensity factor and the fracture toughness.

4.35.4.1 Example Calculation of K_r

This sample calculation is based on the geometry illustrated in **Figure 4** with the following parameters:

Material	AISI Type 304L stainless steel
Temperature	25 °C
Internal radius (R_i)	120 mm
Outer radius (R_o)	132 mm
Wall thickness (t)	12 mm
Crack depth (a)	8.6 mm
Internal pressure (p)	10 MPa

Step 1. Define K_I for the cracked component of interest.

The following equations are used along with the factor parameters G_0 to G_4 given in API 579[4] to define the stress σ and the geometry term Y for the geometry of interest, that is, $R_i/t = 10$ and $a/t = 0.4$.

$$K_I = \sigma Y \sqrt{\pi a} \qquad [10]$$

$$\sigma = \frac{pR_o^2}{\left(R_o^2 - R_i^2\right)} \qquad [11]$$

$$Y = 2G_0 - 2G_1\left(\frac{a}{R_i}\right)_1 + 3G_2\left(\frac{a}{R_i}\right)^2 - 4G_3\left(\frac{a}{R_i}\right)^3 + 5G_5\left(\frac{a}{R_i}\right)^4 \qquad [12]$$

Inserting the geometry parameters of interest and magnitude of the internal pressure into eqns [11] and [12] gives $\sigma = 48$ MPa and $Y = 7.6$. Using these parameters along with eqn [10] gives the Mode I stress intensity factor for this component and internal pressure of $K_I = 60$ MPa √m.

Step 2. Define the fracture toughness K_{mat} of the material at the temperature of interest.

The fracture toughness AISI 304L stainless steel at 25 °C is given as 230 MPa √m in Snead *et al.*[6]. Note that fracture toughness properties can vary from cast to cast, with heat treatment, material processing, test temperature, and specimen size. However, this value is considered suitable for illustrative purposes.

Step 3. Calculate K_r

Only Under primary loading, K_r is defined as K_I/K_{mat}. Therefore, for this component geometry, defect size and internal pressure, $K_r = 60/230 = 0.26$.

4.35.5 The Assessment of Corrosion Defects

This section provides an overview of the guidance provided within the European FITNET procedure for the assessment of corrosion defects.[7] FITNET was a 4-year European thematic network with the objective of developing and extending the use of FFS procedures throughout Europe. The principles of the FITNET procedure are consistent with other assessment methods including BS 7910:2005,[8] R6,[2] and API 579.[4]

The FITNET assessment procedure follows a five-step process:

Step 1: Characterize the nature of the crack
Step 2: Establish the cause of cracking
Step 3: Define the material characteristics
Step 4: Establish data for stress corrosion cracking assessment
Step 5: Undertake structural integrity assessment

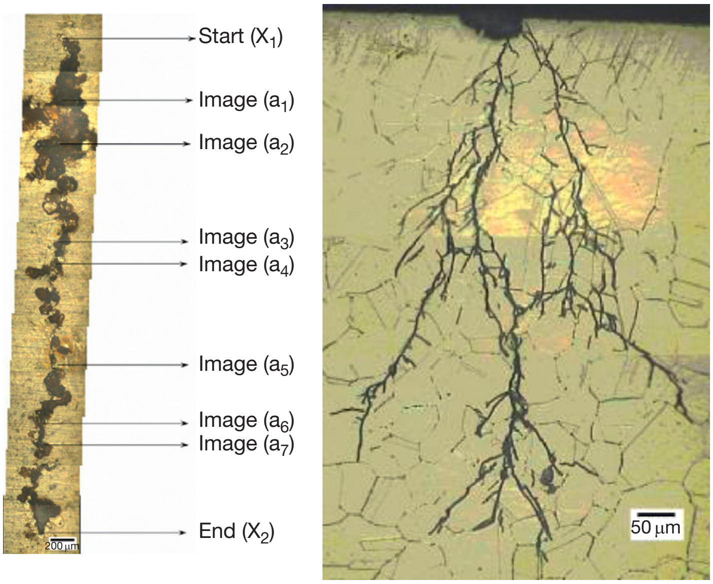
Each of these steps is described in the following sections.

4.35.5.1 Step 1: Characterize the Nature of the Crack

The NDE of plant components by a range of methods is an important aspect to demonstrating FFS. Once a defect is located, as much information as possible should be gathered regarding the nature of the crack (or cracks). This should include (though not necessarily be limited to) the following:

- Crack size and shape, including length and depth
- Crack location
  - Relative to stress concentration, weld, crevice
  - Crack path and crack orientation
- If more than one crack is present
  - Crack number density
  - Spacing between cracks
- State of surface
  - General or localized corrosion damage
  - State of coating (if present)

The information gathered will not only provide valuable inputs for FFS assessment, but will also yield information which may guide the focus of future NDE. Figure 5(a) illustrates the surface of a 304 stainless steel that has been contaminated by magnesium chloride solution and exposed in a humid atmosphere (60% relative humidity) at 60 °C under a tensile stress. Corrosion pits and a linking stress corrosion crack are visible. A metallographic section taken perpendicular to the crack plane reveals the crack to be substantially transgranular and extremely branched in nature, Figure 5(b).



(a) (b)

Figure 5 (a) Surface corrosion damage in 304 stainless steel contaminated with magnesium chloride and exposed to humid air (60% relative humidity) at 60 °C under stress, (b) metallographic section a2 revealing transgranular and branched stress corrosion crack initiated at corrosion pit. Reproduced from, Eble, O.R. M.Sc. Dissertation, *Corrosion and Protection Centre*; The University of Manchester, 2006.

4.35.5.2 Step 2: Establish the Cause of Cracking

Since SCC results from a critical combination of environment, stress and a susceptible material, it is important that these three factors should all be understood. Step 2 focuses on clarifying the first two of these, that is, the service environment and the local stress condition. The nature of the material is considered under Step 3.

4.35.5.2.1 Service environment

An understanding of the service environment is important in helping to understand the nature of cracking. This includes factors such as chemistry (including pH, electrochemical potential, and composition including impurities), humidity and temperature.

While the bulk environment may be well understood and controlled, it is important to note that local environmental conditions can develop within, for example, crevices, under deposits, within dead spaces, etc. Such local environmental conditions are often the cause of corrosion-related problems. Factors that should be considered include the level of impurity ions by ion migration, for example, chloride, and concentration processes, for example, due to evaporation.

Excursions from the normal service environment and (or) temperature during the operation of the plant can result in the development of SCC, even though the normal environment is one which might not normally be a concern. Consequently an understanding of the service history can be critical in providing an understanding of the cause of cracking. Under such circumstances, corrosion monitoring systems can be invaluable in identifying occasions when susceptibility to SCC cracking might have been increased.

4.35.5.2.2 Stress

A knowledge of the service loads is also important both in developing an understanding of the cause of cracking and in providing input data to the FFS assessment. These may include:

- applied stresses such as internal pressure
- thermal stresses due to temperature gradients or thermal shocks
- internal (residual) stresses due to manufacturing processes such as welding.

The presence of significant cyclic stresses may lead to the development of fatigue or corrosion–fatigue cracks. Transient stresses, for example, pressure during the startup or shutdown of equipment, are often important in inducing the propagation of SCC cracks.

In quantifying the stresses, it is important that distinction is made between primary and secondary stresses (as discussed in Section 4.35.3), that is, primary stresses arise from loads that contribute to plastic collapse and secondary stresses arise from loads that do not contribute to plastic collapse.

4.35.5.2.3 Crack morphology

Within the FITNET procedure, environmentally-assisted cracking under both static (SCC) and cyclic (corrosion–fatigue) loading conditions are considered. The morphology of cracking is often different in each case. For example, corrosion–fatigue cracks are often limited to a single crack path, while SCC cracks can exhibit significant branching (Figure 5(b)). Recognition of the crack morphology can thus provide valuable information regarding the cause of cracking.

4.35.5.3 Step 3: Define the Material Characteristics

It is important to ensure that the material that makes up the component is that which was specified during the design and manufacture of the component. In many cases, problems associated with the development of cracks have been attributed to the incorrect selection of material during manufacture, repair, or replacement of the component.

There are a number of particular material factors which will influence the performance of the component. These can arise from the manufacturing process and also from microstructural changes that occur in service. These factors include the following.

4.35.5.3.1 Surface condition

The condition of a surface can significantly influence the subsequent performance of a component. The surface of a material has a number of component parts, which can be divided into four main headings:

- Topography
- Chemistry
- Metallurgy
- Mechanical properties

These may be considered external and internal features. Figure 6, adapted from Griffiths,[9] illustrates the various aspects that contribute to the external and internal features of a surface.

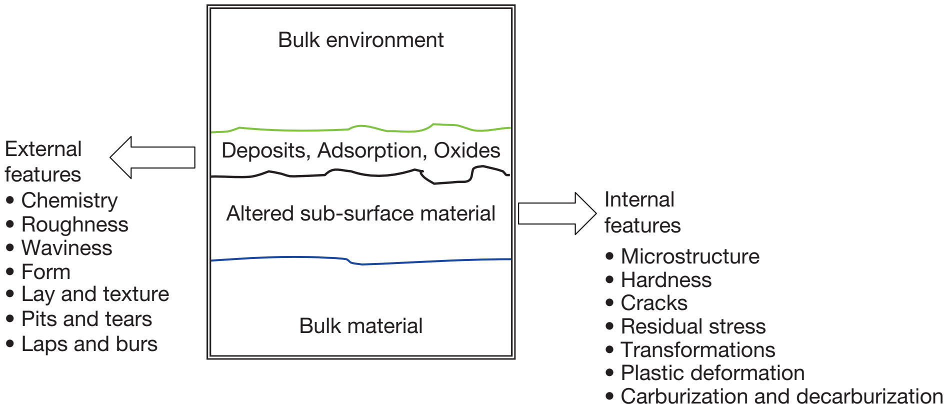


Figure 6 Summary of key external and internal features which characterize a surface. Adapted from Griffiths, B. *Manufacturing Surface Technology: Surface Integrity and Functional Performance*; Penton Press: London, 2001.

With respect to the initiation of SCC cracks, the key features include surface roughness, which in laboratory specimens is used to study corrosion susceptibility and may typically be of the order of 1 μm. In plant components, rough machining by grinding, for example, can result in extremely rough surfaces, which also contain a significant degree of plastic deformation (cold work), microstructural damage, and high internal residual stresses. These can all combine to increase the susceptibility to SCC. Figure 7 illustrates the influence of typical machining (lathe turning) parameters on surface roughness and residual stress in a recent study performed on austenitic stainless steel.[10]

It should be noted that while surface residual stress levels may be tensile, this will be balanced by compressive stresses within the bulk material. Initiating SCC cracks can, under some circumstances, arrest once the tip of the crack reaches the compressive residual stress region.

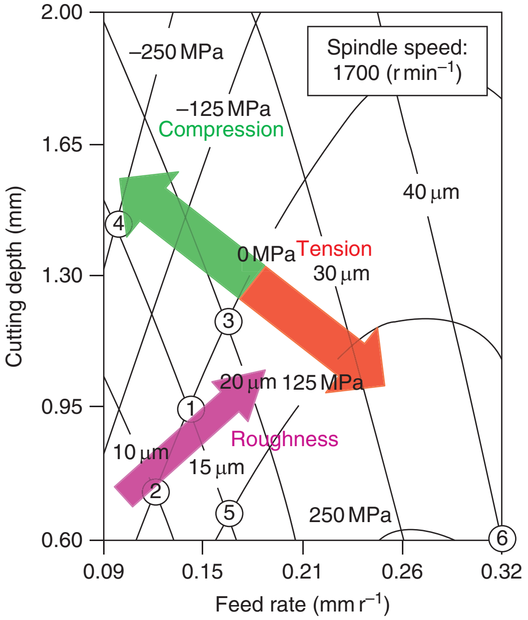


Figure 7 Influence of machining parameters on surface roughness and surface residual stress of austenitic stainless steel. Reproduced from Kuroda, M.; Marrow, T. J. *J. Mater. Process. Technol.* **2006**, *203*(1–3), 396–403.

4.35.5.3.2 Welding

Welds are often a likely region for the development of SCC cracks for two primary reasons. First, weld microstructures are complex and often contain regions of susceptibility to SCC. For example, grain boundary sensitization (chromium depletion) can occur as a result of welding austenitic stainless steels as the parent metal in the heat affected zone (HAZ) cools through the critical temperature range for carbide precipitation ~850–450 °C. Other microstructural factors can include elongated and clustered inclusions and crystallographic texture. Secondly, residual stress levels can be high, particularly in non stress-relieved welds. In such circumstances, the tensile stress level in the vicinity of a weld can be of yield magnitude. Stress concentrating features including undercuts can also provide local geometric features which enhance SCC susceptibility.

4.35.5.3.3 Initial microstructure

In addition to the factors described above, manufacturing history is also an important factor to consider. For example, rolled plates contain heavily elongated grains aligned in the rolling direction. The morphology of the grain structure, including local texturing, combined with its influence of mechanical properties, can influence SCC susceptibility.

4.35.5.3.4 Materials ageing

Material microstructure (and hence properties) can often evolve during service as a result of thermal and (or) environmental factors. For example, extended operation of stainless steels at elevated temperatures can lead to the precipitation of chromium carbides and the consequent local depletion of chromium. Cast austenitic stainless steels, which generally contain some residual ferrite, can undergo a spinodal decomposition of the ferrite with an impact on hardness and toughness. Materials operating in a neutron flux such as core internal components of nuclear reactors, will undergo irradiation-induced microstructural changes which can include grain boundary sensitization (without chromium carbide precipitation) and matrix hardening (due to the formation of lattice defects such as vacancies and interstitials, dislocation loops and copper-rich clusters).

4.35.5.4 Step 4: Establish Data for Stress Corrosion Cracking Assessment

The parameter used to assess SCC crack growth rates is K_{ISCC} which defines the threshold stress intensity factor for sustained crack growth, Figure 8(a). There is a region of applied K_{I} below which SCC crack growth is not well characterized. Within this region the driving force for SCC crack growth may either be too low (and SCC does not occur) or may be stress-controlled. As the applied K_{I} increases above K_{ISCC} the crack growth rate rises rapidly to a plateau. It is important to note that the magnitude of both K_{ISCC} and the crack growth rate plateau are material and environment-dependent. For example, Figure 8(b) reproduced from Cottis[11] shows the influence of copper content on SCC crack growth properties for Al–Cu–Mg alloys. This dependence of SCC crack growth rate with K_{I} is in contrast to other failure modes such as fatigue or corrosion–fatigue. Under cyclic loading, the crack growth rate per cycle is controlled by the difference between the maximum and minimum stress intensity factors, ΔK_{I}. A higher ΔK_{I} leads to a more rapid crack growth rate per cycle.

There are a number of issues which should be considered in the measurement and application of K_{ISCC} data. These include:

- K_{ISCC} will depend on the environment, material condition, and loading configuration used. The conditions used to generate the data should reflect as closely as possible the service conditions of interest.
- The timescales used to generate K_{ISCC} are often shorter than typical plant operation timescales. Rate effects should be considered.
- While K_{ISCC} testing is conventionally carried out under static loading, service loading (as we have seen) often includes periodic unloads and reloads (e.g., due to startup and shutdown). Under such circumstances K_{ISCC} may be affected.

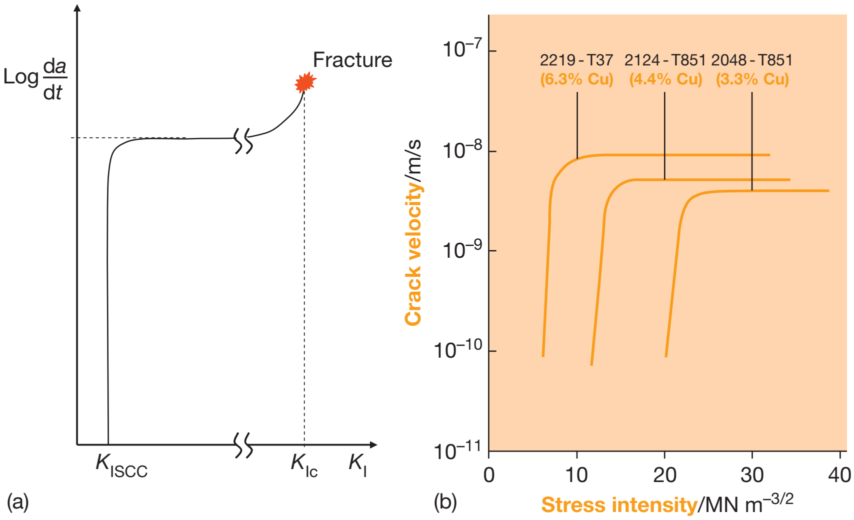


Figure 8 (a) Schematic illustration of SCC crack growth rate as a function of applied K_{I}, and (b) SCC data for Al–Cu–Mg alloys of varying copper content. Reproduced from Cottis, R. A. Guides to good practice in corrosion control: stress corrosion cracking, NPL Report, 2000.

ISO 7539-6: 2003[12] provides guidance regarding the generation of K_{ISCC} data using precracked laboratory specimens loaded under fixed load or fixed displacement conditions.

4.35.5.5 Step 5: Undertake Structural Integrity Assessment

The structural integrity assessment is undertaken with respect to the FAD approach described in detail within the first part of this chapter. Figure 9 summarizes the key elements of the FAD, as described previously.

There are typically five stages in this assessment:

Stage A: Perform a fracture assessment for the initial crack size. If the failure assessment point lies within the acceptable region, and the size of the crack is significantly smaller than the thickness of the component, preventative measures should be considered to limit further growth of the crack. These may include reducing applied stresses and modifying the environmental chemistry or temperature.

Stage B: If preventative measures cannot be applied and subcritical crack growth can be tolerated, steps 1–4 should be followed to fully characterize: (a) the nature of cracking, (b) the environment, stress level, and material of concern, and (c) material properties to quantify SCC crack growth rate for the material/environment combination of interest.

Stage C: Calculate the stress at the crack location, including applied, thermal, and internal stresses as appropriate.

Stage D: Determine the rate of increase of the size of the crack according to the crack growth law appropriate to the material/environment combination of interest.

Stage E: Determine the time for the current size of the crack to reach the critical crack size, including an appropriate in-service safety margin. This is undertaken by performing a series of FFS assessments and plotting a series of failure assessment points, each applicable to a given crack size, on the FAD. The critical crack size is defined when the failure assessment point lies on the failure assessment curve. Inspection intervals can be defined on the basis of such calculations, providing evidence that the growth rate is above or below that used in the assessment.

4.35.6 Worked Example FFS Assessment

A flat plate component of width $2W = 100$ mm and thickness $t = 25$ mm is under a normal operating

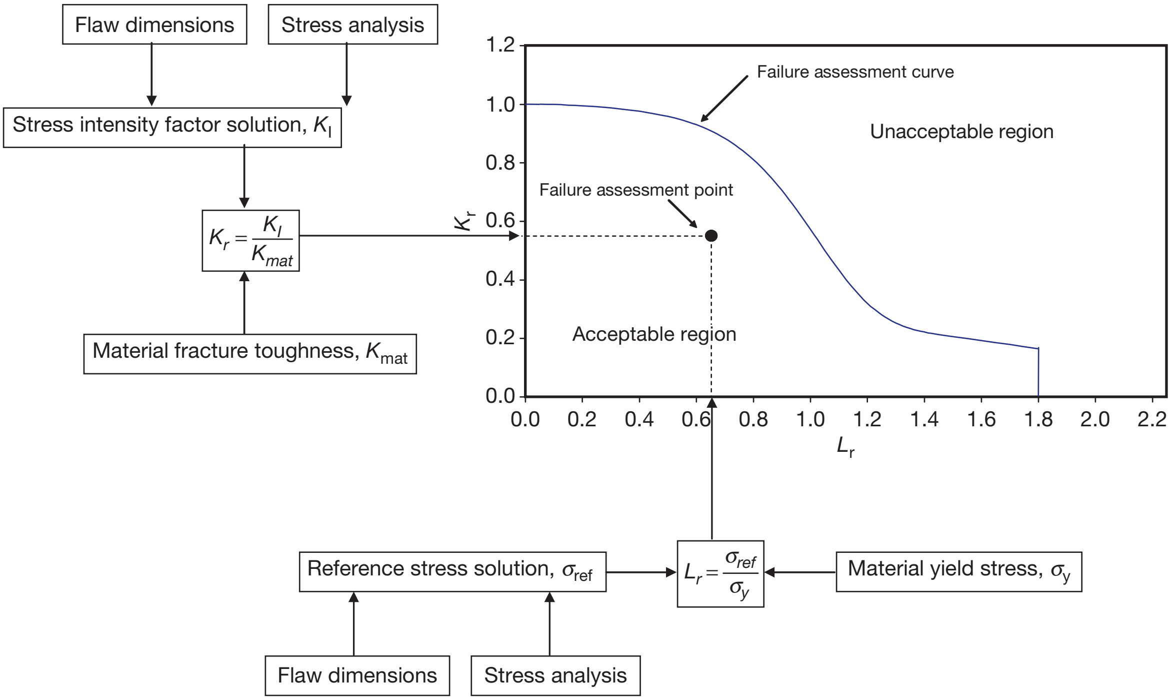


Figure 9 Summary of the key components of the failure assessment diagram.

membrane stress $\sigma_m = 100$ MPa. As shown in Figure 10, a semielliptical flaw of depth $a = 5$ mm and surface-breaking length $2c = 50$ mm has been discovered in the component by nondestructive examination. The material fracture toughness is equal to 40 MPa √m, the yield stress is equal to 450 MPa. Stress corrosion cracking data for the material and environment of interest suggest that K_{ISCC} is equal to 10 MPa √m for this material and environment. Above this stress intensity factor, both a and c will increase at a rate of 1 mm per annum.

a. Plot the failure assessment point on the FAD to demonstrate whether the component is safe to continue operation.
b. Use the FAD approach to estimate: (i) the maximum membrane stress that the component can withstand before failure and (ii) the maximum safe life of the component under normal operating stress.

4.35.6.1 Worked Example Part A

4.35.6.1.1 Calculation of L_r

The reference stress for the geometry shown in Figure 10 is defined by Solution D3.4 in API 579[4] as:

$$\sigma_{ref} = \frac{gP_b + \left[(gP_b)^2 + 9P_m^2(1-\alpha^2)\right]^{0.5}}{3(1-\alpha)^2} \qquad [13]$$

where

$$g = 1 - 20\left(\frac{a}{2c}\right)^{0.75}\alpha^3 \qquad [14]$$

$$\alpha = \frac{a/t}{1+t/c} \quad \text{for } W \geq (c+t) \qquad [15]$$

and P_b is the through-wall primary bending stress component equal to zero in this example and P_m is the primary membrane stress component equal to σ_m in this example. This solution assumes that any induced bending of the plate due to the presence of the defect is restrained.

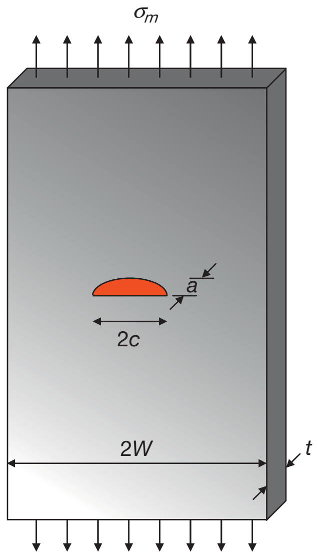


Figure 10 Schematic illustration of a flat plate component containing a semielliptical flaw of depth *a* and surface breaking length 2*c* under an applied tensile membrane stress σ_m.

Using the dimensions of the component and defect, the parameter α is equal to

$$\alpha = \frac{5/25}{1+25/25} = 0.1 \qquad [16]$$

The parameter g is equal to

$$g = 1 - 20\left(\frac{5}{50}\right)^{0.75} 0.1^3 = 1 - 3.556 \times 0.001 = 0.996 \qquad [17]$$

The reference stress is therefore equal to

$$\sigma_{ref} = \frac{0.996\times 0 + \left[(0.996\times 0)^2 + 9\times 100^2(1-0.1^2)\right]^{0.5}}{3\times(1-0.1)^2} = \frac{[89100]^{0.5}}{2.43} = 123\text{MPa} \qquad [18]$$

Since $L_r = \sigma_{ref}/\sigma_y$, for the defect found $L_r = 123/450 = 0.27$.

4.35.6.1.2 Calculation of K_r

The stress intensity factor for the geometry shown in Figure 10 is defined by Solution C3.4 in API 579[4] as

$$K_I = (M_m\sigma_m + M_b\sigma_b)\sqrt{\frac{\pi a}{Q}} \qquad [19]$$

Where M_m and M_b are the membrane and bending correction factors, respectively, σ_b is the applied bending stress (equal to zero in this example) and Q is a geometry factor given by

$$\begin{aligned} Q &= 1.0 + 1.464\left(\frac{a}{c}\right)^{1.65} \quad \text{for } a/c \leq 1.0 \\ &= 1.0 + 1.464\left(\frac{5}{25}\right)^{1.65} \\ &= 1.0 + 0.103 = 1.103 \end{aligned} \qquad [20]$$

The membrane correction factor M_m is dependent upon the plate and defect geometry as well as the location on the defect front of interest. Since the stress intensity factor is maximum at the deepest

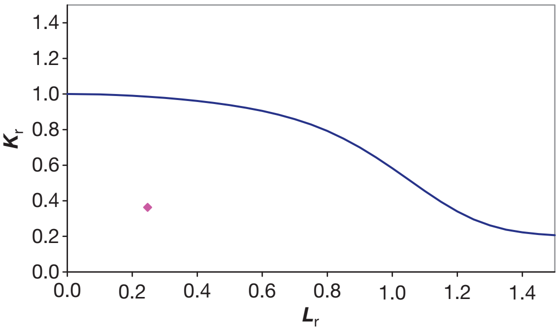


Figure 11 Failure assessment diagram for semielliptical flaw ($a = 5$ mm, $2c = 50$ mm) in a flat plate under membrane stress of 100 MPa.

point of the defect, this location is used to define K_I. Using the equations provided in API 579,[4] the membrane correction factor $M_m = 1.217$.

The stress intensity factor at the deepest point on the defect is thus given by

$$K_I = (1.217 \times 100)\sqrt{\frac{\pi \times 0.005}{1.103}}$$
$$= 121.7 \times 0.119 = 14.5\text{MPa}\sqrt{\text{m}} \qquad [21]$$

Since $K_r = K_I/K_{mat}$, for the defect found $K_r = 14.5/40 = 0.36$

4.35.6.1.3 Plotting failure assessment point on FAD

The failure assessment point for the component shown in Figure 10 is simply plotted on the general FAD using the values calculated for K_r and L_r above, along the general failure assessment curve defined by eqn [1]. The result, illustrated in Figure 11, shows that the point lies below the failure assessment curve and therefore within the 'acceptable' region of the diagram. The component is thus safe to continue operation.

4.35.6.2 Worked Example Part B(I)

The calculation of the maximum membrane stress that the cracked plate can withstand is undertaken by repeating the calculation described in Part (a) for higher stresses, and plotting the resultant family of failure assessment points on the FAD. This is illustrated in Figure 12, which indicates that the failure assessment point moves from the safe and acceptable region of the diagram to the unacceptable region at an applied membrane stress of ~250 MPa.

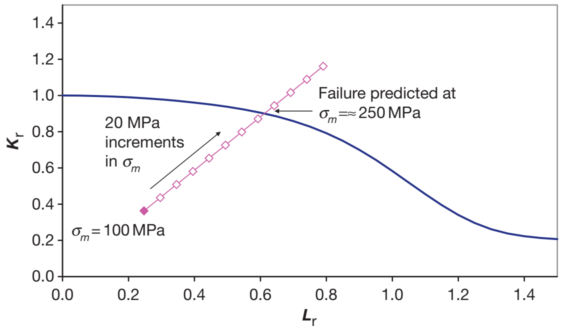


Figure 12 Failure assessment diagram for semielliptical flaws ($a = 5$ mm, $2c = 50$ mm) in a flat plate under an increasing membrane stress. Failure predicted at an applied stress of 250 MPa.

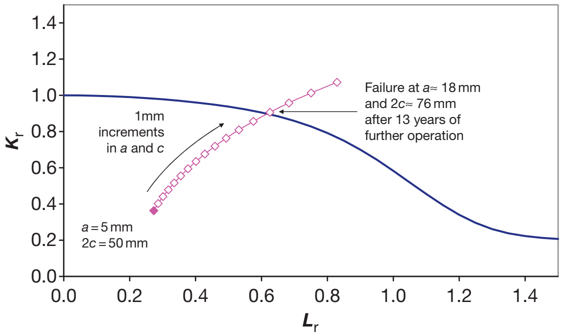


Figure 13 Failure assessment diagram for semielliptical flaws of increasing size in a flat plate under an applied stress of 100 MPa. Failure predicted at a defect size of approximately $a = 18$ mm.

4.35.6.3 Worked Example Part B(II)

The calculation of the maximum safe life of the component is undertaken by first assessing whether the applied stress intensity factor is greater than K_{ISCC}. The value for K_I calculated above was equal to 14.5 MPa √m, see eqn [21]. This is above the value of K_{ISCC} given for this material and environment combination. Therefore the dimensions a and c will both increase by 1 mm year^{-1} by SCC. The second step is to repeat the calculation described in Part (a) for defects of increasing size, and plot the resultant family of failure assessment points on the FAD.

This is illustrated in Figure 13, which indicates that the failure assessment point moves from the safe and acceptable region of the diagram to the unacceptable region at a defect size of approximately $a = 18$ mm and $2c = 76$ mm. As the starting flaw size was $a = 5$ mm and the defect is estimated to propagate at a rate of 1 mm per year, this equates to 13 years of continued operation.

References

1. ASME Boiler & Pressure Vessel Code – Section III – Rules for Construction of Nuclear Power Plant Components, 2007.
2. R6 Revision 4, Assessment of the integrity of structures containing defects, British Energy Generation Ltd., 2006.
3. Lu, M.-W.; Chen, Y.; Li, J.-G. *J. Press. Vess. Technol.* **2000**, *122*, 2–8.
4. API 579. Fitness for Service American Petroleum Institute Recommended Practice, 2000.
5. MatWeb online database, www.matweb.com.
6. Snead, L. L.; Stoller, R. E.; Sokolov, M. A.; Maloy, S. *J. Nucl. Mater.* **2002**, *307–311*(Part 1), 187–191.
7. European Fitness-for-service Network, FITNET Fitness-for-Service Procedure, Final draft Mk. 7, prepared by European Fitness-for-Service Thematic Network – FITNET, 2006.
8. BS 7910:2005. Guide to methods for assessing the acceptability of flaws in metallic structures British Standards Institution, 2005.
9. Griffiths, B. *Manufacturing Surface Technology: Surface Integrity and Functional Performance*; Penton Press: London, 2001.
10. Kuroda, M.; Marrow, T. J. *J. Mater. Process. Technol.* **2006**, *203*(1–3), 396–403.
11. Cottis, R. A. Guides to good practice in corrosion control: stress corrosion cracking, NPL Report, 2000.
12. ISO 7539-6:2003. Corrosion of metals and alloys – stress corrosion testing – part 6: Preparation of pre-cracked specimens for tests under constant load or constant displacement International Standards Organisation, 2003.

4.37 Management of Corrosion of Automobiles

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Glossary

Monocoque A vehicle body fabricated from a single piece of material with no separate load-bearing parts.

Electrocoating A process for applying paint involving application of a DC potential to a submerged work piece to attract paint particles that carry an opposite charge.

Electroendosmosis The movement of the liquid medium of a colloidal solution towards an electrode.

Electrophoresis The separation of ionic molecules by their differential migration through a gel in an electric field, according to the size and charge of the molecules.

Abbreviations

OEM Original equipment manufacture
PVC Polyvinyl chloride

4.37.1 Introduction

No other mass-produced consumer product suffers attack from its service environment as persistently as the modern motor vehicle. A mild-steel car body can be exposed to strong sunlight and high surface temperatures in the summer and to freezing temperatures, surface condensation, frost, ice, and snow in the winter. Rainfall, throughout the year, wets the vehicle regularly, but may not necessarily wash it clean. The paint finish may be damaged by road stone impacts and can be attacked chemically by deicing salts and any aggressive airborne pollutants present in the local environment.

Over the past 25 years, the automotive industry has made significant advances in corrosion engineering management, by adopting an integrated approach to design, material selection, and protective coating technologies, in particular the use of multicoat paint systems and compatible sealants.

The real improvements that have been made in total vehicle corrosion protection have been reflected, most noticeably, in the longer antiperforation warranties now offered, as standard, by most of the volume car makers.

4.37.2 Corrosion of Automotive Bodywork

The bodywork of modern automobiles consists of separate steel panels and reinforcing sections, which are joined together by electrical-resistance spot welds and runs of seam welds. The resulting (monocoque) construction, which will accommodate slight movement and flexing as the vehicle travels over uneven road surfaces, contains a number of small crevices and relatively inaccessible areas. It is in these crevices and localized box sections that the likelihood of corrosion is greatest. Dirt and road salts will, over time, find their way into any unprotected crevices and structural joints. When moist, accumulations of such deposits provide a favorable environment for corrosion to occur and then to advance.

Environmental conditions have a great effect on the rates of corrosion. The rates are at their highest in damp atmospheres, because the dirt and debris present will absorb moisture from the atmosphere more readily. Salt deposits and chemical pollution cause the most rapid corrosion. Condensation and dew will favor corrosion more than heavy rain, as rain water can often wash away surface dirt and road salts, leaving a relatively clean and evenly wetted surface.

Serious corrosion of vehicle bodywork almost always starts from the inner side of the metal surface. The first sign on the outer painted surface of the bodywork is usually localized blistering and lifting of the coating system. If left to advance, the corrosion will result ultimately in perforation of the metal panel and possible structural weakening. Corrosion of the bodywork from the outside, for example, as a result of stone chipping or scratching, is usually slow to advance and may remain 'cosmetic' for a long time, as modern automotive paint systems have good adhesion to the steel surface and good anticorrosive properties. These performance qualities can limit substantially the spread of corrosion by undercutting.

Some typical examples of corroded bodywork are shown in Figures 1–3.

4.37.2.1 Mechanisms and the Most Common Sites of Corrosion

The corrosion that is found most often on automotive bodywork is the result of pitting corrosion. Crevice corrosion and corrosion due to fretting may also occur, and the so-called 'waterline corrosion' can still sometimes be seen on the external bodywork of older vehicles.

Localized pitting corrosion is an electrochemical process involving differential aeration cells. In the presence of an electrolyte, current flows from one area of the bodywork which is not well oxygenated (the anode), to another region which is well oxygenated (the cathode). The corrosion takes the form

Figure 1 Incipient panel perforation.

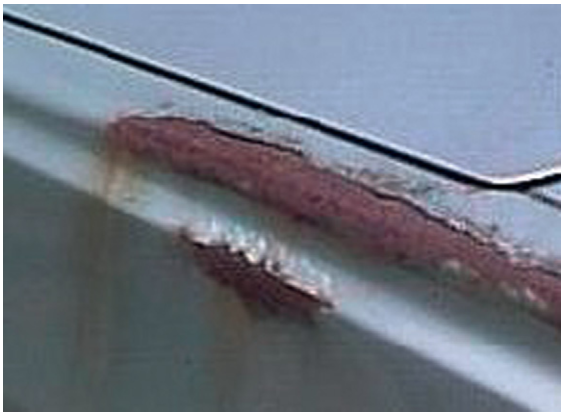

Figure 2 Corrosion along a panel bend.

Figure 3 Corrosion along a door sill.

typically of small pits on the metal surface. Once initiated, these corrosion pits may develop rapidly.

Pitting corrosion may occur wherever particles of dirt have settled on the undersides of the metal bodywork and given rise to a difference in the oxygen concentration, compared with surrounding, cleaner areas. When part of a metal surface is covered by a drop of water, for example, anodic and cathodic regions can be set up as a consequence of differences in oxygen concentrations – the area underneath the droplet is starved of oxygen and becomes anodic; adjacent areas, not starved of oxygen in this way, become cathodic. Metal wastage then occurs in the anodic areas.

When the drop of water contains dissolved salt from the roads, its conductivity is increased and the corrosion rate is accelerated. Microclimates formed within the bodywork during the service life of a vehicle will usually provide the moisture needed for such corrosion reactions to proceed.

Whenever a motor vehicle moves at speed along a wet road, spray produced by the tires is deposited on the undersides, most often in each of the wheel arches. Some wet dirt from the road may also be propelled towards the undersides of the body. This dirt may contain salt in winter months, if deicing of the road has been needed. The faster the speed of the vehicle, the less water is associated with the dirt and the more the dirt will be compacted. In addition, the more the speed of the vehicle, the less the momentum of the road dirt and the more likely it is for the road dirt to be deflected into crevices in the bodywork by the pressure eddies created around a fast moving vehicle by turbulence.

Damp, dirt, road salts, and general debris that are then thrown towards the undersides of a vehicle in this way collect not only over headlights, but also on ledges, some of which may be out of the line of any direct spray. These relatively inaccessible ledges may not then be cleaned when driving subsequently in wet conditions.

The sites on vehicle bodywork most prone to pitting corrosion include, therefore:

1. all underbody areas where road dirt can accumulate and restrict natural drying;
2. beneath mud poultices, wherever they have formed;
3. within poorly protected (or damaged) folds and flanges of the bodywork;
4. beneath poorly adherent, but coherent, paints and protective coatings.

In vehicle bodywork, crevice corrosion can develop, in the presence of moisture, where two metal surfaces have been joined together. The deeper part of the crevice that is formed is often starved of oxygen and so becomes anodic. Most commonly, small crevices are formed when body panels have been joined by spot welding. Over time, these small crevices fill with dirt, preventing evaporation of any moisture present and concentrating electrolyte in a small area. Corrosion may advance rapidly.

Bolted joints are also susceptible to crevice corrosion, unless the two metal surfaces can be separated from each other electrically, by insulating washers. Corrosion will again occur in the least oxygenated regions. In the case of bolted joints, crevice corrosion of the thread will then cause the bolt to seize.

Fretting corrosion (localized corrosion as a consequence of fretting) can occur in motor vehicles. Body panels and structural members in close contact with each other may be subjected to repeated vibration, as the vehicle travels along the road. While such vibrational movement is usually small, it can lead, over time, to fretting of loose particles of metal and paint coatings. If the resulting loose particles then act as abrasives, they may damage otherwise sound surfaces and lead to corrosion. Vehicle doors, bonnets, and boot lids, if too closely fitting, for example, or if distorted as the result of an accident, are susceptible to localized fretting corrosion in this way.

Waterline corrosion in automobile bodywork is sometimes referred to as dirt-wick corrosion. It can develop where condensation may be trapped and collect, within the sills, for example. The lower parts of the doors are also prone to this type of corrosion. The problem is caused usually by rainwater penetrating old window seals in car doors and then collecting in the bottom sections. If dirt and debris also accumulates in these areas and blocks the drainage holes, a moist poultice forms. Wicking action, over time, sets up an unequal oxygen concentration above and below the resulting waterline because oxygen is available freely above the waterline and is restricted below. The rate of waterline corrosion, once established, can be rapid.

Corrosion prediction and prevention in motor vehicles has been described, illustrated, and explained in detail by McArthur.[1]

4.37.3 Advances in the Prevention of Corrosion in Automotive Bodywork

The corrosion resistance of motor vehicles has improved markedly over the past 25 years, permitting longer and longer antiperforation warranties to be offered by the manufacturers, currently up to 12 years.

The improvements have stemmed from significant advances in:

1. design;
2. material selection;
3. protective paint coating systems and application methods;
4. sealants and application methods.

4.37.3.1 Improvements in Design

Many of the choices made by designers of motor vehicles may impact on the susceptibility of the vehicle to corrosion. In recent years, however, corrosion resistance has assumed a much greater prominence, driven by the warranty system, and designers now recognize clearly the consumer's need not only for pleasing, modern body envelopes but also for the best possible corrosion resistance and long-term durability that are achievable commercially.

Vehicle designers, working closely with engineering support teams, now strive to reduce high stresses in bodywork panels, for example, by avoiding the deep pressings needed to produce sharp changes of curvature. Modern body shapes tend to be much smoother and more rounded than they used to be. Smooth body profiles ensure the best possible drainage of water from the surface, not only in the pretreatment and priming stages of manufacture but also in functional use. Smoother body profiles also keep to a minimum awkward corners where dirt and road salts could accumulate and ensure that if there are any unavoidable crevices, they can be reached, in subsequent manufacture, by the robots used to apply sealant.

The avoidance of contact between dissimilar metals and the ensuing risk of bimetallic corrosion on vehicle bodywork have been largely eliminated by the introduction of plastic bumpers, radiator grilles, and door handles and nonmetallic protective side trim.

Problems of bimetallic corrosion are now limited largely to the sophisticated electronic control systems which manage modern engines, regulate antilock braking systems, and stabilize traction.

4.37.3.2 Advances in Materials

For many years, the dominant material of construction for automotive bodywork was carbon steel. Major advances were made initially in the mid-1970s with the introduction of precoated steels, electrogalvanized steels, and other corrosion-resistant materials. Zinc-coated steels (coated on one side only initially) were used to protect the inner surface of body panels, leaving the outer surface uncoated and available for painting.

By the mid-1980s, two-sided electrogalvanized sheet and other zinc alloy steels had become widely available and were being used to manufacture exterior body panels. By virtue of being coated on both sides, the material afforded protection not only from internal perforation corrosion but also from external cosmetic corrosion. It was the introduction of these two-sided zinc/zinc alloy materials that made extended antiperforation and cosmetic corrosion warranties into a reality.

Over the past 15 or so years, a variety of alternative nonferrous materials, predominantly aluminum alloys and plastics, have found automotive applications. Their introduction has presented new challenges. It has driven forward advances in pretreatments for mixed metal assemblies and has helped to define suitable methods of surface preparation, prior to painting plastic bumpers, for example, to color-match the rest of the vehicle bodywork. The use of plastic materials in modern automobiles is increasing, and has contributed significantly to the industry's goal of corrosion avoidance. Plastic components have allowed weight reductions to be made and, as a consequence, savings in fuel consumption and vehicle emissions. Plastic panels present their own design challenges, however, as they contribute very little to the structural rigidity of the vehicle body, as a whole.

Aluminum alloys offer two benefits over carbon steel. First, they are much lighter, and second, they are more corrosion resistant. Aluminum alloys have been used successfully by some vehicle manufacturers for the bonnets and boot lids, primarily to reduce total weight and so improve fuel efficiency.

Improvements in the corrosion resistance of exhaust systems have demonstrated most clearly the benefits of material selection. Stainless steel exhaust systems are known to have very good corrosion resistance and much improved durability. They have not been favored widely by consumers, however, as they are significantly more expensive than their carbon steel counterparts. Aluminized steel silencers, however, are now available widely and represent a good compromise: almost as good performance, at a lower cost. The clear benefit of fitting, as standard, more corrosion-resistant aluminized steel vehicle exhaust systems was advocated by Hoar[2] as long ago as 1971 as a relatively simple and inexpensive way of reducing the overall cost of automobile corrosion. The implementation of his advice by vehicle manufacturers, as the availability of the products increased, has been very successful.

4.37.3.3 Corrosion Protection by the Paint System

The preparation and painting of new automobiles is now a sophisticated, high-speed industrial process, with vehicle bodies passing through the entire coating line in 6–10 h.

The automotive paint systems used have been developed over the past 35 years and provide, today, not only highly durable finishes but also robust corrosion protection. The extended perforation warranties (up to 12 years) offered currently by vehicle manufacturers are a reflection of the considerable advances that have been made.

A typical paint system for a new vehicle consists of:

1. a primer (applied at a dry film thickness of 18–25 µm);
2. a surfacer (applied at a dry film thickness of 35–40 µm);
3. an antichip coating (applied at a dry film thickness of 50–100 µm);
4. a finish (applied at a total dry film thickness of 45–55 µm).

Corrosion protection is afforded primarily by the primer and intermediate coats of the paint system. The function of the finish is to provide good appearance and customer appeal as well as good resistance to weathering, surface scratching, and surface contamination.

Initial cleaning and chemical pretreatment of the vehicle body has also advanced in recent years and provides the foundation needed for the subsequent paint system.

The contributions made by metal pretreatment, primers, surfacers, antichip coatings, and underbody protection (only) to the corrosion protection of the bodywork today on new automobiles will, therefore, be considered further.

4.37.3.3.1 Pretreatment

Metal pretreatment of automotive car bodies has three main purposes:

1. to remove any surface corrosion products, pressing oils, and temporary protective coatings;
2. to improve the adhesion of the subsequent primer coat to the metal surface;
3. to minimize the spread of underfilm corrosion.

The effective removal of the oils and greases used to lubricate body panels during the forming processes has improved the subsequent efficiency of modern, new vehicle coating lines substantially.

Zinc phosphate pretreatment is used almost universally in modern automotive painting plants to provide metal cleanliness and the first stage of the corrosion protection. A typical zinc phosphate process begins with multiple cleaning stages, followed by a titanated activating rinse, zinc phosphate pretreatment, and a sealant rinse. The process is completed by multiple rinses with deionized water. In total, a seven-stage process is now typical, followed by a heated (oven) drying-off stage.

The cleaning and phosphating process is carried out on a conveyorized system. For the cleaning step, a weakly alkaline degreasing solution of aqueous mixtures of salts, wetting agents, and emulsifiers is used. This cleaning solution is applied by a combination of spray and dip treatments, at temperatures of 40–60 °C. The most effective removal of drawing oils takes place in the dip tanks, as full immersion allows the insides of box (strengthening) sections to be reached.

Uniformity of application of the subsequent zinc phosphate conversion coating then takes place in two stages. The clean metal surface is first activated, and the layer of phosphate crystals is then built up, typically to a thickness of 1–2 µm.

There have been a number of developments in pretreatment processes in recent years, primarily to meet the demands of mixed-metal assemblies, energy efficiency, and environmental pressures.

Significant developments have included:

1. nickel- and manganese-enriched zinc phosphates, with controlled fluoride addition;
2. lower temperature processes and chrome-free rinses, for reduced energy cost and environmental impact;
3. optimum control of process parameters through computerized instrumentation;
4. changes from spray-and-dip to full dip processes.

The benefits from these recent developments have included:

1. excellent performance under cathodic electrocoat primers;
2. good phosphate crystal morphology;

3. reduced energy consumption;
4. the requirement for a chrome post-rinse eliminated by the introduction of safer products, such as titanates.

4.37.3.3.2 Priming

The function of the primer is to provide the main corrosion protection for the automotive body. Primers are generally of the ‘inhibitive’ type – containing anticorrosive pigments in a film-forming binder. They are required to inhibit the spread of corrosion on the metal substrate, resulting from any defects in the coating system as a whole; to have good resistance to mechanical damage (notably chipping); and to prevent the spread of corrosion from such points of damage. In order to provide these performance requirements, they must have not only good adhesion to the pretreated metal substrate but also good adhesion to the coating applied subsequently (surfacer) of the full paint system.

The significance of the priming stage in the corrosion protection of automobile bodies is reflected in the number of innovative technological developments by automotive paint manufacturers for original equipment manufacture (OEM) over the last 40 years.

With the advent of welded unit construction of car bodies (monocoque construction) in the mid-1940s, many areas of the individual units were virtually inaccessible to a spray gun, for example, the internals of strengthening cross-members and the front end near door posts. Spray application of primers was no longer feasible, therefore, and dipping processes were introduced. Initially, dipping primers were solvent-borne, but in the 1960s waterborne formulations were introduced, leading ultimately to the development of modern electrocoat primers.

In moving towards electrocoat priming, which is now the most widespread process for applying an anticorrosive primer to mass-produced, new automobile bodies, the automotive industry has progressed from dipping of car bodies up to window level (the so-called ‘slipper’ dip process) to full immersion dip coating which, when first used with early waterborne dip primers, resulted in unwanted runs and sags in the coating on car body panels with complex design curvature.

Electrocoat priming of automobiles began in the late 1960s. Within 5 years, almost all mass-produced vehicles were primed in this way. Electrocoat priming offered several benefits to motor vehicle manufacturers, including:

1. uniform film build (15–35 μm) on all surfaces in contact with the liquid primer, including areas previously difficult to coat effectively: for example, voids in box sections;
2. greater corrosion resistance from improved coverage with a defect-free film of controlled thickness;
3. a highly efficient coating process, with ca. 95% of the coating material deposited in comparison to 50–60% with a conventional dipping primer;
4. greatly reduced solvent emissions and fire hazard.

Electrocoat paints are waterborne coatings containing film-formers (binders), pigments, extenders, and additives. The resulting dispersion will deposit an organic coating on the metal substrate when a direct electrical current is passed. Dispersions stabilized by a negative charge coagulate at the anode and dispersions stabilized with a positive charge coagulate at the cathode.

To enable deposition, the vehicle body is connected to an electrode and is immersed in a tank of the coating dispersion, together with a counter-electrode. The liquid paint is circulated in the tank continuously (forced circulation) to ensure a constant supply of the primer for deposition on the metal surface to prevent the dispersion from settling and, also, to dissipate the heat generated from the flow of the electrical current. The deposition process involves electrolysis, electrophoresis, and electroendosmosis.

Initially, electrocoat primers were of the anodic type, consisting of an acidic film-forming resin solubilized with an organic (amine-type) or inorganic base. In the late 1970s, however, demands for still better corrosion protection, notably in Canada and the colder states of the United States, led to the development of cathodic electrocoating processes. In the cathodic electrocoat process, the acidic component (a carboxylic acid) solubilizes an amine salt of the film-forming resin (epoxy).

The main reasons for the rapid change from anodic to cathodic electrocoat priming were as follows:

1. improved corrosion protection (a 3–4-fold improvement, in conjunction with suitable chemical pretreatment);
2. dissolution of iron no longer being favored;
3. improved ‘throwing power’ (penetration and better coating of voids);
4. corrosion protection at lower film thicknesses (18–22 μm, compared with 25–35 μm for an anodic electrocoat primer).

There have been several generations of cathodic electrocoat primers over the last 30 years. Each new generation has been developed to meet changes in vehicle manufacturing methods and the requirements of increasingly stringent environmental legislation. The most recent formulations are now lead-free and will perform well over low nickel and chrome-free pretreatments. Primers now cure at lower temperatures (130–150 °C) and allow steel components to which plastic parts have already been attached to be co-processed.

The development of electrocoat primers has been described in detail by Ansdell[3] and by Vachlas.[4]

4.37.3.3.3 Seam sealants and anticorrosive waxes

Sealants are usually applied to specific areas of the automotive vehicle body after the electrocoat primer has been applied. Anticorrosive waxes, however, are not usually applied until the final stage of the painting process, often while the painted metal sections are still hot, in order to aid both flow and penetration into cavities and joints.

The application of sealing compounds improves considerably the overall corrosion protection of weld seams and other jointed areas. In most modern car plants, the polyvinyl chloride (PVC) or polyurethane-based sealants used currently are applied by a hot, airless spray. Application is no longer a manual process, as these specialist coating products can be applied more effectively and more consistently by robots.

Anticorrosive waxes, where they are still employed, are also applied by spray. These wax coating products are based typically on polyethylene waxes, with added thickeners and anticorrosive pigments. They are used by some vehicle manufacturers to provide additional corrosion protection, for example, inside door cavities. The waxes are inert, water repellent, and relatively impermeable to moisture.

4.37.3.3.4 Surfacers

Surfacers, sometimes referred to as primer surfacers or filler coats, continue to play an important role in automotive coating systems. They are applied not only to the exterior of the vehicle body but also underneath the bonnet and inside the boot. The vehicle body is given, therefore, an intermediate coating that provides not only an additional defense against corrosion but also protects the electrocoat primer from damage.

The main function of surfacers, however, is still to fill and smooth any unevenness in the exterior bodywork and provide a surface which, with the minimum of sanding (none may be required), can then be coated with the topcoats of the automotive system (basecoat and clearcoat). Surfacers have evolved considerably over recent years to be compatible with new developments in topcoat technologies, meet higher performance standards, and comply with environmental requirements.

In addition to good sandability (and repair), these multifunctional coatings must:

1. possess good mechanical properties – notably flexibility and impact resistance;
2. be resistant to stone chipping, water, and moisture;
3. have good adhesion to the cathodic electrocoat primer, seam sealants, antichip coatings, and the subsequent basecoat of the finish.

Polyester resins, combined with a suitable polyurethane resin, are now recognized as the best binder systems for surfacers. The pigmented surfacer coatings are applied at a typical dry film thickness of 35–40 μm and, increasingly are now color-coded to match the color of the topcoat.

The development of surfacers has been described in detail by Ansdell.[5]

4.37.3.3.5 Antichip coatings

Antichip coatings are now a well-established component of modern automotive paint systems. First introduced some 20 years ago, the primary function of these softer coatings is to provide stone-chip resistance on vulnerable areas of the car body, such as door sills, the bodywork below the front and rear bumpers, the leading edge of the bonnet, and the underbody of the vehicle.

Antichip coatings are applied by spray at typical dry film thicknesses of 50–100 μm, usually 'wet-on-wet' and immediately after application of the surfacer. The two coatings (surfacer and antichip) are then cured at an elevated temperature (stoved), in a common process step. It follows that good compatibility between the antichip coating and the surfacer is needed, so antichip coatings are formulated with similar polyester/polyurethane resins.

4.37.3.3.6 Underbody protection

Underbody coatings are protective coatings applied, by spray, at high film thicknesses (up to 1000 μm) to the underside of finish-painted vehicles to protect the floor panels from corrosion and abrasion caused by impacts of loose road gravel and other surface debris. These coatings need, therefore, to be durable, elastic, and to have good barrier properties. Polyurethane-based formulations have superseded the older types of rubber-based underseals.

Some vehicle manufacturers, however, now favor plastic panels over the spray application of liquid coatings for this service function.

4.37.4 Concluding Remarks

For some 30 years, innovative technology and responses to globalization and market economics have underpinned the automotive industry's successful strategies to control corrosion in motor vehicles. Globalization has accelerated the uptake of new technologies, and manufacturer's warranty schemes have given 'corrosion avoidance' an increasingly high profile in a highly competitive consumer market.

The 'corrosion avoidance' strategy has been very successful, and corrosion problems are now confined largely to the bodywork of motor vehicles over 10 years old.

Corrosion-related failures of some mechanical, electrical, and electronic components, however, continue to occur, and these parts of the supply chain are now under increasing pressure to advance their own 'corrosion avoidance' strategies to the same high level.

Each advance in 'corrosion avoidance' adds directly to the cost of a new vehicle. The most recent study in the United Kingdom into the cost of corrosion,[6] which was reported in 2001, estimated that, in the United Kingdom the overall additional expenditure for improved management of corrosion by the manufacturer was £160 million in 1999. At the equivalent added cost per vehicle of £90, the potential long-term cost benefit to the purchaser is obvious.

Whatever the final outcome of the current global financial downturn, the interplay among new technology, regulatory requirements, and consumer economics will continue to exert a potent influence on the automotive industry, and its suppliers.

Corrosion management will remain a vital element of that process.

References

1. McArthur, H. *Corrosion Prediction and Prevention in Motor Vehicles*, 1st ed.; Ellis Horwood: Chichester, 1988; Chapter 4, pp 77–122.
2. Hoar, T. P. *Report of the Committee on Corrosion and Protection*; HMSO: London, 1971.
3. Ansdell, D. A. *Paint and Surface Coatings – Theory and Practice*, 2nd ed.; Woodhead Publishing: Cambridge, UK, 1999; Chapter 10, pp 422–431.
4. Vachlas, Z. *Automotive Paints and Coatings*, 1st ed.; VCH Verlag GmbH: Weinheim, 1995; Chapter 3, pp 28–71.
5. Ansdell, D. A. *Automotive Paints and Coatings*, 1st ed.; VCH Verlag GmbH: Weinheim, 1995; Chapter 4, pp 72–118.
6. Investigation of the cost of corrosion, risk assessment methodologies and procedures for minimising corrosion costs, Degradation of Materials in Aggressive Environments Programme 1998–2001. Report by Paint Research Association to the Department of Trade and Industry, Report DME 5.3 (3), October 2001.

4.36 Corrosion Monitoring and Inspection

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Glossary

Access fitting Entry-port system for corrosion monitoring sensors, which can be inserted or withdrawn at system pressure using a heavy duty valve and retriever tool.

Barrel US oil industry unit for a container holding 42 US gallons, equivalent to ~159 l or ~35 Imperial (UK) gallons.

Biocide A chemical added to plant and pipelines systems to control and kill bacteria.

Bragg grating Component of optical sensing technology using fiber sensors.

Caliper tool Oil industry term describing a caliper measurement tool for the inspection of corrosion in down-well oil tubing, a specific version of which is the *Kinley caliper tool*.

Corrosion allowance Additional thickness of material provided to ensure that the wall thickness does not drop below the minimum design thickness in service.

Couplant Special grease or liquid (glycerin or oil) applied to the metal surface where an ultrasonic probe is applied to measure metal thickness or detect defects.

Coupon Strip of material that is exposed to a corroding environment to quantify the corrosion rate by weight change.

Electrical resistance Technique for corrosion monitoring based on the measurement of changes in the electrical resistance of metal elements to determine the corrosion rate.

Electrochemical noise Electrochemical technique relying on measurement and analysis of the spontaneous currents/voltages generated between electrodes in an electrolyte.

Electromagnetic acoustic transducer Technique for transmitting and receiving ultrasonic waves to/from the surface of a component without the requirement for contact with an external vibrating transducer.

Fabry–Perot sensor Interferometer using fiber optics for sensing several parameters such as temperature, strain, and acoustic waves.

Fiber optics Technique for sensing a number of parameters including strain.

Fractal and neural analysis Mathematical analysis of shapes and images.

Galvanic probe Electrochemical probe using two different metals electrodes for the measurement of galvanic currents.

Intelligent pigging Use of an intelligent vehicle (PIG) containing instrumentation that travels in the pipeline for assessing both corrosion loss and stress corrosion cracking; also referred to as inline inspection (ILI).

Intrinsic safety The fitting of a sensitive fuse device (zener diode barrier) to electrical equipment in plant handling flammable substances. In UK and other countries, each electrical device must be certificated by a certifying authority.

Iron count Oil industry term describing the total iron content in a fluid stream.

Lateral waves Ultrasonic waves that are compression waves propagating close to the surface of an object, which continually generate a shear wave propagating into the bulk of the object under test.

Lorentz force Force on a point charge due to electromagnetic fields.

Nyquist diagram Diagram displaying the frequency dispersion of impedance.

Piezzoelectric crystal Substance (quartz, lithium sulfate, barium titanate) that emits ultrasonic waves when subjected to an electrical charge.

Planktonic bacteria Bacteria suspended in the bulk of liquid flowing in a plant or pipeline system.

Pressure gland Pressure seal that can be tightened to withstand defined pressures when installing corrosion probes in a system. For safety reasons, a pressure-gland system is regarded as less reliable than an access system with associated retriever tool.

Radiography Technique for examining materials using either X-rays or gamma radiation.

Radio respirometry Instrument system investigating the respiration cycle of different bacteria types.

Raman and Brillouin scattering Light scattering due to time-dependent density variations in a liquid medium.

RSTRENG Calculation to establish the remaining strength of piping or pipeline.

Retrieval tool High-pressure balanced tool used for the retrieval of monitoring devices when a system is under pressure.

Robbin's unit Unit fitted in a length of pipeline, piping, or vessel containing metal studs used for monitoring for the presence of bacteria.

Sour systems Term used by the oil industry to describe a system containing hydrogen sulfide.

Sessile bacteria Colony (or colonies) of bacteria metabolizing on the surface of a metal under scale or other deposits shielded from the fluid.

U-bend coupon A metal coupon bent into a U–shape and exposed to a corrodant to test for susceptibility to stress corrosion cracking.

Ultrasonics Technique using high-frequency sound waves to measure the thickness of material and detect defects.

Abbreviations

ADP Adenose triphosphate photometry

AE Acoustic emission

API American Petroleum Institute

ASNDT American Society for Nondestructive Testing

ASTM American Society for Testing Materials

BG British Gas

BINDT British Institute of Nondestructive Testing

CONCAWE European organization for Conservation of Clean Air and Water

CRA Corrosion resistant alloy

CRT Cathode ray tube

CUI Corrosion under insulation

DOT American Department of Transportation

DPI Dye penetrant inspection

EFC European Federation of Corrosion

EFM Electrochemical frequency modulation

EIS Electrochemical impedance spectroscopy

EMAT Electromagnetic acoustic transducer

EN Electrochemical noise

ER Electrical resistance

FHWA American Federal Highways Administration

FOS Fiber optic sensor

FSM Field Signature Method

HA Harmonic analysis

HSE UK Health and Safety Executive

ICDA Internal corrosion direct assessment

ILI Inline inspection

IRIS Internal rotary inspection system

LPR Linear polarization resistance

LRUT Long range ultrasonic transducer

MFL Magnetic flux leakage

MPI Magnetic particle inspection

NACE National Association of Corrosion Engineers

NRA UK National Rivers Authority

NTD/E Nondestructive testing/examination

NTSB American National Transportation Safety Board

P and ID Process and instrumentation diagram

PIG Pipeline inspection gauge

RBI Risk-based inspection

SCC Stress corrosion cracking

TLA Thin layer activation

TOFD Time-of-flight diffraction

UT Ultrasonic testing

ZRA Zero resistance ammeter

Symbols

b_a and b_c Tafel constants
d Density
i_{corr} Corrosion current density at E_{corr}
t Time
A Area
E Potential
E_{corr} Natural corrosion potential
mil American unit for corrosion loss,
1 mil = 0.001 inch and 40 mil = 1 mm
R_n Noise resistance
R_p Polarization resistance
W Weight
σi_n Standard deviation of the EN current
σV_n Standard deviation of the EN potential

4.36.1 Corrosion Monitoring

4.36.1.1 Definition

Various definitions of corrosion monitoring have appeared since the adoption of industrial corrosion monitoring techniques began to gather pace, first in the USA and later in Europe. Some definitions that have appeared in the literature are as follows:

1. The systematic measurement of the corrosion or degradation of an item of equipment, with the objective of assisting the understanding of the corrosion process and/or obtaining information for use in controlling corrosion and its consequences[1]
2. The assessment of the degradation of a material caused through environmental, chemical, electrochemical, or biological action or reaction[2]
3. Any technique used to observe or measure the progress of corrosion[3]

The author prefers the first definition as it clearly outlines the prime objective of corrosion monitoring and provides important information regarding the benefits obtained in the operation of a corrosion monitoring program. The second definition gives some information regarding both possible corrosion mechanisms and environments. The third definition, although correct, provides no information as to the possible objectives and the advantages of online monitoring in correlating corrosion information with plant conditions and corrosion control techniques.

The ability to correlate corrosion data with operating and process conditions is a very important aspect of corrosion monitoring that differentiates it from inspection, which provides only a snapshot of condition at the time of the inspection. However, some inspection techniques now provide continuous information that bridges the boundary between corrosion monitoring and inspection techniques. Cox *et al.*[4] have pointed out that traditional corrosion control and condition monitoring are still considered to be support services and have presented reasons for this, such as that those involved are mainly technical specialists and enthusiasts, who do not have production responsibility and accountability. The basic techniques of both corrosion monitoring and condition monitoring have been refined, new technologies have been added and their functionality has been augmented by the application of modern computerized data collection, evaluation, and presentation.[4]

Other definitions have emphasized the multidisciplinary nature of corrosion monitoring, covering a wide range of materials, measurement techniques, instrumentation, rules and regulations, standards, logistical support, data analysis communication, and management information. It has been written that if one does not measure (monitor) corrosion, one will not be able to understand it and if one is unable to understand corrosion, one will not be able to control it or improve corrosion control techniques.

4.36.1.2 Benefits of Corrosion Monitoring

The effective management of corrosion in organizations is essential if corrosion risks to safety, health, the environment, and economic viability are to be maintained within acceptable limit values. The wider issue of corrosion management is covered in a separate chapter in this book. Corrosion monitoring and inspection are essential processes in an overall corrosion management system that manages corrosion risks through a combination of proactive and reactive measures[5] that are outlined as follows:

1. Proactive measures are those in which the requirements and implementation of the monitoring system or inspection programs are identified and in place before any corrosion or deterioration has been observed, based either on the outputs of a corrosion risk assessment or on some other review/identification of areas of possible/likely corrosion.
2. Reactive measures are implemented after a problem has been identified, either as a consequence of proactive monitoring or because of an incident or the identification of a problem as a result of inspection.

Corrosion monitoring is of particular benefit in capital intensive industries such as oil and gas (production and refining), petrochemical/chemical manufacture, and electricity generation that are concerned with large volume throughputs where intervals between scheduled shutdowns are generally long and result in large financial penalties. Thus, corrosion monitoring can help to identify and control corrosion regimes that prevail during transient operating periods such as startup and shutdown. It can signal the corrosion implications of altering steady-state operating conditions such as temperature or composition beyond the original design limits. If inspections indicate that a corrosion problem has suddenly developed in service, corrosion monitoring can help to identify the causes of the corrosion damage and/or monitor the effectiveness of proposed treatments.

In several stages of oil and gas production and refining, and in utilities (boilers, cooling water systems, fire water circuits) and power generation, corrosion risk mitigation practices are based heavily on corrosion inhibitor addition. Continuous monitoring can provide criteria to optimize inhibitor dosages with resulting savings in chemical costs. Typically, a plant trial of candidate corrosion inhibitors would be undertaken following laboratory screening during which corrosion rates would be monitored to identify the most effective inhibitor and optimum dosage rates. The coupling of monitoring data output with dosing pumps could be used to automatically control the addition of inhibitors to maintain corrosion rates below specified limits cost effectively.

4.36.1.3 Making a Case for Corrosion Monitoring

To prepare a case for the introduction of corrosion monitoring, some essential information is required in the proposal. The required detail depends on the complexity and scale of the application. In some cases, the application is relatively simple as in the case of a reported increase in corrosion rate in an item of equipment that can be monitored with a few probes and standard equipment, and the case would be relatively simple and amenable to rapid implementation. However, if the application is more complex requiring installation and implementation of a major monitoring scheme in a new or operating plant, there will be a need for a detailed proposal. Any proposal should address and define some key issues.

4.36.1.3.1 Objectives

Corrosion monitoring is usually undertaken with one or more of three objectives:

1. To enable the diagnosis of corrosion problems in operating equipment
2. To monitor and control the effectiveness of corrosion risk mitigation processes such as inhibitor addition in operating equipment
3. To facilitate the scheduling of shutdowns, usually within a risk-based inspection (RBI) strategy

It is beneficial to incorporate into the proposal examples (with references) of relevant, successful industrial corrosion monitoring programs, many of which are available from the literature and other reference sources such as the internet.

4.36.1.3.2 Budgets

Budgets are necessary for the costs of equipment (plus spares), installation and operation, data reporting, and personnel. The delivery time for equipment is required to establish the timing of installation, not least for liaison purposes with maintenance at a shutdown period.

4.36.1.3.3 Choice of technique

The techniques to be adopted for corrosion monitoring and inspection should be defined, including whether invasive (penetrating into equipment/process) or noninvasive (measurements made external to equipment) and whether continuous (data available continuously from probes/sensors exposed to the corrodant) or periodic (sensors exposed to the process but which need to be extracted for analysis such as corrosion coupons or bio-studs).

Factors to be considered include the objective(s) of the proposed monitoring, the appropriateness of candidate techniques in relation to the types of corrosion expected, compatibility with any existing techniques that are used for inspection and monitoring, and the available locations for sensors and the type of instrumentation (portable or automatic) that can be employed. Uniform or general corrosion is the easiest to monitor with a wide choice of monitoring techniques. Localized corrosion has historically been more difficult to monitor in plant or in the field but recent developments in electrochemical techniques, in particular electrochemical noise (EN), have opened the door to the monitoring of localized corrosion, in particular pitting corrosion. However, few engineers receive any training in electrochemistry and they are therefore less receptive to monitoring techniques that are electrochemically based. The electrochemical impedance spectroscopy (EIS) and EN techniques are particularly challenging in this respect and although software can convert complex responses into simple corrosion rates, the lack of understanding of the fundamental basis of the technique inhibits adoption, especially by new users and in remote locations.

Guidance on this aspect is given by Rothwell *et al.*[2] It has been reported[6] that the most successful applications are those in which an integrated system has been installed incorporating several techniques that are the most suitable and appropriate. Of course, there has to be a compromise between the number of techniques used and the total cost including purchase, spares, and operation.

4.36.1.3.4 Awareness of limitations of candidate techniques

All corrosion monitoring techniques have advantages and limitations. Invasive techniques require entries for probes and this may have safety implications depending on the type of plant. A limitation of any monitoring technique that utilizes coupons or probes is that measurements are made on sensor elements or electrodes and not the plant itself. Additionally, the metallurgical condition of the sensor elements or electrodes may not represent the plant metallurgy and temperature differences between the actual plant material and sensor elements or electrodes may be significant.

In the cases of electrical resistance (ER) or electrochemical probes, conductive films or deposits, typified by iron sulfide that may be formed in environments containing hydrogen sulfide, can interfere with operation. An additional uncertainty in the linear polarization resistance (LPR) technique is that polarization resistance (R_p) values are based on laboratory assessment and may not be relevant for certain environments. Galvanic corrosion is very dependent on the anode–cathode ratio, which may not be simulated by the probe.

The monitoring of localized corrosion is difficult and EN is one of the few online techniques for the monitoring of localized corrosion, although LPR systems can sometimes provide a pitting tendency of the environment. However, EN requires expertise for the interpretation of the data obtained. The skills and expertise of the personnel carrying out the monitoring program have important implications in relation to some of the complex electrochemical techniques and this should be borne in mind when the program is being planned.

Although awareness of such limitations is required, they need to be put into perspective. As long as the techniques chosen have some established reliability, these uncertainties are generally accepted bearing in mind that data are unlikely to be more than $\pm 20\%$ accurate. Of course, coupons can be used instead of probes, but although useful for verification, coupon results are also subject to errors, albeit, of a lesser order.

4.36.1.3.5 Personnel management

It is essential that the monitoring program has strong communication links with the inspection function and the corrosion engineer. In larger organizations, it is not unknown for corrosion expertise to be located remotely from the application, which can result in delays and communication problems. If either function is contracted to a third party, a communication and responsibility structure should be established. Liaison with other departments in the organization is also an essential requirement for successful operation. For example, changes in feedstock such as the source of crude oil in an oil refinery can have profound affects on corrosion behavior and all relevant functions involved with the corrosion monitoring should be advised of such changes. Likewise, inspection and allied personnel should advise operations of revised probe locations and any changes to the corrosion monitoring programs.

The corrosion monitoring program should itself be subjected to a periodic review of performance and requirements for change on an ongoing basis. The training of staff relating to current regulations, practices, and guidance is also an ongoing requirement. The availability and commitment of operating personnel are important factors here as the author has witnessed many boxes of corrosion probes lying in half-opened packing cases on the ground in desert oil installations due to nonavailability of personnel for supervision of both installation and operation.

4.36.1.3.6 Data management

The type of data required and its examination require detailed consideration at the design stage. A debate has always existed as to the value of continuous data if the outcome is vast amounts of records that are never examined in detail. The incorporation of corrosion management guidance into overall plant management provides a framework for the data required and the personnel/departments to which it should be directed. Corrosion monitoring and inspection data should be coordinated with operating/process information and evaluated by both inspection and corrosion personnel. Data handling should be standardized and available in a computer reporting format. All the data produced should be incorporated into relevant plant/equipment records and summary reports issued to relevant functions on a quarterly basis. The equipment that is being monitored and the associated data handling system should be reviewed regularly to avoid redundancy, duplication, and/or obsolete information being retained in current records.

Failure to standardize data recording and processing may undermine seriously the effectiveness of corrosion-monitoring programs. For example, some years ago the author carried out an audit of corrosion control measures on a major railway bridge in Scotland. An extensive program of coupon monitoring was in progress. There was a vast amount of coupon records, but no standardized reporting format to describe the appearance of the coupons. When an inspector was absent and another inspector substituted, the differing coupon descriptions resulted in inconsistencies that made accurate comparisons very difficult, if not impossible. Sadly, standards and recommended practices for the systematic recording of coupon corrosion were available but were ignored.

An example where data handling was not coordinated involved the corrosion failure of an overhead line in the saturated gas plant in a UK oil refinery, resulting in a major explosion.[7] The refinery controlled plant degradation mechanisms using a number of measures including materials selection, inspection, sampling for corrosive agents, and corrosion monitoring. An ER probe used for monitoring had shown a high corrosion rate, but this was not followed up.[7] This was one of the several problems with the corrosion monitoring and inspection recording at the refinery. Individual members of the refinery's inspection group did keep records of corrosion-related incidents, but there was no central data base to hold the information.

4.36.1.3.7 Legislation and standards

Legislation regarding corrosion engineering has been produced in several countries and standards and recommended practices relating to corrosion monitoring have been issued by bodies such as National Association of Corrosion Engineers (NACE) International in the USA and the European Federation of Corrosion (EFC). The UK Health and Safety Executive (HSE) has issued specific guidance for the offshore/onshore oil industry as well as for other industries and many other professional organizations have produced published guidance relating to corrosion monitoring, the more significant of which are listed in Appendix 1. Where available, company in-house practices should be followed in addition to national or industry standards.

4.36.1.3.8 Engineering considerations

Regardless of the type of the sensor, commercial probes are available in fixed (screw-in, flanged) or retractable forms. Various hardware systems are available for the insertion and extraction of probes online based on pressure-gland fitting via a 1-inch (25.4 mm) full-bore opening gate-valve and access-fittings used with a retractable tool and valve. Problems such as the welding of access-fitting covers for the hydraulic test after construction need to be anticipated and prevented.

For existing plants, there is usually enough in-plant corrosion experience to identify appropriate locations of sensors. For new applications, and in particular, new processes, the location of sensors can be a complicated and contentious issue. Contractors, in general, have little experience of monitoring and can be reluctant to suggest installation in case clients conclude that their designs are using materials with inadequate corrosion resistance. Clients may have to instruct contractors that a requirement exists for monitoring and define where sensors should be positioned. Discussion with other operators of similar plants can be worthwhile. Chosen locations should be verified for appropriate working. For example, it has been know for locations to be specified at heights requiring scaffolding for reading by portable instruments. The identification of the preferred sensor type to be fitted at each location should be recorded, for example, on the relevant process and instrumentation diagram (P and ID) in the process industries.

The most important consideration when selecting corrosion monitoring locations is that they sample the corrosion risk to be evaluated. For example, within crude oil and wet gas production systems, it is important to find locations where the corrosion coupon or probe will be immersed in any produced water.[8] In pipelines, this is typically at the 6 o'clock position on horizontal sections, because the produced water is heavier than crude oil or gas condensates. Unfortunately, many pipeline and facility engineers have installed monitoring locations on the sides of the pipeline rather than at the bottom. Although side locations provide easier access to retrieval, coupons or probes cannot provide accurate data unless the pipelines are essentially full of water.[8] Operator convenience must not come at the expense of valid results when selecting coupon or probe monitoring locations.

Consideration must be given also to the provision of sufficient room at the proposed location for the operation of retriever tools that require, typically, a minimum of 4–6 feet (1–2 m) clearance.[8]

Intrusive probes should be situated where they can remain in place for extended periods, rather than having to be removed periodically for pigging or other routine operations. Thus, intrusive probes should be installed upstream of pig launchers and downstream of pig receivers. Where this is not possible, flush-mounted probes are required.[8]

Instrumentation must be engineered to minimize the risk of ignition of any flammable substances that may be present from electrical sources. This is particularly relevant to the oil and gas, petrochemical, and chemical industries. This intrinsic safety is engineered by the incorporation of zener diode barriers or an equivalent electrical engineering safety system. There is no technical reason for any corrosion monitoring system not to be engineered for intrinsic safety. Assistance on these matters can be obtained from safety staff in the company. Many countries have organizations responsible for this aspect using either American or European standards.

4.36.1.4 Techniques for Corrosion Monitoring

4.36.1.4.1 Historical development of corrosion monitoring

It has been estimated that the worldwide market for corrosion monitoring equipment (excluding inspection) is of the order of $25 M including ancillary fittings and associated tools. The early US manufacturers of corrosion monitoring equipment were specialty process chemical manufacturers (in particular corrosion inhibitors), who regarded monitoring as a useful adjunct to their chemical products. Instruments were marketed as providing criteria to judge the effectiveness and optimum dosage rates of inhibitors. The instrument manufacturing/supply functions were not seen as profit centers *per se* and were mostly underfinanced, and in general, unsupported at that time.

Some of the earliest applications of corrosion monitoring were in the chemical industry. In the larger chemical companies with in-house corrosion expertise, electrochemical potential measurements were used to monitor the condition of passive materials and although this technique did not provide a rate of corrosion, it did allow operators to alter process conditions to maintain passivity and prevent serious damage. In-house developments in other techniques such as ER enabled construction of sensors/probes that were later licensed for commercial exploitation.

The conservative oil and gas industry was initially skeptical of instrumentation that claimed to provide internal corrosion rate data online. Despite the initial teething problems (selection of the wrong technique, inappropriate sensors or probes for the environment, sensors not sufficiently robust, sensors located in the wrong location), corrosion monitoring systems were slowly introduced for both existing and new plants. This took longer in Europe as most commercial monitoring equipment was of American origin resulting in long deliveries with minimal repair facilities, spares, shortages and more importantly, little if any general guidance and application advice locally.

The experiences of companies using corrosion monitoring in various industries in the UK were surveyed in 1981 and 1984.[6] Unfortunately, no subsequent independent survey has been undertaken and summaries of the data from the original surveys are given in **Tables 1–3**.

The 1981 survey was carried out 10 years after UK oil production had commenced and it is interesting that some of the problems identified in the 1981 survey had been considerably improved by the time of the 1984 survey. Overall, greatest success was obtained by users of integrated systems incorporating several techniques. According to survey returns, the usual package of techniques for monitoring corrosion of industrial

Table 1 Response rate by industrial sectors in the 1981 corrosion monitoring survey

Industry	*Response – no of forms/percentage*	
Oil and gas production	8/22	36%
Oil treating	6/20	30%
Chemical/petrochemical	9/11 (5/50)[a]	82%
Industrial boiler plants	2/4	50%
Industrial cooling water	2/10	20%
Gas distribution	0/5	–
Electricity generation	3/7	43%
Pipelines	0/1	–
Mining	2/5	40%
Process plant contractors	1/5	20%
Miscellaneous	5/20	25%
Total	38 RESPONSES	35%

[a] Five additional responses from a blind survey of 50 companies.
Source: Britton, C. F.; Tofield, B. C. *Mater. Perf.* **1988**, *27*(4), 41–44.

Table 2 Summary of the findings of the 1981 corrosion monitoring survey

Varied response
Widespread concern with the significance of the results and their interpretation
Ruggedness and reliability problems with equipment
Concern with intrinsic safety of equipment
Where corrosion monitoring is successful, several techniques are almost always in use
Widespread interest in new techniques
Universal use of NDT (especially ultrasonics and radiography)

Source: Britton, C. F.; Tofield, B. C. *Mater. Perf.* **1988**, *27*(4), 41–44.

Table 3 Summary of the findings of the 1984 corrosion monitoring survey

Increased awareness of the need for corrosion monitoring requirements to be considered at the design stage
Expanded use of corrosion monitoring in many companies
Greater appreciation of the qualitative nature of corrosion monitoring data and the need to learn by experience
Improved reliability of equipment, but much still to be done
Maintenance costs often too high
Desire to go more automatic and online
Awareness that system installation is expensive
Continuing interest in new techniques

Source: Britton, C. F.; Tofield, B. C. *Mater. Perf.* **1988**, *27*(4), 41–44.

plant at that time comprised corrosion coupons, an appropriate online probe system (either ER or LPR), and a nondestructive testing (NDT) technique, usually ultrasonics.

Since this book was last published in 1994, continuing advances in electronics, software development, and automatic data-handling have resulted in a wider range of techniques for corrosion monitoring from an increasing number of companies worldwide. In addition, much work has been carried out developing the existing monitoring techniques such as ER and LPR particularly in relation to element configuration, data processing, and measurement sensitivity. Electrochemical techniques with simultaneous monitoring of solution resistance enabling online calibration for the determination of Tafel constants are now available in commercial instrumentation. There has been considerable laboratory development of both EIS and EN. There has also been a significant development of ER technology in the form of the field signature method (FSM) that overcomes the fundamental drawback of most corrosion monitoring techniques by measuring the corrosion of the plant component rather than of a sensor or a coupon.

Plants are now routinely fitted with corrosion monitoring equipment in order to comply not only with required company practice but also with the legislation in a number of countries that requires the adoption of appropriate corrosion measurement techniques. Service quality from corrosion monitoring equipment suppliers has improved and delivery and servicing/repair times for equipment have gradually reduced. However, the availability of skilled personnel to operate instrumentation remains a challenge, particularly for the oil/gas industry in offshore and remote desert locations. In particular, the scarcity of expertise in corrosion theory and electrochemistry has been a considerable obstacle to the application of electrochemical monitoring techniques in both field and plant.

In addition to process plant applications, more specialized applications have emerged such as the monitoring of automobile car bodies, aircraft,[9] concrete reinforcement,[10] and atmospheric corrosion.

4.36.1.4.2 Coupons

Coupons are metal samples that are exposed to the corrosion environment to establish the corrosion rate. They are withdrawn from the plant at prescribed intervals and the corrosion rate is determined by gravimetric means involving weighing the coupon before and after the exposure following the removal of the corrosion products. In high temperature applications where metals are exposed to gas mixtures at high temperatures, the coupons may gain or lose weight depending on whether the corrosion products are adherent or show a tendency to spall from the coupon surface and other techniques may be required for corrosion evaluation. Coupons are often used to provide the base-line criteria in a corrosion monitoring program for comparison with instrumented techniques such as ER or the various electrochemical techniques. When confidence is established, the coupon numbers can be reduced.

Coupons are usually strips, flush discs, or cylindrical rods mounted in suitable racks or holders (Figure 1) that are inserted and retrieved at shutdowns, unless inserted in a bypass line or installed in operating plant using full-bore valves or a suitable high-pressure access system.

Coupons are exposed to the corroding environment for defined periods of time and should be insulated electrically from the support system. They are available from commercial suppliers in most

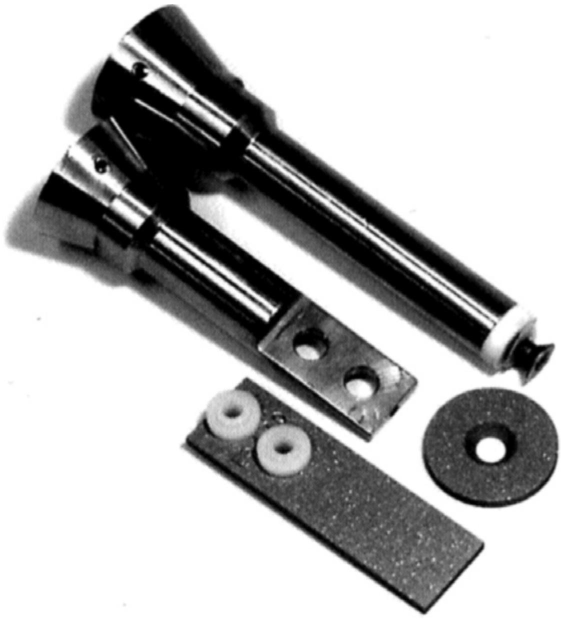


Figure 1 Corrosion coupon holders and corrosion coupons (Courtesy Cormon Ltd).

materials in a variety of geometries and are usually supplied in a surface-treated condition, weighed, and stamped with an identification number. For coupons manufactured in-house at plants, it is advisable to anneal the cut coupons in order to remove residual stresses from the cutting (often guillotining) process. Coupons can be exposed to any type of corrosive environment such as liquid corrosives, high temperature gases, soils, and the atmosphere.

The corrosion product has to be removed following exposure for evaluation and guidance is provided in the chapter on corrosion testing in this book. Errors are introduced if metal is removed in the cleaning process and they are minimized by including corrosion inhibitors in the cleaning solutions. Blank coupons can be cleaned to correct for any metal loss in the cleaning process itself. Large organizations may carry out coupon evaluation in-house but corrosion inhibitor suppliers often include a coupon evaluation service as a part of the inhibitor supply contract. Independent laboratories can also carry out this procedure for the smaller company or plant.

The corrosion rate is expressed in either mm year^{-1} (Europe/Middle East/Asia) or mils year^{-1} (USA) where 1 mm = 39.37 mils. The penetration rate is obtained by calculating the weight loss after exposure to the plant or field environment following treatment for the removal of the corrosion products. The other factors involved are the coupon surface area, metal density, and time of exposure and they are related as follows:

$$\text{Corrosion rate} = 10 \times \frac{W}{dAt}$$

where:

- Corrosion rate: mm year^{-1};
- W (weight loss): g;
- d (metal density): g cm^{-3};
- A (area): cm^2;
- t (time): years.

Special coupons for corrosion testing of welds, crevice corrosion, and for stress corrosion testing (U-bends, C-rings) are available from suppliers or can be assembled by users and guidance on suitable designs can be found in the literature. Errors can occur with coupon evaluation, as in any monitoring technique, and these can only be avoided by familiarity with all standards, codes of practice, and guidance from fellow workers. Coupons can exhibit localized attack such as pitting and crevice attack. If excessive localized attack is present, there is no point in reporting weight loss data. Common sense will determine if localized corrosion will negate the weight loss measurement; however, the representative reporting of coupon appearance is necessary. There is published guidance on the reporting of pitting attack on coupons.[11]

The author has seen many examples where users of coupons have not applied a consistent system for the description of coupon appearance, resulting in meaningless records. It is very difficult to assess coupon results prepared by different personnel without a consistent system for recording coupon appearance. Familiarity with coupon evaluation literature is recommended such as that published by NACE, American Society for Testing Materials (ASTM), and other organizations.[12,13]

The advantages of coupon monitoring include the relatively low cost and the provision of information on forms of localized corrosion such as pitting, crevice corrosion, stress corrosion, and galvanic (bimetallic) corrosion. Although the most common form of coupon is the metal strip, there are other geometries available, including flush-discs that sample conditions at equipment surfaces including the influence of fluid flow. Coupon strips can be exposed on supports in duplicate or in multiple arrays or on coupon-ladder racks allowing a number of coupons in different materials to be exposed at a specific location.

The disadvantages include the labor intensive nature of the technique (especially for offshore application) and the averaging of readings over the exposure period, which may mask possible shorter term excursions in corrosion rate. Automatic recording can minimize this aspect, which can also be mitigated by exposing a series of coupons at one location and retrieving individual coupons at prescribed intervals.

4.36.1.4.3 Electrical resistance (ER)

ER is an online, invasive technique utilizing a metal element made of the metal or alloy of interest mounted in a suitable housing, which is exposed to the corroding environment, as shown in Figure 2.

The increase in ER with time is measured as the element loses cross-sectional area due to corrosion. The use of ER for measuring atmospheric corrosion rate was first suggested in 1928 by Hudson[14] and was in use in laboratory experiments in England in the late 1930s. The technique fell into obscurity, until in 1954 Dravnieks *et al.*[15] demonstrated its potential as a practical field tool. Commercial exploitation was delayed by the need for temperature compensation that was eventually provided by locating compensating resistant elements in the probe body, which were protected from the corroding environment. Early instrumentation was marketed under the trade name Corrosometer™ by Magna Corporation in the US, with the patent relating to temperature compensation. Currently, there are many companies in many parts of the world manufacturing this type of equipment.

Elements are available in a variety of geometries including wires, tubes, and various flush designs incorporating spiral or concentric elements, as shown in Figure 3. ER elements can also be fitted into special spool designs, as shown in Figures 4 and 5.

The element is exposed to the corrosive environment (liquid or gas) and measurements taken at appropriate intervals. Readings can be automatic with transmission to the control room or manual with a portable reader for computer handling on return to the office. Data transmission has been carried out via satellite transmission from offshore platforms to onshore offices. The installation of a spool in a typical plant application is shown in Figure 6.

The data produced average the corrosion rate between measurement intervals, although with automatic readings on sensitive elements the intervals can be very small, and correlation with corrosion mitigation systems or plant variables can be made. The presence of conducting iron sulfide in the corrosion product on the element arising from the presence of hydrogen sulfide in the corrosion environment may invalidate the measurement as iron sulfide is a conductor. However, many corrosion engineers still use ER under these circumstances by applying a correction factor or allowance. In the case of a wire element, any pitting attack will increase the measured corrosion rate but the use of tubular elements reduces this affect by increasing the surface area of the element.

ER elements need replacement when the cross sectional area has decreased by ~50% resulting in a trade off between element life and sensitivity, that is, high sensitivity results in short life, although current

Figure 2 Electrical resistance (ER) probe – spiral wide tip (Courtesy Cormon Ltd).

Figure 3 Electrical resistance (ER) probe – spiral flush element (Courtesy Cormon Ltd).

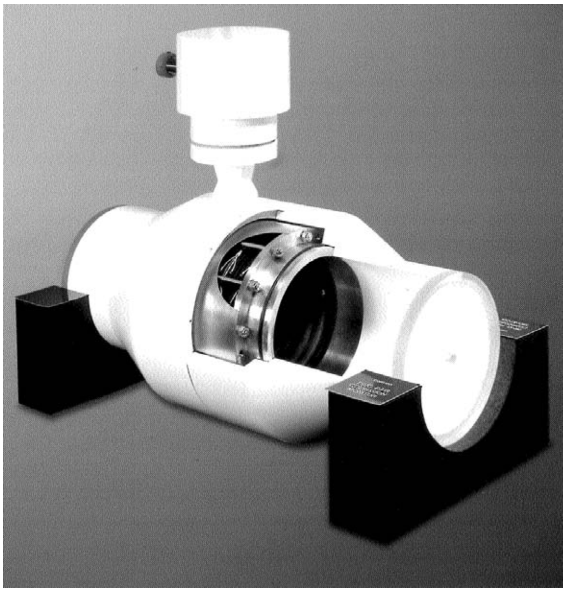


Figure 4 Electrical resistance probe (ER) – ‘Ring-Pair’ spool (Courtesy Cormon Ltd).

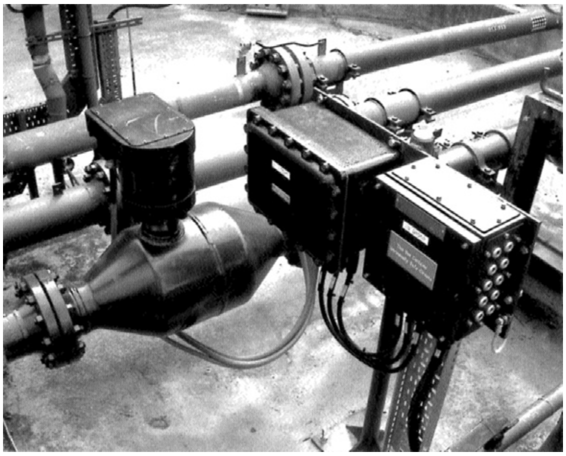


Figure 5 Electrical resistance probe (ER) – ‘Ring-Pair’ spool installation in plant (Courtesy Cormon Ltd).

electronic technology has improved this situation to some extent. Accuracy for the general range of ER equipment is claimed to be 0.1% for a single measurement, but this can be improved very considerably by using special equipment, details of which are available from the manufacturer’s literature or websites. It is important that the element should represent the metal or alloy of interest for the determination of corrosion rate and errors can arise in field/plant applications related to metal composition, metallurgical condition of the element, and heat transfer among other factors, but the technique is well utilized in many industries, in particular the oil and gas industry.

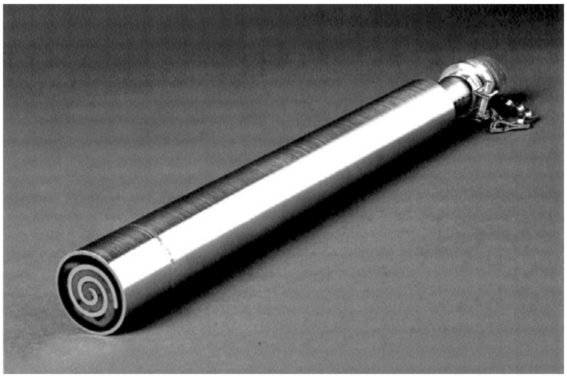


Figure 6 Electrical resistance (ER) probe – fixed attachment to plant (Courtesy Cormon Ltd).

The cost of ER hardware is similar to that of other systems and they can be operated and interpreted by most staff without undue problems. However, noninvolved staff should be acquainted with the locations and sensitivities of probes which have been known to be used as foot supports for climbing on or around the plant.

The advantages of the technique include the capture of data without plant shutdown, the availability of both portable and automatic operation, the reasonable correlation with corrosion variables and process conditions, and the assessment of the effectiveness of corrosion mitigation techniques. Special probe designs are available for use at high temperatures such as in power station boilers, in aircraft components, and in underground pipelines and for the measurement of atmospheric corrosivity.

The disadvantages include problems with conducting corrosion products in sour systems, localized corrosion that can introduce errors in interpretation, and the trade off between element sensitivity and life.

4.36.1.4.4 Electrochemical techniques

Potential measurement

Potential and its variation with time are indicators as to the condition of passive films, but corrosion penetration rates are not obtained. The hardware required consists of an appropriate reference electrode and working electrode, which can be the plant component of interest, and a high-impedance voltmeter. This technique has been used in the chemical industry for assessing the condition of passive materials in some applications. Pioneering work on the technique by Edeleanu[16] demonstrated that potentials of UNS S30400 stainless steel in sulfuric acid varied with pumping speed, temperature, and the presence of impurities. Laboratory determination of polarization characteristics can identify passive and active potential ranges for a given material/environment combination.

The choice of an appropriate reference electrode is a challenge for noncorrosion aware personnel. Ideally, a reversible reference electrode such as a calomel or silver–silver chloride electrode should be used but, in practice, nonreversible electrodes can be deployed as long as they maintain a stable potential. Commercially available polarization resistance probes can be adapted for this purpose.

Potentiodynamic/cyclic polarization

These techniques measure the polarization characteristics of the metal–environment system of interest and laboratory procedures have been outlined and described.[17] Polarization curves are obtained by polarizing a working electrode potential relative to a reference electrode using external current supplied via a counter electrode in a conventional electrochemical cell arrangement. The choice of reference electrode is an issue, as in the case of potential measurement. In theory, this technique allows measurement of the Tafel constants, b_a and b_c, from the slopes of the linear portions of the anodic and cathodic polarization curves for the relevant anodic and cathodic processes that define the corrosion process. Corrosion rates can be measured by extrapolating the linear portions of the curves to intersect at the natural corrosion potential.

Cyclic polarization is a variation of the potentiodynamic technique in which the potential is reversed in the negative direction following an anodic scan. The breakdown potential in the anodic scan and any hysteresis in the anodic segment of the reverse scan can be indicative of the tendency toward pitting and crevice corrosion respectively. Guidelines for carrying out these tests are given in an ASTM standard.[18]

Portable commercial potentiostats are available that allow polarization measurements to be made *in situ* in operating plants. However, polarization characteristics are often relatively complex and these techniques require careful, informed interpretation and are not used routinely for corrosion monitoring.

Linear polarization resistance (LPR)

As aqueous corrosion is an electrochemical process, the measurement of the current involved in the corrosion reactions and the use of Faraday's Law should provide, in theory, a quantitative measurement of corrosion rate. However, it is not practicable to measure the internal corrosion current using an ammeter on the surface of a corroding metal in which the anodic and cathodic sites are inseparable. The current can, however, be calculated from the polarization characteristics of a material in an environment using the Stern and Geary relationship[19,20] developed from the mixed potential theory for a corroding electrode, which defines a linear relationship between applied potential and current density close to the natural corrosion potential:

$$R_p = \frac{\Delta E}{\Delta I} = \frac{b_a b_c}{2.3 i_{corr}(b_a + b_c)} = \frac{B}{i_{corr}}$$

where:

- R_p is the LPR;
- ΔE (equal to E–E_{corr}) is the potential shift from the corrosion potential, E_{corr};
- ΔI is the measured external current flowing due to this potential shift;
- i_{corr} is the corrosion current at the free corrosion potential, E_{corr};
- b_a and b_c are Tafel constants.

The Stern–Geary relationship is valid only for specific experimental and theoretical conditions among which are that ΔE is small, typically $<\sim 20$ mV. The measurements can be completed relatively quickly and are in effect instantaneous, and can therefore be utilized to control corrosion mitigation practices in operating equipment, such as the addition of inhibitors to recirculating cooling water systems or crude distillation column overheads in oil refineries.

Probes for the LPR technique are available in either two- or three-electrode versions, as shown in **Figure 7**, which also shows the access fitting, which is the preferred method for inserting probes into plants.

Two-electrode probes have identical metal electrodes between which the applied voltage (up to 30 mV) is applied and the resulting current measured. The applied voltage is then applied for a second time but with reversed polarity and an average is taken of the readings. A cycle time of around a minute is generally used, after which, in theory, steady state conditions prevail. In three-electrode probes, the potential difference between the reference electrode

Figure 7 Linear polarization resistance (LPR) electrochemical probe and 'access fitting' (Courtesy Cormon Ltd).

and working electrode is sensed and an additional $+/-10$ mV polarization is applied. The three-electrode probe can provide measurements in more resistive solutions but has the disadvantage of measurement error if the current chosen is too large and the working electrode is polarized beyond the $\sim$10 mV level.

Rod-type electrodes are supplied in many metal compositions separately from the probe and electrodes are attached to threaded rods located in the probe. Probes are available in fixed (screw-in), flange fitting, retractable (pressure-gland fitted via a full-bore opening gate-valve) and in versions for commercial retrieval systems. Instrumentation is available in various forms ranging from handheld downloading devices to fully automated systems. Results are converted to penetration rates (mils year^{-1} or mm year^{-1}) using appropriate values of B that are available from the literature for a wide range of material/environment combinations.

The key advantage of the technique is that it is close to instantaneous, giving an estimate of corrosion rate in a short time, typically several minutes, enabling rapid correlation with process conditions.

The disadvantages include the restriction of the technique to conducting solutions, although resistance compensation is available on some systems, and the requirement for values of B for the relevant reactions. Deposits on the probes can interfere with measurements, and errors are introduced if oxidizing or reducing reactions are active that are not involved in the corrosion process. It is good practice to use other corrosion monitoring techniques in a package of techniques to validate and calibrate the technique.

Galvanic current

The galvanic current arising between two different metals can be measured using a zero-resistance ammeter (ZRA) in series between two different electrodes. The current can be related to metal loss using Faraday's Law. This is a long-established laboratory technique that has been extended into plant for the qualitative estimation of galvanic corrosion using, for example, commercial LPR probes fitted with two different metal electrodes.

Electrochemical impedance spectroscopy (EIS)

EIS is similar in approach and hardware to the LPR technique with the exception that an AC rather than a DC perturbation is applied to the electrodes at a range of applied frequencies. The resultant current and phase shift between the applied potential and resulting current are measured. The total impedance comprises contributions from the charge transfer and solution and diffusion impedances, and these can be identified separately and quantified by the use of AC impedance measurements at varying frequencies. The first AC instrument for measuring corrosion was developed by the UK Admiralty Materials Laboratory with the objective of correcting the errors involved with the LPR technique.[21] A fixed frequency of 10 Hz square wave was applied between the electrodes. The working electrode oscillated at $+/-5$ mV about a floating E_{corr} potential using an AC square wave coupled potentiostat. The measurement about a floating rest potential is a major advantage of the AC technique in systems where transients in potential would cause difficulties in measurement using a DC technique.[1] There is an extensive literature relating to the development of EIS as a laboratory/research tool for the investigation of corrosion.[22–24] Current interest is focused on the use of harmonic analysis (HA) of the response of electrodes to the application of a single frequency, from which Tafel slopes and Stern–Geary constants can be determined.

The main advantage of EIS relative to conventional LPR is that measurements at different frequencies allow corrosion rates to be determined in more resistive corrosion environments such as crude oil–water mixtures and concrete. The technique also provides insights into corrosion mechanisms, such as whether corrosion processes are charge or mass transfer controlled and it can be deployed in operating plant using standard, commercially available LPR probes with associated access facilities.

The main disadvantage is the specialized knowledge that is required for the verification of instrument/computer outputs and the interpretation of results, which is an obstacle to the widespread deployment of EIS for industrial applications.

Electrochemical noise (EN)

The EN technique involves the analysis of spontaneous potential or current transients that arise on or between corroding metal electrodes. The EN technique was first identified by Iverson[25] and there is now an extensive literature on applications in corrosion monitoring.[26,27] The theoretical background and development of EN are described elsewhere in this book. In the last edition of this book in 1994, EN applications in power generation plant, cooling water systems, and reinforcement in concrete were reported. Also, it was noted that probes containing combination elements utilizing several electrochemical techniques (AC and DC) had been developed and used for measurements in condensing acid environments.

The development of EN has progressed rapidly particularly due to developments in the electronic equipment that is able to discriminate between natural electrode current/voltage transients and electronic background noise. The interest in the technique derives partly from the prospect of a more reliable and flexible way of measuring corrosion rate but particularly from its unique sensitivity to localized corrosion processes such as pitting crevice corrosion and stress corrosion cracking (SCC) that is not available from other electrochemical techniques. EN is also much more responsive to system changes and upsets than any other monitoring technique, electrochemical or otherwise, which makes it a strong contender for corrosion/process control.

The technique does not perturb the electrodes as is the case with electrochemical techniques involving polarization but detects the natural voltages and currents that are generated on the electrode surfaces in the environment. Measurements can be made in a wider range of environmental resistivity compared with LPR. In the usual configuration, the potential noise and/or the current noise between two identical electrodes is measured. Currents are measured with a zero-resistance ammeter. Data analysis is used to determine the corrosion rate and/or the corrosion mechanism. In theory, corrosion rates can be estimated from EN measurements in a manner analogous to LPR measurements. Corrosion rates are calculated using the so-called noise resistance, R_n, which is equivalent to the LPR polarization resistance, R_p, and is determined using the relationship:

$$R_n = \sigma V_n / \sigma i_n$$

where σV_n and σi_n are the standard deviations of the EN potential and current signals respectively. A variety of techniques can be used to analyze the data including the time basis of the data obtained, statistical analysis, which can provide mechanistic information, frequency domain transformation to characterize localized corrosion, fractal and neural analysis.[28]

An advantage of the technique is that it can be deployed in operating plants using standard, commercially available LPR probes with associated conventional access systems. However, the complex instrumentation can be expensive, and as with EIS, specialized knowledge is required for the verification of instrument/computer outputs and the interpretation and analysis of results. The technique is generally provided by specialized companies/contractors unless there is in-house expertise available in a larger company.

4.36.1.4.5 Field signature method (FSM)

The field signature monitoring technique was developed originally to monitor internal corrosion of pipes and pipelines.[29] A length of pipeline (spool) fabricated from the same material as the parent pipeline is used as the measuring sample to which an array of sensing pins, typically ~3-mm diameter, is stud welded onto the exterior surface. A current is induced in the test spool and the electric field pattern is sensed by measuring the small potential differences among the pairs of sensing pins on the external surface. The electric field pattern depends on the geometry of the test spool and general or localized corrosion on the internal surface produces changes in the electric field pattern. By comparing measured potential differences with baseline values for the uncorroded spool, the distribution and dimensions of corrosion on the internal surface can be computed, as shown in Figure 8. Temperature and current fluctuation effects are compensated for. The original Norwegian patent for the system was issued in 1984 and was later licensed to Corrocean (Norway) for commercial application on a worldwide basis, who

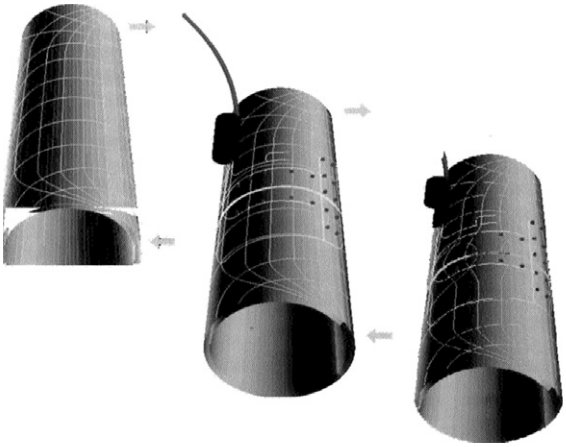


Figure 8 Field Signature Method (FSM) – Schematic (Courtesy iicorr Ltd.).

Figure 9 Field Signature Method (FSM) – Installation on piping at bend/weld on piping (Courtesy iicorr Ltd.).

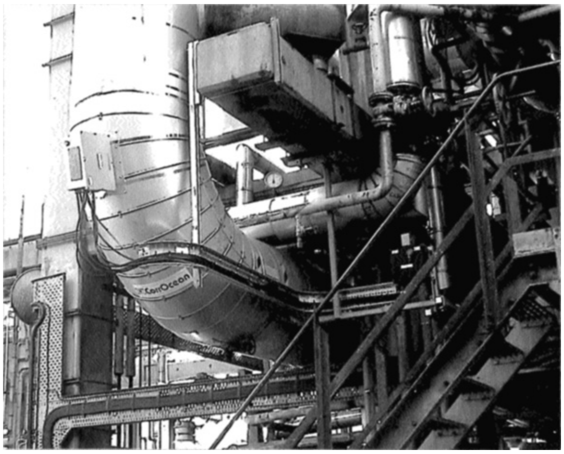


Figure 10 Field Signature Method (FSM) – Installation in oil refinery (Courtesy iicorr Ltd.).

claimed that an accuracy of 0.1% of pipewall thickness could be obtained with a resolution of 0.025 mm for a 25-mm wall thickness. Large areas (several m^2) can be monitored and smaller pin distances result in higher resolution for localized corrosion.

This method has been referred to in the literature as a variation of the ER system. There are now other manufacturers offering similar systems, one of which provides a two-part removable sensor sleeve as an option.

Initial application was directed at the oil and gas industry for the detection and monitoring of corrosion in subsea pipelines, especially for new systems, rather than retrofitting to an existing line, which would involve shutdown and additional cost. Applications in the last decade have expanded into topsides on offshore oil and gas platforms,[30] onshore pipelines/piping, and oil refining equipment[31] as illustrated in Figures 9–11.

An FSM system was fitted to an experimental pressurized pipeline loop in the UK that was used for the testing of oilfield corrosion inhibitors. The operator reported excellent results with emphasis on the accuracy achieved.[32] In one particular onshore oil field installation, considerable savings on corrosion inhibitor cost were made associated with an increase in the interval between inhibitor treatments of 2 weeks.

Advantages relate to the noninvasive nature of the technique, the large areas of actual plant components that can be monitored compared with conventional invasive probes, and the sensitivity that allows the technique to be used to correlate corrosion rates with process conditions such as in the case of naphthenic acid corrosion in crude oil refining.[31] Pitting and SCC can be detected and corrosion monitoring across welds on pipeline welds has been successfully carried out in the North Sea.

Disadvantages include the high cost, which restricts the use of the technique to critical applications and the requirement for specialized data interpretation albeit enabled by custom-supplied software.

The data require careful interpretation since corrosion occurring more than 1 m either side of the sensing unit will not be detected and the generalization of the test spool performance to the system as a whole could be misleading if it has not been located where the corrosion is taking place. Concerns have been expressed relating to the use of FSM at high temperatures (e.g., 60 °C in the shade in the Middle

Figure 11 Field Signature Method (FSM) – Installation on buried pipeline (Courtesy iicorr Ltd.).

East) and whether the sensitive electronics will survive sand and dust in desert environments, which applies to any instrumented system. However, appropriate and regular maintenance may reduce these problems.

Overall, this technique is one of the more interesting developments of corrosion monitoring technology in recent times as exemplified by the number of applications in the oil and gas industry and its progressive use and expansion into other industries.

4.36.1.4.6 *Thin layer activation (TLA)*

TLA was developed originally for monitoring wear and erosion on metals such as in the measurement of the wear of automotive engines and the assessment of the effectiveness of various lubricants. The technique was first utilized for corrosion monitoring in 1983[33] and is based on the creation of a small quantity of a radioactive tracer in a metal surface (one part in 10^{20}) allowing the loss of metal due to corrosion to be measured by the loss of radioactivity. The corrosion product is required to be nonadherent for successful application. Monitoring can be based on measurements of the loss in radioactivity level of the corroding surface or the increase in radioactivity of the corroding liquid environment unless the throughput is so high as to dilute the uptake of radioactive isotopes to levels that cannot be differentiated from background. Plant components can be irradiated, for example, on the inside surface of a pipe, or an irradiated coupon can be exposed invasively. The technique is noninvasive, measurements being possible external to equipment that contains an irradiated internal sample surface.

The requirement that samples or plant components be activated by exposure in a nuclear accelerator and the associated logistics have inhibited the widespread application of the technique, but some successful applications have been reported in subsea, water treatment, and paper-mill operations.[34]

4.36.1.4.7 *Chemical analysis*

The contribution of a well-planned and executed chemical analysis program to corrosion monitoring is often underestimated. Changes in corrosivity may be determined by liquid analysis including changes in process conditions. The most important analyses related to corrosion behavior are levels of oxygen, hydrogen, chloride, trace elements, iron, manganese, corrosion inhibitor, and other treating chemicals such as biocides, oxygen scavengers, and pH. There are a variety of test papers for free water and pH monitoring and hydrogen sulfide and carbon dioxide testing can be carried out on-site. For on-site measurements, the first measurement should be the temperature.

Provision for chemical analysis should be incorporated in the design of process plant in order to give adequate coverage throughout the system, for example, in oil production from the well via processing facilities to the export infrastructure. Correlation with plant parameters such as temperatures, pressures, flow rates, and stream compositions can provide valuable information. Automatic analysis systems, especially those using ionsensitive electrodes with the recording of data, are recommended.

A special case of chemical analysis is the measurement of iron counts, the term used in the oil industry to describe the amount of the element iron in product streams. Results provide a valuable indication of corrosion if carried out on a systematic basis, such as from a reference point upstream and taking samples of fluid at a number of reference points downstream. Samples are analyzed in the laboratory and results are reported as weight of iron per volume of liquid.

Guidelines for iron analysis in oil and gas production are given in the literature.[35]

The loss of wall thickness is not obtained from this technique. However, continuous sampling gives results that provide a good indication of the amount of corrosion taking place, assuming that the corrosion distribution is uniform.

The disadvantages of the technique are that it is less effective for localized corrosion and that clearly the technique is invalidated if iron is already present in the process fluid, for example, in an oil formation. In this case, analysis for manganese can be substituted and results correlated accordingly.

4.36.1.4.8 Hydrogen

Hydrogen is produced from the cathodic reaction in many corrosion systems, particularly where acid environments such as acidizing fluids, sour systems, carbon dioxide, and naphthenic acids promote corrosion. The measurement of the presence and levels of hydrogen can give qualitative indications as to the amount of corrosion occurring. The historical technique for assessing the presence of hydrogen in the oil industry was to place a sample of produced fluids in an empty paint can. The appearance of blisters on the exterior of the can indicate the presence of sour water and consequent hydrogen.

Hydrogen atoms, due to their small size, can migrate easily through a metal lattice. If voids or defects are present in the metal lattice, hydrogen atoms combine to form hydrogen molecules and the continuous formation of molecules leads to increases in internal pressure, which eventually exceed the coherent strength of the material resulting in phenomena such as hydrogen-induced cracking and blistering.

Early probes were based on monitoring the accumulating pressure of hydrogen produced by corrosion. This does not provide a measurement of corrosion penetration directly. However, any increase in the volume of gas indicates that corrosion is underway. Pressure probes are still used in oil production and refining operations and can be installed using the standard access-fittings that are used for other types of invasive probe or coupon, enabling installation and retraction under system pressure. The hydrogen gas requires bleeding from the probe at regular intervals, which is a disadvantage in large oil fields. However, the organization of teams specifically for this purpose has worked well in the Middle East. An outer sheath can be welded onto a pipeline or piping into which hydrogen that is produced by corrosion of the bore diffuses. The pressure generated can be determined with a pressure probe and this allows corrosion of the bore to be monitored noninvasively.

The electrochemical monitoring of hydrogen using Devanathan cells mounted on external surfaces using sealing systems to contain electrolytes was a later development by several manufacturers. Portable versions of the cells extended considerably the scope of this technique and provided a valuable tool for corrosion and inspection engineers. More sophisticated probes are now available that measure the hydrogen flux passing through a metal. Versions are available for both periodic and continuous monitoring and are noninvasive in application. Current instrument systems can measure hydrogen at very low levels with accompanying temperature recording and are available in various versions to fit different geometries.

A recent paper[36] describes the use of hydrogen permeation detection to correlate changes in operating conditions with corrosive conditions in a crude distillation column in an oil refinery. Measurements were taken over a 3-day period. During the monitoring periods, the refinery made adjustments to various operating parameters including chemical injection. The corrosion rates determined by monitoring correlated well with corrosion rates obtained from ultrasonic thickness measurements.

4.36.1.4.9 Test heat exchangers and spool pieces

In cooling water systems, test heat exchangers are often utilized for assessing the effectiveness of the corrosion inhibitor and consequent corrosion behavior of the heat exchanger tubes. These can often be supplied in the overall service package by the corrosion inhibitor supplier. The test unit includes several tubes that can be opened for visual observation and measurements taken of the corrosion rate by destructive, metallographic examination. The units can be isolated by valves allowing removal or replacement of the tubes without interrupting the operation of the cooling water system.

Small lengths of piping (~1 m in length) can be fitted to plants using appropriate flanges and provide valuable data as regards the corrosion characteristics. The spools can be removed at shutdowns or installed in bypass loops allowing more convenient removal and replacement. Caution in the interpretation of the results from bypass loops is required until confidence is obtained that the bypass line mimics mainstream conditions and that allowances are made for any differences.

4.36.1.4.10 Monitoring of bacteria

Bacteria are present in some commercially important processes, including cooling water systems and nearly all areas of oil production. Detecting the presence of bacteria is essential for effective maintenance management that includes treatment with appropriate biocides. In time, bacteria develop immunity to specific biocides and the biocide type requires changing at prescribed intervals to keep bacterial growth under control. The most significant species of bacteria from the corrosion standpoint is sulfate-reducing bacteria, which consume sulfate in its metabolism, producing and expelling hydrogen sulfide, which is very corrosive and can induce cracking in steels. Bacteria can exist in the liquid (planktonic) or under scale/deposits (sessile) and this requires consideration in bacteria-monitoring programs. Techniques of monitoring include bacterial analysis (via filters), sidestreams, vessels, and specially designed corrosion coupons such as the Robbin's device that utilizes metal studs as described in the following paragraph. Note that monitoring in the fluid flow only would not detect the presence of sessile bacteria.

Testing for bacteria is expensive, tedious, and time consuming and considerable effort has been devoted to the development of spot tests that can identify the presence of bacteria within a 10–15 min period, *albeit* without the identification of the bacteria type. Rapid techniques for assessing bacteria include adenosine triphosphate photometry (ADP), fluorescence microscopy, and radiorespirometry. Standards and recommended practices are available.[37–39] The use of a microbiological laboratory is necessary to identify which type of bacteria is present involving transportation with sterile packaging that can be a challenge, particularly for offshore operations.

Coupons and probes (fitted with flush elements) can provide useful information regarding bacteria. The 'Robbin's device comprises a 25 mm diameter stainless steel pipe containing a series of carbon steel studs – any sessile bacteria will deposit on the studs and can be recovered and analyzed.[40] Variations of the 'Robbin's unit are commercially available for insertion into plant using standard access-fittings. Most companies supplying coupons and corrosion probes will be able to supply this equipment.

4.36.1.4.11 Process parameters and conditions

An obvious collection of parameters that influence corrosion processes and require scrutiny but are often ignored, mainly due to communication problems, relate to the process or the product under manufacture. The constituents of feedstocks and process streams should be regularly checked as well as operating plant parameters such as temperatures, pressures, the presences of gases, and flow rates and regimes. This is particularly relevant in gas and oil streams. A change in feedstock and/or source of supply can result in changes in corrosive properties. Sources and quality of water for injection points into the plant in oil refining should be regularly monitored.

4.36.1.5 Industrial Applications and Experience

4.36.1.5.1 Oil and gas industry

Overview

The oil and gas industry is subject to many corrosion hazards in all areas of its operations. In addition to production and refining, the transportation of products is a major operation involving road tankers, extensive pipeline networks, and marine vessels, including coastal vessels and supertankers. Leakage of crude oil presents major environmental risks and leakage of highly flammable refined products can result in explosion and/or fire with consequential risks to life, and because of the scale of industry operations, major financial consequences arising from unscheduled shutdown and loss of production.

Although corrosion risks are mitigated in some areas by the use of corrosion-resistant alloys, the majority of industry equipment is constructed in carbon and low-alloy steels and corrosion inhibition is widely practiced at key stages of the production and refining operations to mitigate internal corrosion risks. The need to monitor and confirm the effectiveness of corrosion control by inhibition is one of the reasons for the industry's being a very large user of corrosion-monitoring equipment. The cost of corrosion to the industry has been estimated in numerous studies at ~40 cents per barrel, exemplified by a study of two oil fields operated by Agip in Europe.[41] A significant element of this cost is the expenditure on corrosion monitoring and inspection, as exemplified by **Table 4**, which shows corrosion-related costs for a major US oil field producing 270 000 bbl day^{-1} (4% of total daily domestic US production) in 1999. The total annual monitoring costs were ~\$1 m as against the total inspection costs of ~\$3.3 m and the inhibitor costs (chemicals alone) of \$13.5 m.

Another major US field operated by the same company producing 246 000 bbl day^{-1} reported

Table 4 Detailed annual costs for corrosion monitoring and inspection and other related corrosion costs for one large US oil field

	Cost ($ x thousand)
Inspection costs	
Overhead	$492
Tangential radial tomography inspection	$1409
Ultrasonic inspection	$361
Other	$1054
Total inspection	$3316
Monitoring costs	
Coupons	$924
Bacteria monitoring	$13
Laboratory analysis	$40
Total monitoring	$977
Repairs	$600
Engineering staff	$1416
Corrosion inhibitor (chemical alone)	$13 533
Total	$19.84 million

Source: www.corrosioncost.com/pdf/oilgas.pdf

Table 5 Costs for monitoring and inspection and control techniques for one US large oil field

Corrosion expense	*Cost ($ x thousand)*
Inspection, monitoring and staff costs	$9625
Repairs	$1350
Corrosion inhibitor (chemical alone)	$7200
Total	$18.175

Source: www.corrosioncost.com/pdf/oilgas.pdf

monitoring and inspection costs as shown in Table 5. In this case, the expenditure on corrosion monitoring and inspection was the largest single item.

Although the industry is regarded as corrosion conscious with a good awareness of corrosion risks and corrosion control practices, serious and costly corrosion incidents continue to occur, for example, in production,[42] refining,[43] pipelines,[44] and transportation.[45]

The engineering design for a new oil field is based on the field fluid analysis. However, field fluid compositions can change radically as the field ages resulting, for example, in higher levels of recovered water and/or field souring (production of hydrogen sulfide at a later date after initial field production) and such factors increase the corrosion risk considerably. The historical approach that initial materials selection supplemented by in service inspection at scheduled shutdowns could be relied upon to mitigate corrosion risks was invalidated progressively by operating experience, not least European offshore experience in the 1970s, which clearly showed the inadequacy of this approach. Increased corrosion risks were usually mitigated by the introduction of corrosion inhibition with the result that online corrosion monitoring was gradually introduced by all the major operators. It came to be recognized that the use of an integrated system for corrosion monitoring, incorporating inspection data such as ultrasonic thickness measurements, was the optimum approach to ensuring successful operation.[6] In today's regulatory environment, the authorities in many countries have introduced legislation requiring oil/gas installations to monitor corrosion, specifying the techniques to be adopted. The USA has introduced a Corrosion Prevention Act, which has the potential to dramatically improve corrosion prevention and control practices in the industry.[46] However, regulatory authorities are reluctant to impose requirements that might result in excessive economic penalties to business operations. For example, there has been a long debate in the USA regarding the frequency with which instrumented inline vehicles (smart pigs) should be used for pipeline inspection.

Regarding monitoring techniques, the industry has from the outset utilized coupons. These were later supplemented by ER probes that were first applied using portable instruments until automatic systems began to appear in the early 1970s. Automatic application took a long time to develop due to the high cost of special cable requirements. When LPR technology was introduced, its application was limited to cooling water systems and streams with some water content. There has always been controversy related to the use of LPR in oil/water streams, although measurements have been made in separated waters in bleed-off pots in crude distillation refinery units and some onshore pipelines. The extensive use of corrosion inhibition requires monitoring techniques that respond rapidly to assess the effectiveness of specific inhibitors and their required dosage rates, and this has provided a considerable impetus for techniques that provide instantaneous information such as EIS, EN, and FSM. Applications of FSM in particular are expanding on both onshore and offshore installations, because it provides accurate corrosion rates for the actual components that are being monitored.

Well-drilling is the first operation in producing oil or gas and can be affected by corrosion if corrosion control is inadequate. Fortunately, tubing used for drilling can be inspected for corrosion on the surface when withdrawn from the well. However, mud-slurries that are used for the removal of scrapings from the drilling operation have to be treated with corrosion inhibitor and oxygen scavenger to counteract the ingress of oxygen into the drill stem. This operation is generally monitored by both coupons and LPR probes that can signal upsets in the corrosivity of the mud and correlation with chemical treatment. Certain dense halide brines are used to balance formation pressures during production operations, which can be corrosive due to dissolved oxygen or entrained air. Also, brines can be corrosive due to acid generation.

Seawater that is injected (squeeze) to recover oil requires treatment to remove oxygen and control bacteria to prevent souring of the formation, otherwise serious corrosion can occur. The water-injection facilities require monitoring on the manifold and elsewhere using coupons and LPR probes to confirm efficient oxygen removal by mechanical degassing and oxygen scavenging. Some operators also use galvanic probes, comprising steel and copper electrodes, which respond rapidly to the presence of oxygen.

Corrosion inhibitors are commonly added throughout the system from downhole (down the well) to the export line and to the water and gas lines downstream of the separators and monitoring is carried out at appropriate locations including wellheads, manifolds, interfield lines, separators (gas outlet, water outlet), export lines, piping, and terminal infrastructure to provide guidance on internal corrosion rates and inhibitor effectiveness. Corrosion monitoring is based mostly on combinations of coupons and ER/LPR probes as appropriate for the location. FSM, EIS, EN, and inspection techniques (including intelligent vehicles) are used selectively to supplement basic monitoring packages. In some installations, primary monitoring relies on the FSM technique if the benefits justify the higher cost.

Difficulties relate to inaccessibility, particularly for offshore pipelines and downhole. Nevertheless, coupons of various designs and caliper tools are available for downhole, albeit with some resulting drawbacks such as the removal of any inhibitor films that are overcome by increasing inhibitor dosage for short periods after the inspection. Subsea facilities present particular challenges related to accessibility and engineering, for which FSM test spools provide potential solutions.

For refineries, each unit needs a risk analysis and the crude distillation unit that provides feedstock to many other refinery units needs particular attention. Crude oil distillation units can suffer severe corrosion, depending on the quality of the crude oil being processed. At one time, a refinery unit handled only one source of crude oil that was selected for its low corrosion risk. For both geo–political and economic reasons, refineries now buy diverse sources of crude oil on the spot market which has increased corrosion risks. The mixing or blending of corrosive crude oil with more benign crude oils is often practiced to reduce the corrosive risk. Any unscheduled shutdown of the distillation unit due to corrosion results in knockon effects on other refinery units with potentially enormous economic penalties. The top of the column and piping carryover to the coolers are vulnerable to corrosion by hydrochloric acid arising from the hydrolysis of calcium and magnesium chlorides. This is controlled by the removal of calcium and magnesium chlorides from the crude oil in desalter vessels upstream of the distillation unit and the addition of ammonia and neutralizing/filming-amine inhibitors to the overhead stream. The pH of the water that separates from the overhead stream is used to control inhibitor addition, and the general target range for pH is 5.5–6.5. LPR probes are also used to monitor corrosion rates in the water stream but hydrocarbon contamination of both pH and LPR electrodes can result in errors if allowed to accumulate.

Hydrogen sulfide and naphthenic acids may also be present and can exacerbate corrosion risks. Naphthenic acids can be extremely corrosive to carbon steel at the temperatures prevailing in distillation columns. Risks are mitigated by either upgrading the metallurgy to stainless steel or adding corrosion inhibitors that are resistant to the temperatures involved.

The management of corrosion in distillation units is based heavily on hydrocarbon and water analysis supplemented by monitoring with coupons and ER/LPR probes to provide advanced warning of system upsets leading to corrosion damage. In addition, there have been isolated applications of FSM and EIS/EN for specialized situations such as corrosion inhibitor trials and the presence of naphthenic acid. Onstream, nondestructive examination is also utilized. As always, no single technique covers all requirements and a number of corrosion monitoring techniques should be used in an integrated system, consistent with the risks involved.

Bacteria present additional corrosion hazards in many areas of oil production operations and bacteria monitoring is essential for adequate control and to assess the effectiveness of the biocide addition. Onshore pipelines are monitored using both coupons and probes with flush elements, although the sensors need to be removed before any online intelligent pigging is carried out. Sensors can also be used in bleed-off pots attached to pipelines.

Overall, corrosion monitoring has made a large contribution to the continuity of operation and safety in the industry, not only by providing data for life prediction of infrastructure but also by enabling optimal corrosion control practices based on corrosion inhibition to be identified.

Case studies

The benefits arising from a well-planned and managed corrosion monitoring program are illustrated by the following cases:

1. *Oil refinery corrosion inhibitor validation* – Corrosion risk mitigation in crude distillation units is based heavily on corrosion inhibition, as already described. ER probes are utilized in many refining units for routine monitoring supplemented by coupons for verification where relevant. Automatic data collection offers the prospect of automatic control and Exxon carried out pioneering work in the USA in their larger refineries, closing the loop from the probe performance to automatic inhibitor control facilities.[47] The main objective for this work was to relieve the corrosion engineer of involvement in routine corrosion upsets (estimated at 60–70% of corrosion incidents) allowing more time for more complex corrosion problems. More recent applications have related to naphthenic acid corrosion, for which corrosion inhibitors were developed that would withstand the higher temperatures involved pending a possible future material upgrade. The data obtained were used to assess effectiveness of the candidate inhibitors and to establish correct dosage rates.[31]
2. *Dehydrated gas pipeline corrosion risk mitigation* – The advantages of using electrochemical techniques that enable online measurement of the Stern Geary factor (*B*) have been reported.[48] One example relates to online, real-time monitoring techniques involving LPR, HA, and EN. Complementary information was obtained on both general and localized corrosion in a range of pipeline environments for steel and other metals. The real time measurements provided valuable information in low water-cut, dehydrated, multiphase, and vapor phase environments for both general and pitting tendencies. The provision of HA enabled measurement of the *B* value and improved the accuracy of the measurements very much providing criteria for optimizing chemical treatments. Vapor phase environments typically exhibit 1–2 orders of magnitude lower general corrosion rate than found in liquid phase environments. The predominant mode of corrosion in the vapor phase has always been observed to be pitting corrosion, shown by high values of pitting factor, corroborated by visual observation. Other factors such as agitation or turbulent flow were correlated together with oxygen excursions.

The following cases highlight the importance of integrating corrosion and monitoring and inspection programs into an overall management system for managing recognized corrosion risks effectively, not least the deployment of monitoring and inspection resources to provide effective corrosion risk mitigation.

1. *Oil refinery explosion due to erosion corrosion* – In 2001, a major oil refinery in the UK, producing high-octane gasoline, experienced a severe explosion and fire in the saturate gas plant resulting from an overhead line rupture. The rupture resulted from local thinning due to erosion corrosion downstream of a water-wash injection inlet after ~13 years of operation. The injection inlet was listed on the inspection data base as in intermittent use and as a result had attracted relatively little subsequent inspection. In 2000, significant wall thinning had been identified and a full inspection of the area was scheduled for 2001. During the erection of scaffolding, the explosion occurred, fortunately on a public holiday, which minimized casualties and no personnel were killed. However, substantial damage was caused to the gas plant and a nearby unit resulting in a loss of production for several months and an increase in the global spot-price of high-octane gasoline. ER corrosion probes had been installed several years previously following receipt of specific information about the vulnerability of carbon steel pipework to corrosion in the vicinity of water injection points, but operators had failed to respond to the indications of increased corrosion in the wash-water feed pipe,[7] and as a result, a recognized corrosion risk was not managed effectively.
2. *Oil transit pipeline failure due to microbiological corrosion* – The Prudhoe field in Alaska is the largest US oil field representing 8% of domestic production. The field was threatened with a complete shutdown of production in August 2006 due to corrosion of a pipeline, resulting in an increase

of 2.2% in the worldwide spot price of crude oil. There are two eight mile (12.9 km) long oil transit lines in the field. The incident was a result of a leak in the 34-inch (86-mm) western transit line, constructed in the late 1970s, which resulted in a leakage of 200 000 gallons of crude oil – the largest spill in the field's history. The hole in the bottom of the pipe measured 0.25 × 0.5 inch (6.4 × 12.7 mm) and the leak went undetected for several days.[42] The line carried hot crude oil from two processing facilities to a facility that blended natural gas liquids and crude oil from the east and west production facilities prior to delivery to the Trans Alaska pipeline. Following the discovery of the leak, the line was immediately closed and clean-up operations initiated. A return to full production was achieved in ~3 weeks. Internal corrosion risk mitigation was based on the use of inhibitors, monitored using coupons, ER probes, leak detection systems, and NDT techniques,[5] including ultrasonics and radiography. The pipeline was accessible above ground excepting cased segments of piping at buried crossings. The US Department of Transportation (DOT) initiated an investigation into the leakage and required further inspection and remediation of the lines, including the running of an intelligent pig (ILI), through the western transit pipeline within 3 months. Intelligent pigging had not taken place in either transit line for several years, in contrast, the Trans-Alaska line is pigged every 14 days. The transit pipeline had been designated initially as a low corrosion risk but due to a reduction in flow rates, debris, and corrosion products that were normally passed through the pipeline deposited on the pipe allowing bacteria to develop beneath, resulting in corrosion. The loss of wall thickness in the pipeline was not identified before leakage occurred despite an extensive corrosion control and monitoring program employing approximately two hundred corrosion professionals and contractors conducting ~100 000 corrosion inspections annually on pipeline and equipment locations throughout the Prudhoe Bay field and facilities, of which 60 000 were for internal corrosion detection.[42] The corrosion problems led to the issue of a subpoena requiring the CEO of the operating company, BP Exploration Alaska to appear before a Congressional Committee in order to describe the incident and its causes. The incident proved a public relations (PR) disaster for the company, which previously had a long-standing reputation for investment in corrosion engineering and research, including corrosion monitoring activities.

4.36.1.5.2 Chemical and petrochemical industry

Overview

In a retrospective view of the chemical process-industries, examples of extreme operating conditions have been outlined by Dean[49] such as the high pressure used in ammonia synthesis of 272 bar (4000 psi), high temperature in ethylene production (1038 °C), low temperature in hydrogen liquefaction (−215 °C), corrosive environment in ammonia oxidation (HNO_3), ammonium nitrate production (exothermic reactions), and the large volumes involved in the processing of petroleum products. Dean has identified a number of major events that have occurred and that have impacted on the chemical industry, shown in Table 6.

The effects of major disasters such as Flixborough (UK) and Bhopal (India) have resulted in increased concern for process hazards in chemical operations, which has focused attention on materials of construction, possible failure mechanisms, and the management, maintenance, and surveillance of chemical manufacturing plants. New standards have been adopted that require positive assurance that equipment is fit for service and degradation processes such as corrosion can no longer be ignored if they cause damage to the structure.[42] As a consequence, interest in online

Table 6 Some trends and vents that caused major changes in the chemical industry

Event	*Dates*	*Results*
Energy crises	1973	Conservation
Ditto	1978	Other energy sources
Passage of OSHA[a]	1970	Safety emphasis
Flixborough[b]	1974	Process safety
Passage of EPA[c]	1970	Environmental concern
Bhopal release	1984	Ditto
Ashland storage tank failure	1988	Mechanical integrity

[a] USA Safety legislation USA.
[b] UK Explosion in chemical plant.
[c] US Environmental legislation.
Source: Dean, S. W. *Stainless Steel World* **2002**, *13*, 62–66.

corrosion monitoring has increased, in particular in devices that provide signals that can be used as control parameters.

Case studies

The benefits arising from a well planned and managed corrosion monitoring program are illustrated by the following cases:

1. *Carbonate plant corrosion inhibitor validation* – A plant in the UK,[1] which had operated for many years, was producing sodium carbonate, using the same process without any serious corrosion problems. A change in a feedstock was made from a by-product of another process to a synthetic source, and laboratory tests on plant liquors indicated that there would be no change in corrosion rate. However, after ~18 months inspection confirmed that serious corrosion had started to occur and although some spares were available, there was a real possibility that production would be severely limited for several months with very serious commercial effects for both the operating company and its customers. Impurities in the original feedstock were identified as having had an inhibitive effect on corrosion. Initial tests had missed this because inhibitor had accumulated in the plant and maintained protection for a period after the feedstock change. ER probes were installed in affected parts of the plant. Some corroded areas were in vapor spaces subject to splashing so that electrochemical LPR probes could not be used directly but were installed in a bypass where continuous immersion occurred. These probes were also utilized in laboratory studies for screening replacement corrosion inhibitors. Possible inhibitors, many selected by analogy with known impurities in the original crude feedstock, were tested in the laboratory, and three were tested in plant trials. The complementary information obtained from the two monitoring techniques simplified the assessment of inhibitor behavior. The most economical inhibitor was identified and its performance monitored in plant trials. A large number of monitoring probes with facilities for automatic scanning and recording of data were used. The equipment cost was correspondingly high but this was justified by the speed with which a solution was found and implemented, resulting in the saving of several millions of pounds of potential lost production and even larger indirect cost to the customers and to their employees. The data obtained were also of value in planning maintenance and shutdown schedules.
2. *Ammonia absorption train corrosion risk mitigation and productivity improvement* – a large coke oven plant experienced significant and unpredictable variations in corrosion rates during normal operations resulting in uncertainty as to the remaining life of the plant.[50] It was recognized that variations in the corrosion rate could be related to poor process chemistry control in the absorption unit, which had implications for the efficiency of ammonia removal. Both LPR and EN corrosion monitoring probes were installed and some typical data over a 1 month period are shown in **Figure 12**.

   The top trace shows weekly temperature excursions that coincided with a process circuit purging cycle. The bottom trace combines both EN and LPR results. The EN responded to pitting attack. On some excursions, increased corrosion rates coincided with the temperature excursion, but on other occasions, the corrosion rate did not increase unduly with temperature. At the start, the measured corrosion rate was reasonably low, but toward the end of the month, the rate increased to a maximum of six to seven times the background rate. Further monitoring revealed a relationship with a particular feature of the plant control involving a faulty pH sensor. Yet further work revealed that excursions in corrosion rate were linked to the molar ratio of two components in the process liquor. The results shown in **Figure 13** identified not only the cause of corrosion, but also that variations in the molar ratio also controlled the efficiency of the ammonia absorption process, thus enabling an increase in the productivity of the plant to be achieved.

4.36.1.5.3 Power generation industry

Coal fired boiler tube corrosion control

Coal remains the most economical and widely available fossil fuel for the base-load generation of electricity.[51] Due to competition and the longer term requirement to minimize the production of greenhouse gases, operators are increasingly trying to maximize the efficiency of pulverized fuel-fired boilers by increasing the interval between scheduled maintenance shutdowns and operating the boilers under optimum conditions by a careful control of combustion parameters. For example, the UK Drax power station, which produces ~10% of the country's base load electricity, has increased the interval between

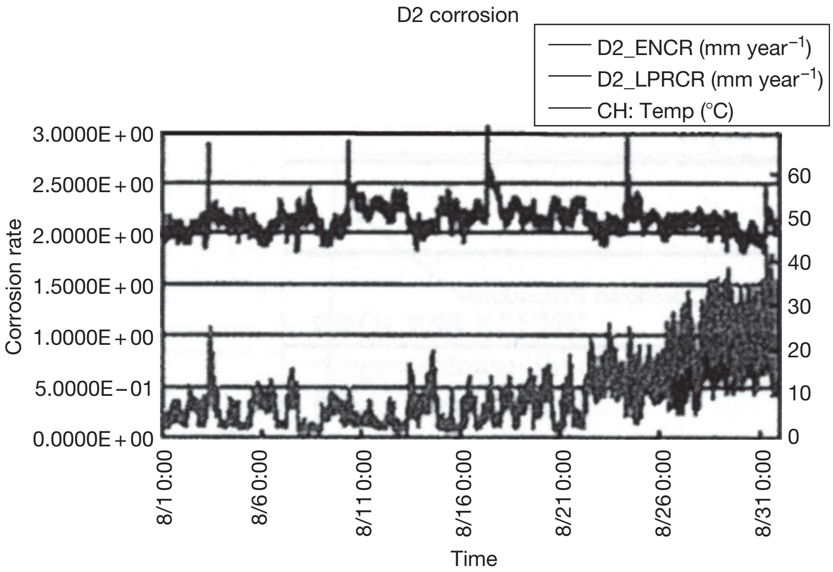


Figure 12 Corrosion behavior in a coal plant ammonia absorber system. Reproduced from Cox, W. M.; Boyce, M.P.; Miyazawa, M.; Tanaka, Y. *Corros. Manage.* **2000**, May–June, 6–10.

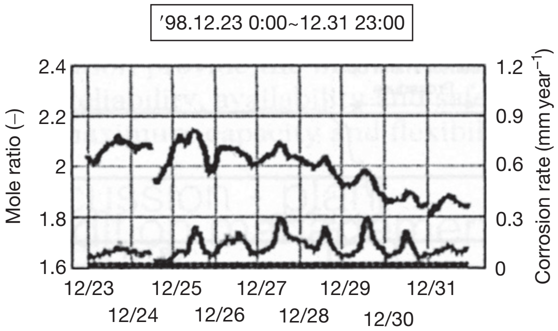


Figure 13 Corrosion behavior in coal plant ammonia absorber system – variations in corrosion process liquor molar ratio (upper trace) rate and corresponding transients in corrosion behavior (lower curves). Reproduced from Cox, W. M.; Boyce, M. P.; Miyazawa, M.; Tanaka, Y. *Corros. Manage.* **2000**, May–June, 6–10.

scheduled maintenance shutdowns from 3 to 4 years and plans to extend this even further in the future. Examples of process improvements include changes in burner configuration, minimizing excess oxygen levels, and optimizing tube-cleaning procedures. The introduction of low NO_x burners over the past few years has produced a corresponding reduction in excess air and an increase in reducing conditions local to the burners. The reduction of excess air has helped thermal efficiency, whereas corrosion and boiler slagging rates have generally increased. Corrosion rates for furnace-walls can be extremely low (<0.1 mm year^{-1}) under oxidizing conditions but may increase to as high as ~9 mm year^{-1} under highly reducing conditions. Historically, manual wall thickness surveys provided data for the prediction of likely tube-wall metal loss between major shutdowns. If this loss resulted in a remaining wall thickness less than an allowed minimum, then tubes were replaced, or a protective, nickel alloy weld overlay applied.

More recently, a range of specialized ER corrosion probes and corrosion scanner systems has been used for monitoring inaccessible surfaces in power stations during normal operations.[51] The sensing elements are welded to the external boiler wall and during the resistance measurement cycle, current is passed directly through the tube wall. The system instrumentation detects small increases in resistance at the nano-ohm level as the tube-wall loses material. Complete maps for corrosion loss can be assembled over large areas of boiler wall. A scanning system was installed in a boiler to monitor the performance of the welded overlay and confirmed that it was performing well, as shown in Figure 14, with very low rates of corrosion (<0.1 mm year^{-1}), in comparison with adjacent nonoverlayed tubing, where corrosion rates were as high as 0.8 mm year^{-1}.

In another monitoring exercise, variations in corrosion rate with the seasons were identified, the precise cause of which was not known other than that some coal stockpiles were thought to contain more moisture during the winter/spring period, as shown in Figure 15.

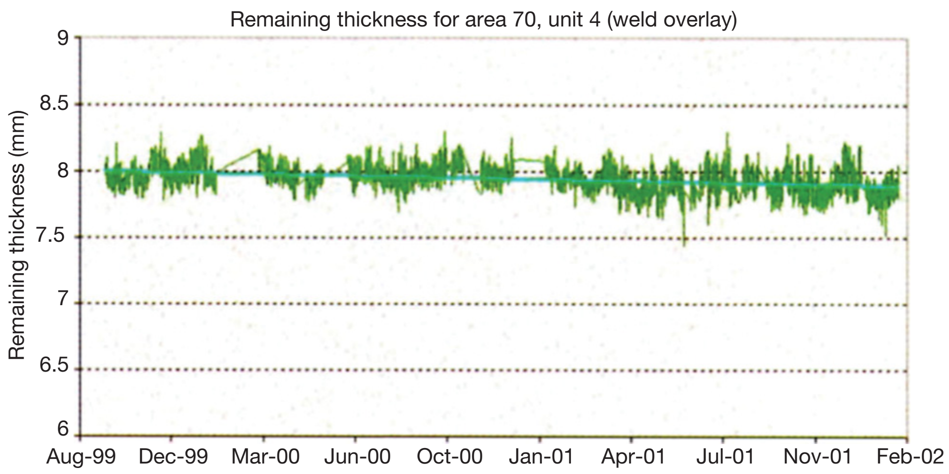


Figure 14 Coal fired power station – monitoring of tube-wall using weld overlayed tubing – thickness trend weld overlay. Reproduced from Farrell, D. M.; Robbins, B. J.; Sikka, P.; Seaman, M. *Corros. Manage.* **2004**, May–June, 16–21.

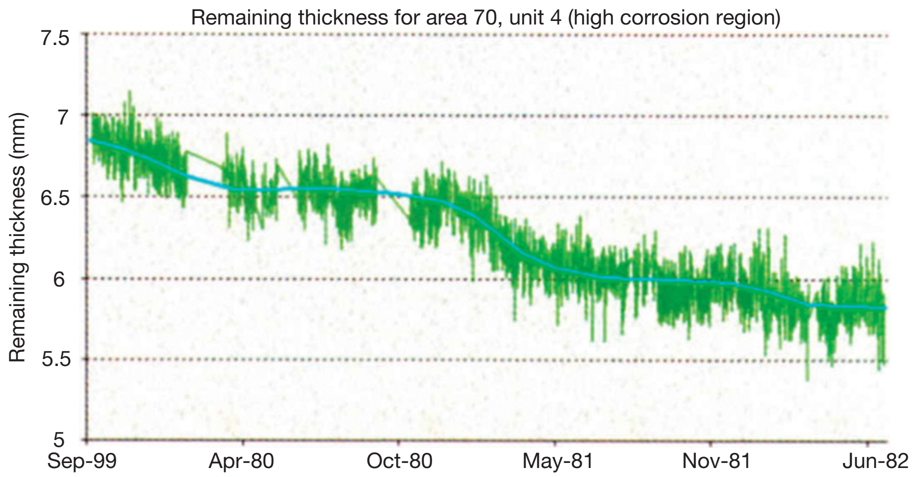


Figure 15 Coal fired power station – monitoring of tube-wall using weld overlayed tubing – high corrosion region. Reproduced from Farrell, D. M.; Robbins, B. J.; Sikka, P.; Seaman, M. *Corros. Manage.* **2004**, May–June, 16–21.

Depending on market conditions and power demand, power plants may be operated in two-shifting mode involving standby during night-time periods. Tube temperatures drop considerably before the plant resumes the next morning and concern had been expressed that this thermal cycling could damage the tube wall scales and accelerate corrosion. However, corrosion monitoring confirmed that this was not the case,[51] as shown in Figure 16.

Flue gas outlet duct corrosion control

Orimulsion® fuel offers power stations an economic incentive for use in industrial boilers.[4] The fuel consists of an emulsion of naturally occurring bitumen in water. However, the fuel has high vanadium and sulfur contents, thus increasing corrosion risks, and produces more ash than conventional fuel. A large power boiler, fitted with a wet scrubber flue gas desulphurization (FGD) unit was using Orimulsion® as fuel and the flue gas outlet duct downstream of the scrubber suffered substantial corrosion damage resulting in heavy expenditure for repairs, lining, and maintenance. A program of online monitoring was initiated to establish when corrosion was taking place and, more importantly, under what conditions the flue gas could become condensing. As the probe metal temperature was lowered, acid dewpoint condensation corrosion took place at temperatures below 65 °C. As soon as this condition was established, very high rates of corrosion would occur on the flue

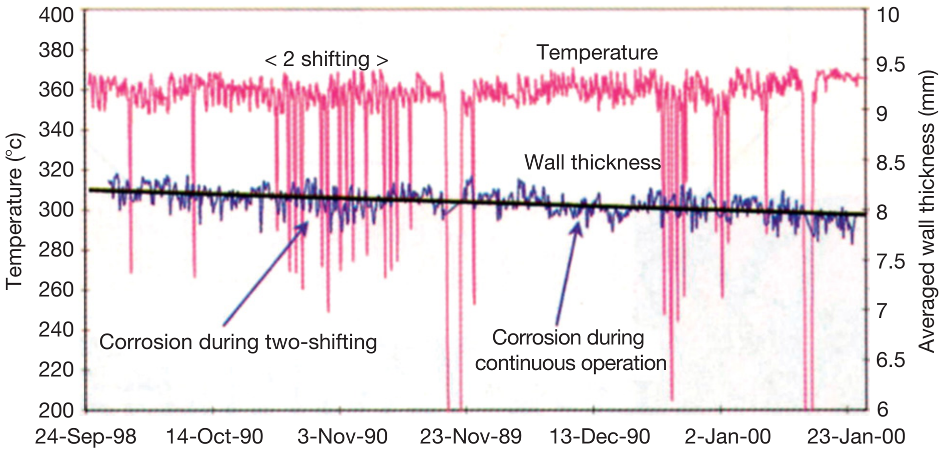


Figure 16 Coal fired power station – monitoring of tube-wall using weld overlayed tubing. Two shifting operation and corrosion trends. Reproduced from Farrell, D. M.; Robbins, B. J.; Sikka, P.; Seaman, M. *Corros. Manage.* **2004**, 16–21.

duct walls. A short program of field trials established that continuous condensation occurred under certain firing conditions of the reheater furnace, especially if moisture removal by the mist eliminators on the outlet from the FGD system was less than optimal.

The field trials were extended to enable the corrosion surveillance instrumentation to remain in service in the plant resulting in significant operational savings, reduced maintenance costs, and the avoidance of expensive plant downtime, all of which previously had contributed significantly to the overall cost of generation.[4]

4.36.1.5.4 Miscellaneous process industries

Desalination

Multistage flash distillation plants provide potable water by the distillation of seawater. These units have substantial amounts of copper alloy tubing for both heat pickup and cooling. The flash chambers that operate at a reduced pressure to obtain as much thermodynamic efficiency as possible are constructed from coated carbon steel. Corrosion of the copper alloy tubing and carbon steel chambers together with severe scaling are common challenges in these plants. Chemical treatments reduce the very severe scaling in these plants.

When the technology for multistage flash distillation was developed in the mid-1960s the copper alloy tubing selected was the same wall thickness as used for power generation. Considerable capital costs savings could be made if the wall thickness could be reduced, but there were concerns as to the robustness of the thinner walled tubing. A trial of both ER and LPR probes in a scaled-down rig gave excellent correlation with destructive examinations of removed tubes. Both systems operated very well and were eventually used in operating plants to monitor the effectiveness of chemical treatments.[52]

Pulp and paper industry

Paper pulp manufacturing processes use very large volumes of water in paper production with many resulting corrosion problems. Some of the variables include temperature, chemical constituents, pH, concentration, size, and quality of the wood fibers. Recycling and environmental concerns may also influence corrosion performance. Conservation of water has resulted in recycling and reuse of water in closed loop systems. This has led to increases in the concentrations of dissolved solids and temperatures and changes in pH that have increased corrosion risks. Traditionally, carbon steel was the main material of construction but over the years, more stainless steel has been introduced. The types of corrosion experienced include pitting, crevice attack, SCC, MIC attack, weld corrosion, and corrosion fatigue.

Monitoring using advanced electrochemical techniques has been widely practiced in these plants. Most of the monitoring methods have been utilized, including coupons and electrical, in particular LPR, probes. EN has been successful in correlating online the effects of process chemistry on corrosion in Kraft continuous digesters.[52]

Cooling water systems

Recirculating cooling water systems using carbon steel tubes are treated with a range of chemicals including corrosion inhibitors. Open recirculating systems present the highest corrosion risks due to oxygen pickup over the tower. These systems are treated with corrosion inhibitors and compatible biocides, and corrosion monitoring is ideal in this application. The cooling water is usually allowed to concentrate by ∼2.5 times for economical operation. Additional concentration would allow excessive chloride content with associated increased corrosion risks. The concentration is held at the given value by discharging a proportion of the water (blowdown) at prescribed intervals and fresh water makeup is added to keep volumes constant. LPR is the most suitable online technique for corrosion monitoring, combined with the use of coupons, which can be reduced in number when confidence in the LPR probes is established. Both probes and coupons are located in the hottest sections of the circuit where corrosion risks peak.

Compact control units for cooling water systems are available commercially that measure water parameters such as conductivity, and pH and incorporate suitable instrumentation for measuring corrosion, usually based on LPR. In the late sixties, a US chemical treatment company introduced a system incorporating an LPR measurement cell and facilities for activating a dosage pump if the preset corrosion rate was exceeded. Recently, a unit has been described incorporating seven different corrosion monitoring techniques (including crevice corrosion) to investigate the relationship between corrosion and water chemistry to facilitate corrosion control in a district heating project in Denmark.[53]

An example of the benefits of corrosion monitoring related to a recirculating cooling water system in a fertilizer plant that used river water and suffered severe corrosion arising from inadequate control and poor maintenance. The system blowdown was discharged to a treatment plant before eventual discharge back to the river. A trial was carried out with a suitable corrosion inhibitor and corrosion monitoring carried out at the exit of the hottest heat exchanger using both coupons and LPR probes. Following the verification of the LPR rates with both coupons and inspection techniques, some reduction in the number of coupons used was permitted. Corrosion rates were below 0.25 mm year^{-1} (10 mpy) for carbon steel. Bacterial monitoring was carried out using spot tests and periodic plate tests.[54]

4.36.1.5.5 Pipelines (excluding oil and gas)

Pipelines are used for many different products other than oil and gas including raw and potable water, seawater and treated wastes. Constructional materials include steels, cast irons, corrosion resistant alloys (CRAs), thermoplastic and reinforced polymers, and concrete. Carbon steel pipelines are often lined with cement and/or coated with organic coatings.

The London water ring main was constructed between 1988 and 1993 to supplement the existing Victorian water mains that have been badly affected by corrosion. Extensions to the new main are already in hand. Corrosion engineering and monitoring are utilized in the overall maintenance program.

In the Man-Made River project in Libya, a pipeline of combined length ∼4000 km has been constructed to carry well-water from the south to the main populated and industrial areas in the northern coastal area. The prestressed concrete coated pipe (4-m diameter and 7.6-m length) is reinforced with steel cabling. The pipes are protected from external corrosion using cathodic protection. Many corrosion problems have occurred with this system varying from corrosion of stainless steel components in the wells to corrosion of the steel reinforcement, which now, hopefully, has been controlled. Extensive corrosion monitoring using a number of techniques is carried out. A particular interest was corrosion failure of the prestressing wires.

4.36.1.5.6 Transportation

One major international car manufacturer has used the ER system for monitoring corrosion on car bodies. Vehicles were driven through salt water on a test track to assess current corrosion control assemblies, materials, and coatings.

Generalized approaches to the corrosion surveillance of aircraft, emphasizing the training of personnel, have been reviewed.[9,55] The development potential of an ER system for civilian aircraft has been examined resulting in a US Air Force initiative of using ER sensors placed in susceptible areas using computer capture of data for a number of different aircraft.[56] In order to establish correlation between operating conditions and corrosion, the Canadian Air Force has used sensors in several aircraft to monitor operating conditions and base locations.[9] Naval flying operations are subject to very severe corrosive environments. The US Navy estimates that every hour of flying requires 27 h of maintenance. A miniature sensor has been developed by the US Navy that can remotely detect and monitor corrosion in inaccessible areas of aircraft, ships, submarines, and weapon containers. The sensor combines bimetallic thin-film microsensor technology with microelectronics with radio frequency communication. The system collects and stores corrosion information that can be retrieved on demand by transmitted radio signals.[57]

4.36.1.5.7 Nuclear waste storage

The nuclear industry has extensive interests in the corrosion of structural materials that are used for the storage of radioactive wastes, where the objective is to minimize moisture and geological storage areas are chosen on this basis. Active waste is stored in both carbon steel and stainless steel drums and considerable work is underway to investigate corrosion monitoring methods for the waste containers in order to maintain integrity prior to and during disposal. The development of an EN-based probe for monitoring nuclear waste containers has been reported.[58]

4.36.1.5.8 Civil engineering

Corrosion measurements using the LPR technique have been reported on a historical building in Chihuahua, Mexico.[59] The building was a railway locomotive roundhouse built in 1910. LPR measurements were made in the building to evaluate the behavior of the metallic materials in the presence of a humid atmosphere. Test-cells were placed in several zones of the building's metallic structure. Data obtained from the *in situ* measurements showed that the corrosion rate was less than 1 mm year^{-1}.

Probes with ER elements have been buried at various depths in concrete to monitor the corrosion of harbor jetties. One application related to naval infrastructure in US Navy dock facilities.[60] Electrochemical techniques for the monitoring of reinforcement in concrete have received much attention and laboratory development has been extensively reported. Advantages and limitations of electrochemical measurements for monitoring the reinforced steel have been reported by Rothman and Tullmin.[2] Details of other electrochemical techniques for assessing concrete reinforcement have been reported by Sykes[61] and Elsenor.[62]

4.36.1.5.9 Atmospheric corrosion monitoring

Special ER probes using printed circuit sensors provide many advantages compared with the conventional coupon technique including remote data capture and overall convenience. Monitoring at specific locations (power plants and other industrial areas) for pollution type monitoring is now mandatory in some countries. An example of location atmospheric monitoring is the monitoring and inspection of radar towers located throughout the USA.[63]

4.36.1.6 Future Developments

An interesting development in an electrochemical technique relates to electrochemical frequency modulation (EFM).[64] In this technique, the potential perturbation signal consists of two sine waves of different frequencies and a corrosion rate can be obtained instantaneously, without prior knowledge of the Tafel constants. An advantage claimed for this method is its inherent data validation control using 'causality factors.' Another advantage claimed is that the method can be used successfully for corrosion rate measurements under various corrosion conditions. Corrosion rates obtained by EFM, LPR, weight loss, and solution analysis (atomic absorption spectroscopy) were in agreement.

There has been a significant increase in the applications of the FSM system and similar systems by other manufacturers in the past decade and this trend is likely to continue because of the advantages of FSM in relation to the accurate monitoring of plant components rather than sensors.

Closing the loop by using online monitoring signals to operate associated control systems will accelerate as new electronic and software developments occur. This is particularly relevant to the oil, chemical, and power industries. A major US company in process control has recently purchased a specialized corrosion control company offering advanced electrochemical monitoring, and this could offer significant advantages to both the manufacturer and the user. Improvements in electronics and analysis have taken their time to induce confidence in online monitoring. Also, the complexity and uncertain morphology of corrosion has not helped the adoption of the technology when compared with the conventional process control, for example, corrosion is not a defined, fixed parameter comparable to the measurement of temperature, pressure, or flow rate. A process control package that includes corrosion monitoring is an exciting prospect that provides for improved service in both hardware development and technical support.

A solicitation issued by the US DOT in 2007 invited research projects based on nanotechnology related to Internal Corrosion Direct Assessment (ICDA) in the pipeline industry. New nanotechnologies for the detection and elimination of internal corrosive species as well as determining the presence and corrosivity of water are a component of the program. In the solicitation, it was stated that currently available technologies are limited because some cannot be applied to all pipelines and others require prior knowledge of where to locate the sensors and costly excavations to replace the sensors.

The oil refining industry[65] has stated the following requirements for a successful corrosion monitoring technique in their operations:

1. Sensitive and reliable;
2. Fast response time;
3. Operate in most if not all environments;
4. Must have online and remote data access;
5. Should be unaffected by iron sulfide (FeS) film formation;
6. Unaffected by noise, vibration, and temperature;
7. Compatible with local plant services.

The provision of a technique that satisfies all of these criteria is a challenging goal for the future.

4.36.2 Inspection

4.36.2.1 Introduction

The definition of inspection is "to look closely at or into" and an inspector is someone who carries out this function. One of the early inspectors was the wheel-tapper, employed by the railway companies, who tapped the wheels of railway carriages with a hammer at larger stations. Any cracks present in the wheel components would alter the tone of the sound reflection. These days this function is carried out at speed by a special testing vehicle fitted with transducers.

Inspection has one of two objectives:

1. To identify defects, flaws, cracks, or changes in physical properties in a component that deviate from the material specification.
2. To periodically inspect operating equipment in order to detect any onset of material degradation and/or mechanical failure, generally referred to as in-service inspection.

There has been much discussion over the years among NDT/E academics, specialists, and inspectors as to the precise definition of the terms flaw or defect. All materials contain flaws but they are significant only in relation to the extent to which they might impair the functionality of a component, not least whether the flaw (or defect) remains the same size or starts to grow in service.

Detailed background information on NDT/E can be obtained from the web sites such as the American Society of Nondestructive Testing (ASNDT) and the British Institute of NDT (BINDT). In practice, NDT/E remains a mixture of black-art and science. An important issue relating to practice is the training levels of NDT/E operatives, especially relevant due to the increasing tendency to buy in inspection services. The establishment of recognized inspection training programs has been a long and tedious process, driven by the relevant professional societies in several countries.

4.36.2.2 Historical Development of Inspection Technology

Inspection has developed over the decades raging from the visual observation of mechanical parts through to the detection of the noise produced by the formation of cracks in industrial plant. Early inspection requirements were directed at moving components that endured stresses and strains particularly the engines, pumps, and compressors that were developed during the industrial revolution in the UK, not least the introduction of steam power, in the nineteenth century. The Second World War led to a massive development due to the requirements of the defense industries, particularly in the USA. Many techniques, including ultrasonics, radiography, acoustic emission (AE), eddy currents, and many others, now employed routinely in a range of industries were developed at that time. However, the new techniques were often oversold and problems with both hardware and data interpretation contributed initially to user disillusion. Confidence was restored with further development stimulated by user feedback. Later developments in electronics made a substantial contribution and further expansion, and development followed the introduction of the computer, in particular, the introduction of the laptop for inspection in the field.

A key issue in relation to the inspection of operating equipment is whether it is necessary to take equipment out of service for inspection. Offline inspection is somewhat easier to carry out than inspection when plant is operating, because equipment can be entered for appropriate inspections using the full range of available inspection techniques. Clearly, size can be an issue such as in the case of piping, but using appropriate borescopes, even small diameter piping can be examined and photographed or viewed by television.

There have been strong economic drivers to develop online inspection techniques, particularly for equipment in high capital cost plants operating for extended periods between scheduled shutdowns, such as in oil production, oil refining, power stations, and chemical plants for which unscheduled shutdown is very costly relating to the cost of lost product. Online ultrasonic thickness measurements (UT) using portable probes were limited in the early days to temperatures that would not destroy the piezzoelectric crystal in the probe. However, the subsequent development and use of special contact greases extended their use to higher temperatures. Water-cooled probes were introduced but proved unwieldy in operation and did not achieve overall acceptance. Welded UT probes were developed by the nuclear industry in the UK for the inspection of some fast reactor components that contained design features to protect the piezzoelectric crystal from excessive temperature. These probes were hardwired to the control room and enabled continuous measurements of wall thickness and this technology soon found applications in the oil industry.

The development of phased arrays of UT probes mounted on a flexible mat, attached by a velcro mat that could be moved from one location to another, was a further useful development. An added benefit with this system related to its use in remote locations capturing data without visits, particularly valuable for the oil industry in dangerous locations subject to terrorist or similar threats. The development of TLA and FSM further extended the battery of available, noninvasive tools. Both are conventionally categorized as corrosion-monitoring techniques but could just as well be categorized as NDT/E techniques, because they bridge the historical boundary between corrosion monitoring and inspection technologies by providing data as to equipment condition continuously.

AE has also developed as a noninvasive, screening tool for identifying damage zones in equipment where 100% inspection would be too costly and/or time consuming. The identified damage zones can be then examined in detail online, using techniques such as ultrasonics. In-line inspection (ILI) vehicles used for pipeline inspection have also seen major development.

4.36.2.3 The Need to Inspect for Corrosion Damage

There are many examples of serious incidents and accidents resulting in fatalities due to corrosion that was not detected because

1. Inspection was not carried out.
2. Inspection was inadequate.
3. The inspector was not sufficiently qualified in the techniques used.
4. Problems regarding the interpretation of the data.

An example of poor, inadequate inspection was the failure of a fairground ride in London in 2000,[66] in which two people were killed and a third person was seriously injured because a seat broke free and flung them through the air before smashing into a kiosk on the far side of the fairground. Examination showed that the ride was riddled with rust and metal fatigue. An inspection of the ride had been carried out 3 weeks before the accident by an independent safety inspector who had reported no defects or deterioration. It was disclosed at the trial that the inspector had two previous health and safety convictions. A subsequent inspection revealed signs of deterioration to the remaining eleven car seats on the ride. The inspector was found guilty of manslaughter. The jury called for tighter regulations covering fairground rides and the introduction of a regulatory body to ensure that inspectors received proper training. This incident emphasizes the importance of adequate training and good professional conduct.

An incident in the marine industry related to a boiler explosion on the cruise liner SS Norway (previously known as the SS France), the world's longest passenger liner carrying 3000 passengers. Within an hour of docking at the Port of Miami in 2003, a massive explosion occurred due to the rupture of one of the four boilers, fatally injuring eight crew members.[67] The steam penetrated the bulkheads on two further decks breaching the crew accommodation areas and seriously burning a further six crew members. A failure examination carried out by the US National Transportation Safety Board (NTSB) showed that a large section of the waterwall header had fractured and broken away. The rupture was caused by extensive fatigue cracking which had initiated at the bases of corrosion pits most likely resulting from improper water chemistry during lay-up periods. From 1990 through 2003, it appears that no NDT/E or appropriate internal visual inspections were carried out on the weld seams of the affected boiler despite a welldocumented history of cracking of weld seams in two of the ship's other boilers in 1996. The ship never returned to service after the explosion and was scrapped.

Neglect of a significant corrosion risk and inadequate inspection resulted in Scotland's worst industrial disaster in May 2004, involving the deaths of nine workers and serious injuries to another

37 personnel at a Glasgow plastics factory.[68] Following an investigation carried out jointly by the UK HSE, prosecutors, and police, a fine of £200 000 was levied on two companies operating at the site. The investigation showed that the explosion was caused by the failure of a buried pipe carrying liquid propane fuel at the factory. A leak outside one of the buildings allowed liquid propane to go through the wall into the cellar area. The pipe had not been inspected since initial installation in 1969. All sections of the buried pipe had deteriorated and corroded, including a cast-iron bend joining two sections of the pipe. No corrosion protection system had been applied to the pipework.

Corrosion risk mitigation by inspection is given a high priority in the air transport industry. However, problems can occur and deficient inspection was a factor in the Aloha Airlines Flight 243 incident[69] involving crevice corrosion allowing water ingress at bonded joints in the airframe. Fatigue cracks occurred, driven by the extensive number of take-offs and landings associated with operating short flights between the Hawaiian Islands, resulting in extensive damage when part of the upper fuselage was torn off. The operating history had exceeded the recommended number of flights, which had not been accounted for by the airline and the manufacturer. Accordingly, the inspection schedule was out of synchronization with that recommended by the manufacturer. In addition, a manufacturer's recommendation of a specific NDT/E test had not been carried out by the airline.

Bridges are at risk from corrosion and inspection is vital to the mitigation of such risks. Following the collapse due to SCC of the Point Pleasant bridge in the USA in 1967, resulting in 46 fatalities, a national policy for bridge inspections was made law in 1968 and a massive inspection program instituted.[70] The recent collapse of the Minnesota freeway bridge in 2007 reemphasized the scale of the problem in the USA. A large number of bridges were built in the 1950s and 1960s and there will be a large requirement for inspection services over the next 20 years. The author was told that the design life of the Forth Bridge, opened in 1890 and providing the main UK east coast railway link between Aberdeen and London, was 'in perpetuity' – the only structure given this classification in the author's experience in any industrial sector. This bridge has received appropriate inspection and corrosion prevention throughout its life. However, the Forth Road Bridge, opened in 1964, has corroded main cables, which will take up to 7 years to replace. Each main cable consists of 11 618 wires and it is believed that ~90% of the wires are corroded. A massive project for inspection and renewal of the wires is expected to cost hundreds of millions of pounds.[71] The Severn Bridge, which provides a road crossing of the River Severn in the UK, is also reported as having cable corrosion with weight restrictions in force until inspection surveys now in progress assess the full extent of the corrosion.[72] The problem was first revealed by inspection in 2004. Special cable inspection techniques are urgently required for bridge suspension cables.

The marine industry relies on vessel certification as the basis for licensed operation. The Erika, a Maltese registered oil tanker on charter to total carrying a cargo of crude oil, broke in half and sank while approaching the Bay of Biscay in a severe storm, resulting in the most severe coastal pollution ever experienced in any country of the European Union. In the ensuing court proceedings, it was revealed that a previous certification authority had refused the issue of a certificate due to severe corrosion of the tanker but the owners had obtained recertification from another authority. Total was fined $550 000 for the maritime pollution caused. Other fines were imposed for other charges relating to the incident and fines were also imposed on the certifying authority and the owners of the tanker.[73]

These failures occurred despite existing legislation relating to the inspection of the relevant infrastructure together with considerable guidance regarding appropriate inspection techniques and practices. Incidents and accidents continue to occur due to failure to recognize prevailing corrosion risks, poor communication, inadequate inspection, and inadequate training of those involved in plant operation and maintenance. These are essentially management deficiencies, the causes of and remedies for which are covered in a separate chapter in this book.

4.36.2.4 Inspecting for Corrosion Damage

Inspection for corrosion damage, or other service deterioration, developed at a later stage on the inspection technology timeline. NDT/E techniques were originally targeted at material defects and manufacturing faults, but as the technology developed, attention was extended to material degradation in service. Several established NDT/E techniques were identified as having potential for the inspection of corrosion including radiography, ultrasonics, and eddy current.

NDT/E as applied to corrosion inspection has the two main objectives of detecting, and if possible, dimensioning corrosion. Inspection staff is not always familiar with all of the many forms of corrosion and good liaison is required between the inspection function and those engaged with corrosion control. General or uniform corrosion is the easiest type of corrosion to detect and measure. Using simple thickness meters, the remaining wall thickness can be measured. For example, subsea pipelines have been inspected by clamping a raster assembly developed by the Danish Welding Institute on the pipeline in which an UT probe assembly can traverse the full circumference of the line. Robotic crawlers can carry UT probes for the inspection of the large storage tanks used by the oil industry. The FSM system has not only been applied for general corrosion but also at a discrete area such as welds.

Some forms of localized corrosion, such as pitting corrosion, proved particularly difficult to resolve with the early ultrasonic instruments and problems are still reported in this respect.[74] The detection of cracks, in particular stress corrosion cracks, was of particular interest to the nuclear power, oil/chemical, and pipeline industries. These are invisible to the naked eye until failure occurs but can be detected using ultrasonics and AE. For pipelines inspection, ILI vehicles are now able to detect cracks as well as reductions in wall thickness, as described in a later section.

Inspection techniques used to detect defects in manufactured products, in particular ultrasonics and eddy currents, have been adapted for the detection of various corrosion types. For example, nonferrous heat exchanger tubing has long been inspected with eddy currents to detect manufacturing flaws (pin-holes) and the technique has been adapted to inspect *in situ*, offline, for corrosion defects that may have developed in service tubing.

Although some of the oldest techniques such as visual examination and mensuration are restricted to shutdown periods, other techniques such as ultrasonics, radiography, and AE can be used online. On-site inspection does not always have the precision associated with manufacturing or workshop conditions but good correlation can be obtained when monitoring and inspection data are compared in a well-organized and integrated inspection and corrosion monitoring program. Choosing the right techniques for inspection is a challenge and generally benefits from experience.

Practical problems inevitably arise and have to be overcome. Lack of access to equipment, in relation to not only the height (requiring scaffolding) but also the close proximity of nearby equipment, can cause problems. In circumstances where access for inspection is completely restricted, corrosion risks have to be mitigated by upgrading materials in the design or at shutdown. The presence of very thick rust can prevent the transmission of ultrasonic waves for single-point ultrasonic measurements in particular. High temperatures can degrade the piezzoelectric crystal in the probe and may require the use of high temperature greases and special probe designs.

Inspection programs are now routinely planned and managed as key components of corrosion management and RBI programs, the development of which are described in separate chapters in this book.

4.36.2.5 Inspection Techniques for Corrosion Inspection

4.36.2.5.1 Visual inspection

A properly executed visual inspection should accomplish the following:

1. Assist in failure analysis.
2. Indicate the need for further exploration.
3. Help to define the search area if further exploration is warranted.
4. Suggest techniques for further exploration.
5. Help to determine the measures needed to prevent or minimize the recurrence of damage.
6. Reduce the possibility of installing faulty fabrications by ensuring that the right materials and fabrication procedures are used and that workmanship is of the proper quality.

Visual observation can be carried with or without optical aids. Typical signs of damage include rust staining, bulging, cracked or distorted coatings/insulation, and hot-spots that are indicative of possible corrosion damage. The value of visual observation cannot be overemphasized as long as the potential limitations of direct eye observations are recognized, including the need for access, tiredness, fatigue, and variability. Simple magnifiers can be utilized ranging to more sophisticated optical equipment using fiber-optic (FO) endoscopes (borescopes), which are used for inspection in restricted areas. These devices can be fitted with cameras or TV cameras and lengths of flexible conduit can be fitted together for the inspection of remote areas and are extensively used for inspection purposes in boilers, buildings, aircraft engines, and process plant. Self-propelled versions of robots with FO equipment attachments and attached umbilical (for power and controls) are used for the inspection of offshore risers, terminal hoses, and short-length pipelines. The introduction of digital cameras has made a major contribution to record keeping and communication purposes. Internal corrosion inspection is generally confined to scheduled shutdown periods, but the examination of external corrosion, often related to coating breakdown, can be carried out when the plant is operating, provided access is available.

4.36.2.5.2 Ultrasonics

Principles

This is one of the most important techniques for corrosion inspection, in particular, for the measurement of metal thickness. Instrumentation varies from simple thickness meters using a single portable ultrasonic probe to more complex equipment using probe arrays with phased-firing probes.

Mechanical vibrations can be propagated in solids, liquids, and gases. If their frequency is within the approximate range of 10–20 000 Hz, the sound is audible. Above ~20 000 Hz, the waves are referred to as ultrasound and their application for measurement as ultrasonics.[75] The waves are produced by a piezzoelectric crystal that is mounted in a suitable probe (holder or an array assembly) and when excited by an electric current, transmits a high-frequency sound-wave. Ultrasound waves have different wavelengths in different materials. The waves arise because of the elastic properties of the material under test and are due to induced particle vibration in the material. If the particle motion is along the line of direction of travel, the resulting wave is called a compressional or longitudinal wave, which can be propagated in solids, liquids, and gases.

It is possible for the particle movements in solid materials to be at right angles to the direction of travel, in which case the waves are called shear waves. The velocity of these waves is around half of that of longitudinal waves. Head waves are shear waves longitudinally polarized that are produced when a wave passes along a free surface at a velocity greater than the bulk wave velocity in the material. Such a wave on a surface or down a crack face converts to shear waves. Other types of surface waves such as Rayleigh and Love waves can be generated in solid materials but are beyond the scope of this chapter.

In the pulse echo system, an electrical pulse is applied to the transmitter probe, producing a short ultrasonic pulse, which is propagated into the material through a couplant layer.[75] The same pulse triggers a timebase generator so that the pulse of ultrasound starts to move through the inspected component at the same time as a spot starts to move across a cathode ray tube (CRT) display screen. Variations in voltage at the transducer due to the ultrasound wave are passed to the amplifier and applied to the Y-axis of the CRT to produce a transmission signal that represents the shape of the generated ultrasonic pulse. The spot continues to move across the screen of the CRT as the sound pulse travels through the component until the electronic pulse reaches a reflecting or scattering surface. In the case of thickness measurement, this would be the opposite surface of the equipment wall. The basis of ultrasonic thickness/depth measurement and some special probes for the purpose are illustrated in **Figure 17**.

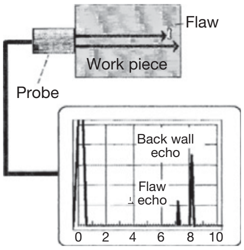
Various types of ultrasonic scans can be created and viewed on a CRT, as follows:

1. A-scan – a linear timebase on the x-axis and ultrasonic signal amplitude on the y-axis is the simplest and commonest, displaying amplitude versus time of flight at a location.
2. B-scan – the apparent size and position of defects is shown on a cross-sectional plane, normal to the surface on the line of the probe scan.
3. C-scan – a two-dimensional display of the test surface in plane view is shown. The probe is scanned mechanically over the surface in a regular raster and the defects are shown as bright patches in their correct plan positions (widely used in immersion water tanks) providing a radiograph type image.
4. D-scan – is a two-dimensional display of a cross-section of the specimen along the line of the scan.
5. P-scan – was designed by the Danish Welding Institute for weld inspection, which produces a simultaneous display of A and B scans.

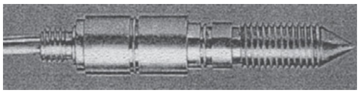
The various scans are illustrated in **Figures 18** and **19**.

Types of probe

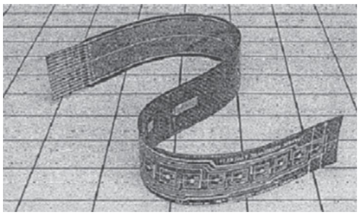
There are different types of ultrasonic probes, depending on the objective of the inspection. The most basic probe contains a single transmitter crystal and requires another probe placed on the opposite surface to receive the compression sound wave. Such an assembly would be used, for example, for the detection of defects in a cast ingot of metal. Two crystals, transmitter, and receiver, can be mounted in a single hand-held probe connected to a portable instrument that allows the measurement of metal thickness from the external surface of the metal component under inspection, such as piping or a process



A scan, amplitude versus time of flight at a location. Compression (longitudinal wave) probes are coupled to surfaces at temperatures up to ~400 °C to detect thicknesses >~0.15 mm at a sensitivity up to >0.01 mm.



Solid coupled probe, welded on to a surface, suitable for temperatures up to ~600 °C, courtesy AEA Technology.



Fleximat probe, 12 transducers glued on to surface suitable for temperatures up to ~120 °C, courtesy AEA Technology.

Figure 17 Ultrasonic thickness/depth measurement.

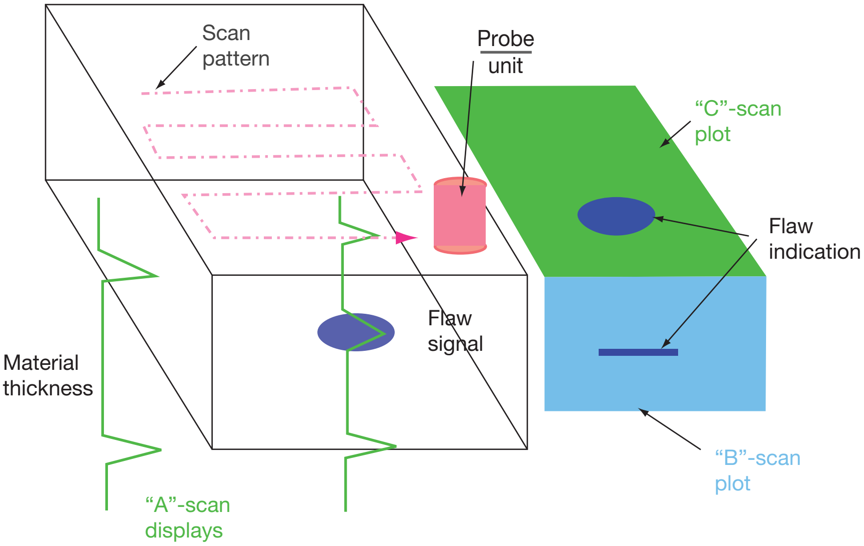


Figure 18 Types of ultrasonic scan: A Scan amplitude versus time of flight at a location. B Scan time of flight versus distance along a transverse scan line. C Scan amplitude or time of flight versus location in scanned area. D Scan time of flight versus distance along a longitudinal scan line.

vessel. The interval between the pulses is displayed digitally, after conversion to a thickness scale using the ultrasonic velocity in the material being tested. The probe is placed on the metal surface and the reading taken. Paint layers, if present, do not generally impede the transmission of the ultrasound waves. If surfaces are thermally insulated, cutouts can be provided at locations that are likely to be vulnerable to corrosion.

Shear probe assemblies transmit shear waves at different angles to those that transmit at 90 degrees to the metal surface. As in the case of compression

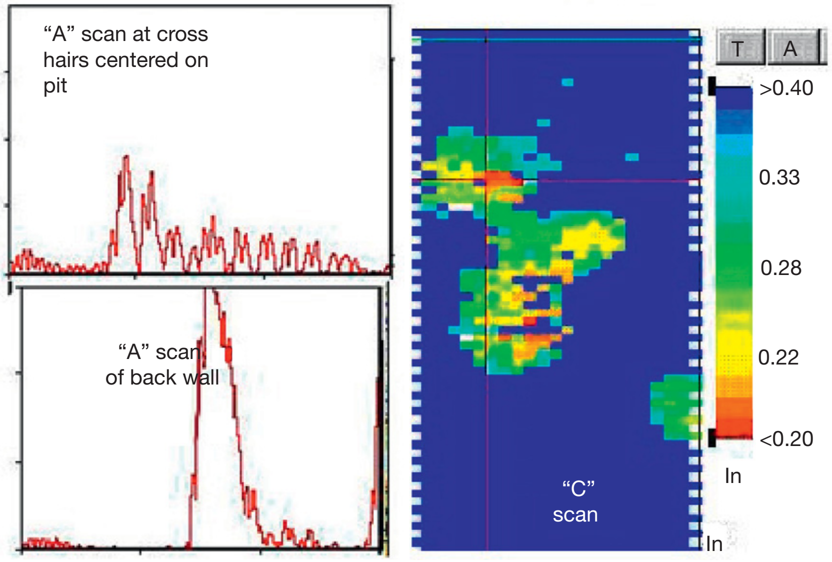


Figure 19 Automated ultrasonic corrosion mapping by the computer control, processing, storage and imaging of ultrasonic signals, courtesy Matrix inspection & Engineering Inc.

probes, either separate or combined transmitter and receiver probes can be used. These angled probes are used commonly for the detection and sizing of crack like defects and weld defects and scanning with angled probes allows defect location/sizing in inaccessible locations. Conventional probes require couplants (grease) for the transmission of ultrasonic waves into the material undergoing inspection to avoid any impedance (blockage) of the ultrasound by an air gap.

Multiprobe (array) systems were developed using computers to process readings from twenty-four probes or more mounted on a single, wrap-around mounting mat, which can be moved around various locations in the plant. There are other forms of arrays such as those mounted on a wheeled trolley that is used to monitor the floors of above-ground storage tanks, now largely replaced by trolleys using the magnetic flux system that does not require water jets for coupling and can tolerate the thicker protective coatings used in tanks. Special assemblies have been developed for certain industries such as the nuclear, oil, and power, industries.

Specialized ultrasonic systems

An ultrasonic internal rotary inspection system (IRIS) for the offline inspection of heat exchanger tubes is available commercially and is widely used. Ultrasonic waves are directed at 90 degrees onto the inner surface of the tube using a 45-degree rotating mirror reflector, as shown in Figure 20. Internal and external wall thinning or pitting can be detected, located, and size estimated. This method has a number of advantages over the older eddy current technique for tube inspection, for example, that tube surfaces under baffles can be inspected, but is considerably slower and the two techniques are, to some extent, complementary.

Long-range ultrasonic transmission (LRUT) has been developed to examine piping for corrosion or erosion. One development consists of a phased array of transducers where the ultrasound is focused on a specific area along the pipe and around its circumference. Three different wave modes are used and propagation distances depend on several factors such as pipe geometry, contents of pipe, and coating and insulation present. However, in general situations, it is not unusual to obtain a range of 30 m (100 ft) in either direction from the transducer. Both internal and external corrosion can be detected, but the method is unable to distinguish between them. Pipe diameters over 50 mm can be inspected. The technique has shown particular promise for the detection of corrosion under insulation (CUI), which is a major problem in industrial plant as described in the chapter on the management of corrosion in the chemical/petrochemical industries in this book. Inspection for CUI is an expensive and tedious operation usually requiring the removal of the insulation for visual inspection. LRUT offers the prospect of inspection of relatively long lengths of insulated piping with only limited, local insulation removal,[76] as illustrated in Figure 21.

Electromagnetic acoustic transducer (EMAT) systems were developed by the nuclear industry. The probes propagate Lorentz waves in a magnetic field and depending on the orientation of the force vector, different ultrasonic wave types can be generated into a metal surface without the need for close contact between the probe and the metal surface under inspection. Both shear and compressional waves can be generated depending on the orientation

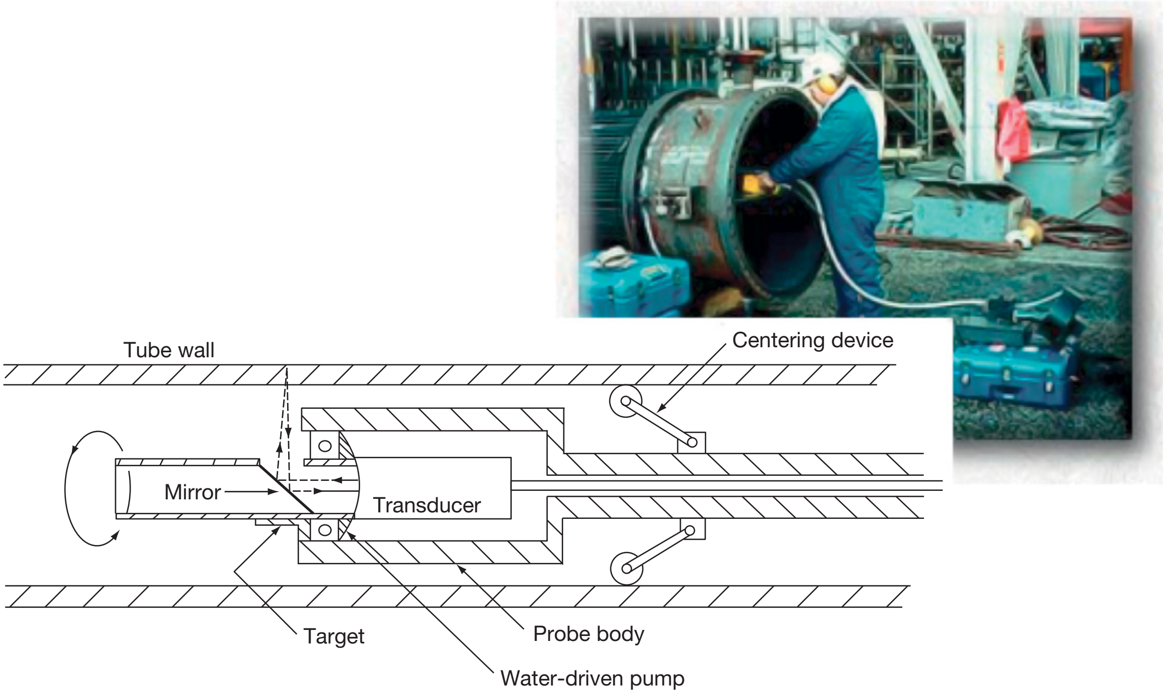
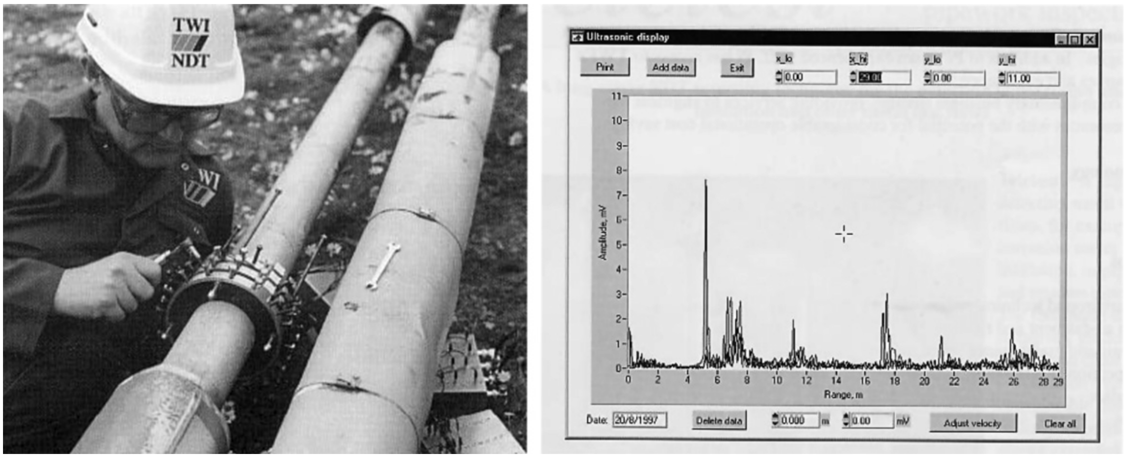


Figure 20 Ultrasonic IRIS for heat exchanger tubing using a probe with a 45° rotating mirror that reflects the ultrasonic beam into the tube wall at 90° to the wall allowing internal/external thinning or pitting to be detected, located, and size estimated.



x_lo 0.00
x_hi 29.00
y_lo 0.00
y_hi 11.00
Date: 20/8/1997
0.000 m
0.00 mV

Figure 21 Long range, guided ultrasonics for the detection of wall thinning due to internal or external corrosion. Rings of piezoelectric transducers, clamped around a pipe, transmit low frequency pulses in both directions. The signal obtained, amplitude versus distance along pipe, is similar to A scan and can detect over distances up to ~30 m in pipes, diameter >50 mm, wall thickness up to 40 mm. Courtesy of The Welding Institute (TWI).

of the magnetic field. There is no need for an external vibrating transducer and coupling. A stand-off from the surface of ~2 mm can be achieved and therefore thin layers of rust or oxide scales can be left as these do not present a barrier. For pipe inspection, a transducer transmits UT signals around the pipe circumference as a self-propelled scanner is carried along a pipe. Up to 500 m of pipe can be inspected in a day and the technique can detect corrosion damage and provide quantitative thickness data.

Time of flight diffraction (TOFD) was also developed by the nuclear industry and is now used in a number of industries. This system has proved useful for assessing in service the preferential corrosion and/or erosion loss at the roots and heat-affected zones of welds. Separate transmitter and receiving probes are placed at an equal distance from the center of the weld. Ultrasound is transmitted at the appropriate angle into the weld by the transmitter probe and at any corrosion (crack), some of the energy is diffracted at its edges and detected by the receiving probe. As the sound strikes the tip of a crack or flaw, this acts as a secondary emitter, which scatters sounds in all directions, some in the direction of the receiving probe. A lateral wave (traveling at the same velocity as the compression waves) is transmitted to the receiver. The time difference between the lateral wave and the diffracted signal from the flaw or crack provides a measure of its distance from the scanned surface. The probes can measure the arrival time of ultrasound diffracted from the upper and lower extremities of a flaw or crack. The technique is useful for monitoring flaw or crack growth provided the variables are closely considered. A variety of systems are available ranging from manual scanning through to fully automated systems. A scan speed of 50 mm s^{-1} is claimed for automated systems. The comprehensive coverage afforded by the wide beams used for TOFD inspections makes it much less dependent on probe position and defect orientation than conventional pulse echo techniques.[77]

4.36.2.5.3 Radiological techniques

Principles

Since the discovery of X-rays in 1895, there has been extensive use of ionizing radiation for the NDT/E of materials as well as human beings.[75] X-rays are a form of electromagnetic radiation and have wavelengths that allow them to penetrate all materials with partial absorption during transmission. They include a fairly wide waveband of radiation from ~10 nm, usually called soft X-rays, which will penetrate only solid materials of very small thickness, to ~10^{-4} nm, often called high-energy or hard X-rays, which will penetrate up to ~500 mm steel. Gamma rays emitted by radioactive substances such as cobalt-60 can exist over a similar wavelength range and are also widely used in industrial radiography. Neutron and protons have also been used for industrial radiography. Radiographs can be taken using portable X-ray machines or for thicker sections, it may be necessary to use radioactive source such as cobalt-60, iridium-192, or cesium-137. Radiography is very useful for confirming and quantifying the presence of corrosion detected by other inspection techniques. However, ionizing radiation can cause damage to living tissue, and therefore, appropriate personnel protection is essential and screening is required as dictated by the relevant legislation pertaining to radiation protection in different countries.

The recording of radiation is carried out using radiographic film or intensifying screens or fluorescent screens. Computer displays are common for displaying radiographic information. No waiting time is required and there is no requirement for photographic laboratory facilities.

Portable systems

Portable X-ray machines are quite small and can be taken around the plant fairly easily. The instrument consists of a filament (for the provision of electrons – a cathode), a target, the anode, a high voltage supply and a containment to enable the anode and cathode to be supported in a very high vacuum.[75] Developments include nonfilament tubes, where the filament is located in a recess in the cathode focusing cup, which helps to produce a narrow, well defined beam of electrons on the anode. The electron beam can be focused with electron lenses, to produce microfocus X-ray tubes. These developments have led to smaller, more robust X-ray tubes compared with the early glass-envelope design. The portable X-ray machines do not present a hazard above normal safeguards but the gamma sources such as cobalt-60 can be hazardous if precautions are not taken using suitable screening.

The development of profile/flash radiography has made it possible to detect CUI on a relatively small diameter piping without the need for insulation removal using small lightweight, battery-operated flash X-ray equipment and X-ray image intensifiers with a primary conversion screen having a very short decay time, and a camera optically coupled to the output screen.

4.36.2.5.4 Magnetic techniques

When a ferromagnetic component is magnetized, the magnetic lines of force (the magnetic flux) are mostly inside the material of the component. If, however, there is a surface-breaking flaw or crack or a subsurface flaw, the field is distorted, causing local magnetic flux leakage (MFL) fields. The flaw or crack causes a sudden local change in permeability.[75] The various methods of magnetization can be grouped as current flow, magnetic flow, or induced current flow where AC current from a magnetic yoke is made to flow in a specimen. This is the basis of the magnetic particle inspection (MPI) technique for detecting surface breaking defects that is described in a later section.

The induced currents produced by magnetic fields, which vary with time in conducting materials are called eddy currents. The eddy currents set up secondary magnetic fields, which oppose the original magnetic field in direction, so that the magnetic field inside the component undergoing test decreases in intensity with distance below the surface.

For inspection purposes, there are various ways to achieve magnetization such as residual magnetism, current flow techniques, or the use of a threading bar or cable. The choice of the technique is dependent on the shape and size of the specimen, the expected directions of critical flaws, and whether an overall or a local examination is to be performed.

Examples of interest to the corrosion engineer are MFL developed for ILI vehicles for the inspection of pipelines and a trolley used for inspecting the floors in above-ground storage tanks.

4.36.2.5.5 Electrical techniques

Application of eddy current techniques involves the interaction of a coil carrying an AC current with a test piece of metal. The current passed through the coil generates circulating eddy currents in the metal test piece near the surface, which will affect the exciting current in the coil due to mutual induction. Any variation in material thickness or localized defects such as pinholes will affect the strength of the eddy currents. Coils can be single or in a double configuration used as a bridge balancing circuit. The coil can be mounted in a suitable probe, which is moved over the test sample. The system was developed originally for the inspection of defects and pinholes in nonferrous heat exchanger tubes on the assembly line following manufacture. At a later stage in the development of the technique, coils were wound on a bobbin and mounted in a suitable holders for insertion into the bores of heat exchanger tubes, allowing them to be inspected in service when offline. Despite complications at the locations of baffle plates used for tube support, valuable data were obtained.

A system for CUI inspection uses pulsed eddy currents without the necessity for the removal of the insulation. A special coil is positioned on top of the pipe insulation. The coil incorporates a transmitter and receiver coil and a magnetic field is established in the steel wall. The receiver coil measures the time of arrival of the eddy currents at the back wall. At places with wall loss, the arrival time will be earlier than at places with no wall loss. From this time of arrival, the average wall thickness can be calculated. The system can measure wall thickness through up to 100 mm insulation, including chicken wire as well as steel and aluminum sheeting. The time of measurement is 2–5 s and up to 1000 measurements can be made daily. In addition to insulated piping, the method has been applied to vessels, elbows, tank walls, and tank roofs.

4.36.2.5.6 Dye penetrant (DPI) and magnetic particle (MPI) surface crack detection

Penetrant testing is a low-cost technique that is widely used to detect flaws and defects that penetrate the surface. The technique can be used on any nonabsorbing surface. Following surface cleaning, a liquid that wets the surface is applied and migrates into defects and cracks by capillary action. Any excess liquid is removed and then the liquid in the crack is drawn out by a suitable developing agent. The liquid incorporates either a red-dye or a fluorescent substance, in which case, observation is carried out using ultraviolet light. For field testing, the technique is applied on a manual basis. The technique is particularly effective for the detection of SCC, which shows very little visible evidence at the surface in contrast to other forms of corrosion attack that reveal themselves by surface corrosion products.

Magnetic particle testing (MPI) is a related technique for the detection of surface breaking cracks/defects in ferromagnetic materials. The specimen is magnetized, usually with portable electromagnets. Surface flaws distort magnetic fields, causing local MFL around the flaw. White matt paint is applied, following which finely divided magnetic particles are applied to the test area in air or a liquid suspension, which decorate the line of the flaw. Fluorescent particles aid visual discrimination in ultraviolet light. The technique is rapid, low cost and more tolerant of surface finish than the dye penetrant method. However, it is restricted to ferromagnetic materials.

Both the techniques are limited to surface temperatures that are less than ~60 °C.

4.36.2.5.7 Acoustic emission

AE has been used to detect and locate flaws in metal or FRP-pressurized systems in a wide range of applications in several industries. It was universally adopted when first introduced but controversy related to interpretation and cost resulted in user disillusion. However, confidence returned after a few years following overall improvements in both hardware sensitivity and data interpretation, although a recent view was that the technique remains closer to its infancy than to full maturity.

The technique involves raising the pressure beyond design/previous operating levels during proof or in-service inspection. This induces elastic deformations and defect micropropagation processes release stored elastic strain energy, partly in the form of propagating elastic waves (AEs). Surface-mounted piezoelectric probes detect emissions and emission amplitude is a guide to severity. Triangulation techniques position emissions within ~10 mm. Defects must propagate to provide a signal response. Existing defects that do not propagate will not give a response and will therefore remain undetected. The technique has gained wide acceptance for the testing of pressurized systems provided that they can be pressurized above their operating pressure and an adequate number of appropriate sensors can be applied externally. Typically, for a sphere of 16 m (53 ft) diameter, ~30–40 sensors are required. If insulation is present, only small holes in the insulation are required. An examination can be carried out in 1 day after installation and setup.

Hardware developments have been mainly associated with improvements in electronics enabling differentiation of acoustic noise from overall background noise. However, the major advances have related to signal classification, and emissions are usually graded as a function of the number of hits and their amplitude in categories that range from very minor, to be noted for future reference, to intense, requiring immediate shutdown and follow up NDT/E methods such as surface crack detection and ultrasonic testing to locate and dimension defects, as illustrated in Figure 22.

From the corrosion standpoint, the identification of cracks is of much interest and finger-prints of the cracks can be compared at prescribed intervals to see whether crack growth is occurring.[78] The use of AE to detect active corrosion (progressive loss of wall thickness) in above-ground storage tanks has been reported.[79]

AE testing is carried out onsite by specialist companies and is not routinely available from NDT/E contractors. The level of operator training is most critical to correct interpretation of data. A Euro-funded project to develop an AE system for assessing corrosion in marine oil tankers is now in progress.[80]

4.36.2.5.8 Thermography

Infrared cameras are very effective for remote temperature measurements, which are extensively used in plant for checking the efficiency of insulation, boiler component temperatures, and flare tips. In some plant applications, a direct relationship has been established between temperature excursions and corrosion. The technique has been used for assessing the thickness of oxide films on the fire-side of power station boiler tubes when offline. This is somewhat tedious with the requirement for scaffolding but the method gave interesting results and provided criteria to assess the progress of corrosion.

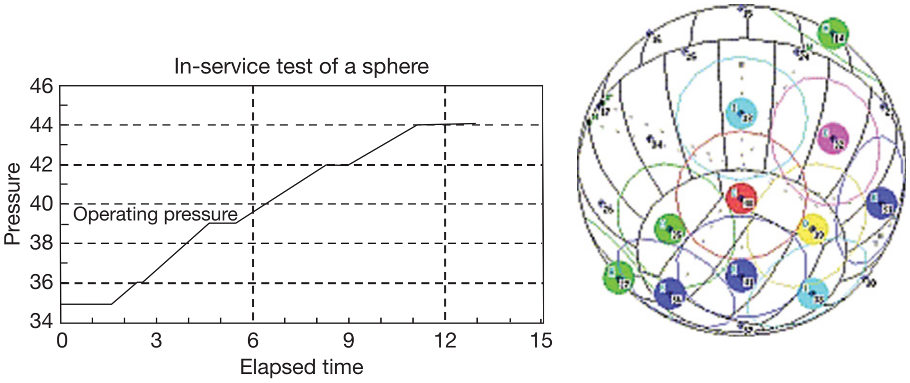
The examination of insulation to detect broken or missing insulation using infrared cameras has proved useful for the detection of CUI.

4.36.2.5.9 Fiber optics

Structural monitoring has attracted special interest in the technical press regarding the detection of failure modes in structures such as the cracking of materials. Sensors utilizing fiber optics have been tested and installed in a number of constructions, in particular bridges, for example, in Canada where bridges have had fiber optic sensors (FOS) fitted since 1998.

Sensors using FOS have been fitted to pipelines and can detect pipe movement by monitoring any change in the neutral plane of the pipe from its initial reference state and can also measure any bending strains that occur due to pipe movement. Monitoring these strains and associated stresses can provide warnings of potential pipe failures. FOS systems can measure structural displacements, strains, pressure, vibration, and temperature. Types of sensor include point sensors such as fiber Bragg gratings and Fabry–Perot sensors. Changes in wavelength that occur are proportional to the strain induced in the structure. Fabry–Perot sensors also respond to strain. Sensors referred to as distributed include Raman and Brillouin Scattering and measure a change in wavelength of scattered light.

FOS are now available for detecting the presence of wall thinning due to general corrosion or erosion



Category	AE source	Action
A	Very minor	Note for future reference
B	Minor	Inspect visually for surface defects
C		Follow up NDE
D	Significant	Immediate follow up NDE
E	Intense	Immediate shut down and follow up NDE

Figure 22 Acoustic emission assessment based on grading emissions as a function of the number of hits and their amplitude as applied to storage sphere.

and allow monitoring of a pipe section to ensure fitness for service. The sensors are noninvasive and can be mounted on pipes and pressure vessels. Sensors are designed to precisely measure temperature, pressure, and the localized swelling of pipeline walls that signal the presence of corrosion.

Corrosion monitoring using FOS has been carried out in a Middle East gas processing plant and oil refining operations for hard-to-reach areas or remote locations. A FOS system was installed on a 12-inch (305-mm) by 20-inch (508-mm) reducer, connecting a gas feed line into a large pressurized vessel. Because of the diameter change from top to bottom, the geometry presents a difficult shape to monitor and to analyze the data. UT monitoring was carried out simultaneously and a trend of wall thickness was demonstrated with both UT and FOS.[81]

4.36.2.6 ILI of Oil and Gas Pipelines

4.36.2.6.1 Background

In 1996, a European organization, Conservation of Clean Air and Water (CONCAWE) produced figures for oil pipeline spills in Europe for 1994, reporting that eleven incidents of spills totaling more than 15 000 bbl occurred, one of the costliest spill years on record. Cleanup operation recovered less than 2500 bbl of oil. Final costs for cleanup were reported as \$9.7 million, with two spills accounting for \$9.1 million. The actual cleanup costs for the same year would have been higher because costs for the second largest spill were not reported. Corrosion was the third highest cause of incidents with third-party damage being the largest cause.[82] In 2005, 6226 km or 18% of the total length of the European inventory was inspected by various types of inline inspection (ILI) vehicles. Inspections were split among the individual classes of vehicle, as follows:

1. Metal loss ILI – 5860 km in 105 sections
2. Crack detection ILI – 2132 km in 34 sections

CONCAWE has given the reason for improved performance and lower spills as increased use of ILI. The same situation prevails in the USA and many other countries. The benefits of ILI technology cannot be overestimated in its contribution to the safety of ageing pipeline systems.

In the USA, there has been much debate relating to a compulsory requirement for ILI and various Bills have been discussed by the US Congress without a final conclusion yet regarding the contentious aspect of inspection frequencies, in particular, whether the interval between ILI inspections should be 3 or 5 years or some other interval. Many US pipelines are now approaching 50 years of age and European landlines will soon approach these lifetimes with offshore pipelines somewhat younger at ~35 years. The consequence of high-pressure pipeline failure due to corrosion can be catastrophic and much effort has been devoted worldwide to the development of inspection devices for pipelines.

An early pipeline failure in the UK involved a 12-inch (305-mm) pipeline supplying the Shell Stanlow oil refinery when 150 tons of crude oil polluted a 32-km stretch of the Mersey estuary due to a pipeline fracture and killed an estimated 300 birds with a further 3000 at risk. In the first major prosecution by the National Rivers Authority (NRA), Shell pleaded guilty to spilling the oil. The court heard that a 6.5-inch (165-mm) crack in the pipe had been caused by the wrinkling of a protective sleeve. Tests found no weakness in the pipe although it had been planned to adapt it, at a cost of £100 000, to enable the use of a fault-detecting device known as an intelligent pig.[83]

A far more serious major pipeline event occurred in 2000 in the USA and involved a gas line carried under a bridge in Arizona. An underground pipeline, owned by the El Paso Energy Co. and installed in 1952, ruptured and discharged flammable gas, engulfing an adjacent campsite in flames and killing eleven tourists. The incident was investigated by the DOT and was shown to be due to be internal corrosion. The pipeline had been inspected in 1996. The company was fined $2.52 M by the DOT.

Many other incidents of pipeline failure have occurred in the USA such as the gasoline leakage at Bellingham, WA in the summer of 1999 when a pipeline failed due to damage from construction activity near the pipeline, which contributed to the rupture resulting in the deaths of three young people. The two companies involved, Olympic Pipeline Co. and Shell Pipeline Company LP, were likely to face fines each totaling $18.6 m. This incident prompted the US Senate to pass the Pipeline Safety Improvement Act of 2000, aimed at increasing penalties for safety violations, increasing state oversight of pipelines within their borders, and requiring pipeline companies to publicly disclose information about pipelines on the internet.

The corrosion of pipelines can occur on both internal and external surfaces if appropriate and adequate corrosion control measures are not carried out and monitored. Although some material upgrading from carbon steel has taken place, particularly offshore, the major proportion of pipelines are still constructed from carbon steel. In addition, pipelines can be subject to SCC and although this failure mode is more difficult to monitor, there are now ILI versions available for the detection of cracks.

External inspection using ultrasonic wall thickness will not give a comprehensive picture of the degradation (if any) at inaccessible locations of the pipelines as both onshore and subsea pipelines have an uneven elevation and debris and water can collect at discrete points within the pipelines and cause corrosion to be initiated. John *et al.*[84] point out that corrosion monitoring data will only provide an assessment at the actual location where the probes or coupons are located.

To overcome some of the above problems, an approach to modeling the metal loss within pipelines has been attempted by combining an assessment of the historic operating parameters over the life of the pipeline and calculating a cumulative metal loss since commissioning, while also allowing for the unknown variations in operating parameters by the incorporation of uncertainty analysis. Two case histories have been reported using this approach on a subsea line in the Middle East and a pipeline in the North Sea.[84]

4.36.2.6.2 Development of ILI vehicles

An ILI vehicle for the inspection of pipelines is referred to in the oil and gas industry as a pipeline inspections gauge (PIG), a device incorporating onboard instrumentation that is propelled under pressure from the product being transported through pipelines and which collects and records inspection data relating to both internal and external corrosion.

From the beginning of the oil industry, pipeline operators have utilized devices that are passed through the pipelines for cleaning the interior and removing paraffin waxes and sludge. Later, devices incorporating mechanical feelers that were used to detect mechanical damage such as dents or ovality were introduced. Vehicles containing various NDT/E sensing equipment using magnetic saturation arrived in the mid-sixties. However, pipeline operators became disillusioned with these devices due to the number of false positive signals. Excavation to verify suspect areas often revealed little corrosion, if any, and initial interest shown by pipeline operators and oil companies soon diminished. In addition, the classification of the corrosion information was very qualitative in nature. For one model, the corrosion indication was only classified into three categories designated as low, medium, and severe corrosion.

An up-rated ILI was developed on behalf of British Gas (BG) in the late eighties using MFL. Prior to the introduction of the improved device, BG tested their high-pressure lines hydraulically, which required the line to be taken out of service. This was the first time that an ILI was available that could be judged in performance terms on a quantitative measurement of corrosion. The early development gave a defined specification for sensitivity, as shown in Table 7.

The BG vehicle design provided a benchmark for the industry and high-resolution versions based on magnetic flux and ultrasonics were subsequently developed in Canada, Germany, and Japan. The development of these vehicles was a major advance in pipeline inspection made possible by improved computer power and developments in electronics. The detection of cracking has been a long-held objective of pipeline operators and versions are now available for this purpose using EMAT systems.

Intelligent vehicles are inserted and removed from pipelines through pig-traps. Essentially, the vehicle comprises two or more sections, one section contains the sensing equipment, the sensors and other sections contain the electronics and batteries. The rear section contains the odometer wheels to measure the speed and distance of the vehicle. The improved ILI vehicles could not be used at first, because they were too large for the existing pig traps. This was the case for offshore platforms initially, where space is always at a premium. However, later designs of platforms and pipelines took account of the additional size and appropriate pig-traps were installed.

Not all pipelines can be inspected by ILI vehicles for reasons that include economics (costs of inspection), varying pipeline diameters and geometry (angles, sharp bends), or other constraints inside lines. It is generally considered that the minimum size of line is 152 mm (6 inch) but special caliper devices may allow the inspection of lines down to 76 mm (3 inch) diameter.

Table 7 British gas ILI vehicle-magnetic flux leakage (MFL) – specification for corrosion detection (Data supplied by British Gas)

	Detection sensitivity	*Sizing accuracy*
General corrosion	0.2t	+ or – 0.1t
Pitting corrosion	0.4t	+ or – 0.1t

Where t = nominal pipe wall thickness (seam welded pipe) and pitting corrosion defined as corrosion affecting a surface area of pipe contained within a square of dimensions 3t x 3t.

Intelligent vehicles use several techniques for their operating mode. MFL continues to be the most common for inspection of pipelines.[85] Accuracy for these vehicles is estimated at ±10% at the 80% confidence factor. Ultrasonic vehicles were developed because MFL vehicles were not accurate enough to allow calculation of the remaining strength. The ultrasonic vehicles are better able to measure the wall thickness and the results can be used directly in calculations (e.g., RSTRENG) to determine the remaining strength. Note that ultrasonic methods require a liquid in the line for operation (unless they are in a liquid slug) for the transmission of the ultrasound. Each technique has advantages and disadvantages and the usual strategy adopted by pipeline operators is to alternate inspections between the different systems.

Vehicles using elastic waves have been produced for crack detection with liquid-filled wheels for the transmission of the waves into the line but it is reported that too many false positives are produced. Vehicles using EMAT systems have also been developed for SCC obviating the need for a transmission medium.

4.36.2.7 Management of Inspection Programs

Many organizations undertake visual inspection and metal thickness measurement in-house. Inspection functions are generally well managed and have clearly defined roles in the company structure. Communication is a vital component of success and is more difficult for oil and gas operations compared with land-based, permanent sites. Coordination and liaison are most important regarding process information, corrosion data, and inspection schedules as well as everyday factors relating to overall operations. A UK HSE investigation into the inspection functions in oil refineries suggested that inspectors should be embedded in units in order to improve liaison. The introduction of RBI (risk-based inspection) has improved overall cooperation; however, it still requires continuous monitoring on a quarterly basis to avoid problem areas. The updating of records as well as management of contractors should have high priority. The regular issuing of the minutes of meetings should also be given priority. Resistance to changes in previous practices can be avoided by fully describing reasons for the changes and providing evidence that there needs to be such changes.

Specialized contractors make a large contribution in the inspection sphere but they have to be supervised and managed effectively. In some cases, the total inspection function will be contracted out (as is the case for most offshore oil/gas production) with the contracting workforce embedded at the plant premises and producing daily and monthly reports for the plant management. An important factor is the training received by the contractor's technicians as well as reliable record keeping and overall technical ability. Continuous training is required and on-the-job training is not sufficient. Operatives and supervisors need to be qualified and supervised on an ongoing basis. The selection of contractors requires careful consideration, including, of course financial stability. The author has had good experience working with NDT/E over many years with contractors chosen by personal recommendation wherever possible.

The cost of inspection is similar to any other high-tech service for high capital cost equipment and relates to the complexity of the equipment used and the degree of training required for its operation and interpretation. Reference has already been made relating to the qualifications of personnel involved and how the ASNDT (US) and BINDT (UK) have been instrumental in raising the level of qualification and assessment of examinations. Costs have steadily increased due to the resulting improved qualifications of NDT/E personnel, which most of industry has welcomed.

The existence of international, national, and company standards coupled with legislation relating to maintenance and inspection of industrial infrastructure is of considerable assistance, but presents a challenge to those engaged in the inspection process. Accordingly, systems and procedures require regular appraisal and revision. There are many sources of standards and codes of practice. In addition to the main societies relating to NDT in both the USA and Europe, many countries have their own standards to which reference should be made first, followed by those produced by relevant engineering and scientific bodies. The standards of the European Economic Community are issued as ISO documents. The Russian Federation has a considerable expertise and reputation in this technology, and despite an emphasis on the academic interest, some of this experience has trickled down into the industrial sphere. Some of these standards are very specific to certain materials and environments. Some organizations of particular relevance are:

1. International Standards Organization (ISO).
2. American Petroleum Institute (API) has responsibility for the infrastructure used for the extraction of oil and gas, storage, transportation, and downstream infrastructure in refining crude oil. The use of pipelines for both subsea and onshore is also considered.
3. American Society of Mechanical Engineers (ASME) issues recommendations relating to inspection, especially relating to boilers.
4. ASTM is mainly, but not exclusively, oriented to laboratory R & D.
5. Institute of Petroleum (IP) based in London has a number of technical committees that issue both guidance and recommendations for general practice in the industry.
6. British Standards – reference should be made to BS: EN 10204:2004 Metallic Materials. Types of Inspection.

Nonmetallic materials such as plastic/polymer and FRP materials can be inspected using some of the methods described in this chapter. Standards exist for some of these materials.

Close liaison between the inspection and safety functions within organizations is essential. Most inspection equipment requires electrical power, and therefore, compliance with intrinsic safety legislation, and there is no reason why any instrumented system cannot be engineered to meet the requirements. The usual plant safety rules regarding access to heights and entry to confined spaces must be complied with. The use of ionizing radiation requires precautions, particularly relating to shielding.

It is particularly important that precautions are taken to check that dangerous gases have been purged from equipment and that vessels are tested for the presence of sufficient oxygen. Fatalities have resulted from entry into vessels where the oxygen level was insufficient to support life. For example, a cruise-ship crew member died recently from suffocation during an inspection of tanks for corrosion, prior to departure from Southampton in the UK and another crew member had to be rescued from the tank.[86]

4.36.2.8 Specific Industries

4.36.2.8.1 Oil and gas industry equipment

Inspection functions are usually influential in oil and gas companies because plants have to operate for long periods between scheduled shutdowns and there is a strong interest in onstream inspection. Communications are more difficult in production compared with refining due to the remoteness of production fields, both onshore and offshore. The introduction of RBI has focused the inspection process to a great extent than in earlier days when the approach was more random.

The most common inspection technique is observation utilizing the human eye and measuring equipment of various kinds such as calipers and gauges. These techniques are supplemented by cameras and TV and sometimes with borescopes and similar equipment, albeit such techniques are generally restricted to shutdown periods with corresponding drawbacks.

Downhole inspection presents particular problems due not only to the high temperatures and pressures but also to limited access. A widely adopted inspection system for downhole corrosion involves the Kinley mechanical caliper (involving a number of feelers), which, apart from resolution problems (inadequate coverage of the 360 degree tubing circumference), is still widely used in the industry. A major problem involves mechanical damage to the oil-tubing surface, which can damage any inhibitor films that are present. This is overcome to some degree by increasing the dosage rate of the inhibitor for a short period when production resumes. Downhole cameras and television are available for visual examination as well as various types of electrical instrumentation. Increasing use of CRAs downhole will reduce the requirement and/or frequency of such inspections, although acid treating of wells to remove scale and formation damage will still need verification that damage to the metal has not occurred.

Ultrasonics, usually undertaken by contractors, is commonly used for thickness measurement and for detecting cracks in pipelines and vessels. Welded probes and phased array probe system, which can provide a continuous signal are also used in critical situations and can mitigate the need for operators to visit remote and/or dangerous locations. Aboveground storage tank walls and roofs can be inspected online, using automatic crawlers held to the steel surfaces by magnetic attraction.[87] Infrared cameras are useful for surveying hot-spots in equipment and for locating insulation failures. There have been many examples where a correlation has been made between increased corrosion and an increase in temperature. AE by specialist contractors at intervals is used for the assessment of both the onset of cracking and crack growth.

4.36.2.8.2 Chemical and petrochemical plants

As in the oil and gas industry, plants are operated for long period between scheduled shutdowns, and hence, the approach to inspection is very similar. The shutdown period is utilized for much visual and hands-on inspection to verify that materials behavior complies with expectations from online inspection. Plants utilize extensive amounts of CRAs that increase the focus on localized corrosion failure modes such as cracking and pitting corrosion. The plants commonly use waste heat to raise steam and require extensive water cooling systems, which introduce additional inspection requirements.

4.36.2.8.3 Power plants

Unscheduled outages in these high capital cost facilities can be very costly as power has to be bought from other suppliers at high cost and some material upgrading, for example, the introduction of titanium condenser tubes, has occurred over the years to reduce corrosion risks.

Fossil fuel and gas-fired stations are subject to corrosion in boiler tubes (water and fire-side) and water circuits, which have to be inspected using most of the available NDT/E techniques. The inspection challenge is greater in nuclear stations. The first series of UK advanced gas cooled (AGR) nuclear reactors (Magnox) have a relatively poor record regarding corrosion. Excessive corrosion of some carbon steel fasteners in the gas cooling conduits was experienced, which required an operating temperature reduction and consequent loss of efficiency.[88] A later design (Dungeness AGR) also experienced corrosion problems with carbon steel linkages and where zinc-coated wires embrittled stainless steel tubes necessitating a downrating. More recently, some of the nuclear power stations (Hartlepool and Heysham 1) have had to be shutdown due to corrosion problems in wiring corrosion in steel and concrete boiler units attached to the reactors. It is believed that up to $10 M will be required to investigate corrosion in the 54 km of wire involved in the units.[89] The root cause is believed to lie in the original design and construction. In total, eight reactors are experiencing corrosion and cracking related to ageing and these problems have presented considerable inspection challenges. In addition to the conventional range of NDT/E techniques, special systems have been designed solely for the nuclear industry.

An interesting NDT/E device designed for the inspection of high-voltage transmission lines for corrosion (loss of zinc coating on the steel core) involves

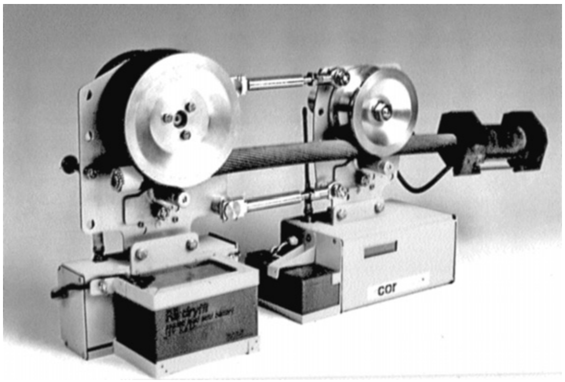


Figure 23 High voltage cable corrosion detector (Courtesy Cormon Ltd).

the use of eddy currents. The lines can be inspected when carrying current using a trolley-carriage that traverses the lines, as shown in Figure 23.

The device was developed in the UK and has been widely used in the UK, France, Ireland, and Sweden.

4.36.2.8.4 Defense

Many corrosion problems are experienced in defense infrastructure and systems. Individual countries have their own specifications and standards. Corrosion is particularly severe in naval operations and corrosion protection and inspection are well organized and implemented but problems still occur from time to time. Accordingly, most of the NDT/E techniques are implemented. Military aircraft are appreciably ageing compared with civil aircraft and present a severe challenge to the inspection function. One historical aspect relating to fuselage inspection relates to the use of primer (where fuselage panels are riveted together), which can mask the penetration of X-rays – now largely replaced with techniques using eddy currents.

Military missiles now have casings made from carbon fiber, Kevlar, or other materials wound in layers, which results in weight savings of up to 40% compared with metals. Their light weight also makes them less expensive to ship and easier to handle. However, the missiles are sometimes damaged when struck by rock and debris kicked up by helicopter rotors or when mishandled during shipping or maintenance. Unlike metals, which usually show external signs of damage (such as cracks or dents), the filament-wound composite materials may not reveal telltale signs. A new monitoring system developed in the USA (Purdue University) uses a mathematical model to pinpoint the location and severity of impacts based on vibration data collected by a triaxial accelerometer. The objective of the project is to have a permanently installed system to monitor the structural health of the missile. The information obtained enables the monitoring system to determine within seconds whether an impact is beyond the design threshold. The technique also would determine how durable the material is after long-term storage and exposure to humidity, UV radiation, and other environmental conditions. Materials under examination include sandwich metallic materials, woven composites, ceramics, and filament-wound materials. Components of particular interest are wheels and spindles.

4.36.2.8.5 Marine

The progressive use of higher strength steels for shipbuilding has resulted in significant weight savings by reducing thickness but has inevitably exacerbated corrosion risks. Accordingly, inspection has become more critical than in previous years.

Major ocean-going vessels require a fit-for-purpose certification at prescribed intervals in order to operate. This process involves much inspection mainly in the area of coating inspection. However, not only has the vessel integrity to be established, usually in dry dock, but also the onboard facilities such as boilers and fire, cooling, potable, and discharge water systems among others. Vessels change cargoes at short notice and tanks require complete cleaning between each change of cargo. Other marine infrastructure such as dock facilities, jetties, cranes, and oil-loading facilities also require inspection.

4.36.2.8.6 Road transportation

Transportation includes road vehicles (private and industrial), rail transport (wheel and track inspection being the main priority), and aircraft. Road vehicles can suffer from body corrosion, now mostly designed out. Trucks can suffer from various corrosion problems, especially road tankers used for potentially aggressive liquid cargoes that require periodic internal inspection. Regular inspection of pipes carrying hydraulic brake fluid is necessary as corrosion degradation is not unknown and incidents have caused loss of life.

4.36.2.9 Future Developments

The resolutions and response times of some inspection and corrosion monitoring techniques are shown in Table 8. These define the state-of-art and the current challenge for the future development of inspection technologies.

Table 8 Resolution and response time for some corrosion monitoring and inspection techniques

Technique	*Resolution*	*Response time at 1 mpy (1/40 mm year^{-1}) corrosion rate*	*Response time at 40 mpy (1 mm year^{-1}) corrosion rate*
Electrochemical	1 μA	minutes	minutes
FSM™ 25 mm wall thickness	0.025 mm	1 year	days
Electrical resistance	0.00025 mm	4 days	minutes
Ultrasonic thickness transducer (fixed)	0.1 mm	4 years	40 days
Weight loss coupon	1 mg	months	days

Source: Joosten, M. W.; Fischer, K. P.; Strommen, R.; Lunden, K. C. *Mater. Perf.* **1995**, *34*(4), 44–48.

General improvements in data capture and handling combined with developments in electronics, in particular relating to miniaturization, should bring exciting developments and improvements in inspection technology. This will apply to most of the existing techniques for inspection such as ultrasonics, eddy current, and AE. The detection and monitoring of cracks is of much interest and will receive particular attention in the future. Some specific likely developments are as follows:

1. Miniaturization is of much interest regarding the internal inspection of process piping with hopefully the sensitivity approaching that of intelligent vehicles presently used for buried and offshore pipelines. There are still problems to be solved, with the sharp bends and the many obstructions present in a process plant piping, but this is the most interesting area of activity.
2. Development of the EMAT systems and better performing portable ultrasonic array systems will receive attention.
3. Interest has been expressed in fiber optic strain sensors used for civil engineering structures that could be adapted for use in process plant for corrosion detection and measurement.[90] As corrosion or other chemical reactions occur, the transverse strain is relieved and the peak-to-peak spectral separation changes allow a measurement of corrosion. Different metals and stretchable plastics can be used as a component to support the measurement of a variety of corrosion events.
4. A research program organized by the Southern Illinois University Carbondale Material Technology Center is in progress to develop an internet-based wireless sensor network that will provide real-time data and analysis on the structural soundness of transportation infrastructure, such as bridges.[91] The three-year project, initiated in October 2007, is funded by a $1 M grant from the US Federal Highway Administration (FHWA) Intelligent Transportation System's program. The concept involves placing several types of sensors on a structure to detect variable such a stresses, elongation, deformation, vibration, cracking, and corrosion. Sensor technology includes existing sensors such as strain gauges, accelerometers, and pH sensors as well as new sensor technology developed in conjunction with the project.
5. It is possible that other data sets may be added to ILI vehicles in the future, which should assist the operator's ability to proactively detect possible corrosion threats to pipeline integrity other than metal loss.[92]
6. In 2007, a new Research Center in Nondestructive Testing was established in the UK with initial funding of $3 M over 5 years. Participating universities are Imperial College, Strathclyde, Bristol, Bath, Nottingham, and Warwick. It functions as an industrial club and carries out research projects of interest to club members.

Appendix 1 Standards and Codes of Practice

British Standards/ISO

PD 8010 2:2004 Code of practice for pipelines. Subsea pipelines.

PD 8010 1:2004 Code of practice for pipelines. Steel pipelines on land.

BS EN 1473:2007 Installation and equipment for liquefied natural gas. Design of onshore installations.

BS EN ISO 19903:2006 Petroleum and natural gas industries. Fixed concrete offshore installations.

DD ISO/TS 24817:2006 Petroleum, petrochemical and natural gas industries. Composite repairs for pipework. Qualifications and design, installation, testing, and inspection.

BS ISO 12732:2006 Corrosion of metals and alloys. Electrochemical potentiokinetic reactivation measurement using the double loop technique (based on Cihal's technique)

BS EN ISO 9934–2:2002 Non-destructive testing. Magnetic particle. Detection media.

NACE International Standards, Recommended Practices and Test Methods

RP0102–2002 In-line Inspection of Pipelines

RP0189–2002 Online Monitoring of Cooling waters

RP0192–98 Monitoring Corrosion in Oil and Gas Production with Iron Counts

RP0197–2004 Standard Format for Computerized Electrochemical Polarization Curve Data Files

RP0198–2004 The Control of Corrosion Under Thermal Insulation and Fireproofing Materials – A System Approach

RP0205 Recommended Practice for the Design, Fabrication and Inspection of Tanks for the Storage of Petroleum Refining Alkylation Unit Spent Sulfuric Acid at Ambient Temperature

RP0296–2004 Guidelines for Detection, Repair and Mitigation of Cracking of Existing

Petroleum Refinery Pressure Vessels in Wet H_2S Environments

RP0497–2004 Field Corrosion Evaluation Using Metallic Test Specimens

RP0502–2002 Pipeline External Corrosion Direct Assessment Technique

RP0775–2005 Preparation, Installation, Analysis, and Interpretation of Corrosion Coupons In Oilfield Operations

SP0106–2006 Control of Internal Corrosion in Steel Pipelines and Piping Systems

SP0206–2006 Internal Corrosion Direct Assessment Technique for Pipelines Carrying Normally Dry Natural Gas

SP0294–2006 Design, Fabrication and Inspection of Tanks for the Storage of Concentrated Sulfuric Acid and Oleum at Ambient Temperatures

SP0590–2007 Prevention, Detection, and Correction of Deaerator Cracking

SSPC-VIS2 Standard Technique of Evaluating Degree of Rusting on Painted Steel Surfaces

TM0106–2006 Detecting, Testing, and Evaluation of Microbiological Influenced Corrosion

(MIC) of External Surfaces of Buried Pipelines

TM0169–2000 Laboratory Corrosion Testing of Metals

TM0193–2000 Laboratory Corrosion Testing of Metals in Static Chemical Cleaning Solutions at Temperatures below 93 °C

TM0194–2004 Field Monitoring of Bacterial Growth in Oilfield Systems

TM0286–2001 Cooling Water Test Unit Incorporating Heat Transfer Surfaces

TM0299–99 Corrosion Control and Monitoring in Seawater Injection Surfaces

TM0398–98 Laboratory Corrosion Testing of Metals in Static Chemical Cleaning Solutions at Temperatures Above 100 °C

TM0498–2006 Evaluation of the Carburization of Alloy Tubes Used for Ethylene Manufacture

TM0499–99 Immersion Corrosion Testing of Ceramic Materials

European Federation of Corrosion – EFC (Incorporating ISO) Standards

EN ISO 6509 1995 Corrosion of metals and alloys – Determination of dezincification resistance of brass (ISO 6509:1981)

EN ISO 7441:1995 Corrosion of metals and alloys – determination of metallic corrosion in outdoor exposure corrosion tests (ISO 7441:1984)

EN ISO 7539 Corrosion of metals and alloys – Stress corrosion testing, Parts 1–7 1995: 1989

EN ISO 8565:1995 Metals and Alloys – Atmospheric corrosion testing-general requirements for field tests (ISO 8565:1992)

EN ISO 9400:1995 Nickel-based alloys–Determination of resistance to intergranular corrosion (ISO 9400: 1990)

EN 10229:1998 Evaluation of resistance of steel products to hydrogen cracking (HIC)

EN ISO 11306:1998 Corrosion of metals and alloys – Guidelines for exposing and evaluating metals and alloys in surface sea water (ISO 11306:1998)

Provisional Europeans Standards (As at June 1994)

pr EN ISO 8044 Corrosion of metals and alloys – Basic terms and definitions

pr EN 12500 Protection of metallic materials against corrosion – Corrosion likelihood in atmosphere environment – Classification, determination and estimation of corrosivity of atmospheric environments

American Society for Testing Materials (ASTM)

ASTM G4–01 (2008) Standard Guide For Conducting Corrosion Tests in Field Applications

ASTM G96–90 (2008) Standard Guide for Online Monitoring of Corrosion in Plant Equipment (Electrical and Electrochemical Methods)

ASTM G102–89 (2004) Standard Practice for Calculation of Corrosion Rates and Related Information from Electrochemical Measurements

ASTM G1–03 Standard Practice for Preparing, Cleaning and Evaluating Corrosion Test Specimens

American Petroleum Industry (API)

API MPMS 10.3 Sediment for Water – Standard Test Technique for Water and Sediment in Crude Oil by the Centrifuge Technique (Laboratory Procedure)

API RP 2201 Safe Hot Tapping

API 653 Inspection and Storage Tanks Standard

API 598 Valve Inspection and Testing

API 570 Piping Inspection Code

API 661 Air Cooled Heat Exchanger for General Refinery Service – Inspection

API 1163 Guidance Provided by Inline Inspection Standards

References

1. Hines, J. *Industrial Corrosion Monitoring*; Committee on Corrosion, Department of Industry H.M.S.O.: London, 1968.
2. Rothwell, N.; Tullmin, M. *The Corrosion Monitoring Handbook;* Coxmoor Publishing Co.: Kingham, Oxford, UK, 2000.
3. Glossary, National Corrosion Service, National Physical Laboratory (NPL), Teddington, London, UK.
4. Cox, W. M.; Boyce, M. P.; Miyazawa, M.; Tanaka, Y. *Corrosion Management* **2000**, May–June, 6–10.
5. *Review of Corrosion Management for Offshore Oil and Gas Processing*; UK Health and Safety Executive, Chapter 4, Planning and Implementation, 4.8 Implementation in Offshore Technology Report 2001/044, 2001.
6. Britton, C. F.; Tofield, B. C. *Mater. Perf.* **1988**, *27*(4), 41–44.
7. UK HSE Report. *Public Report of the Fire and Explosion at the ConocoPhillips Refinery on 16 April 2001,* Health and Safety Executive: UK, 2005.
8. Powell, D. E.; Ma'Ruf, D. I.; Rahman, I. Y. *Mater. Perf.* **2001**, *40*(8), 50–54.
9. Roberge, P. R.; Tullmin, M. A. A.; Grenier, L.; Ringas, C. *Mater. Perf.* **1996**, *35*(12), 50–54.
10. Britton, C. F. Private Communication.
11. *Standard Guide for Examination and Evaluation of Pitting Corrosion*; ASTM G46–94, ASTM International, 2005.
12. *Standard Guide for Conducting Corrosion Tests in Field Applications*; ASTM G4–01, ASTM International, 2005.
13. *Field Corrosion Evaluation Using Metallic Test Specimens*; RPO497–2004; NACE International: Houston, TX, USA, 2008.
14. Hudson, J. C. J. *Inst. Met.* **1928**, *40*, 294.
15. Dravnieks, A.; Cataldi, H. A. *Corrosion*; **1954**, *10*, 224.
16. Edeleanu, C. *Anticorros. Methods Mater.* **1955**, *2*, 204–208.
17. Publication EFC4. *Guidelines for Electrochemical Corrosion Measurements,* European Federation of Corrosion, 1990.
18. *Standard Test Method for Conducting Cyclic Potentiodynamic Polarization Measurements for Localized Corrosion Susceptibility of Iron-, Nickel-, or Cobalt-Based Alloys*; ASTM-G61–86, ASTM International, 2003.
19. Stern, M. *Corrosion* **1958**, *14*, 440t–444t.
20. Stern, M.; Geary, A. J. *Electrochem. Soc.* **1957**, *104*, 56–63.
21. Moreland, P. J.; Rowland, J. C. *Br. Corros. J.* **1977**, *12*, 72–79.
22. Richardson, J. A. *Innovations in Techniques for Corrosion Monitoring*; Proceedings of the Conference on Advances in Materials Technology for Process Industries Needs, Atlanta, National Association of Corrosion Engineers, 1984.
23. Mansfield, F. *Corrosion* **1988**, *72*(12), 856–868.
24. Dawson, J. L.; Callow, L. M.; Hladky, K.; Richardson, J. A. In *Corrosion Rate Determination by Electrochemical Impedance Measurement*; Proceedings of the Conference on On-Line Surveillance and Monitoring of Process Plant, London, Society of Chemical Industry, 1977.
25. Iverson, W. P. J. *Electrochem. Soc.* **1968**, *115*, 617–618.
26. Hladky, K.; John, D. G. In *Using Electrochemical Noise*; Proceedings of the 2nd International Conference on Corrosion Monitoring and Inspection in the Oil and Petrochemical and Process Industries, London, Oyez Scientific and Technical Services Ltd., London, 1984.
27. Kane, R. D.; Eden, D. C.; Amidi, S.; Delve, D. *Implementation of Real-Time Corrosion Monitoring With Industrial Process Control and Automation;* Paper 07268, Corrosion 2007; NACE International: Houston, TX, 2007.
28. Rothwell, N.; Tullmin, M. *The Corrosion Monitoring Handbook;* Coxmoor Publishing Co, Kingham, Oxford, UK, 2000; Chapter 3, pp 69–70.
29. Strommen, R. D.; Horn, H.; Wold, K. R. *Mater. Perf.* **1994**, *32*(3), 50–54.
30. Britton, C. F. Private communication.
31. Riley, J. from information provided by Kettle, A., FSM Presentation relating to Texaco Refinery, Pembroke, UK, available at http://committees.api.org/standards/cre/sci/minutes/docs/spring04/fsm.pdf.
32. Britton, C. F. Private Communication.
33. Asher, J.; Conlon, T. W.; Tofield, B. C.; Wilkins, N. J. M. *On-line Surveillance and Monitoring;* Ellis Horwood: London, 1983.
34. Britton, C.F. Private communication.
35. *RP0192–98 Standard Recommended Practice-Monitoring Corrosion in Oil and Gas Production with Iron Counts*; NACE International: Houston, TX, 1998.
36. Addington, F. Paper 08548, *Corrosion 2008*; NACE International: Houston, TX, 2008.
37. *TM0194–2004 Field Monitoring of Bacterial Growth in Oil and Gas Systems*; NACE International: Houston, TX, 2004.
38. TM0106–2006. *Detecting, Testing, and Evaluation of Microbiological Influenced Corrosion (MIC) of External Surfaces of Buried Pipelines;* NACE International: Houston, TX, 2006.
39. EFC Publication 29. *Microbial Corrosion*; Sequeira, C. A. C., Ed.; European Federation of Corrosion, 2000.
40. *Methods of Studying Biofilms,* Paper 20 in Microbial Biofilms, Ghannoun, M. A., Ed.; ASM Press, 2004; p 392.
41. Cavassi, P.; Cornago, M. *PCE* **1998**, 24–30.
42. Gretchen, J. A. *Mater. Perf.* **2007**, *46*(8), 27–34.
43. Ahluwalia, H.; Sharp, S. *Mater. Perf.* **2008**, *47*(8), 83–85.
44. US National Transportation and Safety Board, (NTSB). *Natural Gas Pipeline Rupture and Fire Near Carlsbad, New Mexico* 19th August, 2000, available at www.ntsb.gov/publictn/2003/PARA0301.pdf.

45. *Erika Oil Spill Trial: Landmark Ruling for the Environment*, available at www.humaniteinenglish.com/spip.php?article 810.
46. *Mater. Perf.* **2007**, *46*(3), 6, 10.
47. Britton, C. F. Private Communication.
48. Biedermann, A.; Williams, G. W.; Kane, R. D.; Eden, C.; Eden, D. A.; Trillo, E. A. *Oil Gas J.* **2005**, *103*, 56–62.
49. Dean, S. W. *Stainless Steel World* **2002**, *13*, 62–66.
50. Cox, W. M.; Boyce, M. P.; Miyazawa, M.; Tanaka, Y. *Corrosion Management* **2000**, May–June, 6–10.
51. Farrell, D. M.; Robbins, B. J.; Sikka, P.; Seaman, M. *Corros. Manage.* **2004**, May–June, 16–21.
52. Pawel, S. J. Oak Ridge National Laboratory, August 2004, Report ORNL/TM-2004.
53. Anderson, A.; Hilbert, R. L. *Proceedings of the 13th Scandinavian Corrosion Congress*; University of Iceland: Reykjavik, 2004; p 10.
54. Britton, C. F. Private communication.
55. Brown, A. S. *Mater. Perf.* **1992**, *30*(9), 55–58.
56. US Patent 134292. Batelle Memorial Institute, 1993.
57. Aircraft Sensor for Corrosion. US Navy *Mater. Perf.* **1999**, *38*(4), 16.
58. Edgemon, G. L.; Nelson, J. L.; Bell, G. E. C. Paper No 175, Corrosion 98; Nace International: Houston, TX, 1998.
59. Neri Segura, F. J.; Almeraya Calderon, F.; Borunda, T. A.; Gaona Tiburcio, C.; Martinez Villafana, A. *Mater. Perf.* **2007**, *46*(1), 60–62.
60. Britton, C. F. Private Communication.
61. Sykes, J. *Corros. Sci.* **1985**, *28*, 1051.
62. Elsenor, B. *Corros. Sci.* **2005**, *47*, 3019.
63. Britton, C. F. Private Communication.
64. Bosch, R. W.; Hubrecht, J.; Bogaerts, W. F.; Syrett, B. C. *Corrosion* **2001**, *105*, 60–70.
65. NACE Technical Co-Ordination Committee. *Gap Analysis Sector Report on Petroleum Refining; Mater. Perf.* **2008**, *47*(8), 83–85.
66. London Times. 28th November, 2002.
67. National Transportation and Safety Board, (NTSB), Accident No. DCA-03-MM-032, NTSB/MAB-07/03, 25th May, 2003.
68. BBC Radio 4, *You and Yours,* 27th December, 2007.
69. *Aloha Flight* 243 (available on www.absoluteastromony.com/topics/Aloha_Airlines_Flight_243).
70. Wearne, P. *Collapse: Why Buildings Fall Down,* Channel 4 Books, **1999**, 43–53.
71. Larson, K. R. *Mater. Perf.* **2008**, *47*(4), 30–33.
72. UK Highways Agency, Press Release, (SW/725/06) The Government News Network, 20th October, 2006.
73. London Times. 17th January, pp 52, 2008.
74. Papavinassam, S.; Doiron, A.; Revie, R. W. *Mater. Perf.* **2008**, *47*(2), 58–62.
75. Halmshaw, R. *Non-destructive Testing*; Edward Arnold: London, 1987.
76. *Long Range Ultrasonic Inspection Technology*; The Welding Institute: UK (available at www.twi.co.uk).
77. *Time of Flight Diffraction (TOFD) Inspection Technology*; The Welding Institute: UK (available at www.twi.co.uk).
78. Ennaceur, C.; Laksinni, A.; Herve, C.; Cherfaoui, M. *Int. J. Pressure Vessels Piping* **2006**, *83*(3), 197–204.
79. Lackner, G.; Tscheliesnig, P. *Corros. Manage.* **2007**, May–June, 8–12.
80. Veazey, M. V. *Mater. Perf.* **2004**, *43*(2), 16–19.
81. Al-Taie, I.; Al-Musalami, F.; Al-Daajani, B. F.; Al-Bakhat, A.; Morison, D.; Cherpillod, T. *Oil Gas J.* **2007**, *105*, 50–55.
82. *Oil and Gas J.* **1996**, *4*, 69.
83. Daily Telegraph, (London) 23/02/90 and 24/02/90.
84. John, D. G.; Oliver, K. E. Paper 07124, Corrosion 2007; NACE International: Houston, TX, 2007.
85. Teitsma, A. Technology Assessment for Delivery Reliability for Natural Gas Inspection Technologies: RFEC, Contract DE-FC26–04NT42266, Pipeline Inspection Technology, Gas Technology Institute, Des Plaines, IL, USA.
86. Report on the investigation of the fatality on board passenger cruise ship SAGA ROSE in Southampton, England, on 11 June, 2009, Marine Accident Investigation Branch, Southampton, UK, Report No1/2009, January 2009.
87. Rose, R. *UT Crawlers for Above Ground Inspection*; Posting on NDT Forum, 10th July 2001, available at www.ndt.net/forum.
88. Trethewey, J. Magnox reactors/AGR. In *Corrosion for Science and Engineering*, 2nd ed.; Longmans: Harlow, Essex, England, 1995; Chapter 17, pp 414–415.
89. London Times, UK Business. pp 53, 14th November, 2007.
90. US Patent, 250/227. 14–18, 385/37, Issued November 7, 2000.
91. *Mater. Perf.* **2008**, *47*(3), 9–10.
92. Schroder, S. *Oil Gas J.* **2008**, Supp. *106*(7), 10.

4.38 Management of Corrosion of Aircraft

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Abbreviations

AGARD	Advisory Group for Aerospace Research and Development
CAA	Chromic acid anodizing
CCC	Chromate conversion coating
CFRP	Carbon fiber reinforced plastic
HE	Hydrogen embrittlement
HVOF	High-velocity oxy-fuel
L	Longitudinal direction
LT	Long transverse direction
NDE	Nondestructive evaluation
PMS	Plastic media stripping
PVD	Physical vapor deposition
RH	Relative humidity
SCC	Stress corrosion cracking
ST	Short transverse direction
UTS	Ultimate tensile strength
VOC	Volatile organic compounds

Symbols

K_{1SCC}	Stress intensity for stress corrosion cracking (MPa.m$^{0.5}$)

4.38.1 Airframe Corrosion

4.38.1.1 Introduction

This chapter is concerned with the management of corrosion on fixed wing aircraft and helicopters. It concentrates on the corrosion and protection of aircraft structures and does not consider the complex corrosion problems associated with the protection of materials used in aircraft engines. Although the references and discussion are mainly concerned with aircraft, the approaches described are also applicable to other aerospace structures such as guided weapon systems and airships.

The principal materials used in the construction of the modern aircraft are aluminum alloys, titanium alloys, high-strength steels, corrosion resisting steels, magnesium alloys, and composite materials.

Weight has always been the main consideration in airframe construction. The structure must be light, but strong enough and rigid enough to withstand the applied loads and stresses. The specific strength and resistance to buckling are important factors in the selection of airframe materials. For these reasons, extensive use of aluminum alloys has traditionally been made in the aerospace industry. With the development of composite materials, such as carbon fiber reinforced plastics, the volume of aluminum alloys employed on the modern civil transport aircraft and military fast jet has been significantly reduced. As will be discussed later in this chapter, this will have an impact on aircraft corrosion and protection.

High-strength steels are used in a number of applications. In areas where size is critical, steels have advantages over aluminum alloys. Landing gear components, for example, have to be stowed away into relatively small volumes. To achieve the necessary load carrying capacity, parts are frequently manufactured from steels having tensile strengths in excess of 1800 MPa. Many fasteners used on aircraft are also manufactured from steel.

Strength is not always the overriding criteria. Some applications require a high level of stiffness and this can be obtained through the use of thick section. Gearbox housings are one example in which it is more advantageous to use a magnesium alloy casting. The same part manufactured in an aluminum alloy would be 1.5 times heavier. Titanium alloys are also finding increasing applications in airframe components and are replacing steels in some areas. Titanium alloy fasteners are also extensively used on modern aircraft.

Corrosion can have a major impact on the structural integrity and hence safety of all types of aircraft. To implement a successful corrosion management program, an understanding of the operating environment and the potential corrosion risks associated with the various materials used in the airframe structure is essential.

Neglecting to manage corrosion may lead to the eventual grounding of an aircraft because it is structurally unsound and unsafe to fly. A planned approach to the management of corrosion on aircraft is therefore necessary to ensure safety and reliability and begins at the design stage of the aircraft.

4.38.1.2 The Operational Environment

Aircrafts are frequently operated in highly corrosive environments. For example, many military aircrafts fly from coastal bases and carryout low level missions over the sea. Aluminum alloys, high-strength steels, and magnesium alloys are highly susceptible to various forms of corrosion in the presence of chloride ions if they are not adequately protected.

The AGARD Aircraft Corrosion Handbook[1] has summarized the relative rates of corrosion for different types of atmosphere. It lists tropical, industrial, and marine environments as highly conducive to corrosion, while rural and arctic locations are considered to give a low rate of corrosion. Moderate corrosion occurs when flying is in temperate or suburban regions. Some desert areas have high levels of salt and are potentially highly corrosive.

In addition to contaminants from the environment, there are a number of compounds and liquids that are used on the aircraft, such as hydraulic fluids, fuels, and oils, which can degrade protective treatments and may lead to the onset of corrosion. In addition, spillages from galleys, toilets, and batteries and breakages in freight-holds have all been identified as initiating corrosion. These areas need particular consideration in terms of design and protection to minimize the risk of corrosion in-service. Condensates from passengers and livestock will also promote corrosion. Mitchell[2] has described a UK airline's experiences with many of these contaminants. Reference is made to the soundproofing adjacent to the fuselage, which was found to absorb up to 400 kg of moisture, presenting a major corrosion threat.

During maintenance, a range of chemicals is used for washing, cleaning, and removing paint from the exterior and interior surfaces of the aircraft. These materials if not used correctly and in the right concentrations may lead to corrosion, particularly if allowed to enter the internal structure of the aircraft. Specifications covering cleaners, etc., for use on aircraft include corrosion tests designed to ensure that potentially corrosive materials are excluded. Similarly deicing materials used on aircraft and for clearing runways must satisfy these corrosion tests.

Early studies conducted by Kohler and Scott[3] demonstrated that significant levels of chloride ions and other corrodents can accumulate in the internal structure of military aircraft operated in a maritime role. The levels were sufficient to initiate pitting corrosion and other forms of localized attack on aerospace aluminum alloys. Future aircraft corrosion control plans will need to take into account the likelihood of corrosion developing in internal parts of the structure, which cannot be inspected by conventional methods.

Although corrosion will occur primarily when an aircraft is sitting on the ground, flying at 30 000 ft will contribute to degradation of the protective treatments used on the external surfaces. At these altitudes, the external temperatures fall to $-60\,^\circ\mathrm{C}$ reducing the paint flexibility. This can lead to paint cracking around fasteners, permitting the ingress of moisture. Further, the ozone and ultraviolet levels are high, causing degradation of the exterior paint schemes. The temperature cycling experienced by the aircraft, especially when operating in hot humid environments, will lead to a continuous buildup of moisture in internal regions.

The protective treatments applied must be capable of preventing corrosion on aircraft structures when exposed to the various operating environments and contaminants listed earlier.

4.38.1.3 Summary of Main Corrosion Types

The airframe materials employed exhibit a number of different types of corrosion. A key part of the management of aircraft corrosion is the knowledge of the conditions under which a specific form may develop, and the steps that should be taken to prevent or control it. Table 1 summarizes the various forms of corrosion that have been found. They may be divided into three groups as follows:

- corrosion occurring in the absence of an applied stress,
- corrosion occurring in the presence on an applied stress,
- corrosion resulting from poor design and protection.

Detailed information about the mechanisms of the different types of corrosion identified may be found elsewhere in this book. Sections 4.38.1.3.1, 4.38.1.3.2, and 4.38.1.3.3 summarize the main aspects of each form of corrosion as they relate to airframe materials.

4.38.1.3.1 Corrosion occurring in the absence of an applied stress

General corrosion is included in Table 1 for completion, but in practice relatively few examples of general corrosion are found on airframe materials. More usually the type of attack that develops can be described as localized corrosion. This may take the form of pitting, intergranular, or exfoliation corrosion. In the case of aluminum alloys, the surface is protected by a thin adherent oxide film. One hypothesis is that flaws preexist in the oxide film and provide sites for the initiation of corrosion attack. The flaws may be associated with precipitates, impurities, or grain boundaries in the matrix. The dissolution of aluminum is localized and leads to the formation of corrosion pits particularly if chloride ions are present.

Pitting is often a precursor to further localized attack. In intergranular corrosion, the grain boundary areas behave anodically with respect to the bulk of the grains. The corrosion follows paths along the grain boundaries of the material and can proceed at a high

Table 1 Summary of corrosion types found on aerospace materials

Type		*Description*	*Susceptible materials*
Absence of applied stress	General	Corrosion uniformly distributed over exposed surface	
	Pitting	Localized attack, which leads in the formation of deep and narrow cavities	Aluminum alloys Magnesium alloys
	Intergranular	Corrosion attack propagating along the grain boundaries of the material	Aluminum alloys
	Exfoliation	A form of intergranular corrosion occurring in materials with elongated grain structures. Leads to blistering and surface lifting and flaking	Aluminum alloys
	Microbial corrosion	Corrosion developed as a result of microbiological growth	Aluminum alloys in contact with fuel
Presence of applied stress	Stress corrosion cracking	Cracking process involving the conjoint action of a stress and a corrodent	Aluminum alloys High-strength steels Titanium alloys
	Corrosion fatigue	Accelerated fatigue growth on exposure to a corrosive environment	Aluminum alloys
	Hydrogen embrittlement	Cracking of statically loaded components resulting from the absorption of hydrogen	High-strength steels
	Fretting corrosion	Form of wear resulting from movement or vibration between two surfaces	Titanium alloys
	Solid/liquid metal embrittlement	Cracking of statically loaded components resulting from direct contact with liquid or solid metals	Aluminum alloys High-strength steels Titanium alloys
Corrosion arising from poor design and protection	Crevice corrosion	Corrosion resulting from the ingress of moisture into crevices or gaps between components	Aluminum alloys Corrosion resisting steels
	Galvanic corrosion	Corrosion resulting from the contact between two metals of different electrochemical potential immersed in an electrolyte	Direct contacts between aluminum alloys, steels, magnesium alloys in contact with titanium and CFRP materials
	Filiform corrosion	Thread-like corrosion developing under organic coatings	Painted aluminum

rate because of the large difference in cathode to anode area. If the grains are elongated in shape as in the case of plate and extruded materials, the corrosion may run parallel to the surface causing flaking and blistering. This type of attack is known as exfoliation corrosion and many examples of it have been found in-service. Often, the first indication that there is a problem arises when it is noticed that the paint film adjacent to fastener holes is lifting. At this stage, the attack may be well established and extensive repair work may be required.

In addition to aluminum alloys, magnesium alloys and steels may exhibit pitting corrosion when exposed in an aircraft environment.

Microbial corrosion is a type of attack initiated by the presence of organisms such as fungi and sulfur-reducing bacteria. Examples of this form of corrosion have been found in fuel tanks. Bowden[4] describes the action of *Cladosporium resinae*, a fungus which may live in water droplets present in fuel tanks. The acidic by-products produced by the fungus may breakdown the protective treatments applied to the interior of fuel tanks and lead to the attack of the aluminum alloy substrate. Sludge developed as a result of the microbial action may lead to blockage of fuel pipes and pumps.

4.38.1.3.2 Corrosion occurring in the presence of an applied stress

Stress corrosion cracking (SCC) and corrosion fatigue result from the synergistic action of an applied stress and a corrosive environment. In the case of SCC, a static tensile stress is present, while in corrosion fatigue the stress is fluctuating in some manner. Stress corrosion failures have occurred in-service mainly with the high-strength aluminum–zinc–magnesium alloys such as 7075 and examples of failures have been seen on landing gear components. The stresses responsible for cracking are generally either residual stresses introduced as a result of the material manufacturing process or stresses arising from poor alignment during assembly. Once initiated, the stress corrosion crack can propagate rapidly and catastrophic failure may eventually occur.

The mechanism or mechanisms of SCC in aluminum alloys continue to be the subject of much research and discussion and are covered in some depth elsewhere in this book.

In addition to high-strength aluminum alloys, high-strength steels and titanium alloys may also suffer SCC. Steels with an ultimate tensile strength greater than 1450 MPa are generally considered to be susceptible to SCC in aqueous environments. Failures have occurred with titanium alloys when exposed to specific environments.

Fatigue is familiar to all aircraft designers and operators. The presence of a corrosive environment can accelerate the process by shortening the initiation stage and/or by increasing the growth rate of fatigue cracks. Most of the concerns and research into corrosion fatigue on airframe materials have been with aluminum alloys. The need to understand this type of corrosion has gained particular importance in relation to ageing aircraft. It is now recognized that the interaction between fatigue and corrosion is crucial in determining the integrity of aircraft structures.

On airframes, hydrogen embrittlement is normally associated with high-strength steels. Cracking takes place in statically loaded components, resulting from the absorption of hydrogen, which may be introduced as a result of corrosion occurring on the surface or from hydrogen introduced during surface finishing treatments. Rapid crack growth takes place, leading to the eventual catastrophic failure of the component. It is widely accepted that the mechanism of SCC in high-strength steels is one of hydrogen embrittlement.

The fourth type of corrosion occurring in the presence of an applied stress (identified in Table 1) is fretting, which is a form of wear resulting from the movement or vibration between two surfaces. The movement is very small, often leading to the formation of fine particles or debris. Titanium alloys are particularly sensitive to this type of degradation.

4.38.1.3.3 Corrosion arising from poor design and protection

Crevice corrosion arises in-service, largely as a consequence of poor design. Crevices provide an area in the structure where water, hydraulic fluids, and other contaminants may become trapped. The diffusion of oxygen into the crevice is restricted so that the second cathodic reaction involving the reduction of water to form hydrogen ions is favored. This increases the acidity of the solution at the tip of the crevice and will lead to accelerated corrosion of structural materials such as aluminum alloys, magnesium alloys, and corrosion-resistant steels. The proper use of sealants and jointing compounds, to fill crevices and prevent the entry of fluids, can eliminate this type of corrosion.

Galvanic corrosion can occur when two dissimilar metals are joined. Some indication of the likely risk of coupling two different metals together can be gained by comparing their corrosion potentials. If there is a large difference in potential between the two metals, for example, 2014-T6 aluminum–copper alloy and steel, the corrosion of the more negative material, in this case the aluminum alloy, will be accelerated, while the corrosion of the steel will be reduced. The occurrence of this type of corrosion in an aircraft can be limited if coatings such as electroplated cadmium are applied to steel parts. The corrosion potential of cadmium is similar to 2014-T6 aluminum–copper alloy and therefore the driving force for corrosion is much lower.

Filiform corrosion is a form of attack that develops under organic coatings applied mainly to aluminum alloys. It appears as long filaments that spread from areas of surface damage such as cracks or chips in the coating. The development of this form of corrosion is dependant on the surface cleaning and treatments applied to the substrate.

4.38.1.4 In-Service Corrosion

Corrosion is likely to take place within the aircraft structure at areas where moisture and other corrosive contaminants become trapped. The main problem areas have been documented in the open literature[1,2,5] and are summarized as follows.

- Areas where fluids may collect
- Areas partly exposed to the environment
- Areas into which fluids may leak

Examples of corrosion found in-service on civil transport aircraft associated with the build up of fluids include areas below toilets, galleys, and cargo-holds. The corrosion of seat tracks arising from the spillage of drinks continues to be a major problem area. Some areas such as undercarriage bays, freight doors, access doors, and flap shrouds are regularly exposed to the environment. Leakages from hydraulic systems and batteries can rapidly degrade protective treatments.

4.38.1.5 Impact of Corrosion on Structural Integrity

Corrosion can degrade the integrity of the aircraft structure in a number of ways as listed in Table 2.

Exfoliation corrosion, which is often found to develop in components manufactured from plate

Table 2 Examples of the effects of corrosion on the integrity of airframe structures

Corrosion type	*Impact on structural integrity*
Intergranular and exfoliation corrosion and most forms of corrosion	Reduction in section leading to loss in strength/load bearing capacity, ductility, stiffness, etc.
Corrosion pitting	Failure of hydraulic pipes, fuel lines – leakage of fluids into areas causing breakdown of protective treatments and further corrosion
Corrosion pitting and fretting	Introduction of stress raisers leading to reduced fatigue life
Crevice corrosion	Generation of stresses at joints resulting from corrosion product wedging – breakdown of bonded joints
Galvanic or dissimilar metal corrosion	Accelerated corrosion attack of aluminum and steel components
SCC and hydrogen embrittlement	Catastrophic failure of stressed components
Microbial corrosion	Leakage from fuel tanks, blockages

aluminum alloys, can lead to a major loss in section, and hence, load bearing capacity. Pitting corrosion and intergranular attack may accelerate the initiation of fatigue cracking. The areas where attack occurs act as stress raisers and greatly reduce the fatigue life of the structure. In hydraulic and fuel pipes pitting attack can cause perforation and eventual fluid loss.

Some of the aluminum alloys employed in older aircraft are susceptible to SCC. This form of attack can develop if the component is under stress and is exposed to a corrosive environment. The stresses may be residual stresses introduced during the manufacture of the part or they arise as a result of misalignment during assembly. Once initiated, SCC may develop very quickly resulting in the catastrophic failure of the part or structure.

In some instances, corrosion may contribute to the degradation and eventual failure of adhesively bonded joints. At present, much research is being directed towards understanding the mechanisms involved in the failure within adhesively bonded lap joints on ageing aircraft and developing methods for the early detection of breakdown.

4.38.2 Corrosion Management During Manufacture

4.38.2.1 Introduction

The approach adopted in the management of corrosion during the initial manufacturing stage is based on the following:

- the selection of materials with inherent resistance to corrosion,
- the application of protective treatments to individual parts and components,
- careful design and assembly to minimize potential problems such as crevice and galvanic corrosion,
- the application of additional protective treatments in high corrosion risk areas.

Each of these aspects is considered in this section.

4.38.2.2 Materials Selection

4.38.2.2.1 Introduction

In many cases airframe materials were initially selected to provide specific strength levels, fatigue resistance, fracture toughness properties, etc. Corrosion resistance was often only a secondary consideration. The philosophy adopted was basically to assume that the inherent poor corrosion resistance of the material could be compensated for by the application of a protective coating, typically an inhibited primer or metal coating. This assumed that the coating would remain intact and undamaged throughout the life of the component. The reality is that coatings in the form of both paints and metal deposits suffer from cracking and degradation during the operational life of an aircraft. Examples of undercarriage components manufactured from 7000 series aluminum–zinc–magnesium alloys heat treated to the high-strength T6 temper that suffered catastrophic failure in-service have been referred to earlier. In these instances the surface treatments applied failed to prevent the onset of SCC.

The approach now adopted is to take into account the inherent corrosion resistance of the material to be employed. Guidance data are available from several sources[6,7] on the susceptibility of airframe to various types of corrosion, in particular, resistance to SCC and exfoliation corrosion.

4.38.2.2.2 Aluminum alloys

As indicated in Section 4.38.1.3 airframe aluminum alloys are susceptible to various forms of corrosion including localized attack and SCC. The alloy composition, heat treatment, and product form will control the type and distribution of precipitates as well as the grain size and shape of the grains. The microstructure of the component material, together with the nature of the environment and loading applied, will determine the type and extent of the corrosion attack that takes place. During the material selection process, the resistance of aluminum alloys to exfoliation corrosion and SCC is taken into account. Extensive laboratory testing combined with service experience has enabled the relative susceptibilities of aerospace aluminum alloys to exfoliation to be given a rating as indicated in Table 3 based largely on Defence Standard 00-970.[6]

Sheet aluminum alloys are generally considered to be immune to exfoliation corrosion and have an 'A' rating. Some intergranular attack may take place but the grain structure is normally equiaxed and true exfoliation corrosion will not develop. Alloys with C ratings should be avoided wherever possible. As discussed in the following section, surface treatments must be applied to minimize the risk of corrosion occurring. Several alloys such as plate 2024-T3 aluminum–copper, which has frequently been used for bottom wing skin applications, and plate 7075-T651 aluminum–magnesium–zinc which has been used for the manufacture of upper wing skins and undercarriage components are very susceptible to exfoliation corrosion and have a 'D' rating. The policy now is to avoid the selection of these materials wherever possible.

Table 3 Exfoliation ratings applied to aluminum alloys

Rating	*Description*
A	Immune to exfoliation corrosion
B	Resistance to exfoliation corrosion under normal service conditions but could occur under extreme conditions
C	Susceptible to exfoliation corrosion if appropriate design precautions are not taken
D	Very susceptible to exfoliation corrosion

Source: Defence Standard 00-970 Part 7/2 Section, Detail Design and Strength of Materials, Ministry of Defence, Directorate of Standardization, Kentigern House.

Table 4 compares the susceptibility of several materials that have been widely employed in airframe structures. The data have been taken from Defence Standard 00-970[6] and ASTM Handbook,[7] which should be consulted for more detailed information. Table 4 indicates that with the 7000 series plate alloys, the susceptibility may be reduced by using a material in the over-aged T73 or T76 condition. In these tempers, however, the strength of the 7075 alloy is reduced by up to 10% compared with the peak aged T6 temper. The 7010 and 7050 alloys were developed to provide materials that matched the strength of the peak aged 7075 alloy and were resistant to exfoliation corrosion. Recent developments in both high-strength 7000 series alloys and damage-tolerant 2000 series alloys have been aimed at producing products with improved mechanical properties and a resistance to corrosion.[8,9]

The resistance of plate aluminum alloys to SCC is often assessed by determining a threshold stress below which failure will not occur. For this purpose, alternate immersion/emersion testing in 3.5% sodium chloride solution or outdoor marine exposure trials are conducted using C-ring or tensile bars cut from the plate material. Table 5 gives typical values published in the literature for three commonly used plate materials. The susceptibility to SCC in these materials is orientation dependent and is mainly a consequence of grain shape. Plate materials are most susceptible when the stress is applied in the short transverse direction (ST) as shown in Table 5. The

Table 4 Examples of the exfoliation corrosion susceptibility of some aerospace aluminum alloys

	Rating			
	A – Immune	*B – Resistant. Slight exfoliation may be induced under extreme conditions*	*C – Susceptible to exfoliation. Can occur in-service*	*D – Very susceptible to exfoliation*
Product form				
Sheet		2014-T6, T3 2024-T3, 7075-T6		
Plate	7075-T7351	7010-T7651 7010-T73651 7050-T7651 7050-T73651	2014-T6	2024-T3 7075-T651
Extrusion			2014-T6	

Table 5 Typical threshold stresses for plate aluminum alloys (MPa) exposed in a marine environment

Material	*Direction*		
	L	*LT*	*ST*
2014-T651	310	210	<55
2024-T3	170	140	<55
7075-T651	340	310	<55
7075-T73	349	330	300

Table 6 SCC ratings applied to aluminum alloy

Rating	*Description*
A	Immune to SCC
B	Resistance to SCC under normal service conditions but could occur under extreme conditions
C	Susceptible to SCC if appropriate design precautions are not taken
D	Very susceptible to SCC

Source: Defence Standard 00-970 Part 7/2 Section, Detail Design and Strength of Materials, Ministry of Defence, Directorate of Standardization, Kentigern House.

effect of overaging the 7075 alloy to the T73 temper is to increase the SCC threshold stress from less than 55–300 MPa.

The data presented in Table 5 are derived from tests conducted on smooth specimens and basically relate to the initiation of stress corrosion cracks. The rate at which a stress corrosion crack propagates may also be studied. The usual approach is to determine the crack growth rate as a function of the stress intensity. A value of stress intensity K_{1SCC} can often be measured below which the crack does not grow effectively.

The threshold stress data and K_{1SCC} data are used together with service experience to assess the susceptibility of aerospace aluminum alloys to SCC. As discussed in the following section, susceptibility is dependent on the product form, that is, sheet, plate, tube, extrusion, etc., alloy composition, and the heat-treatment that has been carried out.

Data comparable to those available for exfoliation susceptibility are detailed elsewhere,[6,7] listing the SCC resistance of aluminum alloys. A similar rating system is employed as indicated in Table 6.

As previously discussed, the susceptibility to SCC in wrought aluminum alloys is orientation dependent. Plate aluminum–zinc–magnesium alloys heat treated to the T6 condition are particularly sensitive when loaded in the short-transverse (ST) direction. Heat treating material to the T73 and T76 tempers will improve the SCC resistance of an alloy such as 7075 from a ‘D’ to an ‘A’ or ‘B’ rating but with some loss in strength. The 7010 and 7050 alloys offer high strength and improved resistance to SCC. By applying a duplex ageing treatment, consisting of up to 24 h at temperatures in the range 120–135 °C followed by a shorter period at a higher temperature (160–170 °C),[10] the strength 7075 alloy in the T6 peak aged condition can be obtained but with much improved resistance to SCC. These alloys contain zirconium rather than chromium or manganese to inhibit recrystallization.

More recent developments in 7000 series airframe materials are described elsewhere.[8,9,11] Alloys such as 7449 are being considered in various product forms and tempers for use in upper wing skins, upper and lower wing stringers and wing box applications. The material gives improved strength combined with good resistance to corrosion.

4.38.2.2.3 High strength steels

Steels employed in airframe manufacture fall broadly into the following groups:

- non-corrosion resisting mild steels and low alloy steels,
- intermediate alloy steels,
- high-alloy steels,
- precipitation and transformation – hardening steels (stainless).

The main concerns with high-strength steels are their susceptibility to hydrogen embrittlement (HE) and SCC. The wealth of available experimental data indicates that the mechanism of SCC in steels is one of hydrogen embrittlement. Hydrogen is generated during surface corrosion some of which will diffuse into the steel substrate.

Steels with ultimate tensile strength (UTS) levels up to 1100 MPa are considered to be immune to these forms of corrosion but above this strength level, the susceptibility increases as the UTS is raised. Undercarriage parts, for example, are often manufactured from low alloy steels such as 300M and AISI4340 that have strengths of 1800 MPa or above. Steels heat treated to these strengths are very susceptible to hydrogen embrittlement and SCC. In an identical way to that used for aluminum alloys, steels may be given an SCC rating of ‘A’ through to ‘D.’ Based on the guidance information given in Defence Standard 00-970[6], the bar and tube product forms of 300M are given a ‘D’ rating, that is, very susceptible to SCC, while AISI 4340 is less susceptible and has a ‘C’ rating. Within the four groups of steels, there are some variations in SCC susceptibility, but there is an overall trend showing that susceptibility increases with increasing UTS.

In selecting steels for aerospace applications, the tables given in Defence Standard 00-970[6] and ASTM Handbook[7] should be referred to in order to determine the potential SCC and hydrogen embrittlement risks. Where a choice of materials is available, the more corrosion-resistant materials should be selected. As discussed in **Section 4.38.2.3.3**, steel parts must be protected against corrosion and wear. The choice of cleaning, pretreatment, and finishing processes available are greatly influenced by the SCC and HE susceptibilities.

4.38.2.2.4 Magnesium alloys

The use of magnesium alloys is now largely limited to castings. Sheet alloys were used at one time for skinning on both fixed wing aircraft and on helicopters. Major corrosion problems were experienced in-service, particularly around fasteners where the protective treatments had cracked or flaked off. This resulted in reskinning programs replacing the magnesium alloy with sheet aluminum alloys. For many military applications, the use of magnesium alloy sheet is not permitted. Their lower density compared with aluminum alloys and their superior casting properties have made magnesium alloys particularly attractive for the production of gearbox housings for helicopter applications.

Unprotected magnesium alloys are susceptible to pitting corrosion but are not prone to intergranular attack. The presence of cathodic impurities such as iron, nickel, and copper has significant effects on the pitting behavior and improvements in corrosion resistance have been achieved by developing materials with lower impurity levels. The corrosion rate of a AZ91C magnesium–aluminum–zinc alloy, for example, may be reduced from 0.022 to 0.006 mm year^{-1} in a marine–rural environment by lowering the iron level from 350 to 10 ppm.[12] In selecting magnesium alloys consideration should be given to choosing materials with lower impurity levels. Care must also be taken in processing materials in order to minimize the risk of surface contamination, which could initiate corrosion.

Some differences in corrosion behavior also exist between the main types of magnesium alloys employed for aerospace purposes. For example, the AZ63A magnesium–aluminum–zinc alloy has a corrosion rate of 0.018 mm year^{-1} compared with a rate of 0.028 mm year^{-1} for the EZ33 magnesium–rare earth–zinc alloy. For further information see ASTM Handbook[12] and manufacturer data sheets.

A key problem with magnesium alloys is the potential risk of galvanic corrosion when in contact with other materials. This requires the application of effective barrier coatings.

4.38.2.2.5 Titanium alloys

Titanium alloys are relatively resistant to corrosion mainly due to the presence of a thin highly protective air formed oxide film. In terms of material selection there are no significant differences between the various types of titanium alloys to aqueous corrosion. However, the following points should be taken into consideration when selecting titanium alloys for airframe applications

Galvanic corrosion

Titanium alloys can promote galvanic corrosion when coupled to other airframe materials such as aluminum alloys, steel, and magnesium alloys. Precautions must be taken during assembly to reduce the contact between parts made from titanium alloys and other structural materials.

Fretting corrosion

Where small repeated movements take place between a titanium alloy part and parts made from either aluminum alloy or steel, there is a possibility that fretting damage may be induced in the titanium alloy surface. This can lead to early fatigue crack initiation. The risk of fretting can be minimized through the application of a suitable antifret surface treatment. A number of treatments are available commercially and include surface coatings and ion implantation treatments.

Stress corrosion cracking

While titanium alloys are generally resistant to both corrosion and SCC in marine environments, there are a number of chemicals and contaminants which are commonly found on aerospace structures that may induce corrosion and SCC.[13] These include chlorinated hydrocarbons, methanol and phosphate ester fluids at temperatures above 120 °C. It is good practice to avoid the use of titanium alloys in areas where contact with these chemicals is a possibility.

Solid metal embrittlement

Titanium alloys may be susceptible to solid-metal embrittlement when in contact with cadmium. Embrittlement may occur at ambient temperatures, but it is likely the embrittlement process that is accelerated at elevated temperatures. Failure of the component will take place under an applied stress if there is intimate contact between titanium alloy and cadmium plating.[14] For airframe applications, direct contact between cadmium and titanium should be avoided. At one time cadmium plating was often used on titanium alloy fasteners to improve lubricity and to reduce the

Table 7 Methods currently employed in the protection of aerospace components

Method of Protection	*Examples*	*Applications*	*Substrate*
Corrosion Inhibitors	Chromates	Chromate pigmented primers	Aluminum alloys
		Conversion coatings	Aluminum alloys Aluminum coatings
		Passivation treatments	Cadmium coatings Zinc coatings
Sacrificial metal coatings	Cadmium	Electrodeposited and physical vapor deposited cadmium plating	High-strength steel Corrosion resisting steel
	Zinc	Electrodeposited zinc plating	Steel
	Aluminum	Aluminum and Aluminum–zinc cladding	Sheet aluminum alloys
	Aluminum	Physical vapor deposited aluminum plating	Steel Titanium alloys Aluminum alloys
Barrier coatings	Epoxy coatings	Thick dense coating	Magnesium alloys
	Anodic films	Thick oxide coating	Magnesium alloys
	Sealed anodic films	Dense oxide coating	Aluminum alloys
	Nickel plating	Electroless nickel plating	Steels Aluminum alloys
	Chromium plating	Hard chromium electroplating	Steels

likelihood of dissimilar metal corrosion when used with aluminum alloys. This practice is no longer permitted and cadmium plated steel parts and fasteners should not be in direct contact with titanium alloy parts.

Other metals that have been identified as causing solid-metal embrittlement under certain circumstances are zinc and silver.

4.38.2.2.6 Composite materials

While generally resistant to degradation from the chemicals employed on aircraft and to the environments to which aircraft are exposed, composite materials may contribute to the corrosion of other airframe materials. CFRP (carbon fiber reinforced plastic) composite materials behave in a similar manner to titanium alloys when coupled to less noble metals in so far as they will accelerate the corrosion of steel, aluminum alloys and magnesium alloys. There is also concern that some composite materials will absorb moisture, which may lead to the loss of mechanical properties.

4.38.2.3 Protective Treatments

4.38.2.3.1 Introduction

Following manufacture, normal aerospace practice is to apply a protective treatment to parts made from aluminum alloys, magnesium alloys, and steels. Parts made from titanium alloys and composites may also be protected depending on the location on the airframe and environment to which the part is likely to be subjected. The method of protection employed varies according to the substrate material as indicated in Table 7.

In the following sections, the protective treatments applied to aerospace components are described in detail.

4.38.2.3.2 Aluminum alloys

Current protective treatments

The standard protective treatments currently applied to aerospace aluminum alloys are based on the use of chromate containing pretreatments and chromate pigmented primers. As indicated earlier, aerospace aluminum alloys are susceptible to localized corrosion particularly in the presence of chloride ions. Strontium chromate is a very effective corrosion inhibitor for aluminum alloys particularly on exposure to salt containing atmospheres. This is demonstrated by published data showing that, in 3.5% sodium chloride (a chloride level equivalent to that of seawater), the addition of 0.02 mmol l^{-1} of chromate is sufficient to prevent the onset of corrosion on a 2000 series aluminum alloy.[15]

Figure 1 illustrates the protective scheme used on parts manufactured from aluminum alloys.

Prior to the application of the pretreatment, the part is degreased and cleaned using a suitable process such as alkaline degreasing, abrasive cleaning, organic solvent degreasing, and chromic–sulfuric acid etch. For fatigue critical parts it should be

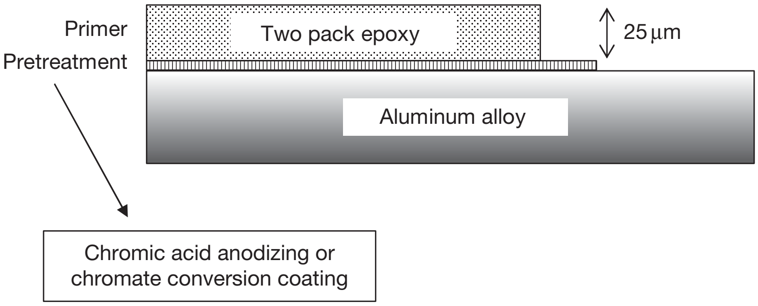


Figure 1 Standard protective treatment applied to aluminum alloy components.

noted that surface etching may have an adverse effect on fatigue life. Pretreatments normally used include chromic acid anodizing (CAA) and chromate conversion coatings (CCC). The purpose of these is to produce a protective film, which consists basically of alumina and, in the case of CCC, incorporates chromates and chromium oxide. In addition these coatings enhance paint adhesion by promoting mechanical keying.

CAA is usually conducted in a bath containing a concentration of 30–100 g l^{-1} chromic acid. The anodizing voltage depends on the composition and temper of the alloy but is typically in the range 20–50 V. Times of up to 40 min are required to produce suitable films. Further details may be found in the appropriate process specifications. The anodic films produced by chromic acid anodizing consist of a thin barrier layer with a thicker porous outer layer. To achieve maximum paint adhesion, it is normal practice to paint within 8 h of anodizing. An alternative approach is to seal the anodic films prior to painting by immersing the part in near boiling water. This improves the protective properties of the film but probably at the expense of the paint adhesion.

Chromate conversion coatings fulfill the same role as anodizing but are generated by immersing the part in an acidic chromate bath. Details of the chemistry of the conversion coating process may be found elsewhere.[16] The films generated vary from colorless through yellow, iridescent, to brown depending on the film weight. The heaviest films, which are brown in appearance, are used when no further protection is to be applied. However coatings applied as a pretreatment for painting are normally yellow. Usual practice is to apply primer paint within 16 h of filming. A number of commercial treatments are available, which are approved to various aerospace and defense standards employed by the aerospace industry.

As indicated in Figure 1, the main protective treatment applied to airframe aluminum alloys is a chromate pigmented primer. In most instances, this will be a two-component epoxy paint but polyurethane primers are also used. One of the functions of the primer is to act as reservoir of strontium chromate corrosion inhibitor, which will be leached from the paint when the surface comes into contact with moisture. The presence of the inhibitor prevents corrosion from occurring at areas where the paint film has become damaged and the aluminum alloy is exposed. Laboratory experiments indicate that the amount of chromate leached out of the primer is well above the minimum concentration required to inhibit corrosion.[15] Primers used for aerospace applications are required to meet various performance criteria such as adhesion, resistance to fluids, corrosion, drying times, etc. For detailed information, specifications such as BS 2X33[17] or the equivalent European EN or US Military Standards should be consulted.

Epoxy primers have been employed on both civil and military aircraft for many years. Developments in the mid 1980s were concerned with improving the adhesion and fluid resistance of the standard primer. This was mainly in response to corrosion problems occurring on civil transport aircraft. Leakage of hydraulic fluids led to the degradation of the standard protective coatings and the eventual corrosion attack of the underlying aluminum alloy substrate. New generation primers were developed by leading aircraft paint manufacturers, which, in addition to giving improved resistance to aircraft fluids, gave better adhesion. Both types of primer are covered by standards such as BS 2X33. Normally the primers will be applied to components by spraying and this may be followed by a baking treatment.

Recent developments in primers have focused on reducing the level of solvents released. The primers originally used typically had a volatile organic compound (VOC) emission level of 600 g $\mathrm{l^{-1}}$. Within the European Union, legislation was introduced in the 1990s reducing the permissible levels of VOC in aircraft paints. For epoxy primers the level was set at 350 g $\mathrm{l^{-1}}$. High solid primers are now available, which meet these requirements and have been applied to UK military aircraft.

The other area of concern is the formulation of chromate-free conversion coatings, anodizing treatments and primers. Chromates together with other hexavalent chromium compounds have been identified as carcinogens and the use of chromates in aerospace surface treatments and coatings is likely to be prohibited in the future. Several alternative treatments are available commercially but their use so far has been restricted to exterior surfaces on aircraft operating in benign environments. Progress towards chromate-free treatments includes the development of modified sulfuric acid anodizing processes, such as boric–sulfuric anodizing[18]; conversion coatings formulated using cerium salts, zirconates, vanadates, and molybdates; pretreatments based on sol–gel technology[19] and appliqués[20] as potential replacements for conventional paint finishes. Several paint primer standards have been published covering chromate-free systems, which specify a range of corrosion performance requirements that will need to be fulfilled.

Aluminum coatings and cladding

In addition to chromate-based protective treatments, aluminum coatings are used for the protection airframe aluminum alloys. The coating may be applied by a physical vapor deposition (PVD) process or may take the form of a thin clad layer applied in the manufacture of the alloy. PVD aluminum coatings have sometimes been used to protect fatigue critical components. Normal cleaning treatments such as chromic/sulfuric acid etching, and anodizing and chemical conversion pretreatments, often cause a reduction in fatigue strength, which may be as large as 10%. With PVD aluminum coatings, the surface is sputter cleaned prior to deposition and the loss in fatigue strength is small. Typically the aluminum coating is 12–25 μm thick.

Clad sheet aerospace aluminum alloys are commercially available and find applications mainly in the construction of civil aircraft. The cladding is applied during the manufacture of the alloy and consists of a thin sheet of aluminum on either side of the alloy (see **Figure 2**). Typically the thickness of the cladding on each side is 5% of the total sheet-thickness. For 2000 series aluminum–copper alloys, a commercially pure aluminum cladding is used while for 7000 series aluminum–zinc–magnesium alloys a aluminum–zinc cladding is employed. The cladding is corrosion resistant and isolates the alloy from the environment. Additionally, the cladding provides sacrificial protection if the underlying alloy becomes exposed as a result of surface damage. Clad alloys have lower strengths than the equivalent unclad material and are less resistant to fatigue damage. As a result, they tend not to be selected for use on military aircraft. Depending on the operating environment, parts made from clad materials may be further protected using the standard scheme outlined earlier.

4.38.2.3.3 Steels

For most applications, passivated cadmium plating is the preferred protective treatment for high-strength and corrosion-resistant steels. **Figure 3** shows schematically the protective coating applied to steel parts.

Cadmium plating offers a unique range of physical and mechanical properties, which are so far unmatched

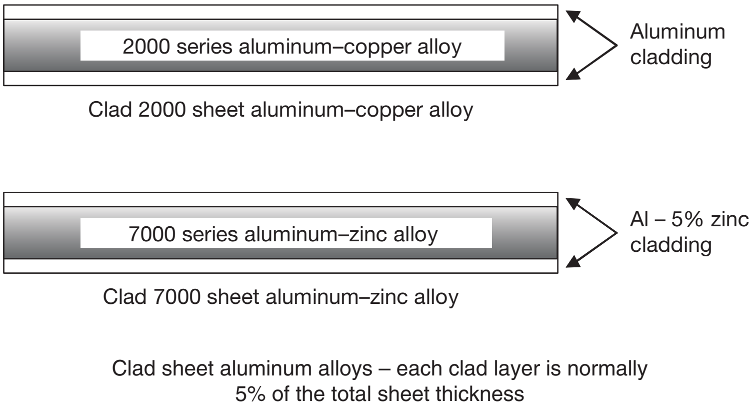


Figure 2 Structures of clad 2000 and 7000 series sheet aerospace aluminum alloys.

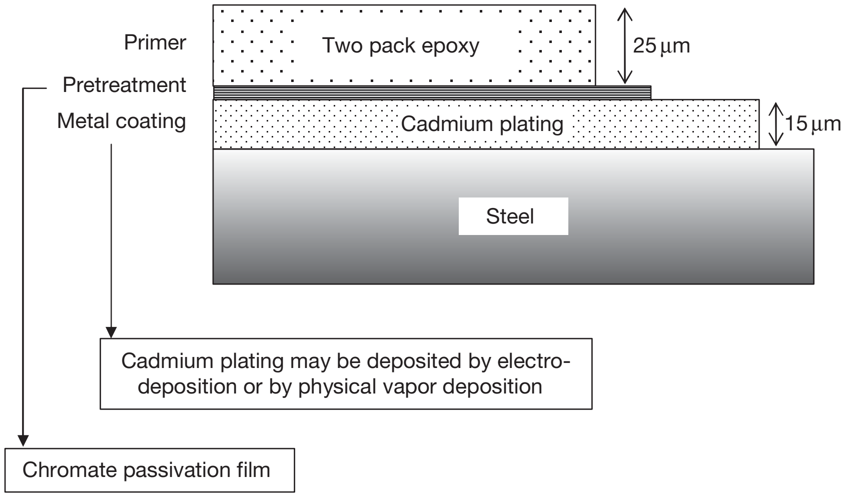


Figure 3 Standard protective treatment applied to steel components.

by other protective treatments. Cadmium provides a sacrificial coating that is galvanically compatible with aerospace aluminum alloys and has a high lubricity. The latter is an important property when the coating is used on fasteners or threaded parts.

The coating is normally applied by electrodeposition from a cyanide-based plating bath, which permits dense uniform coatings to be deposited on to complex surfaces with threaded areas, recesses, etc. The thickness of cadmium required is dependent on application. Defence Standard 03-19[21] proposes that for normal requirements on noncorrosion resisting steels a minimum average thickness of 14 µm should be employed, while for threaded items a minimum average thickness in the range 4–7.5 µm depending on the nominal average thread diameter is necessary.

Like most electrodeposition processes, cadmium plating is less than 100% efficient and significant levels of hydrogen may be generated. As discussed earlier, high-strength steels are susceptible to hydrogen embrittlement and the susceptibility increases with increasing UTS. Following plating, a de-embrittlement baking treatment is conducted, which reduces the level of hydrogen.

For processing purposes, high-strength steels may be divided into four strength categories as follows:

- Category 1 up to 1100 MPa
- Category 2 1101–1450 MPa
- Category 3 1451–1800 MPa
- Category 4 1801 MPa and greater

Steels falling into the category 1 are not considered to be susceptible to HE and a baking treatment is not regarded as necessary. For steels in category 2, a minimum post plating treatment of 8 h at 190–230 °C is employed. For categories 3 and 4, the minimum baking times are increased to 18 and 24 h respectively. In addition to determining the baking conditions, the range and types of cleaning treatments, which may be carried out prior to plating, are dependent on the strength category. As the UTS of the steel increases, processes that may generate hydrogen should be avoided.

For steels with category 3 or 4 strengths some constructors prefer to use cadmium plating prepared by PVD. This is a nonaqueous process involving the deposition of cadmium by evaporation within a vacuum chamber.

After plating, a chromate passivation treatment is applied to improve the corrosion resistance of the cadmium and to act as a pre-treatment for subsequent painting. The process is carried out by immersing the part in a bath containing a sodium dichromate/sulfuric acid solution to produce a yellow film. Fasteners are used in the plated and passivated condition while components are normally primed before assembly.

In situations where parts may become heated to temperatures above 230 °C, zinc plating may be used rather than cadmium plating. Areas that are difficult to electroplate, for example, the internal bore of a tube, are sometimes phosphated rather than plated.

The main problem with cadmium plating is the toxic nature of cadmium compounds, which can cause fetal damage as well as damage to the kidneys, lungs, and liver. Legislation banning the use of

Table 8 Possible alternatives to cadmium plating

Coating type	*Coating composition*	*Method of application*	*Major limitations*
Aluminum based	Aluminum	Physical vapor deposition	Plating in recesses/holes may be difficult
	Aluminum	Electrodeposition from an organic bath	Limited commercial availability
	Aluminum–manganese	Electrodeposition from molten salt bath	Not generally available
Zinc based	Zinc–nickel (low)	Electrodeposition	Commercially available
	Zinc–nickel (high)	Electrodeposition	Post plating treatments such as hydrogen de-embrittlement and passivation required.
	Zinc–cobalt	Electrodeposition	Limited coating lubricity
	Zinc–cobalt–iron	Electrodeposition	
Metallic–ceramic	Al and Zn flakes in an inorganic matrix	Electrostatic spraying, dipping or spin coating	Tend to be thick coatings – generally unsuitable for fasteners
Manganese based	Manganese alloys	Electrodeposited	Limited availability commercially – mainly laboratory processes. Low bath efficiencies

cadmium plating for many engineering applications was introduced within the European Union some years ago but its use on aircraft components is still permitted. Continuing concerns about the harmful effects of cadmium has led to a number of studies aimed at identifying possible replacements. While it is unlikely that a single replacement coating will be found, a number of coatings are available commercially that could be used as alternatives to cadmium plating for specific applications. Table 8 details the range of coatings that have been considered together with some of their limitations.

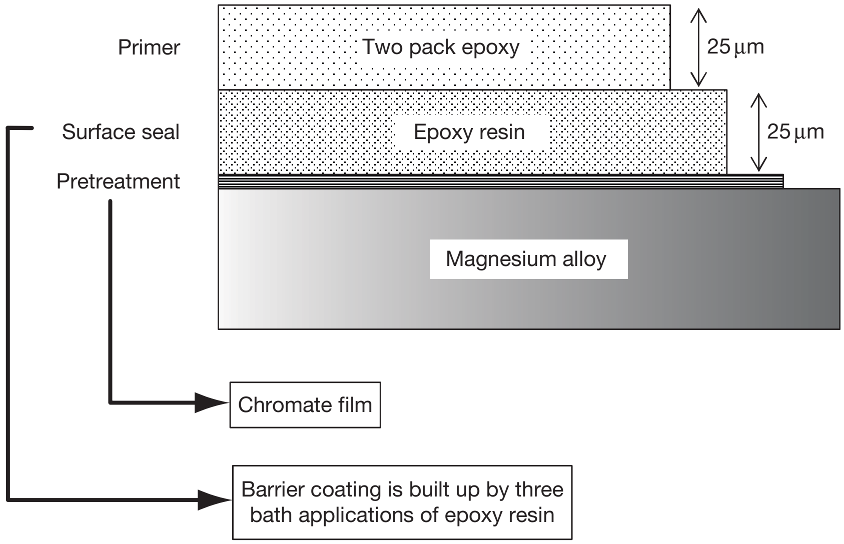
The coatings fall into four groups, all of which provide a level of sacrificial protection. The aluminum- and zinc-based coatings are normally given a passivation treatment after plating to improve the corrosion resistance. These tend to be chromate solutions but some nonchromate treatments are now becoming available. The metallic–ceramic coatings group covers several commercially available types consisting of an inorganic matrix incorporating aluminum or zinc flakes or powders. The feasibility of electrodepositing manganese alloy coatings was demonstrated more than 60 years ago, but it is only relatively recently that their use as alternatives to cadmium plating has been investigated. In some instances, the alternative coatings are thicker than the cadmium plating in order to achieve the same level of protection.

The results of a number of major programs examining alternatives to cadmium plating for aerospace applications are available in the literature.[22–24] In addition to the corrosion aspects of alternative coatings, other important properties such as lubricity, torque–tension behavior, hydrogen embrittlement, effects on fatigue, paint adhesion, and coating repair have been investigated. Depending on the particular application, some of these aspects must be taken into account when selecting an alternative coating system. Some general guidance on cadmium replacements can be found elsewhere.[25]

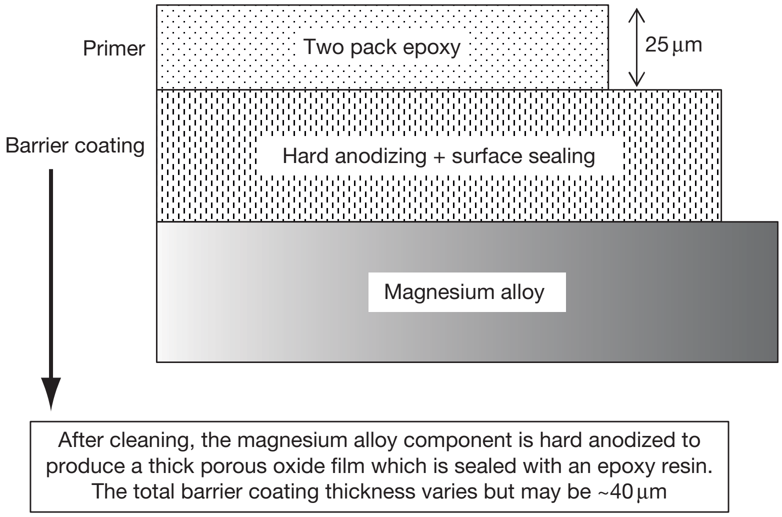
4.38.2.3.4 Magnesium alloys

The normal approach adopted for the protection of parts made from magnesium alloys is to isolate the component from the environment through the use of a barrier coating. The standard protection scheme consists of a nonpigmented epoxy resin as indicated in Figure 4(a). The part to be protected is first cleaned to remove all traces of contamination. The cleaning processes employed include solvent and vapor degreasing, mild alkaline treatments, and various acid pickles. Fluoride anodizing is also employed as a cleaning treatment. The part is anodized in an ammonium bifluoride solution using alternating current to produce an anodic film. This is removed by immersing the part chromic acid to leave a surface free of contamination.

Prior to carrying out the sealing treatment, a chromate filming treatment is applied to the component to improve the corrosion resistance and promote the adhesion of the epoxy resin. Generally, a thick layer of resin is applied by dipping the component which has been preheated to around 200 °C into a bath maintained at 60 °C containing the resin solution. After removal from the bath, the resin is stored at 180 °C for 45 min. The process is repeated three times to build up a resin thickness of about 25 µm.



(a) **Use of chromate filming treatments.**



(b) **Use of hard anodizing treatments.**

Figure 4 Examples of protective treatments applied to magnesium alloy components.

As indicated in Figure 4, two pack epoxy primer paint is applied to the part before assembly.

Several new protective processes have been introduced using anodizing treatments, an example of which is given in Figure 4(b). These have been adopted by several manufacturers for the protection of gearbox housings. The anodizing treatments generate films which are up to 40 µm thick and which may be subsequently surface sealed.

Other protective treatments, which either have been used or are being considered for magnesium alloy parts, include metallic–ceramic coatings and thick hard anodic films formed by high voltage anodizing.

4.38.2.3.5 Titanium alloys

As previously stated, titanium alloys have a high resistance to corrosion in the presence of moisture and most of the contaminants found within the aircraft structure. If used in isolation, titanium alloy parts require only the minimum in terms of corrosion protection. This could be a single coat of primer

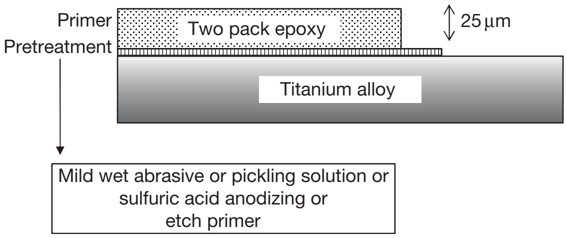


Figure 5 Protective treatments that may be applied to titanium alloy components.

applied to the surface of the component as indicated in Figure 5.

To promote paint adhesion, the surface would normally be cleaned using a mild wet abrasive treatment or a pickling solution. Etch primers and anodizing treatments are also sometimes used. The main problem with titanium-based alloys arises when contact is made with other metals and precautions must be taken to reduce the risk of galvanic corrosion. Zinc plating or zinc shims are often employed for this purpose when contact has to be made with magnesium alloy parts.

4.38.2.3.6 Composite materials

Composite materials used in the manufacture of airframe parts and panels do not suffer corrosion degradation but items made from plastics reinforced with carbon fiber may have an adverse effect on the corrosion of some metal parts with which they are in direct contact. Measures that should be taken to minimize this risk are described in Section 4.38.2.4 dealing with the design and assembly aspects of corrosion management.

Where a part made from composite materials is being used internally, surfaces may be left untreated. Where the part forms part of the external surface of the aircraft, a suitable pretreatment is applied followed by a paint scheme consisting of a primer and top coat. As a pretreatment, mechanical scuffing followed by degreasing is adequate if an epoxy primer is to be used. Since the paint is not providing corrosion protection to the composite substrate a chromate-free epoxy primer or epoxy filler may be employed.

4.38.2.3.7 Wear and fretting resistant coatings

In locations where there my be some movement or rubbing between parts it is often necessary to use a coating or surface treatment to minimize the risk of fretting or wear developing. Examples include landing gear components and flight control actuators. Electroless nickel and hard chromium coatings are often employed for this purpose particularly on steel parts and hard anodizing is sometimes used on aluminum alloys. Specialized treatments such as ion implantation and high voltage anodizing are also available and are beginning to find applications on airframe parts. Metal coatings such as electroless nickel and hard chromium plating while primarily used to reduce wear or fretting do provide some level of corrosion protection. The coatings act purely as a barrier layer, which isolates the substrate from the environment. Generally, these coatings are much thicker than cadmium, aluminum, and zinc plating, but provide no sacrificial protection once the substrate is exposed. Developments in wear resistant coatings have mainly been concerned with the incorporation of fine ceramic particles into electrodeposited coatings and the deposition of hard metal sprayed coatings. To some extent this has been driven by the need to replace hard chromium and eventually nickel coatings with environmentally compliant treatments. Sartwell *et al.*[26] describes recent research assessing the use of HVOF thermal spray coatings on landing gear.

4.38.2.4 Design Considerations

Careful design of the airframe to prevent the buildup and ingress of moisture and other corrodents into the structure will prevent the development of several potentially damaging and expensive corrosion problems. This can be achieved through the use of drain holes or filler materials in areas where moisture could collect. Sealing joints will also greatly reduce the risk of both crevice and dissimilar metal corrosion. Table 9 lists some of the potential corrosion problem areas and the design approach to reducing the risk.

In the case of dissimilar metal contacts, guidance material is available from several sources, including PD 6484:1979[27] and US Military Standard,[28] enabling potential problem areas to be identified. The corrosion between different metal couples is rated by the degree to which the corrosion of one metal is increased by contact with a second. For example, if a titanium alloy is in contact with an aluminum alloy, the corrosion of the titanium alloy is not increased but the corrosion of the aluminum alloy is markedly increased.

Table 10 details some of the dissimilar metal contacts that are likely to cause corrosion problems and gives examples of procedures, which may be employed to minimize the risk. In the examples given, there is a marked increase in the corrosion rate of the more active material due to the large difference in corrosion potential between the two metals. In order to reduce the risk of corrosion occurring, parts are protected and assembled to prevent metal-to-metal contact.

Experience has shown that many of the corrosion problems found in-service are often in internal areas that are difficult to inspect. Access for examination is an important design consideration, which will reduce inspection times and costs.

Table 9 Examples of potential corrosion problems and possible design solutions

Potential problem	*Design solutions*
Crevices	Static joints should be sealed to eliminate crevices – May be achieved by the use of wet assembly
Dissimilar metal contacts	Metal coatings, shims, wet assembly to reduce differences in galvanic potential and electrically isolate parts
Water traps	Incorporation of a drainage scheme to prevent the accumulation of fluids. Consideration of the inclusion of drain holes and the use of inert fillers
Leakage from galleys and toilet areas.	Use of non-metals, drain paths, sealed floor coverings

4.38.2.5 Final Assembly and Finishes

As discussed in Section 4.38.2.3, it is normal practice to apply an appropriate protective treatment to all parts prior to assembly. Where necessary, additional procedures will be carried out to reduce the risk of dissimilar metal corrosion as outlined in Section 4.38.2.4. In general, wet assembly methods will be employed to prevent the ingress of moisture at joints and prevent the occurrence of crevice and dissimilar metal corrosion. As indicated, certain areas within the fuselage, wings, undercarriage bay, and tail plane may be especially prone to the collection of aircraft fluids, leakage from galleys and toilets or to the build up of moisture and corrosive contaminants. These areas will require additional protection during assembly such as a further epoxy primer coat or a finish coat. One approach described by Voss[29] is to divide the aircraft structure into zones. In the example given, a military fast jet, three zones were identified as follows:

- Zone A – Interior surfaces, not to be subjected to permanent condensation
- Zone B – External and internal surfaces, to be exposed to wet condensation
- Zone C – Fuel wetted surfaces

For areas falling into the Zone A classification further protection is not necessary. For Zone B, some additional protection is applied, for example,

Table 10 Corrosion at dissimilar metal contacts and assembly procedures to be employed

Contact	*Corrosion*	*Protective treatment*	*Assembly*
Corrosion resisting steel coupled with Aluminum alloy	No increase in corrosion rate Corrosion rate may be markedly increased	Cadmium plating + Painting (optional) Pre-treatment + primer	Wet assembly
Corrosion resisting steel coupled with Magnesium alloy	No increase in corrosion rate Corrosion rate markedly increased	Cadmium plating + painting Full protective scheme	Wet assembly
Titanium alloy coupled with Magnesium alloy	No increase in corrosion rate Corrosion rate markedly increased	Zinc or aluminium coating + painting Full protective scheme	Wet assembly
Titanium alloy coupled with Aluminum alloy	No increase in corrosion rate Corrosion rate markedly increased	Painting or aluminium coating Pretreatment + primer	Wet assembly
Titanium alloy coupled with High strength steel	No increase in corrosion rate Corrosion rate markedly increased	None required Coated with Al, Al rich coating or cadmium	Wet assembly
Carbon fiber reinforced composite coupled with Aluminum alloy	No corrosion Large increase in corrosion rate	Pretreatment + primer Standard protective scheme	Adhesive bonding or wet assembly

a polyurethane finish coat while in areas such as fuel tanks (Zone C) special sealants and paint schemes need to be employed. If there is a risk of microbial corrosion occurring, the use of paints containing a biocide might be considered.

The normal finish coat employed is a two pack polyurethane paint. Polyurethane finishes have been available for aerospace applications for many years and continue to be widely used on both civil and military aircraft. As indicated in Section 4.38.1.2, one of the main sites for corrosion initiation is around fasteners on external surfaces where the development of cracks in the paint film allows the ingress of moisture. One of the important advances in polyurethane finishes has been the formulation of paints with increased flexibility, which are less prone to cracking. Current specifications for polyurethane finishes[30] identify two types of materials one intended for interior and exterior use where the maximum resistance to fluid attack is required and one intended for exterior use where increased tolerance to flexing is needed.

Acrylic finishes were used on some military aircraft for a number of years. They were introduced in the 1970s partly to fulfill a requirement for a paint scheme, which could be more readily removed than polyurethane finishes. The latter are highly resistant to fluids and very aggressive paint strippers must be employed to remove the polyurethane finish. The life of the acrylic finishes is relatively short (2 years) compared with polyurethane schemes (5 years) and the trend has been to phase them out in favor of polyurethane finishes.

The external painting of an aircraft is not solely for corrosion protection purposes. On military aircraft, the finish coat is used for camouflage purposes while on civil aircraft it is used to identify the airline or operator. On large transport aircraft, the paint applied to the external surfaces makes a significant contribution to the overall weight, which in turn will have an impact on fuel costs, passenger numbers, etc. Boeing[31] estimate for a 747-400 the weight of the paint applied to the fuselage and tail is approximately 252 kg. Some airlines have preferred to operate aircraft with polished rather than painted skins. In these cases, clad aluminum alloys are used for the skinning and the surface is treated with a clear conversion coating. Boeing has calculated that the fuel cost savings are offset by the higher costs of washing and polishing unpainted aircraft.

On some areas of the aircraft, specialized finishes may be employed. These include walkways, high temperature areas around engines and radome surfaces. For further information on these finishes, national and international specifications as well as manufacturer data sheets should be consulted.

4.38.3 Corrosion Management In-Service

4.38.3.1 Introduction

During the manufacture of an aircraft, the procedures broadly outlined in Section 4.38.2 are applied to produce a structure that is resistant to corrosion degradation. The approach is based on the selection of materials with a good resistance to corrosion, the application of protective treatments to individual components, and careful design to avoid potential corrosion problems. The airframe is wet assembled using sealants, jointing compounds, etc. to prevent moisture ingress into joints and other parts of the structure. External surfaces and internal areas, likely to suffer high levels of moisture build up or leakage of aircraft fluids, are given further protection by painting with a primer or a finish coat. In-service protective treatments can become degraded or damaged; drain-holes and drainage systems may be blocked and changes in operational role and life extensions can subject the airframe to environments for which it is not adequately protected. Corrosion management in-service is therefore concerned with maintaining the integrity of the aircraft throughout its operational life. It includes the cleaning and washing of exterior surfaces to remove harmful contaminants, inspecting for early signs of corrosion, corrosion rectification, the application of supplementary protective coatings, and the repainting of aircraft.

4.38.3.2 Aircraft Washing and Cleaning

Lewin[32] has described in some detail the way in which corrosive contaminants may build up on the surface of aircraft in-service. For example, during normal maneuvering on the ground, the exterior surfaces of aircraft may become covered with dust and salt, which may mix with moisture to form a clay-like structure, which adheres to the aircraft exterior. In-flight Lewin suggests that electrostatic forces generated will cause light dust to be deposited on aircraft skins. In addition engine contaminants such as oils, fluids, and carbonaceous films form on surfaces. If these contaminants are not removed from the aircraft surface, they will contribute to the eventual breakdown of the protective coatings and corrosion of the airframe.

Freshwater rinsing is often used on military to reduce levels of chloride and other contaminants present following maritime operations. Land-based aircraft may taxi through dedicated spray units on landing to remove surface salt.

Aircraft cleaning is generally carried out by first flushing exterior surfaces with water to remove loose dirt or other residues. The cleaning solution is sprayed on to an area of the aircraft and soft brushes may be used to remove surface contaminants. The area is then rinsed with fresh water and a new area cleaned. At the end of the cleaning operation, the whole aircraft is rinsed with water and dried off. Various types of cleaners approved for aerospace applications are available commercially. National standards identify different types of cleaners designed to remove different levels of contamination. Part of the approval process involves subjecting the cleaners to different corrosion tests to ensure that they will not cause damage to the airframe and engine materials.

4.38.3.3 Inspection for Corrosion

The early detection of corrosion remains a major priority for the in-service management of corrosion. At present, much reliance is still placed on visual inspection, often with hand lenses, looking for evidence of paint blistering, paint cracking, and filiform corrosion, particularly around fasteners. For internal areas where access is difficult, mirrors and endoscopes may be employed to facilitate the visual inspection. In some instances, the paint is removed from structurally critical areas to allow the metal substrate to be examined more thoroughly.

Many of the areas on an aircraft are difficult to inspect visually without dismantling parts of the airframe structure. The early stages in the development of corrosion and fatigue in fuselage lap joints present on many older transport and military aircraft, for example, are almost impossible to detect visually. To that end, nondestructive evaluation (NDE) techniques employing ultrasonics, eddy current measurements, radiography, and thermography are being employed to search for the evidence for the onset of corrosion and fatigue damage. NDE techniques are also used to assess the extent of the corrosion damage on hidden surfaces and to determine the depth of corrosion and the remaining wall thickness. This information is crucial in deciding the manner in which specific corrosion problems should be managed. Much research into developing improved NDE techniques for the early detection of corrosion is in progress.

The frequency and level of inspection undertaken vary according to the aircraft type and examples for civil transport aircraft are given elsewhere.[33,34] On a daily basis, areas would be examined for evidence of fuel leaks, cracking, surface damage, etc. Every 4 or 5 days, a more detailed visual inspection would be carried out of the interior and exterior surfaces and at longer intervals (typically 30 days) access panels may be removed to allow inspection of specific areas. Inspections employing NDE techniques are generally carried out at 12–18 month intervals, and every 3–5 years major checks involving removal of interior panels are conducted to allow careful examination of structural parts for signs of corrosion and cracking.

4.38.3.4 Corrosion Rectification

4.38.3.4.1 Corrosion removal

At present aircraft operators adopt a ‘find-and-fix’ approach to airframe corrosion. Often corrosion and fatigue damage are found during the scheduled maintenance of the aircraft. The occurrence of damage in a particular location may necessitate a fleet-wide inspection for similar damage on other aircraft.

With the find-and-fix approach a repair scheme is implemented, as soon as practical. The extent and depth of the corrosion that is found will determine whether a repair can be made, whether components must be replaced, and the time-scale in which they must be carried out. For aerospace structures, three levels of corrosion have been specified and are detailed elsewhere.[35] Level 1, for example, refers to relatively minor corrosion damage found between inspection periods that may be blended out within the limits specified by the manufacturer. Level 2 is concerned with corrosion that requires work or blending out which exceeds the manufacturer’s limits, while level 3 corrosion is sufficiently serious that there are urgent airworthiness implications.

For corrosion damage falling within ‘Level 1,’ repair often involves the blending away of corrosion damage, probably using a combination of mechanical and chemical methods, and then applying a protective coating to the blended area. Typically the allowable limits are 10% of the thickness for wing and fuselage skins. Mechanical methods commonly employed include rubbing with metal wool, abrasive pads or small abrasive wheels, and abrasive blasting with glass beads or alumina grit. Portable abrasive blasting units are available, which allow corrosion removal to be carried out *in situ*. The units recycle the spent abrasive and separate out the corrosion products.

When the corrosion found exceeds the allowable limits (Level 2), it may be necessary to replace components or carry out a structural repair. For corrosion damage identified as 'Level 3,' other similar aircraft in the operator's fleet would be inspected and the findings reported to the appropriate regulatory authority.

Problems may arise when corrosion occurs on areas that have already been blended and reprotected. This may result in the total depth of corrosion exceeding the allowable limits set by the manufacturer.

4.38.3.4.2 Reprotection

Once the corrosion has been blended out, the metal surface is reprotected using a suitable protective scheme. Often it is not possible to apply the original scheme, but rather a modified treatment. Table 11 gives examples of repair schemes that are employed to various substrates.

For aluminum alloys it is normal to use a conversion coating as a pretreatment for painting. The use of etch primers for the repainting of the air intake of an aircraft following paint stripping and removal of the corrosion damage has been described.[36] In this instance, an etch primer was chosen as the pretreatment rather than the normal chromate conversion coating. The choice was made to avoid the need to deoxidize the surface and water rinse the intake before and after the application of the conversion coating. There was concern that aggressive solutions could have been washed into the internal structure of the aircraft.

Small areas of damage on cadmium plated steel parts may be repaired after removal of corrosion products using an approved paint scheme. Brush plating techniques allow the localized repair of small areas of damaged coatings such as zinc, nickel, and cadmium electroplating. The process depends on the establishment of a plating cell between an anode (usually a graphite rod) wrapped in an absorbent material saturated with electroplating solution, and the damaged area, which is the cathode. During plating, the anode is rapidly moved backwards and forwards over the damaged area in order to build up a uniform deposit. Often brush plating may be carried out *in situ* greatly reducing the cost of corrosion rectification. One aerospace application has been the repair of damaged cadmium plating on landing gear components. High-efficiency solutions are available, which greatly reduce the risk of hydrogen evolution and absorption. After plating the cadmium plating is passivated and then painted with an appropriate paint scheme. The repair of cadmium replacement coatings such as electroplated zinc alloy and PVD aluminum is an area that is currently being studied.

As described in Section 4.38.2.3.4, the protection of magnesium alloy components involves a series of complex cleaning and coating procedures. When extensive corrosion is found, the component must be removed from the aircraft and where possible disassembled. After cleaning using some form of abrasive blasting to remove corrosion products and degraded resin, the magnesium parts are reprotected using the schemes outlined in Section 4.38.2.3.4. If the corrosion found is limited to a few small areas, it may be possible to repair *in situ*. This involves removing any damage mechanically, and then cleaning chemically using an acid chromate solution. The area is then repainted with a primer and top coat. More detailed information on procedures that should be undertaken is given in national and international standards.

The protective finishes applied to the top and lower wing skins play an important role in preventing the initiation of localized corrosion within fastener countersinks and in fastener holes. As discussed in Section 4.38.2.5, epoxy primers and polyurethane finishes with improved flexibility are available, which reduce the occurrence of cracking around fasteners and prevent the ingress of moisture. In some instances these coatings have not been found to give adequate protection, and alternative protective schemes using self curing polysulfide elastomeric coatings have been employed. These may be used directly as a primer or

Table 11 Examples of protective schemes used in the repair of damaged coatings

Substrate	*Original protective treatment*	*Repair schemes*
Aluminum alloys	Chromic acid anodizing or chromate conversion coating + epoxy primer (+finish coat)	Swab applied conversion coating + coat of primer paint (+finish coat) Etch primer + coat of primer paint (+finish coat)
Steels	Cadmium plating + passivation treatment + primer + finish coat	*In situ* repair using low HE cadmium brush plating + passivation and paint scheme
Magnesium alloys	Pretreatment + barrier coating + paint scheme	Etch primer + 2 coats of primer + finish coat

alternatively may be applied over a conventional epoxy primer. The elastomeric coatings are typically 150–250 μm equivalent to a coating weight of 270 g m^{-2} compared with a weight of 70 g m^{-2} for standard schemes. For this reason the coatings are used selectively, for example, along fastener runs, rather than over the whole surface to minimize the weight penalty. After applying the polysulfide coating the surface is painted with a flexible polyurethane finish.

4.38.3.5 Use of Supplementary Protection

The corrosion repair of internal areas may prove a much greater challenge requiring parts of the structure to be broken down to permit access for rectification to be carried out. In such cases, it may be possible to control the corrosion by applying a supplementary protective coating. These function by forming a barrier layer, which separates the substrate from the immediate environment. Several types are available commercially, which may be used on aircraft structures. These may be applied by brushing or spraying. Some of the products have water displacing properties, which leave a thin oily film after the solvent has evaporated, while other products must be applied to dry surfaces and produce a wax-like coating. At best supplementary protection will prevent the further spread of corrosion and may enable rectification work to be delayed to a time when the aircraft is undergoing major servicing.

4.38.3.6 Paint Removal and Repainting

The polyurethane finishes that are widely employed on the external surfaces of civil and military aircraft are highly resistant to fluids and are generally effective for up to 5 years. In-service, the paint films are subjected to large fluctuations in temperature, exposure to high levels of UV radiation, flexing during flight, and exposure to aggressive environments, leading to the crazing, cracking, and degradation of external paint schemes. For many years, the polyurethane paint schemes could only be removed for repainting or inspection purposes by using aggressive chemical paint strippers many of which were based on methylene chloride with a phenol additive. These materials are extremely hazardous to use, posing many health and safety issues.

Mechanical methods of paint removal such as plastic media stripping (PMS) are now extensively used. In the PMS process, small plastic beads are impacted onto the painted surface causing the paint film to crack and flake off from the substrate. Commercially available equipment allows the plastic beads to be blasted at the work surface at a controlled velocity and to recycle spent beads removing dust and paint particles. Some operators and maintenance organizations have installed facilities that allow small components as well as complete aircraft to be stripped. There are some limitations in place regarding use of PMS on thin metal sheet, clad alloys, and composite materials. Other blasting media such as dry ice and wheat starch have been evaluated. There is also interest in laser techniques, possibly for removing paint in around fasteners.

Another approach employed to simplify paint removal has been the use of selectively removable paint schemes. These permit the polyurethane top coat to be removed while leaving the primer intact. The schemes use 8–12 μm-thick intermediate coats, which are painted over the epoxy primer. The polyurethane finish is then applied to the intermediate coat. A comparatively simple paint stripper may be used to remove the finish and intermediate coats, but leave the primer intact. The use of such schemes on commercial aircraft has been described.[37] Aerospace paint standards have been issued covering both the intermediate coating[38] and the paint remover.[39]

4.38.3.7 Dehumidification

The corrosion found on an aircraft occurs mainly when it is parked on the ground or sitting in a hangar. Aircraft operated by the civil airlines spend a high percentage of their time flying, while many military aircraft are designed with a low number of flying hours but are required to remain operational for many years. In addition, many military airfields are very close to the coast and at these locations the atmosphere may be very corrosive.

The rates of corrosion of many airframe alloys exposed to the atmosphere are dependant on the relative humidity (RH), that is, the amount of moisture present in the air. There is often a critical RH typically ~50% above which the rate of corrosion increases rapidly with increasing RH. Below this critical RH, the corrosion rate is low and diminishes to an insignificant level when the RH is reduced to 10% or less. To reduce the risk of corrosion, dry air dehumidification has been employed to lower the humidity within the aircraft to less than 10% RH. Examples are given in the literature of both complete and partial dehumidification being employed in the management of military aircraft.[40,41] In some instances, localized dehumidification has been used to reduce the risk of corrosion in areas where electronic equipment is housed, on turbines, and parts of the airframe especially susceptible to corrosion. Whole aircraft dehumidification using dedicated shelters has now become a regular procedure for maintaining both fixed wing aircraft and helicopters.

4.38.3.8 Future Trends in Aircraft Corrosion Management

In-service aircraft structures are subjected to both fatigue and corrosion degradation. While the damage due to fatigue is primarily a function of the number of flights and the number of flying hours, corrosion is more closely related to the physical age of the aircraft. Many of the protection schemes applied to the internal areas of the fuselage and wings when the aircraft was built cannot be renewed without carrying out major dismantling of the airframe structure. Primer paints, for example, applied during the initial build are expected to provide corrosion protection throughout the life of the aircraft. Often these will become damaged or degraded due to the leakage of aircraft fluids or the build up of condensation and moisture. As the operational life of the aircraft is extended, the probability of corrosion developing is greatly increased.

Many of the aircraft currently in-service have exceeded their design operational life. This applies to both military and civil aircraft. Statistics published in 2000[42] indicated that more than 2500 commercial aircraft in the United States were flying beyond their 20-year design life. Figures published by the US Federal Aviation Authority suggested that 7% of the aircraft, which would be covered by the proposed Aging Airplane Safety regulation, are more than 40 years old. As the operational life of an aircraft is extended, there are increased maintenance costs. For example, statistics published for USAF aircraft[43] show that the total cost of corrosion rose from $926 million in 1990 to $1518 million in 2004 despite a reduction in fleet size.

The present find-and-fix approach to aircraft corrosion management is expensive both in terms of cost and the time aircraft are taken out of service. Two organizations, the United States Air Force and the Australian Department of Defence, have proposed changing from the find-and-fix approach[44,45] to a more structured method of managing corrosion. The alternative approaches, described as 'anticipate-and-manage' by USAF[44] and 'identify-and-manage' by the Australian DoD,[45] have similar aims of lowering maintenance costs and reducing aircraft nonavailability times. These aims may be achieved by rescheduling corrosion rectification work where possible so that it is carried out during normal servicing and maintenance periods.

To implement the new approaches to corrosion management, a number of areas have been identified where improvements in current technology are required. These include more sensitive methods for detecting corrosion, the development of a better understanding of the impact of corrosion on structural integrity, and more effective supplementary protective materials to halt the spread of corrosion.

To detect the early stages of corrosion, improved NDE methods are required together with corrosion sensors to locate the onset of corrosion in 'difficult-to-inspect' areas. It has been proposed that sensors should be installed in potential corrosion problem areas within an aircraft during its manufacture. These would permit the first signs of corrosion to be detected and its progress to be monitored. In parallel with improved detection, there is a need for accurate, reliable models for predicting the long-term effects of corrosion on fatigue and static strength. These would allow decisions to be made concerning the scheduling of inspections and corrosion rectification. The application of better supplementary protection would further allow work to be delayed until programmed maintenance periods.

The new approaches to aircraft corrosion management are aimed at lowering the cost of ownership by reducing the time spent on unscheduled maintenance.

References

1. Wallace, W.; Hoeppner, D. W.; Kandachar, P. V. *AGARD Corrosion Handbook, Vol. 1: Aircraft Corrosion: Causes and Case Histories;* AGARD NATO, Neuilly-Sur-Seine: France, 1985; AGARD-AG-278, Vol. 1.
2. Mitchell, R. G. *Corros. Prevent. Control* **1981**, 11–17.
3. Kohler, R.; Scott, J. *The corrosion properties of airframe contaminants*, D. Mat Report No. 179; Ministry of Defence (PE) Directorate of Materials R & D (Aviation), 1971.
4. Bowden, D. Attack of the fungi, *Flight Safety Australia* Sept–Oct 2005, pp 50–51.
5. Akdeniz, A. *Aircraft Eng. Aerospace Technol.* **1996**, *68*(3), 3–7.
6. Defence Standard 00-970 Part 7/2 Section, Detail Design and Strength of Materials, Ministry of Defence, Directorate of Standardization, Kentigern House.
7. *ASM Handbook Volume 13B Corrosion: Materials*, ASM International, 2005.
8. Lapasset, G.; Barbaux, Y. *1st ONERA-DLR* Aerospace Symposium Paris; France, June 1999.

9. Lequel, P.; Lassince, P.; Warner, T.; Raynaud, G. M. *Aircraft Eng. Aerospace Technol.* **2001**, *73*(2), 147–159.
10. Polmear, I. J. *Light Alloys – Metallurgy of the Light Metals*; Arnold: London, 1995.
11. Lequel, P.; Lassince, P.; Macé, R.; Warner, T. Aeromat 2004 Conference, Seattle WA, June 2004.
12. *ASM Handbook Volume 13B Corrosion: Materials, Corrosion of Magnesium and Magnesium Base Alloys*; ASM International, 2005.
13. Blackburn, M. J.; Smyrl, W. H.; Feeney, J. A. In *Stress-Corrosion Cracking in High Strength Steels and in Titanium and Aluminium Alloys*; Brown, B. F., Ed.; Naval Research Laboratory: Washington, DC, 1972.
14. Fager, D. N.; Spurr, W. F. *Corrosion* **1970**, *26*(10), 409–419.
15. Smith, C. J. E.; Baldwin, K. R.; Hewins, M. A. H.; Gibson, M. C. In *Progress in the Understanding and Prevention of Corrosion*; The Institute of Materials, 1993; Vol 2, pp 1652–1663.
16. Wernick, S.; Pinner, R.; Sheasby, P. G. *The Surface treatment of Aluminium and Its Alloys*; ASM International, 1987.
17. *BS 2X33, Specification for Two Component Epoxy Primer for Aerospace Purposes*; British Standards Institution: London, 1998.
18. Jones, J. H. *Plating Surf. Finishing* **1990**, 20–22.
19. Khobaib, M.; Reynolds, L. B.; Donley, M. S. *Surf. Coatings Technol.* **2001**, *140*, 16–23.
20. Ihbe, T. Recent advances in appliqué film technologies for aerospace coatings Presentation at DoD Maintenance Symposium and Exhibition October, 2002.
21. Defence Standard 03-19. Electrodeposition of cadmium *Ministry of Defence*; Directorate of Standardization: Kentigern House, 2005.
22. Baldwin, K. R.; Smith, C. J. E. *Trans. IMF* **1996**, *74*(6), 202–209.
23. Validation of alternatives to electrodeposited cadmium for corrosion protection and threaded part lubricity applications; Engineering and Technical Services for Joint Group on Pollution Prevention (JG-PP) Projects Joint test report BD-R-1-1, 2002.
24. Legg, K. Evaluation of cadmium replacement alternatives for aircraft Presented at Aeromat Meeting, 2002. www.rowantechnology.com/Tech-Info-Cadmium.
25. Defence Standard 03-36. Guidance to the use of cadmium alternatives in the protective coating of defence equipment, Ministry of Defence, Directorate of Standardization, Kentigern House, 2005.
26. Sartwell, B. D.; Legg, K.; Bretz, P. E. Proceedings of AESF Aerospace Plating and Metal Finishing Forum, 2000; pp 131–139.
27. PD 6484:1979. Commentary on corrosion of bimetallic contacts and its alleviation British Standards Institution: London, 2003.
28. US Military Standard MIL-STD-889B. Dissimilar metals 1976.
29. Voss, H. J. AGARD Conference Proceedings 565, Corrosion Detection of Advanced Airframe Material 1995; pp. 21-1–21-18.
30. *BS 2X33: Specification for component polyurethane finish for aerospace purposes*; British Standards Institution: London, 1998.
31. Painting versus polishing of airplane exterior surfaces, Boeing Corrosion.
32. Lewin, J. B. G. In *Treatise on Coatings*; Myers, R. R., Long, J. S., Eds.; Marcel Dekker: New York, 1975; Vol. 4. Formulations Part 1, Chapter 1.
33. Boeing: Commercial Airplanes – Jetliner Safety – Airline's Role in Aviation Safety – Aircraft Maintenance Inspections. http://www.boeing.com/commercial/safety/airline_role.html.
34. Miller, D.; Irwin, S. *Materials Performance* **1991**, 10–13.
35. Koch, G. H.; Brongers, M. P. H.; Thompson, N. G.; Virmani, P.; Payer, J. H. Corrosion costs and preventative strategies in the United States, Appendix P Aircraft; CC Technologies Laboratories Report WA-RD-01-156, September 2001.
36. Smith, C. J. E.; Higgs, M. S.; Baldwin, K. R. RTO Meeting Proceedings 25, New Metallic Materials for the Structure of Aging Aircraft, 2000; pp 15.1–15.8.
37. Blackford, R. In Proceedings of 3rd Aerospace Corrosion Control Symposium, Amsterdam, Sawell Publications: England, 1994.
38. BS X35: Specification for Selectively removable intermediate coating for aerospace purposes, British Standards Institution, London, 1998.
39. BS X36: Specification for Paint remover for air drying selectively removable paint scheme for aerospace purposes, British Standards Institution, London, 1998.
40. Benavides, S. 9th FAA/DoD/NASA Aging Aircraft Conference 2005.
41. Senter, J. 9th FAA/DoD/NASA Aging Aircraft Conference 2005.
42. Cederquist, S. C. *Materials Performance* **2000**, 21–25.
43. Kinzie, R. 9th FAA/DoD/NASA Aging Aircraft Conference 2005.
44. Kinzie, R. C.; Peeler, D. T. 9th FAA/DoD/NASA Aging Aircraft Conference 2005.
45. Clark, G. RTO Meeting Proceedings 79(II) on Ageing Mechanisms and Control, 2003; 9-1–9-8.

4.39 Management of Corrosion of Infrastructure

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Abbreviations

ALWC Accelerated low water corrosion
CCTV Closed circuit television
GI General inspection
PI Principal inspection
SI Special inspection
UV Ultraviolet

4.39.1 Introduction

The term ‘infrastructure’ covers a wide range of industries involved in establishment and maintenance of an effective and functional industrialized society. These include structures such as bridges and tunnels for road, rail, and canal traffic, water treatment facilities for clean and dirty water, ports and harbors, and power generation and distribution systems. This accounts for a vast range of structures manufactured from a relatively small number of materials.

The materials employed in the construction of the infrastructure are predominantly masonry, structural steel, and reinforced concrete with certain materials dominating particular periods of infrastructure development. For example in the United Kingdom, the big push in the water industry in the Victorian era has left a large legacy of predominantly masonry built facilities, whereas the boom in highway construction in the 1960s resulted in large numbers of reinforced concrete bridges and other highway structures.[1]

During the second half of the twentieth century, the increased use in reinforced concrete allowed rapid and affordable construction of the much needed infrastructure in postwar Europe, but as discussed in the **Chapter 3.30, Degradation of Cement and Concrete** in this book, such materials are not without their own durability problems and corrosion risks.

4.39.2 Causes of Degradation

The commonest causes of degradation result from exposure to the environment, most notably UV radiation, water, and chloride ions. For marine structures, the chlorides are present in abundance in the surrounding environment. For nonmarine structures, the chlorides can come from deicing salts or admixtures in concrete. During winters, in much of Europe and North America, many hundreds of thousands of tons of rock salt is spread onto the road networks in an attempt to clear snow and ice. This is rarely followed up in the spring by any attempt to remove residual salt from the associated infrastructure, resulting in considerable chloride-related collateral damage in the following years.

Other branches of infrastructure have their own aggressive environments with which to deal. The water industry has to cope with a wide range of natural and artificial chemical environments. Freshwater can be acidic and soft, which can dissolve concrete and carbonaceous masonry and prevent the formation of calcareous scales upon which cast iron pipes rely for their corrosion protection. Anaerobic bacteria in sewage and other organic waste materials generate hydrogen sulfide, which can be oxidized into sulfuric acid by aerobic bacteria. Hydrogen sulfide is incredibly aggressive to ferrous materials, while sulfuric acid will attack most materials, including concrete.[2]

4.39.3 Consequences of Failure

There is a common thread that links the majority of infrastructure. The consequences of failure of infrastructure are often too great to contemplate, and typically a large number of people and livelihoods are affected. The results of a failure can be marked and potentially life threatening. However, there is a general cozy assumption in most societies that bridges do not collapse, power stations will continue to operate come what may, and the water supply will always be safe and available. This idyllic view relies totally on the quality of the inspection and maintenance regimes adopted for the infrastructure.

The basic management approach is that repair requirements are identified primarily via routine inspection programs. However, the fundamental problem is that repair work is severely constrained by the fact that the infrastructure is generally subject to public funding. In addition to cost limitations, infrastructure, by its very definition, often cannot readily be taken off stream. For a major road, it can only be closed for maintenance if there is a suitable alternative route. As a consequence, works often have to be carried out at night, or using innovative access methods. All of this can have a significant impact on the cost of the works, such that access and traffic management can often cost more than the actual repair.

Politically, funding for the maintenance of infrastructure is often given a relatively low priority. Such works are seen as disruptive, and given the general public perception that infrastructure does not deteriorate and is essentially maintenance-free, it may prove attractive to delay such works until absolutely essential. As a result of this, maintenance is commonly underfunded and there is often a significant backlog of critical maintenance. For example, a recent study identified that between 30% and 60% of bridges in the United States are deficient as the result of corrosion aggravated by the lack of proper maintenance programs.[3]

The management of infrastructure spending is often complex and involves allocating limited resources in the most efficient manner. This will usually be linked to a program of inspection, which feeds into a maintenance plan where works are prioritized. The development of effective inspection and reporting methods are, therefore, key to the operation of an effective infrastructure maintenance system. An example of such procedures is given later with respect to the inspection of highway bridges in the United Kingdom.[4]

4.39.4 Inspection Requirements

The basic procedure most commonly adopted is to use routine visual inspection by experienced personnel. This is an efficient method of gathering data but is aggravated by the nature of most infrastructure in being large and in near-constant use. Access for visual inspection may therefore be difficult and will often have to take advantage of temporary closures or offpeak working.

An additional factor is that most structures built more than 20 years ago did not necessarily consider the requirements for future inspection. In some cases, it was assumed that inspection would not be required. Structures were typically designed to prescriptive codes that were meant to ensure durability; however, material properties and safety factors and sometimes even exposure conditions changed over time. It was only when corrosion was being observed on a more widespread scale that it began to be considered as an issue, but even then the perception remained that if a structure was designed to the relevant code it will achieve the design life. The concept of design life is in fact not related to a period that a structure is expected to survive but rather a return period for a statistical loading regime, for example, a 1-in-100-year storm, or traffic loading.

As durability and future inspection was not considered to be an issue, access for such inspections was not incorporated into the design. The aim was to achieve a structure that was simple and cheap to construct. As a result, details are commonly encountered that are particularly vulnerable to deterioration, but all impossible to inspect.[5] A classic example in a bridge is the half joint as shown in **Figure 1**.

Joints are required to allow for thermal movement and are sealed to prevent debris and water from penetrating to the substructure. However, the material used as a sealant is typically not sufficiently durable, and the action of traffic and thermal movements of the structure will ultimately result in leaks. The water, plus any deicing salts or other aggressive chemicals present

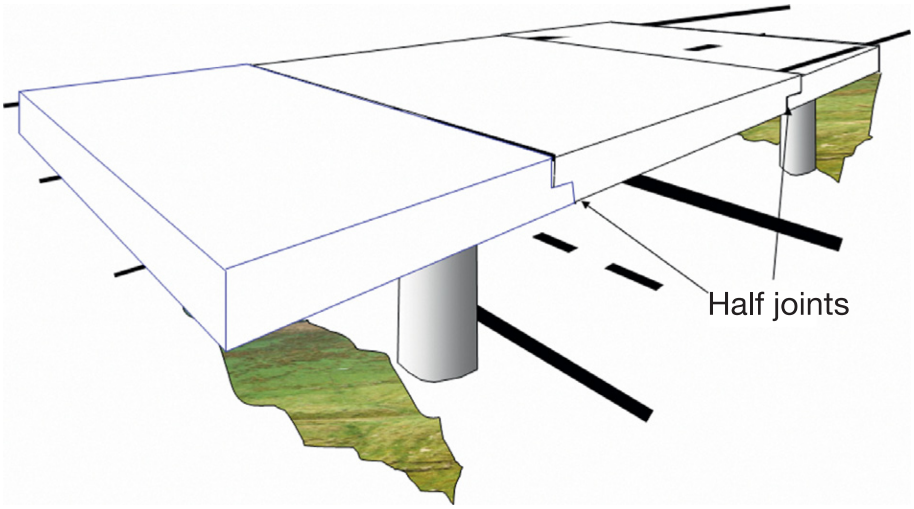

Figure 1 Bridge half-joints.

on the road surface, penetrates the joint and pond on the bearing shelf below where the bearings, now sat in a solution of chlorides and hydrocarbons, start to corrode. Chloride-laden water may also be running down the columns supporting the deck, penetrating the concrete and initiating corrosion of the steel reinforcement. The deck itself will be supported by beams of either steel or reinforced concrete, neither of which will benefit from exposure to the salty, contaminated water running through the joints.

Ports and harbors have obvious limitations on visual inspection, as large parts of the structures can be immersed. For steel sheet piling, corrosion is normally addressed by employing a corrosion allowance in the form of additional thickness of steel for tidal and atmospherically exposed areas. For the permanently submerged areas, the lack of oxygen at depth can stifle corrosion, but the action of microbes in the environment can lead to a phenomenon known as accelerated low water corrosion (ALWC) where large section losses in excess of 1 mm year^{-1} can be found in the vicinity of the lowest astronomical tide. This is far in excess of the corrosion allowance, and coincides with the area of highest structural load and the least inspectable part.

Similar problems occur for underground transit systems. These are often constructed from cast iron or reinforced concrete segments bolted together to form a tunnel. There may be a hydrostatic pressure across the joints between segments and rings, and the water may be contaminated with chlorides, sulfates, and other aggressive species.

There is a wide range of equipment available for assisting experienced personnel in carrying out visual inspections, such as endoscopes and CCTV equipment. Together with improved access equipment, these make the inspection of infrastructure safer and more effective. Figure 2 shows a hydraulic underbridge unit in use on a bridge inspection.

4.39.4.1 Inspection Methods

Besides any initial visual inspection, the inspection methods adopted may be destructive or essentially nondestructive. Commonly employed nondestructive tests for reinforced concrete that are able to assess structural integrity and remaining long-term performance are delamination tests, rebound hammer (compressive strength), covermeter survey, dust sampling, and half-cell surveys. Destructive concrete breakouts allow the inspection of the reinforcement and the determination of the depth of carbonation. The type and extent of the inspection usually depends on the initial visual observations.

Delamination tests can be carried out using a hammer to identify areas where cover concrete has spalled due to the expansive reaction of reinforcement corrosion. The formation of the more voluminous steel corrosion products, that is, the rust, results in the delamination of the cover concrete caused by induced stress exceeding the concrete tensile strength.

The depth of carbonation, a natural process by which carbon dioxide in the air forms carbonic acid which neutralizes the alkalinity, can be established by

Figure 2 Underbridge unit. Photo courtesy of Wemo-Tec GmbH.

applying phenolphthalein indicator to a freshly broken section of concrete. The change from colorless to purple indicates that the pH of this area is above 9, which in turn demonstrates that any steel reinforcement in the concrete should be protected from corrosion by the alkaline environment. Colorless areas show the concrete to be carbonated and the reinforcement to be at risk of corrosion. It should be noted that reinforcement can still corrode in an alkaline environment in the presence of chloride ion contamination.

The bar size and cover depth of reinforcement can be identified by means of a covermeter which generally use electromagnetic or eddy current techniques to locate the steel. Figure 3 shows an electromagnetic covermeter being used to locate prestressing tendons in precast concrete beams. Their use is limited to certain depths, which may be affected by the presence of a screed. Where the absolute size, depth, and condition of reinforcement need to be identified for the purposes of structural assessment, covermeter readings should be used in conjunction with destructive breakouts.

To determine the risk or occurrence of reinforcement corrosion, the structure can be tested with respect to chloride ion content and electrochemical activity of the steel within the concrete. The chloride content is usually determined from concrete dust samples obtained from different depths using a percussion drill.

The immediate surface is discarded, as it is likely to contain contaminants that are not representative of the bulk of the concrete. Incremental samples are then taken at depths that typically represent the cover, the environment adjacent to the steel, and the concrete beneath.

Half-cell potential surveys are a rapid method of establishing any corrosion ‘hotspots’ within key reinforced concrete elements. These may be defined as areas where corrosion of the reinforcement is likely to be occurring and differs in electrical potential from an adjacent area by more than 100 mV. There is considerable guidance on the use of this and other associated electrochemical techniques, and they provide a useful method of scanning large areas and identifying locations for other testing.[6] A typical output of a half-cell potential survey at 0.25 m centers where the red areas indicate highest corrosion risk is shown in Figure 4.

The Schmidt Hammer or rebound sclerometer test is a simple and quick nondestructive method to obtain an estimate of the compressive strength of concrete. It is a device that impacts a concrete surface with a sliding mass at a given energy as generated by a spring under a preset compression. The rebound of the sliding mass or hammer is governed by the hardness of the concrete

Figure 3 Electromagnetic covermeter used to locate steel reinforcement.

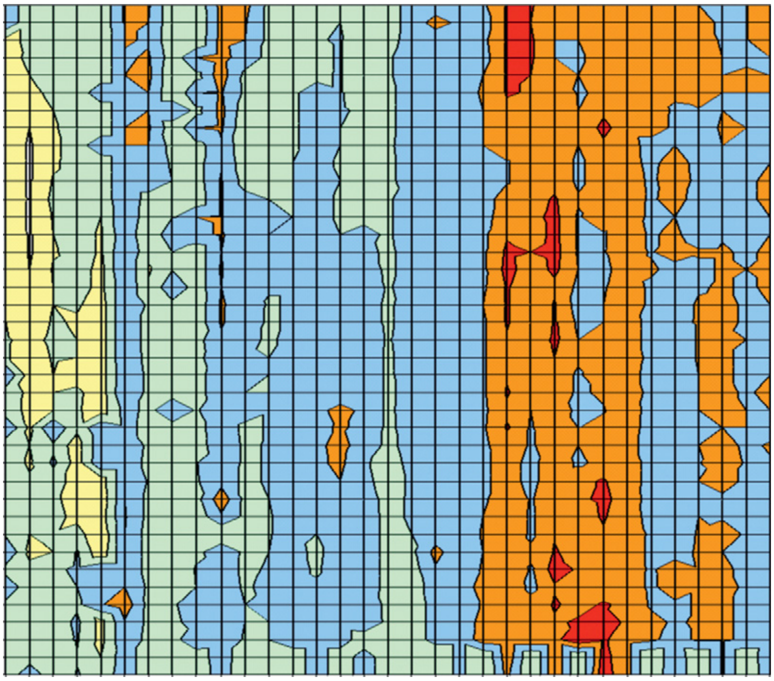

Figure 4 Typical results of a half-cell potential survey at 0.25 m centers, where the red areas indicate highest corrosion risk.

structure. As there is a relationship between hardness and compressive strength, the values obtained from the Schmidt Hammer can be converted into strengths for the area of concrete tested. The test should be carried out in accordance with relevant standards.[7] The results should be considered as an estimation of the actual strength and verified with conventional strength tests on cubes or cores taken from the structure.[8]

4.39.4.2 Remote Monitoring

There is a considerable range of embeddable probes currently available that can be employed to detect the onset and development of corrosion in large structures.[9] Such probes work best when installed at the time of construction, but in many cases, they are required to be retrofitted to existing structures wherein some degree of corrosion or other degradative process may already have occurred.

Selecting areas for the inclusion of probes is not without its problems. It is often relatively simple to identify the areas most likely to suffer from corrosion, such as under a joint, or elements where corrosion would constitute a significant risk, such as post-tensioned tendons. A specific length of motorway may have many thousands of potentially vulnerable areas, some of which will fail, while the majority will not. The chlorides from deicing salts will leak on to the substructure and then spread over the surface of the concrete and penetrate into the steel. A specific area, possibly less than a few square centimeters, may then start to corrode. The precise location of probes is therefore always going to be difficult as there is a significant chance that corrosion may be missed unless a large number of probes are employed in combination with regular visual inspections and other complementary monitoring techniques. Considerable effort is being directed towards the development of more effective monitoring systems that can assist in the long-term maintenance of complex infrastructure systems.[10]

4.39.4.3 Structural Considerations

The wide variety and complexity of infrastructure encompass a wide spectrum of loading requirements. For example, in pipelines the loading is relatively uniform and so areas of greatest concern are those areas where corrosion is most likely to occur and such areas therefore may be targeted for risk-based inspections. For liquid retaining structures, the load increases with depth and so at the design stage the structural capacity will increase with depth to accommodate this. For bridges, the loading similarly varies across each element and so the design will also vary to accommodate the necessary structural properties. As a consequence, for any given amount of corrosion each area will be affected to a different degree. A loss of 2 mm of steel thickness may not be considered significant in one location, but may be critical in another and, whereas a structural member may be able to tolerate the full loss of section in some areas, a pipeline cannot be allowed to form even the smallest perforation. As a result, the inspection cannot simply focus on areas of highest corrosion but must review the whole structure.

This is further aggravated by changes in the design approach adopted by the relevant statutory or advisory bodies. Over a period of time, the approach to the specific design requirements often changes as other factors become more significant. The purpose of parapets, for example, initially used to be essentially to form an edge to a structure. They are now required to provide effective vehicle restraint to faster and heavier impacts. The predicted loading has changed from simply being able to support the self weight and survive wind loading, to restraining a vehicle impact at 50 kph. Changes in the guidance and requirements mean that many structures will fail to achieve the standards laid down by the design codes. It can be tempting to adopt the approach of ‘it has not yet fallen down,’ but then all unexpected collapses are preceded by a prolonged period of inactivity, and hence the requirements for well-defined and carefully managed inspection regimes.

4.39.5 Highway Infrastructure

The 1980 Highways Act[11] established a statutory obligation to maintain public highways in the United Kingdom. However, the responsibility and procedures to be employed in this maintenance depended on the ownership of the structure. The primary routes are maintained by the Highways Agency, which is an executive agency of the Department of Transport. The remaining bridges fall under the responsibility of a wide variety of parties, such as local authorities, the railway and canal network, and other utilities where their structures pass over the highway.

The absence of a common code of practice has led to a range of different approaches being taken, which was less than desirable. To help clarify this situation, a document entitled ‘The Management of Highway Structures’ was published in 2005.[12] Its stated aims were “. . . to encourage and assist highway authorities and other owners to implement Good Management Practice, harmonise practices, coordinate approaches and share their experiences and practices.” Three key themes were identified, these being asset management planning and resource accounting, maintenance planning and management, and engineering processes.

Asset management may be defined as a strategic approach that identifies the optimal allocation of resources for the management, operation, preservation, and enhancement of the highway infrastructure to meet the needs of current and future customers. The asset management plan is a long-term view. Maintenance planning and management involves the development and implementation of cost-effective maintenance plans for highway structures that support the safe operation of the network while delivering the required levels of service. The maintenance plans typically cover both short- and medium-term actions and requirements.

The engineering processes are the necessary practical measures and data collection exercises. These include inspections to identify the current condition, assessments to identify the current capacity, and the approach to be taken to manage abnormal loads. These themes are supported by data and information, which are normally stored within a computerized bridge management system. This enables the data to be interrogated and manipulated to provide useful information on the structures and network.

Central to all of this is the inspection procedure. It is not possible to accurately assess a future maintenance requirement unless the existing condition is known. In order to achieve this, the code of practice proposes the following series of inspections, all of which are carried out by appropriately skilled and competent professionals.

1. General inspections (GI) are required every 2 years. They are primarily visual inspections carried out from readily accessible areas. As such, it is not expected that these will provide a comprehensive and detailed view of each part of the structure.
2. Principal inspections (PI) are carried out every 6 years, and the intention is that they are carried out within touching distance of all elements, unless suitable alternatives can be justified, for example, remote CCTV inspection of areas with difficult access.
3. Special inspections (SI) are carried out as and when deemed necessary. They can include inspections required as part of the assessment process. They can also include inspections carried out under the grounds of public safety, or inspections relating to acceptance of repair work or at a handover stage where maintenance responsibility is being transferred.

The Management of Highway Structures contains 17 recommendations, which, it states, should be implemented in a measured way. Three milestones are proposed.

1. Milestone 1 covers the adoption of processes necessary to provide highway structures that are safe to use, inspect, and maintain.
2. Milestone 2 adds the broad inclusion of additional processes necessary to provide highway structures that are fit for purpose and meet government requirements.
3. Milestone 3 imposes the adoption of processes necessary to deliver the agreed level of services at minimum whole-life costs and represents the full implementation of the good management practice set out in the code. It is stated that ideally the milestones should be implemented in order, but it is considered appropriate to progress to some actions in Milestone 3 before Milestone 2 is fully achieved.

The German standard for bridge monitoring and inspection states that GI of easily accessible areas should be carried out every 3 years and PI of the entire structure every 6 years.[13] SI should be carried out after certain events have occurred, such as flooding, hurricane, and accidents. The standard notes that all structural components such as protectively enclosed elements are to be inspected. The standard is based on a guidance from 1930 which dealt with the monitoring and inspection of cast iron highway bridges.

In Italy, an equivalent standard covers the inspection of highway structures.[14] It recommends that an inspection of those elements of the bridge visible from accessible areas should be systematically carried out. The aim of this inspection is to identify all the possible signs of deterioration such as cracking, superficial deterioration, moisture staining, exposure of steel bars, difference in color of concrete surfaces, and structural deformation. Depending on the result of this first inspection and on the structural characteristics and importance of the bridge, a more detailed inspection should be planned. The detailed inspection should be carried out at touching distance on all the elements of the structure including the foundations and the embankments.

Similar guidance is available in all countries with a significant highway-based infrastructure.

4.39.6 Other Infrastructure

Multiple storey car parking structures have featured in a number of high-profile failures in recent years.

The traditional approach of managing car parks has typically been to carry out the minimum level of maintenance possible, and owners, often private companies, have appeared unaware of the consequences of degradation. Innovative designs and rapid construction methods coupled with poor construction practices have often exasperated the problems. Many date from the early 1970s when the designs often did not include for a degree of robustness. This, combined with a lack of understanding of the corrosion processes, has resulted in many corroding structures with low factors of safety and an increased risk of failure or collapse. Figure 5 shows the typical appearance of such structures with patching of the damaged areas.

Following on from the collapses, guidance documents were produced in the United Kingdom with regard to the design, maintenance, and refurbishment of multistorey car parks.[15] The guidance followed similar lines to those contained within the bridge management code of practice, namely that the current condition and load-carrying capacity should first be established and a more active inspection and maintenance regime be implemented. This included benchmarking using appropriately qualified and competent personnel to establish the current condition. In addition, routine inspections were recommended by on-site staff to identify areas such as blocked drainage which would produce future durability issues.

The majority of other maintainers in the United Kingdom and elsewhere are generally private companies. These tend to be left to carry out their own procedures, although obviously any major incidents would be investigated. Shortfalls that result in the health and safety of employees or the public being put at risk or those that adversely affect the environment would be expected to result in criminal prosecutions under the relevant statutes.

Street lighting and signage is another area that at first glance would not appear to be a significant problem other than periodic maintenance of the luminaires. However, the lights and signs are typically fixed at height to large posts which are generally fabricated from metal or reinforced concrete and therefore subject to corrosion in aggressive environments, as well as suffering occasional unreported impact damage.

Inspection of the posts for internal and external corrosion is not in itself particularly onerous or technically challenging. It is the shear number of units requiring inspection that lead to concerns. Kent County Council in the United Kingdom with an area of 3736 km^2 and a population of 1.6 million reports having a total of 113 000 street lights, 14 000 lighted signs, and 5500 bollards. Extrapolated to the

Figure 5 Multiple patch repairs to car park deck.

whole country, this would equate to something in excess of 4 million lighting and signage posts requiring periodic inspection and maintenance. With such large numbers to deal with, the occasionally reported failures must represent a very small percentage of the whole.

References

1. Baldwin, P.; Baldwin, R. *The Motorway Achievement. Volume 1: Visualisation of the British Motorway System: Policy and Administration*; Thomas Telford Publishing: London, 2004.
2. Lambert, P.; Ecob, C. R. *The Degradation and Protection of Reinforced Concrete Sewers*; Coatings & Linings for the Water Industry: Prague, Czech Republic, 1995; p 65.
3. Larsen, K. R. *Mater. Perform.* **2009**, *8*, 30.
4. The Highways Agency. *Inspection Manual for Highway Structures. Volume 1: Reference Manual*; The Stationary Office: UK, 2007.
5. Lambert, P.; Norris, P. *Struct. Faults Repair, Edinburgh* **1993**, *1*, 111.
6. The Concrete Society. *Electrochemical Tests for Reinforcement Corrosion*, TR 60; The Concrete Society: UK, 2004.
7. BS EN 12504 Part 2. Testing Concrete in Structures. Non-Destructive Testing. Determination of Rebound Number, British Standards Institute, 2001.
8. BS EN 13791. Assessment of In-Situ Compressive Strength in Structures and Pre-Cast Concrete Components, British Standards Institute, 2007.
9. Song, H.-W.; Saraswathy, V. *Int. J. Electrochem. Sci.* **2007**, *2*, 1.
10. Buenfeld, N. R.; Davies, R. D.; Karimi, A.; Gilbertson, A. L. *Intelligent Monitoring of Concrete Structures*; CIRIA: London, 2008.
11. Department of Transport. *Highways Act*; The Stationary Office: UK, 1980.
12. Department of Transport. *Management of Highway Structures*; The Stationary Office: UK, 2005.
13. DIN 1076. Highway Structures – Testing and Inspection, Deutsches Institut Fur Normung, 1999.
14. Italian Standard No. 34233. Planning, Execution and Testing of Bridges; Circolare del Ministero dei Lavori Pubblici, 1991.
15. Institute of Civil Engineers National Steering Committee. Inspection and Maintenance of Multi-Storey Car Parks, Thomas Telford: London, 2002.

4.40 Management of Corrosion in the Petrochemical and Chemical Industries

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Abbreviations

AE Acoustic emission
API American Petroleum Institute
EAC Environmentally assisted cracking
ECN Electrochemical noise
ESCC External stress corrosion cracking
FEP Fluorinated ethylene propylene
FFS Fitness for service
FRP Fiber reinforced plastic
FSM Field signature monitoring
HB Brinell hardness number
HDPE High-density polyethylene
HIC Hydrogen-induced cracking
HV Vickers hardness number
LDPE Low-density polyethylene
MSD Materials selection diagram
NACE National Association of Corrosion Engineers
NDE/T Nondestructive examination/testing
PE Polyethylene
PEEK Polyetherketone
PIR Polyisocyanurate
PP Polypropylene
PTFE Polytetrafluoroethylene
PVC Polyvinyl chloride
PVDF Polyvinylidene fluoride
PEC Pulsed eddy current
PWHT Post-weld heat treatment
RBI Risk-based inspection
SCC Stress corrosion cracking
SCW Super critical water
SHE Safety, health and environment
SOHIC Stress-oriented hydrogen-induced cracking
SSC Sulfide stress corrosion
TLA Thin layer activation
UT Ultrasonic testing

Symbols

bar Pressure of $10^5\,\mathrm{N\,m^{-2}}$
°**C** Temperature, degrees Centigrade
mm Millimeter
t Tonne, metric ton, 1000 kg

4.40.1 Industry Scope

Petrochemicals and chemicals manufacture comprises a major sector of most developed and developing economies. The primary feed-stocks are oil, gas, and naturally occurring materials that are processed in large quantities in world scale plants to produce refined oil products and commodity chemicals. Downstream processing is undertaken in progressively smaller plants to produce the wide range of complex chemical products that are demanded by developed economies. Value is added through each stage of processing so that at the end of the chain, fine chemicals and pharmaceuticals, although manufactured in relatively small quantities, are very significant economically because of their high intrinsic value.

The industry is driven by the usual commercial imperatives. It strives to create value through new and improved products and processes, increased energy and resource efficiency, and improved manufacturing performance. At the same time, the industry is acutely aware of its societal obligations to comply with safety, health, and environmental (SHE) expectations and regulations that preclude loss of containment incidents.

4.40.2 Risks to Industry Equipment

Process plants, typified in Figure 1, are assembled from standard equipment items that are subdivided conventionally as follows:

1. storage tanks;
2. pressure vessels – reactors, heat exchangers, columns for distillation/fractionation/stripping, storage spheres/tanks, etc.;
3. fired equipment – furnaces, heaters, boilers, etc.;
4. machines – gas/steam turbines, compressors, expanders, pumps, etc.;
5. piping – including valves, venturi tubes, orifice plates, etc.;
6. instrumentation – measuring temperature, pressure, concentration, flow, etc.;

Industry equipment operates over wide ranges of temperature and pressure as well as in a wide range of corrosive environments. Operating conditions for some common items of industry equipment are summarized in Figure 2. Thus, liquefied hydrocarbons are stored at atmospheric pressure at extremely low, subzero temperatures, while furnace tubes may operate at significant pressures at temperatures around 1000 °C. Crude oil is distilled at atmospheric pressure, or even under vacuum, while hydrocrackers and ammonia/methanol converters operate at pressures in the range 200–300 bar at temperatures that can be well above 400 °C. Some processes for the manufacture of low-density polyethylene (LDPE) operate at pressures as high as 3000 bar.

At the extremes, the temperatures and pressures at which industry equipment is required to operate present significant challenges to the properties of available engineering materials. Design codes for industry equipment provide protection against mechanical failure due to ductile overload, brittle fracture, fatigue and creep mechanisms. However, industry equipment is also vulnerable to failure modes associated with the full range of corrosion and/or wear mechanisms during operation, and design codes offer only very general guidance as to the mitigation of such risks in specific applications.

Historically, piping and storages have proved the likeliest types of equipment to give rise to major incidents,[1] as recorded in Figure 3. This is to some

Industry scope:

- Petroleum refining
- Petrochemicals
- Commodity chemicals
- Fine chemicals
- Pharmaceuticals

Equipment

- Storage tanks
- Pressure vessels
- Fired equipment
- Machines
- Piping
- Instrumentation

Figure 1 Process plants, regardless of size/complexity, are assembled from standard equipment items.

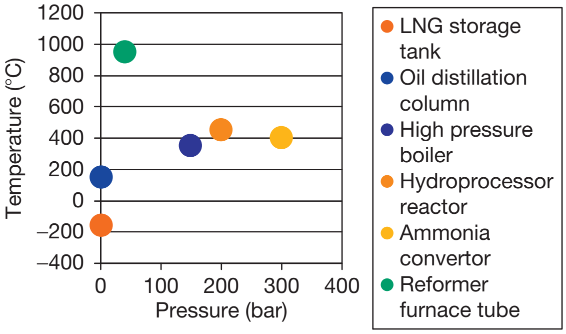


Figure 2 Operating conditions for common items of petrochemical/chemical industry equipment.

extent counterintuitive and is probably a reflection of their lower historical priorities in the management of structural integrity compared to more obviously vulnerable equipment types such as pressure vessels or machines. Regarding mechanisms of failure, periodic surveys have confirmed that cracking, in particular environmentally assisted cracking (EAC), and general corrosion are the commonest causes of equipment failure in the industry as, for example, in a recent survey of the refining/petrochemical industry in Japan[2] from which **Figure 4** is adapted.

These corrosion risks have to be managed to preclude major incidents and eliminate avoidable costs. A number of sources provide comprehensive overviews of the mitigation of corrosion risks in the process industries.[3–8] The challenge is to select materials, protection procedures, and fabrication procedures for equipment that enables value creation while containing SHE risks within acceptable limits. Corrosion management is a life cycle process, the available tools for which are:

1. At the equipment design stage, selecting corrosion-resistant materials and protection practices and adopting good design practices for equipment that mitigate corrosion risks.
2. Throughout the operating life, dimensioning and understanding the corrosion performance of

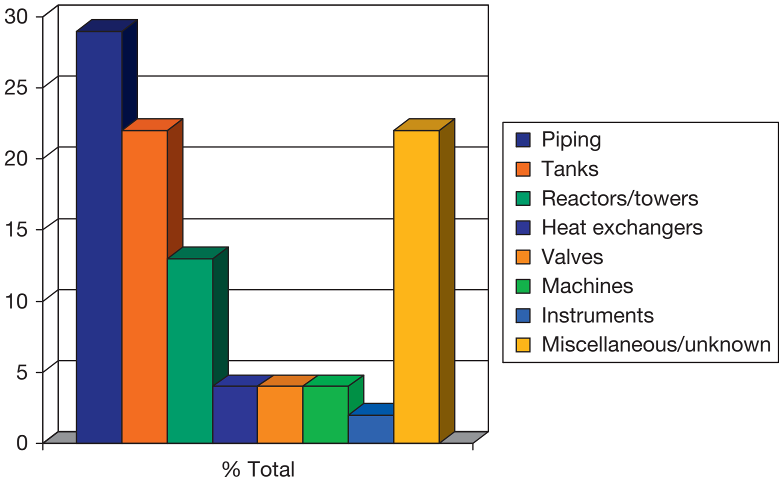


Figure 3 Types of process equipment involved in 170 major industry losses over 30-year period. Adapted from Garrison, W. G. *Hydrocarb. Process.* **1988**, *67*, 115–122.

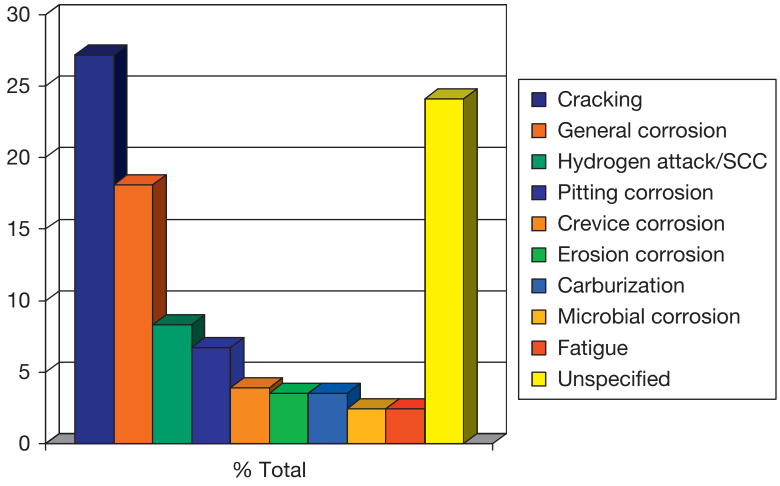


Figure 4 Causes of failure in refining/petrochemical equipment. Adapted from Katsumi, Y. *Corros. Eng.* **2004**, *53*, 185–189.

equipment and managing corrosion control practices to assure structural integrity and provide increased reliability and availability.

3. At all stages, promoting awareness and commitment among engineers and managers.

4.40.3 Materials and Protection Practices for Process Equipment

4.40.3.1 Materials

Most classes of materials find use in process industry equipment because of the wide ranges of temperatures, pressures, and corrosive environments that have to be tolerated. The approximate capabilities of the more important classes of material as a function of temperature are charted in Figure 5. The needs of the process industries for equipment to withstand ever more demanding conditions have provided significant drivers for the development of new and improved grades of engineering materials across all classes that are too numerous to mention here but are described in detail in this book in the relevant chapters on materials.

The strength and ductility required for the safe operation of pressurized equipment are confined mostly to metallic materials, although some lower-pressure/temperature systems are constructed in thermoplastic and fiber reinforced plastic (FRP) materials. Carbon and carbon–manganese steels are workhorse materials for process equipment because of their low relative cost, but they have limited strength and ductility at high and low temperatures respectively, as well as poor corrosion resistances. A number of low-alloy steels also find significant usages:

1. Chromium–molybdenum–vanadium steels provide improved strengths at the temperatures that are required for handling environments such as steam and that occurring in hydroprocessing. They also provide increased resistance to hydrogen-containing gases at elevated temperatures.
2. Chromium steels provide improved resistance to high temperature corrosion, particularly in gases containing hydrogen sulfide.
3. Nickel steels provide improved ductility for low-temperature duties, in particular for the storage of liquefied gases and hydrocarbons.

Higher-strength medium- or high-carbon grades of steel generally lack the ductility for pressure containment duties but find uses in machines as materials for shafts, gears, punches, extrusion dies, cutting tools, etc.

The austenitic and duplex stainless steels and nickel alloys provide acceptable strengths and ductility over much wider temperature ranges than steels as well as much greater corrosion resistance, and they are widely used for process equipment.

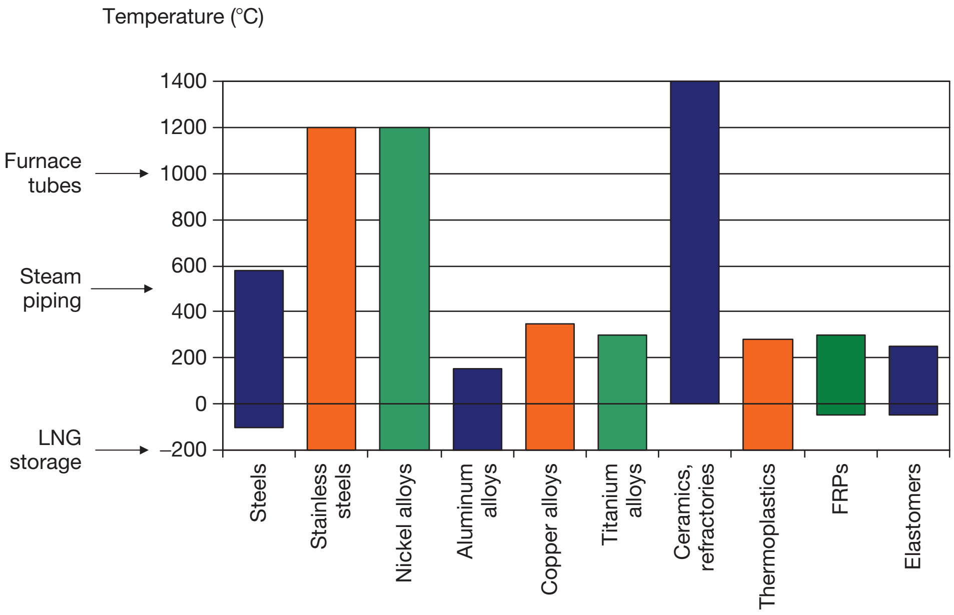


Figure 5 Approximate temperature capabilities of materials in process equipment.

Specific grades have been developed to address specific corrosion risks in the process industries such as resistance to stress corrosion cracking and pitting/crevice corrosion, reducing and oxidizing acid corrosion and specific high temperature corrosion phenomena. Ferritic, martensitic, and precipitation hardening stainless steels also have useful corrosion resistance but have weldability and potential ductility issues that constrain their use for pressure containment. Ferritic stainless steels find most uses in relatively thin section components such as heat exchanger tubing. Martensitic and precipitation hardening stainless steels find uses where stronger materials are required such as shafts, impellers, valve springs, bolting, etc.

The other alloy classes find niche uses in process equipment:

1. Titanium, zirconium, and tantalum alloys have excellent corrosion resistance, but their applications are constrained by their relatively high cost and limited strength at higher temperatures that are offset to some extent by deploying them as linings on steel substrates.
2. Aluminum alloys have restricted corrosion resistance and are mostly confined to relatively noncorrosive applications such as storage tanks and silos.
3. Copper alloys find niche applications arising from their corrosion resistance in relatively low-temperature applications including heat exchanger tubing and tube plates, and pumps and valves.
4. Cobalt alloys are used mostly for their excellent resistance to wear in equipment that handles solids and slurries.
5. Lead alloys find continuing but declining uses as lining materials for tanks and vessels handling principally sulfuric and phosphoric acids.

Nonmetallic materials find important and increasing usage in process equipment, some of which are illustrated in Figures 6 and 7. Refractory linings are deployed routinely as thermal protection for steels, allowing them to operate at the temperature ranges within which they have adequate strength for pressure containment. For corrosion resistance, chemically resistant brick and glass linings have also found significant application. In general, solid engineering ceramics lack the ductility to deploy directly for pressure containment. However, they are highly corrosion resistant and find increasing usage as internal components of equipment for corrosive duties as illustrated in Figure 6. These applications include heat exchange duties in the cases of impervious graphite and silicon carbide that are thermally conducting.

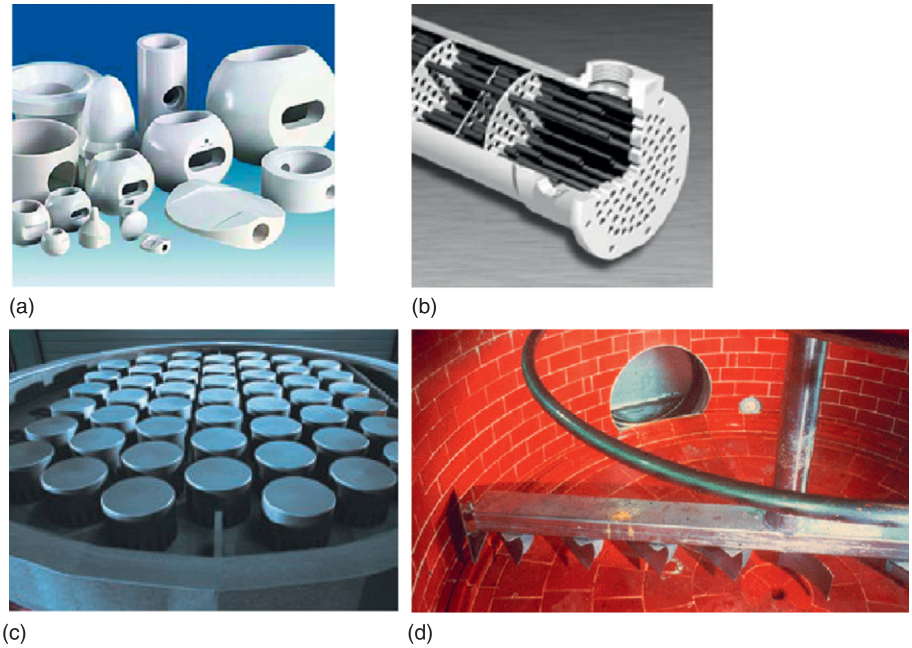


Figure 6 Process equipment internal components constructed in engineering ceramics: (a) partially stabilized zirconia valve components,[9] (b) silicon carbide heat exchanger tubing,[10] (c) impervious graphite bubble cap tray,[11] (d) acid-resistant brick-lined vessel.[12]

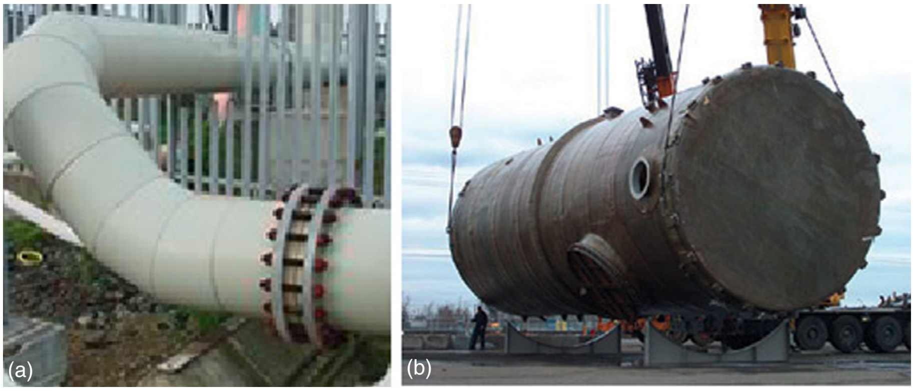


Figure 7 Process equipment items constructed in plastics (a) 60 cm diameter polypropylene piping. Reproduced from www.ianflockton.co.uk (b) ~1000 m^3 PVDF-lined GRP vessel. Reproduced from www.chemicalprocessing.com

Thermoplastic and FRP materials have also found significant and increasing usage in process equipment because of their wide ranging corrosion resistance. Some of the more common materials (polyethylene (PE), polypropylene (PP) and polyvinyl chloride (PVC)) compete favorably with steel on cost. In the case of the higher-performance thermoplastic materials such as the fluoropolymers (PVDF, FEP, PTFE) and polyetheretherketone (PEEK), useful properties persist up to relatively high temperatures, albeit at a cost. There are available design codes for solid thermoplastic and FRP tanks, vessels, and piping systems. Allowable combinations of pressure and size are constrained by the relatively low strengths and temperature tolerances of the relevant materials, but at low temperatures and pressures, relatively large fabrications are achievable as illustrated in Figure 7. Pressure and size restrictions are overcome to some extent by deploying the materials as coatings and linings on stronger, tougher substrates. Thermoplastic linings can be used on FRP substrates in so-called dual laminate constructions. Alternatively, thermoplastic, FRP and elastomeric linings are used on steel substrates. Elastomers also have essential uses in sealing materials.

4.40.3.2 Protection Practices

4.40.3.2.1 Coatings and linings

Thin paint coatings, generally <0.5 mm thick, are used routinely for the protection of structural steelwork and external surfaces of steel equipment against atmospheric corrosion and also find uses for the internal protection of process equipment.[13] Thicker coating systems up to ~2 mm[14] are available for the internal protection of storage tanks, vessels, and pipelines based on heat-cured fluoropolymer and other resin systems that may be reinforced with wire mesh and antipermeation layers for particularly corrosive duties.

Metallic coatings also find uses. Dipped zinc and zinc/aluminum coatings are commonly used for the protection of structural steelwork in chemical plants, but their use on equipment surfaces is constrained by any attendant risks of liquid metal embrittlement (LME). Thermal spray coatings of, for example, aluminum or stainless steels sealed with organic materials are sometimes used for repair and protection against relatively low corrosion rates. Thermal spraying is also used to apply a wide range of erosion-resistant coatings, including nickel- and cobalt-based alloys, sometimes incorporating hard materials such as carbides.

Relatively thin coatings are more likely to contain defects than thicker linings which are generally favored as the more prudent option for protection where substrate corrosion rates are likely to exceed ~0.5 mm year^{-1}. Linings are used where the cost and/or mechanical properties of the corrosion-resistant material preclude its use in solid form. Metallic linings are applied by one of the following processes:

1. Roll bonding; routine for stainless steels and nickel alloys on steel, typically 1.5–5 mm thick.
2. Explosive bonding; especially for metals that cannot be fusion bonded to steel such as titanium, zirconium, and tantalum, 3–25 mm thick.
3. Weld overlaying; mainly stainless steels, nickel alloys, and hard surfacing alloys, up to 25 mm thick.
4. Wallpapering; in which thin sheets, typically 1.5 mm thick, are welded intermittently to substrates and sealed with overlaps that are welded continuously,

for stainless steels and nickel alloys on large areas such as ducts.

5. Loose lining; for expensive materials such as tantalum, typically 0.5 mm thick.

Thermoplastic, FRP and elastomer linings, up to ~5 mm thick, are preferably bonded to the substrate, usually steel, but in some applications rely on mechanical bonding such as in the case of swaged thermoplastic linings in steel pipes. Bonded glass linings up to ~2 mm thick and much thicker brick linings continue to find significant uses.

4.40.3.2.2 Inhibitors

The principal uses of inhibition in chemical plant is in the control of corrosion in steam raising and cooling water systems that are covered in separate chapters in this book. However, inhibition finds niche uses in the control of process corrosion, such as in the control of crude unit overhead corrosion[15] and the control of corrosion in CO_2 removal systems.

4.40.3.2.3 Electrochemical protection

Cathodic and anodic protection are described in separate chapters in this book. Cathodic protection finds conventional uses for the control of external corrosion of immersed and buried steel infrastructure and pipelines. Anodic protection is based on the development and/or consolidation of protective films on steel and stainless steel equipment to control corrosion at acceptable rates and prevent unacceptable contamination of process fluids with corrosion products. The main commercial applications of anodic protection are in sulfuric acid storage tanks, piping and coolers and in pulp digesters and storage tanks handling caustic kraft liquors in the pulp and paper industry.

4.40.3.3 Selection of Materials and Protection Practices for Process Equipment

The procedures that are used to select materials and protection practices and to factor costs into the selection process are described in separate chapters in this book. One of the more important requirements is that the level of risk inherent in the outcome is understood and aligned to the overall philosophy for managing technical and commercial risks in the specific application. The extent to which such risks need to be quantified rigorously depends upon the application and, in particular, the consequences of corrosion failure.

In the process industries, the SHE risks inherent in the selection of materials and protection practices are embedded in the hazard study methodologies[16] that are deployed throughout process and equipment design at its various stages. Such methodologies attempt to ensure that the risks are contained within the acceptable, defined limit values. Risks, including those arising from the selection of materials and protection practices, are evaluated and mitigated by teams of functional professionals, including materials/corrosion engineers.

In the process industries, the semiquantitative evaluation of corrosion risks is normally regarded as sufficient, based on the essentially empirical corrosion data that is used to predict corrosion performance, the reliability of which is normally classified as of high, medium or low reliability, depending on the source. For example, the American Petroleum Institute classifies the reliability of corrosion data as follows[17]:

1. High-reliability sources – extensive field data through inspection, test coupon data from >5 years' exposure in operating equipment.
2. Moderate reliability sources – laboratory testing with simulated process conditions, limited operating plant corrosion coupon testing.
3. Low-reliability sources – published data, corrosion rate tables.

It is vital that the selection of materials and protection practices are documented to capture the know-how that they embody, record any changes that are required and render the information accessible to the wider community of engineers and managers concerned with the design and operation of process equipment. The use of materials selection diagrams (MSDs) is being adopted increasingly for these purposes.[18] MSDs comprise simplified process flow diagrams showing relevant operating conditions together with materials selection information and any associated corrosion protection practices. These diagrams capture the information needed to ensure that materials selection decisions for the many specific items of equipment that comprise the final plant (vessels, piping, machines, instrumentation) incorporate the outcomes of corrosion-risk identification and evaluation, together with any necessary mitigation practices, for the relevant operating conditions. This is particularly important to mitigate the risks of deficient information transfer across organizational boundaries when materials selection decisions are spread across several supplier organizations.

4.40.4 Mitigation of Corrosion Risks by Good Detailed Design, Procurement, and Construction Practices

The extent to which detailed design may have a significant influence on corrosion risk and its mitigation is covered in a separate chapter in this book that includes many examples of bad and good practices relating to the design of process equipment, particularly in relation to environmental, thermomechanical, geographic or geometric, and galvanic compatibility factors. Probably, the greatest corrosion risk to process equipment at the design stage arises from the difficulties in anticipating and defining the development of aggressive local chemistries under the following influences:

1. Concentration by repeated wetting/drying cycles on hot surfaces under thermal insulation, on heat transfer surfaces, and at wind and water lines.
2. Concentration in crevices and beneath scales/deposits.
3. Condensation onto surfaces below critical dew points.

Examples of the first two risks and their mitigation in relation to the design of heat exchangers are given in this book in the chapter on design. An example of condensation-induced risk is summarized in **Figure 8** which shows a section through the bottom of a steam reformer tube where the tube is welded to a branch on a refractory-lined header beneath a furnace base. The tube has cracked along the fusion line between a nickel alloy weld joining the low-alloy steel header branch to the cast stainless steel reformer tube, resulting in leakage of process gas. The cause of the problem is that the section of tube around and below the dissimilar weld behind some insulating refractory operates intermittently below the dew point of the process gas that is nominally ~160 °C. The condensate is acidic because of its CO_2 content resulting in corrosion of the low-alloy steel branch bore, and environmentally assisted cracking of hard material that is formed during welding along the fusion line between the nickel-alloy weld and the low-alloy steel branch. The root cause of the problem lies in the design that allows a damaging microenvironment to develop around a dissimilar metal weld as a result of repeated condensation/dry out events. The risk is mitigated by changing it to a 'hot bottom' design for the reforming furnace in which the temperature of the dissimilar metal weld is maintained permanently above the dew point of the process gas.

During the procurement and construction stages, additional corrosion risks may be incurred if the correct materials and protection practices are not procured or deployed according to specification. An example of the very expensive consequences of failure to implement correctly a specified corrosion-risk mitigation practice is shown in **Figure 9** that relates to an economizer on a nitric acid plant. The vertical, tubular

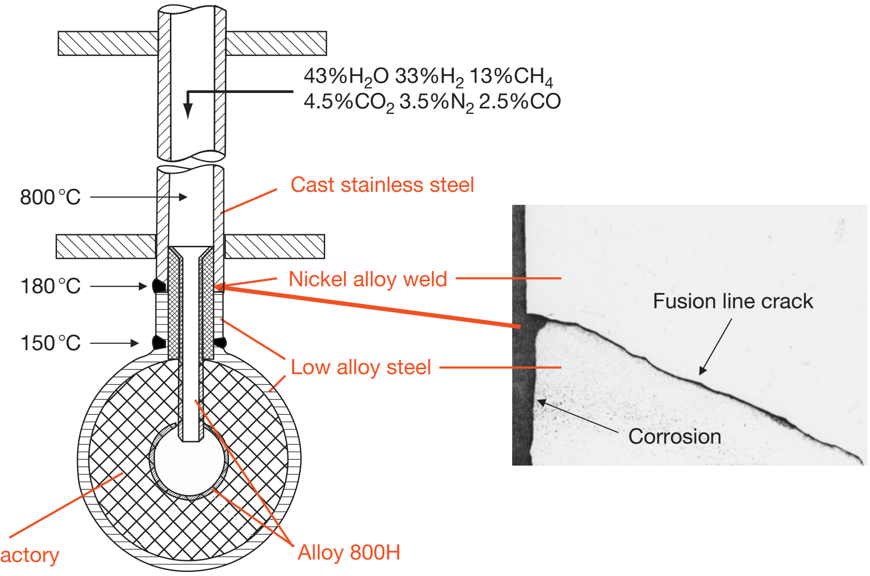


Figure 8 Environmental cracking of a dissimilar weld attaching a reformer tube to a header resulting from intermittent condensation of the process gas, dew point ~160 °C, behind insulating refractory.

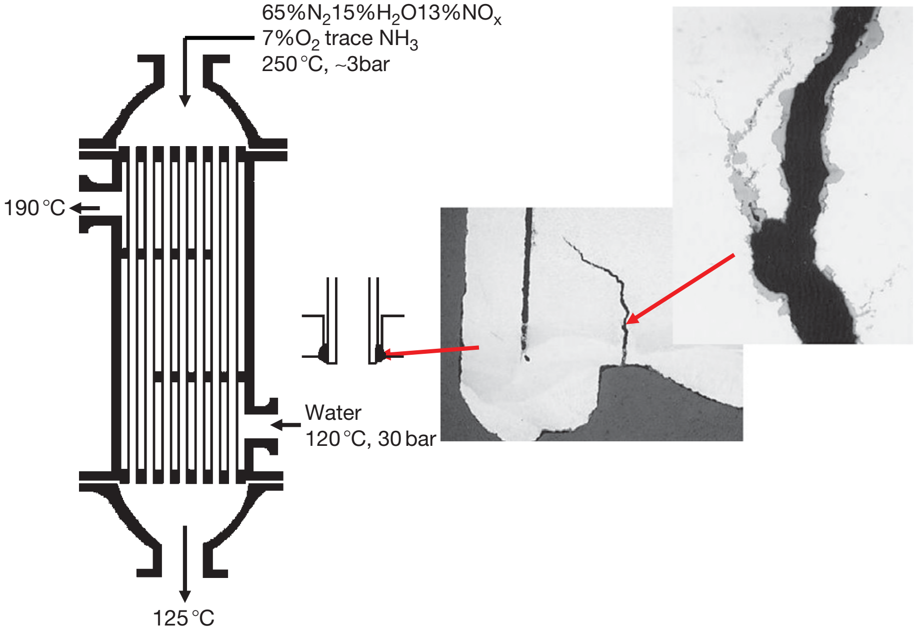


Figure 9 Nitrate stress corrosion cracking of steel tube plate of a nitric acid plant economizer during plant startup because of poor thermal stress relief during fabrication.

heat exchanger is used to preheat boiler water with the hot, gaseous products of ammonia oxidation. Such vessels are routinely constructed in carbon steel and are operated sufficiently hot in service to preclude condensation of nitric acid that would result in severe corrosion. However, during startup there are significant amounts of unreacted ammonia present in the process gas and condensation of ammonium nitrate solution can occur on the relatively cool bottom tubeplate, presenting a risk of nitrate stress corrosion cracking to stressed carbon steel. The risk was mitigated by revising the stress relieving procedure in collaboration with the fabricator to ensure that the vessel be thermally stress relieved as a last stage of fabrication. In the case of the failure summarized in Figure 9, the vessel was inadequately stress relieved and, as result, suffered such rapid nitrate stress corrosion cracking that the bottom tube plate leaked during the startup procedure. The risk was mitigated by reviewing the stress-relieving procedure with fabricator to ensure that residual stresses were reduced below the SCC threshold.

4.40.5 Mitigation of Specific Corrosion Risks

4.40.5.1 External Corrosion Risks

Carbon steel and reinforced concrete infrastructure such as structural steelwork and pipe bridges is vulnerable to atmospheric corrosion in chemical plants that may be exacerbated by contamination of the atmosphere by process fumes and/or fluids and is mitigated by the use of appropriate coatings. More insidious corrosion risks arise on carbon and low-alloy and stainless steel equipment surfaces beneath fireproofing and thermal insulation materials. Passive fireproofing materials are based normally on Portland cement or lightweight concretes (e.g., vermiculite). The most commonly used thermal insulation materials are organic foams such as polyisocyanurate (PIR) foam, mineral wool and calcium silicate that are preferred for cold (below ambient), warm (typically $<\sim 350\,°C$) and hot (typically $>\sim 350\,°C$) duties, respectively. The insulation is normally overlaid with mastic or clad with metal to prevent water ingress.

Corrosion risks arise when water from rainfall, cooling tower spray, leakage or spillage, fire deluge systems or other sources penetrates through cracks in the fireproofing or gaps in the outer insulation system arising from the loss of weatherproofing because of poor design and/or construction, deteriorated seals or mechanical damage. Corrosion risks are increased if water is entrapped on horizontal surfaces without drainage or in the annular spaces between equipment surfaces and deteriorated protective coatings, thermal insulation or fireproofing. The corrosivity of the entrapped water depends on the composition of the fireproofing or insulation material. Portland cement and calcium silicate produce relatively alkaline solutions that are least aggressive. Mineral wool produces relatively neutral solutions but organic foams can produce relatively acid extracts that are particularly aggressive. The corrosivity is further increased by acid fumes and accumulations of chlorides from coastal atmospheres, road salt and other sources which are further concentrated on hot equipment surfaces by repeated wetting/drying cycles.

Carbon and low alloy steels are vulnerable to general corrosion in the temperature range −5 to ∼150 °C. Below −5 °C, corrosion rates are very low and above ∼150 °C surfaces are dry, although thermal cycling across the boundary temperatures can reintroduce corrosion risks. Corrosion rates peak in the temperature range 80–100 °C within which corrosion rates up to ∼5 mm year^{-1} have been recorded. Particularly, vulnerable design features include penetrations of the insulation cladding at vents, drains, hangers, supports, valves, ladders, platforms and similar features, steam-traced systems, stiffening or insulation support rings and other water trap features and improper sealing at flange terminations, or hardened, cracked, or separated sealants. A classic example of corrosion of a warm vessel shell that experienced sustained exposure to water held up in a non-draining stiffening ring is shown in Figure 10(a). Austenitic stainless steels under thermal insulation in the temperature range ∼50–150 °C are significantly vulnerable to external, chloride-induced, stress corrosion cracking (ESCC). Above ∼150 °C, the risk is negligible because surfaces are dry although periodic cycling to lower temperatures reintroduces the risk. Below ∼50 °C, the initiation and propagation of stress corrosion cracks are possible, depending on the hygroscopicity of the salts that are present, but operating experience confirms that the practical risks are very small for most process applications. A typical example of ESCC of an austenitic stainless steel pipeline from which the insulation has been removed is shown in Figure 10(b).

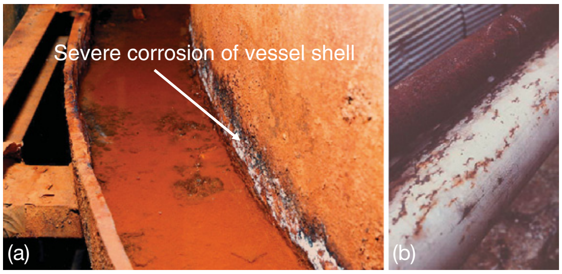


Figure 10 External corrosion under thermal insulation (a) general corrosion of carbon steel vessel shell and (b) external stress corrosion cracking of austenitic stainless steel pipe.

In a recent study of the costs of corrosion to the UK chemicals and petrochemicals sector,[19] external corrosion emerged as the largest individual source of expenditure on corrosion in the industry. This is, in large measure, a legacy cost associated with the remediation of elderly assets that were designed and constructed to standards that are now recognized as deficient in relation to the mitigation of external corrosion risks. The industry has devoted considerable effort to the mitigation of external corrosion risks and the resulting guidance has been codified.[20–22] For new equipment, the options are

1. Design of equipment to prevent water ingress by shedding water away from joints that are sealed effectively, and to prevent water hold-up by the provision of effective drainage.
2. Application of coatings that may be organic, if compatible with the service temperature range, or metallic; particularly, thermally sprayed aluminum (TSA) coatings and aluminum foil[23] have been identified as cost-effective for carbon and stainless steels, respectively.
3. Selection of corrosion-resistant materials for equipment; for small pipe sizes, austenitic stainless steel is an economic alternative to protected carbon steel for service temperatures below ∼50 °C, and for equipment that operates at temperatures in the vulnerable range for ESCC, duplex grades of stainless steel may be an economic alternative to protected austenitic stainless steel.
4. Control of insulation composition, principally by the avoidance of PIR foam for warm insulation systems; inhibited insulation materials with controlled chloride levels are available but are not widely used.
5. Construction supervision, in particular the technical supervision and inspection of coating, fireproofing, and insulation operations to ensure compliance with specifications.

For existing equipment, risks are mitigated by appropriate inspection and repair or replacement. Risk-based inspection (RBI) methodologies may be used to identify high-risk locations[24] that are examined after local insulation removal using surface crack detection and/or ultrasonic thickness measurement. There are available NDE techniques that do not require insulation removal, such as infrared thermography to detect areas of inadequate insulation, flash (profile) radiography to detect wall thinning of carbon steel pipework or small vessels and long-range, low-frequency ultrasonics to detect wall thinning of carbon steel pipework.

4.40.5.2 Internal Corrosion Risks

Industry equipment is required to operate in a plethora of chemical environments that consist of or contain mixtures of organic chemicals and acids, mineral acids, alkalis, salts and gases. The recognition and mitigation of the attendant corrosion risks presents significant challenges but is enabled by the major progress that has been made in understanding and dimensioning the corrosion performance of engineering materials and good corrosion control practices in industry equipment. This work has inevitably focused on specific chemicals or common process fluids or operations that present significant SHE or financial risks in the event of failure due to corrosion during storage and/or processing. Much of this learning has been codified in the standards, and recommended practices of technical organizations that industry professionals use for collaborative work and guidance is available on the mitigation of corrosion risks arising from the major recognized corrosive environments including:

1. organic chemicals[38,53] and acids[26,45];
2. mineral acids including sulfuric,[25,41,43,54,55] hydrochloric,[27,33,46] hydrofluoric,[28,47] nitric,[29,33,44] phosphoric,[31,34,51] carbonic[35] and mixed acids[32];
3. alkalies including sodium,[30,32,49] potassium,[39] and ammonium[30,39,49] hydroxides;
4. salts, including chlorides,[37,42] hypochlorites,[34] sulfates,[40] and mixed salts[52];
5. gases, including hydrogen chloride,[27,46] hydrogen fluoride,[28,47] chlorine,[48] ammonia,[30,39,50] hydrogen,[56] and hydrogen sulfide[57];
6. specific process fluids or operations in the petroleum refining sector such as crude unit overheads,[15] naphthenic acids,[58] hydroprocessing,[59] hydrofluoric acid alkylation,[60] and sour water stripping.[61]

A particular focus of collaborative industry work has been the mitigation of EAC risks that present the most significant risks of loss of containment, the mechanisms of which are described in other relevant chapters in this book. Figure 11 summarizes the more common alloy/environment systems that are vulnerable to EAC in process equipment. A recent industry survey,[62] summarized in Figure 12, concluded that ∼60% of industry EAC failures are associated with stainless steels, despite the fact that most process equipment is constructed from carbon and low alloy steels. This is a reflection of the vulnerability of austenitic stainless steels to chloride-induced stress corrosion cracking (SCC), particularly under thermal insulation and fireproofing.

- Steels
  - Alkalis
  - Nitrates
  - Anhydrous ammonia
  - Carbonate/ bicarbonate
  - Aqueous CO/CO_2
  - Hydrogen cyanide
  - Hydrogen sulfide
  - Hydrogen
  - Amines
  - Boiler water
  - Ethanol…
- Copper alloys
  - Ammonia
  - Amines…
- Stainless steels
  - Alkalis
  - Chlorides (waters)
  - Polythionic acids
  - Hydrogen sulfide
  - Hydrogen…
- Nickel alloys
  - Alkalis
  - Hydrogen…
- Titanium alloys
  - Anhydrous methanol
  - Anhydrous nitric acid
  - Hydrogen…
- Zirconium alloys
  - Sulfuric acid…

Figure 11 Some alloy–environment systems that are vulnerable to EAC in process equipment.

The majority of industry guidance and recommended practice for the mitigation of EAC risks to process equipment relates to the performances of carbon and low alloy steels. The interrelation of the various cracking risks that arise in corrosive petroleum refining environments is summarized in Figure 13, which is adapted from a recommended practice[63] that is widely used in the industry. Guidelines are available for the detection, repair and mitigation of cracking in existing equipment that operates in wet hydrogen sulfide service.[64,65] For new or replacement equipment, mitigation of cracking due to hydrogen charging is based on the control of base metal chemistry and the hardness of welds and heat-affected zones (HAZ) within the threshold levels and, if appropriate, post-weld heat treatment (PWHT).[66] Sulfide stress cracking (SSC) risks are mitigated by hardness control according to NACE standard MR0103,[67] which was developed recently to differentiate downstream fluids (containing ammonia and/or hydrogen cyanide) from upstream fluids (containing CO_2 and/or chloride) that were used historically for defining both upstream and downstream sour service according to the long-established NACE standard MR0175. For ASME IX P1 or 2 steel grades, from which most equipment is constructed, there are no base material hardness requirements, but welds and HAZs are controlled within hardness number limits of 200 HB on the Brinell scale and 248 HV on the

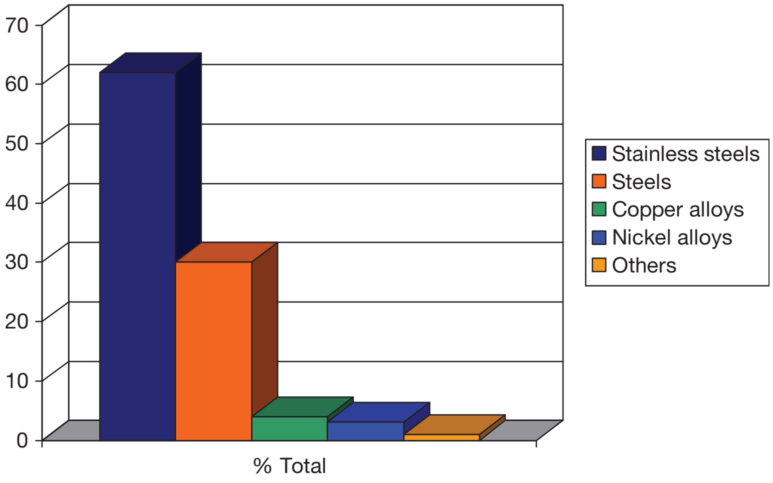
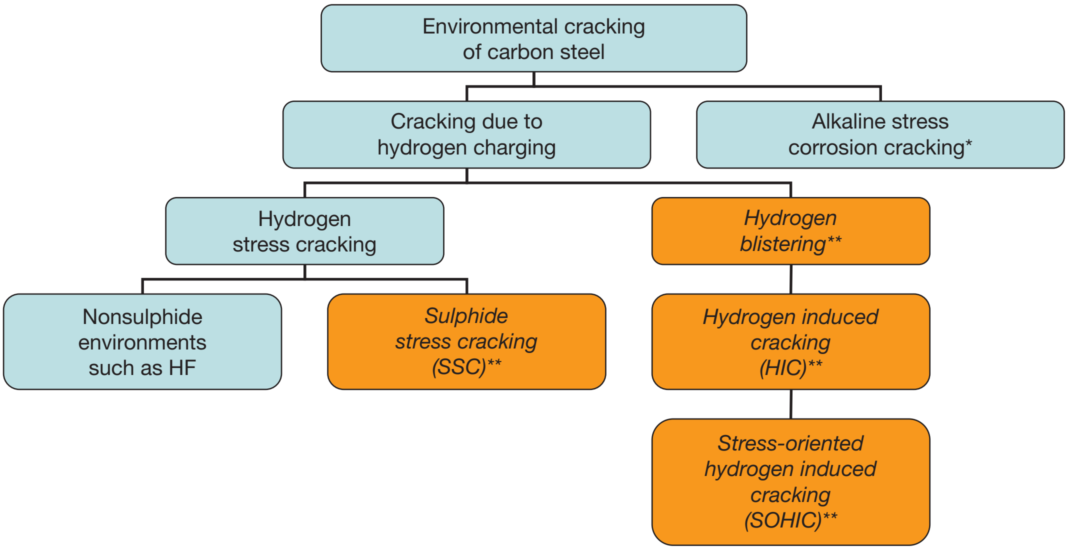


Figure 12 Frequency of EAC in process equipment as a function of alloy class. Reproduced from Puyear, R. B. *Corrosion Failure Mechanisms in Process Industries - A Compilation of Experience*; MTI Publication 9502-R4, Materials Technology Institute of the Process Industries, 1997.



*Environments such as caustic, alkanolamine solutions containing CO_2 and/or H_2S, alkaline sour waters containing carbonates.

**Italicised mechanisms referred to collectively as ‘wet H_2S cracking’ when they occur In wet hydrogen sulphide environments.

Figure 13 Interrelationships of the various EAC mechanisms for carbon steels in corrosive petroleum refining environments. Adapted from NACE Standard Recommended Practice RP0472-2005: *Methods and Controls to Prevent In-service Environmental Cracking of Carbon Steel Weldments in Corrosive Petroleum Refining Environments*; NACE International, 2005.

Vickers scale, respectively. The corresponding risks of hydrogen-induced cracking (HIC) and stress-oriented hydrogen-induced cracking (SOHIC) in the base materials are mitigated by controlling steel chemistry and microstructure (including limits on sulfur content and inclusion shape control) and manufacture (in particular, rolling conditions), and confirming resistance by appropriate testing.[68–70]

A typical example of damage to a carbon steel vessel in a wet hydrogen sulfide environment is shown in Figure 14, which relates to failure of a nonstress-relieved vessel for storing crude propane, operating at 17 bar and ~50 °C. The steel vessel contained type II MnS inclusions and anomalous microstructures that rendered it vulnerable to HIC and blistering damage in an H_2S-containing aqueous phase that separated out in the vessel base within the vulnerable temperature range (commonly 15–35 °C, but possible up to ~120 °C). There was no associated SSC, because weld and HAZ hardnesses were below the threshold levels for cracking. By the time this damage was detected by internal inspection, the vessel was beyond repair but was rendered fit for short-term operation, while a new vessel was procured by drilling the more severe blisters externally to relieve internal stresses. EAC risks were mitigated for the replacement vessel by selecting an HIC-resistant grade of steel and appropriate welding procedures and specifying PWHT of the vessel to further mitigate the risks of SSC of the welds.

Hydrogen-related EAC mechanisms for carbon and low-alloy steels are more prevalent in the petroleum refining and petrochemical sectors than in the wider chemical industry, where SCC mechanisms dominate. There is available industry guidance on the mitigation of SCC risks that are also of interest to the petroleum refining and petrochemical sectors such as in caustic[71] and amine[72] environments, boiler feed waters[73] and fuel-grade ethanol.[74] However, guidance on the mitigation of other SCC risks for carbon and low-alloy steels such as those that arise in solutions of nitrate,[75] carbonate/bicarbonate,[76] CO/CO_2[77] and hydrogen cyanide[75] tends to be more organization-specific and/or more widely scattered in the open literature. Nevertheless, practicable design and operating practices that mitigate SCC risks have been developed for all of these systems based on experience and experimental research to understand and dimension the factors that control initiation and propagation of cracking, as can be illustrated for the case of SCC of steels promoted by anhydrous ammonia.[78]

Anhydrous ammonia is stored and transported in large quantities around the world in carbon steel tanks and vessels that are mostly nonstress-relieved and operating under conditions that range from atmospheric pressure at a temperature of −33 °C to significant pressures at ambient temperatures. In the early 1980s, it was recognized that such storage equipment is at significant risk of SCC of welds and HAZs, as summarized in Figure 15. Industry-sponsored research[79] established that

1. Crack initiation risks increase with temperature above −33 °C and with steel strength.
2. Crack initiation risks increase with oxygen content and decrease with water content of the ammonia. However, water partitions preferentially into the liquid phase, so condensates from the vapor phase above a water-inhibited liquid phase may still initiate cracks.
3. Cracks propagate at relatively low velocities that reduce with time.

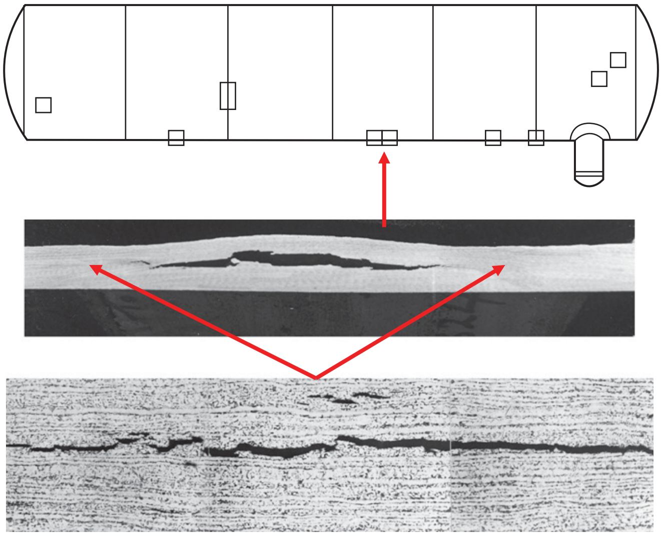


Figure 14 HIC/blistering of a propane accumulator vessel base because of contact with an H_2S-containing aqueous phase but no associated SSC because the weld/HAZ hardnesses were below threshold levels.

The risk mitigation options that emerged from the research work were:

1. Reduction of initiation risks by specifying relatively soft steels and welds and/or stress relieving new vessels, if practicable, and by controlling ammonia composition in service by eliminating oxygen and/or adding a threshold amount of water if practicable.
2. Reduction of risks arising from crack propagation in service by the management of inspection and repair.

On the basis of these findings, various approaches have emerged for the management of SCC in anhydrous ammonia storages typified by that developed in Australia,[80] summarized in **Table 1**. Clearly, mitigation by the use of relatively soft steels is impractical for most situations. For relatively small transport vessels, where it is impractical to control ammonia composition because of the frequency of filling and emptying operations, mitigation is achieved by a combination of thermal stress relief and relatively regular, mandatory inspections. On the other hand, for large storage vessels for which thermal stress relief is impractical, mitigation is based on the control of ammonia composition together with appropriate inspection or repair policies that may include probabilistic approaches to scheduling inspection and maintenance.[81]

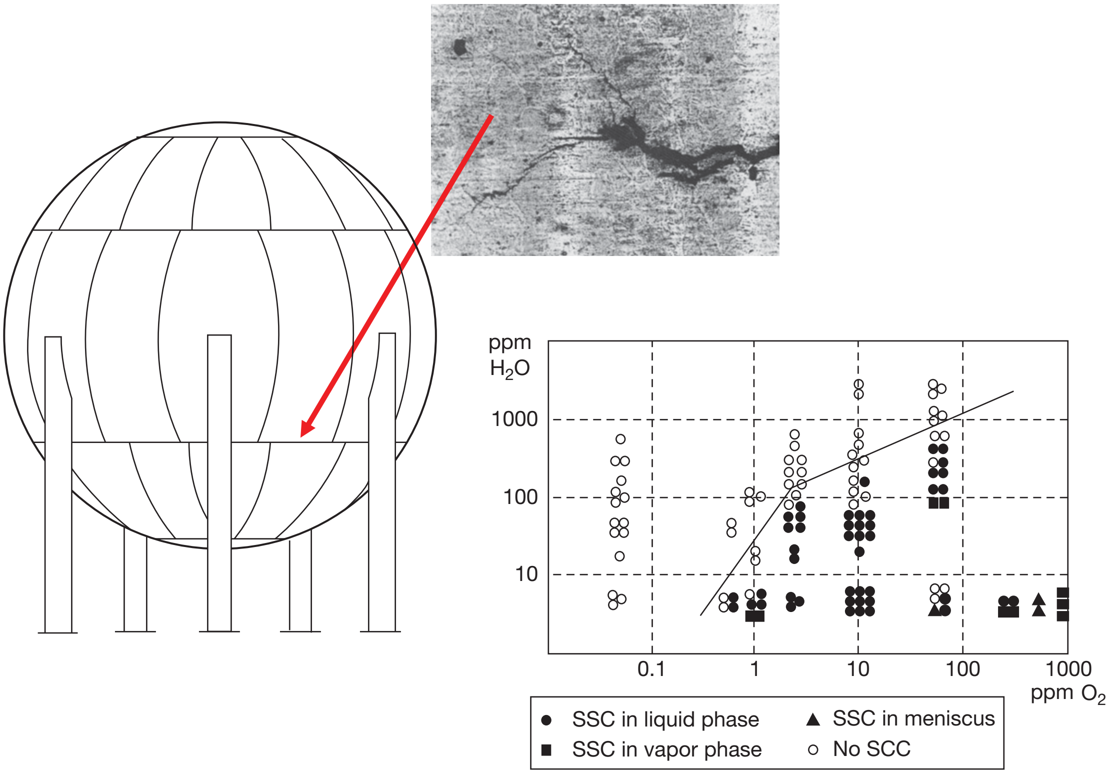


Figure 15 Welds in nonstress-relieved anhydrous ammonia storages may be vulnerable to SCC, depending on the relative contents of oxygen and water in the ammonia.[78,79]

Table 1 Australian[80] approach to the management of carbon steel storage and transport vessels to mitigate risks arising from SCC promoted by anhydrous ammonia

Mitigation option	*Storage tanks*	*Road/rail tankers*
Use steels <300 MPa yield	Most steels stronger	Most steels are Q & T and stronger
Stress relieve	Impractical	Mandatory if >300 MPa yield
Eliminate oxygen	Minimize inspection frequency, control recommissioning	Impractical
Add 0.2% water	Normal practice	Vapor space?
Manage inspection/ repair	Develop noninvasive inspection and fitness for service (FFS) approaches	Mandatory internal inspection every 1 or 2 years

Regarding the mitigation of industry EAC risks to materials other than steels, stress relief is rarely used and mitigation is more focused on the avoidance of material/environment combinations that present risks. Guidance also tends to be more organization-specific than for steels and/or more widely scattered in the open literature, as for the avoidance of the most frequent cause of failure, the chloride-induced SCC of austenitic stainless steels. Some sources are comprehensive in scope[75] while others relate to specific process duties such as thermal insulation[20] and water-cooled heat exchangers.[82] Guidance on the avoidance of caustic cracking of stainless steels is more limited but there are sources that define environmental conditions that present risks.[83] However, there are detailed recommended practices for mitigating the risks of polythionic acid-induced SCC of austenitic stainless steels and other austenitic alloys during the shutdown of refinery equipment[84] and for avoiding sulfide-induced stress cracking (SSC) of stainless steels and nickel, cobalt, titanium, aluminum, and copper alloys in corrosive petroleum refining environments containing H_2S.[67]

The author's own unpublished survey of EAC experience over a 20-year period within a world scale chemical company concluded that EAC failures arose principally (~70% of all cases) from failure to identify or control environments that presented a significant threat due to lack of awareness of the EAC potential of an environment, inadequate chemistry definition, inadequate chemistry control, or unpredicted contamination with EAC-promoting chemicals. The biggest single cause of unpredicted EAC failure was the development of EAC-promoting microenvironments at specific equipment locations and stages of operation, and of this group the commonest example (~30% of all cases) was ESCC of austenitic stainless steels. Of the remaining cases, ~20% arose from materials causes, either selection of the wrong material or of the right material in the wrong condition, and a small minority (~10% of all cases) arose from failure to control stress, principally, as a result of inefficient stress relief.

4.40.6 Mitigation of Corrosion Risks During Operation

Operating process equipment is not managed by corrosion engineers but by other professionals whose goals include the development and maintenance of equipment to provide increased availability and reliability without jeopardizing the organization's SHE obligations that require the avoidance of incidents and assurance of structural integrity. The processes that may be adopted to manage corrosion are reviewed in detail in a separate chapter in this book. However, in most organizations the management of corrosion is not a separate functional activity but is integrated into more familiar asset management functions such as production and maintenance. Within this framework, the management of corrosion during operation is defined by two key objectives:

1. Ensuring that the design intents in relation to the mitigation of corrosion risks are delivered during operation. This requires that processes are operated within the design envelope in relation to all of the factors that can influence corrosion risks such as the compositions, temperatures and velocities of process fluids, the intensities of heat fluxes, etc. It also requires that corrosion control practices that were specified in design, such as inhibitor addition, electrochemical protection, etc. are operated continuously to design specification.
2. Dimensioning and understanding the corrosion performance of equipment by inspection and monitoring, and embedding corrosion performance data in asset development and maintenance databases so that corrosion risk mitigation is integral to the maintenance management processes that capture history and learning in pursuit of reduced maintenance costs and increased reliability and availability.

The delivery of these objectives requires the promotion of corrosion awareness and commitment amongst production and maintenance personnel who are accountable for delivering manufacturing performance. Effective corrosion management derives from influential corrosion professionals operating within the appropriate management systems.

Central to the management of corrosion during operation is assurance of the structural integrity of process equipment and this has been enabled by continuing developments in protocols and techniques for the inspection and monitoring of process equipment that are described in separate chapters of this book:

1. RBI procedures[85–87] are now the norm for process equipment. Large companies have developed their own protocols, and proprietary procedures are available from numerous sources. An essential first stage for any organization is the calibration of the risk/consequences matrix by defining acceptance criteria for the probability and

consequences of failure within a specified timescale. This is a team activity, requiring contributions from equipment specialists and inspectors, process engineers, and operations and maintenance personnel in addition to materials/corrosion specialists. The required effort and cost of an RBI process increases with the period under consideration and a common practice is to focus on a limited number of turnaround periods rather than the full design life of equipment. It is important that the risks of external as well as internal corrosion are evaluated for equipment items. As indicated previously, the semiquantitative evaluation of corrosion risks is normally regarded as sufficient for process equipment, based on the mostly empirical corrosion data that are used to predict corrosion performance, the reliability of which is classified as high, medium, or low, depending on the source.[88] The contributions of materials and corrosion specialists are crucial to the accurate evaluation of risks. Key outputs of RBI processes are risk rankings for equipment items and corresponding inspection plans and other risk mitigation activities to be adopted. Inspection plans detail the inspection methods to be adopted in defined areas and locations, and the timing of examinations. Other risk mitigation activities include fitness for service (FFS) evaluation based on codified[89] defect and remnant life assessment procedures that are described in a separate chapter in this book, the adoption of methods to monitor deterioration rates and their variation, and equipment repair or replacement, or modification or redesign. Anticipated reductions in risk levels are predicted after inspection plans and other risk mitigation activities are implemented. The key benefit of RBI has been to focus management attention and effort on the most significant risks to the structural integrity of equipment, including corrosion risks. However, RBI has also delivered significant economic benefits, due not least to improvements in the planning and scheduling of maintenance.

2. Noninvasive NDE technologies are available, including acoustic emission (AE) and scanning ultrasonics (UT) that allow the condition of equipment to be established while the equipment continues to operate, without the need to shut down and prepare equipment for entry. AE detects and locates internal flaws in metal or FRP-pressurized systems by detecting acoustic emissions from defect micropropagation processes with external, surface-mounted, piezoelectric probes. Emissions are triggered by raising the pressure beyond the design or previous operating levels and their amplitude is a guide to the severity of the defect. The entire structure is assessed in one; rapid operation and triangulation techniques allow emissions to be positioned within ~10 mm. Defects that have been located by AE can be sized using external ultrasonic techniques online if permitted by access and operating temperatures. Automated C-scan ultrasonic techniques allow mapping of corrosion distribution by computer control, processing, storage and imaging of ultrasonic signals. P-scan techniques produce 3-D reconstructions of defect locations and sizes from robotic manipulation of probes and computer processing of signals. Having been located and sized, defects can be assessed for their significance using appropriate FFS[89] procedures, allowing the entire structural integrity evaluation process to be undertaken without interrupting production.
3. Online corrosion monitoring technologies are available that are noninvasive and allow monitoring of equipment directly without having to resort to probes, including hydrogen permeation,[90] thin layer activation (TLA),[91] field signature monitoring (FSM)[92] and pulsed eddy current (PEC).[93] Technologies are also available based on electrochemical noise (ECN)[94] that is sensitive in real time and to localized corrosion. Examples of the uses of corrosion monitoring to deliver increased plant availability are illustrated in Figures 16 and 17. The case illustrated in Figure 16 relates to a well known hydrocracker corrosion problem in refineries. As shown in the simplified process flow diagram, reactor effluent, a mixture of hydrogen, hydrogen sulfide, hydrocarbons and salts such as ammonium bisulfide (NH_4HS), is cooled in air coolers upstream of which water is injected to prevent corrosive salt accumulation in equipment. In the particular case,[95] the air cooler exit pipework constructed in carbon steel suffered NH_4HS-induced, flow-assisted corrosion at higher rates than anticipated in the design. Corrosion rates were monitored online using PEC sensors that were strapped onto pipes as shown in Figure 16. PEC offers significant advantages over ultrasonic determinations of wall thickness because of its greater repeatability, which allows corrosion rates to be determined more rapidly. Data typified by that shown in Figure 16 for an elbow in an exit pipe provided justification for an extended runtime while replacement material was procured and a shutdown was planned. The case illustrated in

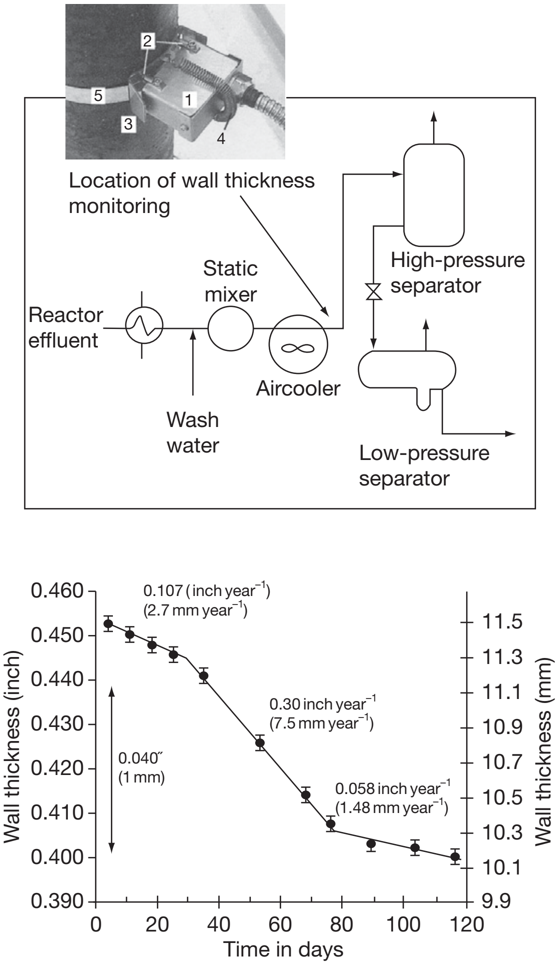


Figure 16 Online, pulsed eddy current (PEC) monitoring of carbon steel piping wall thickness provides justification for an extended hydrocracker run-time to procure replacement material and plan a shutdown. Reproduced from Crouzen, P. C. N.; Munns, I. J.; Verstijnen, W.; Hulsey, R. C. In *Corrosion 2006*, NACE International, 2006; Paper 06312.

Figure 17 relates to the start-up stage of an ethylene dichloride (EDC), fluidized bed reactor. Reactors are constructed typically in carbon and low alloy steels and relevant process flows in the reactor are shown schematically in Figure 17. The greatest risk of corrosion occurs during plant start up in the event that condensation of the hydrochloric acid feed occurs on steel surfaces. In the particular case,[96] steel reactor internals had suffered excessive corrosion and real-time ECN monitoring using an appropriate multielement corrosion probe established that corrosion rates up to ~50 mm year^{-1} were experienced during start up due to condensation because the catalyst feed temperature (100 °C) was too low and the time interval between the hot (160 °C) air and catalyst feeds to the reactor was too short. Typical temperature and corrosion rate profiles before and after adopting a revised startup procedure involving a higher catalyst feed temperature (140 °C) and a longer time interval are shown in Figure 17. As a result of these changes, corrosion rates during start up were reduced by a factor of five resulting in extended lives for carbon steel internals and a significant (2%) increase in the availability of the reactor.

4.40.7 Corrosion Risk Management Costs and Benefits

A recent study[19] of the UK petrochemicals/chemicals sector estimated that total expenditure on corrosion management amounted to ~4.5% of industry turnover. The majority of this expenditure was spent optimally and beneficially, comprising the inevitable costs of mitigating the corrosion risks associated with the processing corrosive and hazardous fluids to add value without incurring unacceptable financial or SHE consequences. However, two areas of avoidable expenditure were identified:

1. In the cases of ageing, individual plants and sites that were designed, fabricated and protected to standards now recognized as inadequate, estimated expenditure on corrosion management as high as ~9% of turnover was identified. The great majority of this expenditure was associated with historical deficiencies in the awareness and management of external corrosion of carbon and stainless steels under thermal insulation and fireproofing that have resulted in major remedial expenditure to mitigate risks. This emerged as the largest individual corrosion cost to the industry but it should be a one-off legacy cost that declines as the risks to replacement or new equipment are mitigated by improved design, specification and fabrication practices.
2. It was estimated that ~15% of the total expenditure on corrosion was associated with problems for which there are proven, economic solutions and was avoidable by better application of existing corrosion control technology and management practices. Some of the wasted expenditure arose from deficient materials selection and design practices relating to the mitigation of risks such as the localized corrosion of stainless steels and nickel alloy equipment, particularly at welds; erosion and

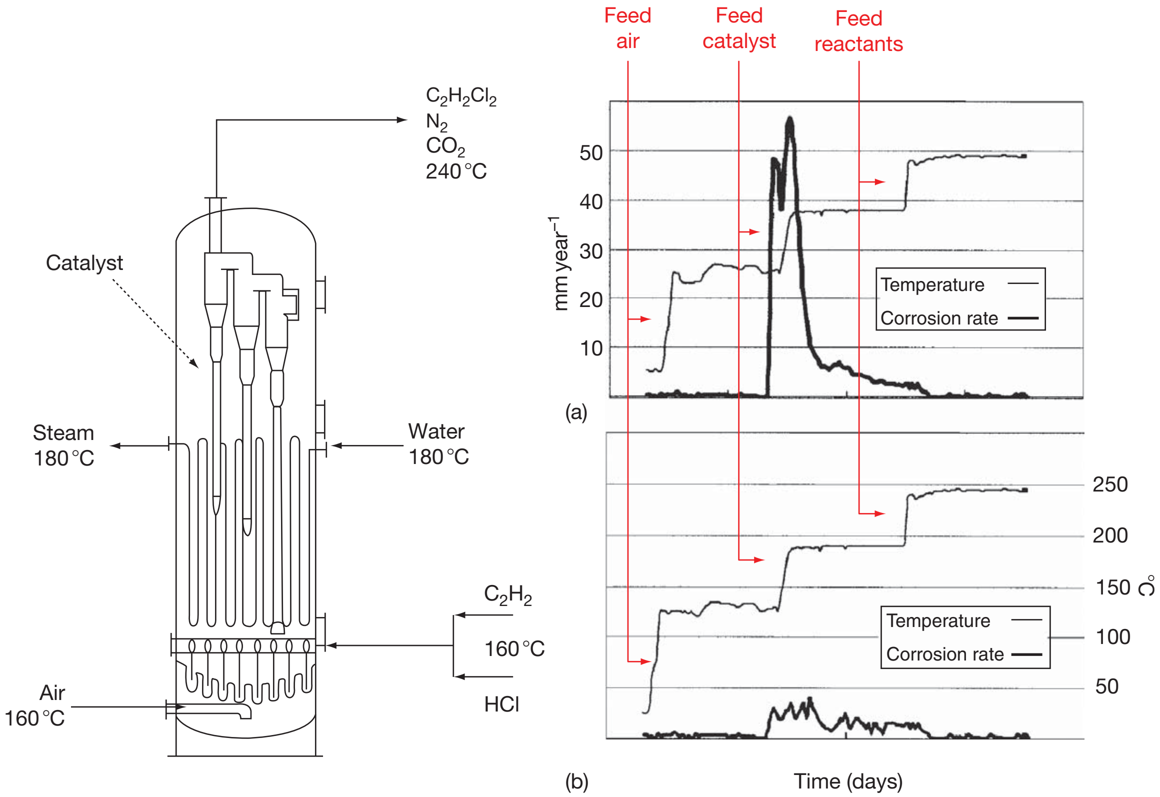


Figure 17 Corrosion rate profiles obtained by ECN monitoring during start up of an EDC reactor (a) before and (b) after implementing measures to prevent condensation of HCl on internal steel coil/pipe surfaces. Reproduced from Ohtsu, T.; Miyazawa, M. In *Corrosion 2007*, NACE International, 2007; Paper 07266.

erosion corrosion in piping and heat exchangers; galvanic corrosion, particularly at specified transitions from one material to another in piping; the corrosion of heating/cooling coils in batch vessels, etc. Other wasted expenditure arose from deficiencies in the management of corrosion in operation, not least the control of corrosion in cooling water and steam raising equipment.

The UK study also identified several developing and new processes for which corrosion risks present significant barriers to commercialization because cost-effective mitigation practices have yet to emerge, typified by processes that promote metal dusting and organic oxidation processes undertaken in supercritical water (SCW):

1. Metal dusting is described in a separate chapter in this book and is a risk under process conditions that favor carbon deposition as a result of the disproportionation and/or reduction of carbon monoxide in gas mixtures that also contain hydrogen as summarized in Figure 18. A common example is synthesis gases that are formed by the steam reforming of hydrocarbons. Carbon deposition is catalyzed on surfaces that contain iron, nickel, and cobalt and the rate of carbon uptake is a balance between thermodynamic and kinetic driving forces. Metal dusting is a relatively low-temperature phenomenon with rates that generally peak in the temperature range ~400–800 °C. Penetration of carbon reduces ductility and results in transformation to a mixture of oxide, alloy and carbon particles which can shed resulting in general or localized corrosion that can be very rapid.[97] All high temperature alloys are vulnerable to metal dusting but risks can be mitigated to some extent by the incorporation of strong oxide promoters such as chromium, aluminum and silicon, either in the alloy itself or on the surface by appropriate coating processes. In theory, risks may also be mitigated by increasing the ratio of steam or including catalyst poisons such as hydrogen sulfide in the process gas. However, process efficiency considerations favor lower rather than

higher steam ratios and catalyst poisoning concerns preclude sulfide additions. At the current state of art, robust and cost-effective materials solutions have yet to emerge and the migration of several world scale processes to the most efficient operating conditions remains inhibited by metal dusting risks.

2. Over the past ~10 years there has been considerable interest in the potential of SCW as a solvent. Solubility behavior is reversed in SCW so that organic materials are soluble and inorganic salts insoluble, allowing single-phase oxidation of organic materials (SCWO). Much of the early research interest has been focused on the development of processes for the destruction of hazardous wastes, as summarized in Figure 19. However, there has also been interest in the development of SCWO processes that may offer economic advantages over

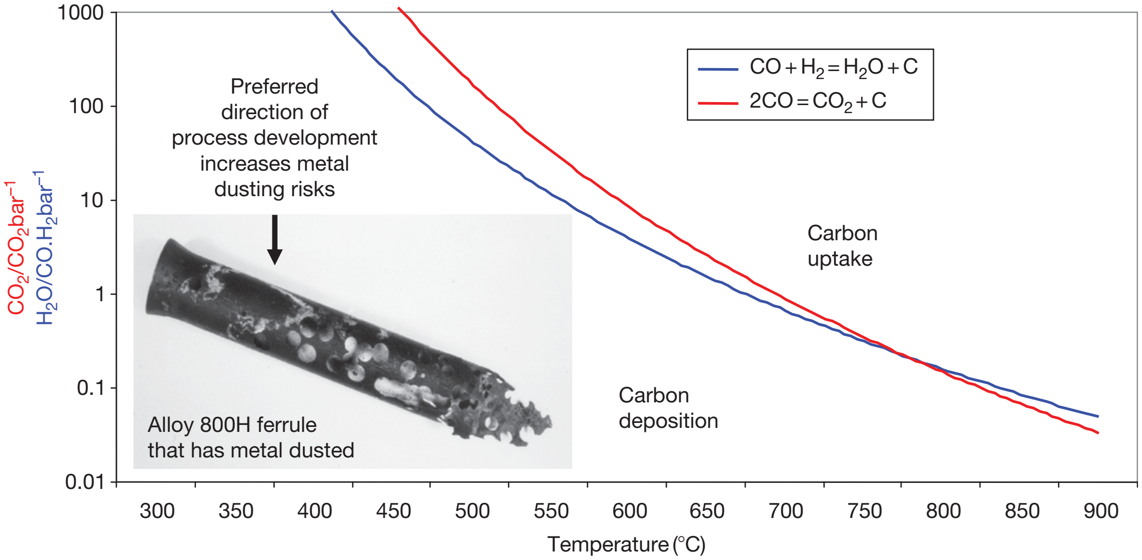


Figure 18 Equilibrium ratios at unit carbon activity versus temperature for CO disproportionation and reduction processes – metal dusting threatens equipment operating at temperatures below unit carbon activity in any gas composition.

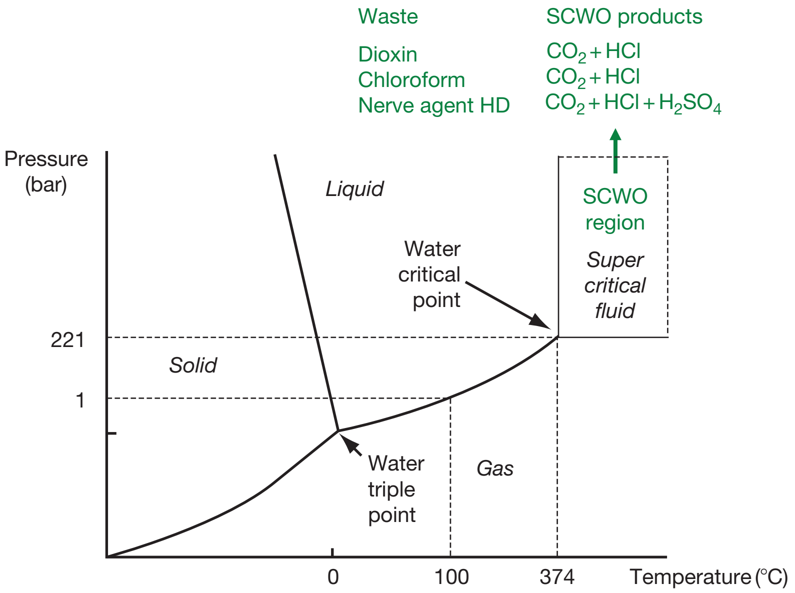


Figure 19 Typical conditions and products of organic waste destruction by supercritical water oxidation (SCWO).

conventional processes for commercially important organic oxidations such as the oxidation of paraxylene to terephthalic acid.[98] Commercial application of SCWO technology requires materials that are resistant to corrosion under super- and subcritical conditions, at temperatures above ∼300 °C. In processes where mineral acids are significant products of SCW oxidation, such as those summarized in Figure 19, corrosion is a potential show-stopper. In general, stainless steels are insufficiently resistant to corrosion, nickel alloys have shown major corrosion vulnerabilities, and although titanium and zirconium have shown useful corrosion resistances, they have other limitations relating to their strength and resistance to ignition at the prevailing temperatures and high oxygen pressures. Economic, robust, long-term materials solutions have proved elusive.[99]

4.40.8 Future Trends in Process Equipment

The current trend to increasingly large, single stream plants seems likely to continue in the refining, petrochemical and commodity chemicals industries. For example, single stream sulfuric acid plants are currently under construction with capacities of $4\text{–}5000\ \mathrm{t\,e\,day^{-1}}$. There are challenges relating to the fabrication of extremely large vessels and the logistics of transporting them around the world, not to mention the operability of extremely large equipment and the high cost of unreliability. However, large capital cost savings provide the incentive that favors the trend.

Against the trend, there is growing interest in the advantages of microscale manufacture using micro-equipment, of the type shown in Figure 20. A key advantage of microequipment[98,99] is the possible reduction of manufacture, reaction and transport to the same timescales. Diffusion distances are reduced to minimize residence times, obviating the requirements for mixing/velocity in conventional equipment. This requires small flow channels, typically submicron to 1 mm with high surface-to-volume ratio and reduced residence times and process volumes. Lower diffusion resistances favor high catalyst selectivity. A manufacturing plant comprises a multitude of small or lab scale reactors.

Materials and fabrication techniques are drawn from the microelectronics and semiconductor industries. Materials include silicon, glass, ceramics and polymers as well as metals, fabricated with techniques that include lithography, electroplating, molding, etching,

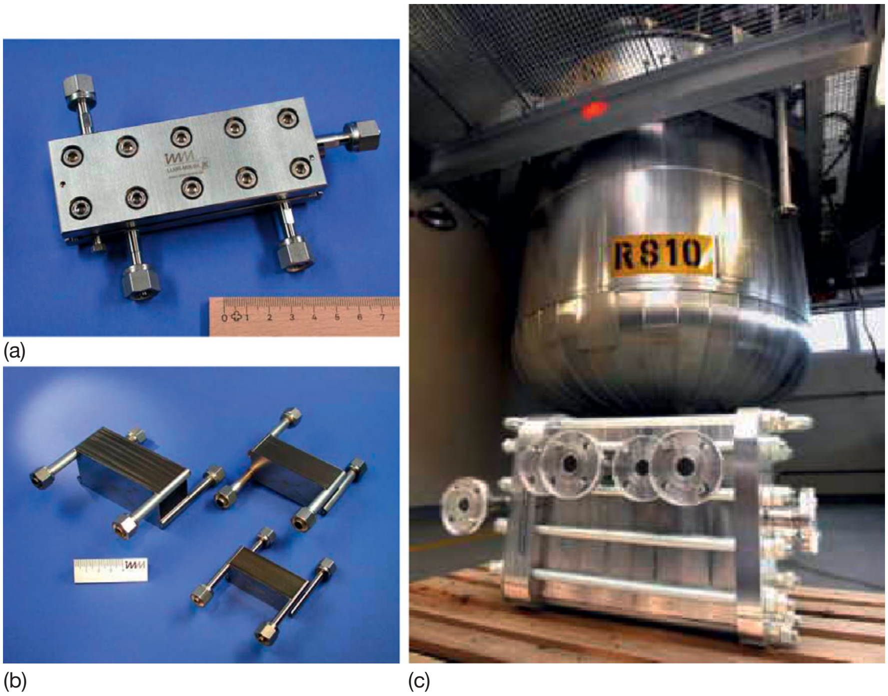


Figure 20 Microprocess equipment for fine chemicals/pharmaceuticals manufacture: (a) liquid–liquid reactor,[99] (b) heat exchangers,[98] and (c) microstructured reactor with equivalent throughput to continuous stirred tank reactor in the background.[99]

micromachining, laser ablation, etc. Catalysts are applied using surface enhancement techniques such as anodic oxidation, or impregnation using PVD/CVD or ion implantation. This is clearly very different territory from traditional materials and corrosion engineering!

It remains to be seen what impact microscale manufacture will have on the industry as a whole. To date, interest seems to be focused mainly in the fine chemicals and pharmaceuticals sectors, where it has been strong enough to promote acquisitions of companies that specialize in the fabrication of such equipment.

4.40.9 The Current Corrosion Risk Management Scorecard

The petrochemical/chemical industry has seen major advances in equipment reliability, availability, and SHE performances because of advances in corrosion understanding, control technology and management practices. However, unpredicted, SHE-threatening and/or expensive incidents continue to occur. Most are avoidable, arising from deficiencies in awareness and/or management of recognized corrosion risks for which there are proven, economic solutions, but some arise from problems for which there are not yet proven, economic solutions. Significant corrosion challenges/opportunities remain to be addressed.

References

1. Garrison, W. G. *Hydrocarb. Process.* **1988**, *67*, 115–122.
2. Katsumi, Y. *Corros. Eng.* **2004**, *53*, 185–189.
3. Moniz, B. J.; Pollock, W. I. Eds. *Process Industries Corrosion*; National Association of Corrosion Engineers, 1986.
4. White, R. A. *Materials Selection for Petroleum Refineries and Gathering Facilities*; NACE International, 1998.
5. Harston, J. D.; Ropital, F. *Corrosion in Refineries (EFC 42)*; European Federation of Corrosion, 2007.
6. Dillon, C. P. *Corrosion Control in the Chemical Process Industries*; Materials Technology Institute, 1994.
7. Garverick, L., Ed. *Corrosion in the Petrochemical Industry*; ASM International, 1994.
8. In *ASM Handbook – Corrosion: Environments and Industries*; ASM International, 2006; Vol. 13C, pp 652–1037.
9. www.mtcmelbourne.com
10. www.hexaloy.com
11. www.sglgroup.com
12. www.nori-acidbrick.com
13. Society for Protective Coatings/NACE Joint Standard No. 11/SSPC-PA8: *Thin Film Organic Linings Applied in Carbon Steel Process Vessels*; NACE International, 2003.
14. www.edlon.com.
15. *Crude Unit Overhead Corrosion Control;* Refining Industry Corrosion Information Compilation Series; NACE International, 2001.
16. Kletz, T. A. *HAZOP and HAZAN: Identifying and Assessing Process Industry Hazards*, 4th ed.; Institution of Chemical Engineers: UK, 1999.
17. API Publication 581: *Base Resource Document on Risk Based Inspection*; American Petroleum Institute, 2000.
18. NACE Standard Practice SP0407-2007: *Format, Content and Guidelines for Developing a Materials Selection Diagram*; NACE International, 2007.
19. McIntyre, P. Corrosion and associated costs in the UK chemicals and petrochemicals sector, Degradation of Materials in Aggressive Environments Programme (DME), Report NRW/PM/CORRO/D1; Paint Research Association, 2001.
20. NACE Recommended Practice RPO198-2004: *Control of Corrosion Under Thermal Insulation and Fireproofing Materials – A Systems Approach*; NACE International, 2004.
21. Ahluwalia, H. In *ASM Handbook – Corrosion: Environments and Industries*; ASM International, 2006; Vol. 13C, pp 654–658.
22. Winnik, S., Ed. *Corrosion Under Insulation (CUI) Guidelines (EFC 55)*; European Federation of Corrosion, 2008.
23. Richardson, J. A.; Fitzsimmons, T. In *Corrosion of Metals Under Thermal Insulation*, ASTM SP 880; Pollock, W. I., Barnhart, J. M., Eds.; American Society. For Testing and Materials, 1985; pp 188–198.
24. Chauviere, M. M.; Krynicki, J. W.; Richert, J. P.; In *Corrosion 2007*; NACE International, 2007.
25. *Materials Selector for Hazardous Chemicals: Concentrated Sulphuric Acid and Oleum*, 2nd ed.; MTI Publication MS-1, Materials Technology Institute of the Process Industries, 2005; Vol. 1.
26. *Materials Selector for Hazardous Chemicals: Formic, Acetic and Other Organic Acids*; MTI Publication MS-2, Materials Technology Institute of the Process Industries, 1997; Vol. 2.
27. *Materials Selector for Hazardous Chemicals: Hydrochloric Acid, Hydrogen Chloride and Chlorine*; MTI Publication MS-3, Materials Technology Institute of the Process Industries, 1999; Vol. 3.
28. *Materials Selector for Hazardous Chemicals: Hydrogen Fluoride and Hydrofluoric Acid*; MTI Publication MS-4, Materials Technology Institute of the Process Industries, 2000; Vol. 4.
29. *Materials Selector for Hazardous Chemicals: Nitric Acid*; MTI Publication MS-5, Materials Technology Institute of the Process Industries, 2004; Vol. 5.
30. *Materials Selector for Hazardous Chemicals: Ammonia and Caustic Soda*; MTI Publication MS-6, Materials Technology Institute of the Process Industries, 2004; Vol. 6.
31. *Materials Selector for Hazardous Chemicals: Phosphoric Acid*; MTI Publication MS-7, Materials Technology Institute of the Process Industries, 2004; Vol. 7.
32. *DECHEMA Corrosion Handbook: Sodium Hydroxide, Mixed Acids*; Wiley-VCH, 2004; Vol. 1.
33. *DECHEMA Corrosion Handbook: Hydrochloric Acid, Nitric Acid*; Wiley-VCH, 2004; Vol. 2.
34. *DECHEMA Corrosion Handbook: Hypochlorites, Phosphoric Acid*; Wiley-VCH, 2005; Vol. 3.
35. *DECHEMA Corrosion Handbook: Carbonic Acid, Chlorine Dioxide, Seawater*; Wiley-VCH, 2005; Vol. 5.
36. *DECHEMA Corrosion Handbook: Atmosphere, Industrial Waste Gases*; Wiley-VCH, 2006; Vol. 6.
37. *DECHEMA Corrosion Handbook: Sodium Chloride*; Wiley-VCH, 2007; Vol. 7.
38. *DECHEMA Corrosion Handbook: Chlorinated Hydrocarbons*; Wiley-VCH, 2007; Vol. 8.

39. *DECHEMA Corrosion Handbook: Potassium Hydroxide, Ammonia, Ammonium Hydroxide*; Wiley-VCH, 2007; Vol. 9.
40. *DECHEMA Corrosion Handbook: Sodium Sulphate, Sulphur Dioxide*; Wiley-VCH, 2008; Vol. 10.
41. *DECHEMA Corrosion Handbook: Sulphuric Acid*; Wiley-VCH, 2008; Vol. 11.
42. *DECHEMA Corrosion Handbook: Iron Chlorides*; Wiley-VCH, 2009; Vol. 12.
43. Brubaker, S. K. In *ASM Handbook – Corrosion: Environments and Industries*; ASM International, 2006; Vol. 13C, pp 659–667.
44. Ahluwalia, H.; Eyre, P.; Davies, M.; Yau, T.-L. In *ASM Handbook – Corrosion: Environments and Industries*; ASM International, 2006; Vol. 13C, pp 667–673.
45. Scribner, L. A. In *ASM Handbook – Corrosion: Environments and Industries*; ASM International, 2006; Vol. 13C, pp 674–681.
46. Crum, J. R. In *ASM Handbook – Corrosion: Environments and Industries*; ASM International, 2006; Vol. 13C, pp 682–689.
47. Jennings, H. S. In *ASM Handbook – Corrosion: Environments and Industries*; ASM International, 2006; Vol. 13C, pp 690–703.
48. Liening, E. L. In *ASM Handbook – Corrosion: Environments and Industries*; ASM International, 2006; Vol. 13C, pp 704–709.
49. Davies, M. In *ASM Handbook – Corrosion: Environments and Industries*; ASM International, 2006; Vol. 13C, pp 710–726.
50. Davies, M. In *ASM Handbook – Corrosion: Environments and Industries*; ASM International, 2006; Vol. 13C, pp 726–735.
51. Ross, R. W. Jr. In *ASM Handbook – Corrosion: Environments and Industries*; ASM International, 2006; Vol. 13C, pp 736–741.
52. Sridhar, N. In *ASM Handbook – Corrosion: Environments and Industries*; ASM International, 2006; Vol. 13C, pp 742–749.
53. Ahluwalia, H.; Thodla, R. In *ASM Handbook – Corrosion: Environments and Industries*; ASM International, 2006; Vol. 13C, pp 750–753.
54. NACE Recommended Practice RP0391-2001: *Materials for Handling and Storage of Commercial Concentrated (90–100%) Sulphuric Acid at Ambient Temperatures*; NACE International, 2001.
55. NACE Standard Practice SP0254-2006: *Design, Fabrication and Inspection of Storage Tank Systems for Concentrated Fresh and Process Sulphuric Acid and Oleum at Ambient Temperatures*; NACE International, 2006.
56. API Recommended Practice RP941: *Steels for Hydrogen Service at Elevated Temperatures and Pressures in Petroleum Refineries and Petrochemical Plants*; American Petroleum Institute, 2008.
57. Gutzeit, J. In *Process Industries Corrosion – The Theory and Practice*; National Association of Corrosion Engineers, 1986; pp 367–372.
58. *Naphthenic Acid Corrosion – Refining Industry Corrosion Information Compilation Series*; NACE International, 2001.
59. *Hydroprocessing Units – Refining Industry Corrosion Information Compilation Series*; NACE International, 2001.
60. API Recommended Practice RP751: *Safe Operation of Hydrofluoric Acid Alkylation Units*; American Petroleum Institute, 2007.
61. API Document 950: *Survey of Constructional Materials and Corrosion in Sour Water Strippers*; American Petroleum Institute, 1983.
62. Puyear, R. B. *Corrosion Failure Mechanisms in Process Industries – A Compilation of Experience*; MTI Publication 9502-R4, Materials Technology Institute of the Process Industries, 1997.
63. NACE Standard Recommended Practice RP0472-2005: *Methods and Controls to Prevent In-service Environmental Cracking of Carbon Steel Weldments in Corrosive Petroleum Refining Environments*; NACE International, 2005.
64. NACE Standard Recommended Practice RP0296-2004: *Guidelines for Detection, Repair and Mitigation of Cracking of Existing Petroleum Refinery Pressure Vessels in Wet H2S Environments*; NACE International, 2004.
65. API Document 939-B: *Repair and Remediation Strategies for Equipment Operating in Wet H_2S Service*; American Petroleum Institute, 1994.
66. NACE Publication 8X194: *Materials and Fabrication Practices for New Pressure Vessels Used in Wet H_2S Refining Service*; NACE International, 2006.
67. NACE Standard Material Requirements MR0103-2007: *Materials Resistant to Sulphide Stress Cracking in Corrosive Petroleum Refining Environments*; NACE International, 2007.
68. NACE Standard Test Method TM0177-2005: *Laboratory Testing of Metals for Resistance to Sulphide Stress Cracking and Stress Corrosion Cracking in H_2S Environments*; NACE International, 2005.
69. NACE Standard Test Method TM0284-2003: *Evaluation of Pipeline and Pressure Vessel Steels to Hydrogen Induced Cracking*; NACE International, 2003.
70. NACE Standard Test Method TM0103-2003: *Laboratory Test Procedures for Evaluation of SOHIC Resistance of Plate Steels Used in Wet H_2S Service*; NACE International, 2003.
71. NACE Standard Practice SP0403-2008: *Avoiding Caustic Stress Corrosion Cracking of Carbon Steel Refinery Equipment and Piping*; NACE International, 2008.
72. API Recommended Practice RP945: *Avoiding Environmental Cracking in Amine Units*; American Petroleum Institute, 2003.
73. NACE Standard Practice SP0590-2007: *Prevention, Detection and Correction of Deaerator Cracking*; NACE International, 2007.
74. API Document 939-D: *Stress Corrosion Cracking of Carbon Steel in Fuel Grade Ethanol: Review and Survey*; American Petroleum Institute, 2000.
75. McIntyre, D. R.; Dillon, C. P. *Guidelines for Preventing Stress Corrosion Cracking in the Process Industrie*; MTI Publication No. 15, Materials Technology Institute of the Process Industries, 1985.
76. Smith, R. F.; Richardson, J. A. In *Corrosion 91*, National Association of Corrosion Engineers, 1991; Paper 576.
77. Berry, W. E.; Payer, J. H. In *Symposium on Line Pipe Research*, Houston, TX; American Gas Association, 1979.
78. Hewerdine, S. *Ammonia Storage Inspection*; The Fertiliser Society: London, 1991; Proceedings No. 308.
79. Lunde, L.; Nyborg, R. *Stress Corrosion Cracking of Carbon Steel Storage Tanks for Anhydrous Ammonia*; The Fertiliser Society: London, 1991; Proceedings No. 307.
80. McGowan, P. *Plenary Address*; Australasian Corrosion Association, 2000.
81. Saugerud, O. T.; Angelsen, S. O. In *Life Prediction of Corrodible Structures*; Proceedings of the Conferences, Cambridge, UK, 23–26 September 1991 and Kauai, Hawaii, 5–8 November 1991; Parkins, R. N., Ed.; National Association of Corrosion Engineers, 1991; paper 67.
82. Haruyama, S. *Mater. Perform.* **1982**, *21*, 14–19.

83. Craig, B. D.; Anderson, D. S. Eds. *Handbook of Corrosion Data*, 2nd ed.; ASM International, 1995; p 787.
84. NACE Standard Recommended Practice RP0170-2004: *Protection of Austenitic Stainless Steels and Other Austenitic Alloys From Polythionic Acid Stress Corrosion Cracking During the Shutdown of Refinery Equipment*; NACE International, 2004.
85. API Recommended Practice RP580: *Risk Based Inspection*; American Petroleum Institute, 2002.
86. API Publication 581: *Risk Based Inspection Resource Document*; American Petroleum Institute, 2000.
87. Valbuena, R.; Aller, J.; Renner, M.; Feigel, G. *Implementing and Evergreening RBI in Process Plants*; MTI Publication 9526. Materials Technology Institute of the Process Industries, 2005.
88. API Document 579-1: *Fitness for Service*; American Petroleum Institute, 2007.
89. Menendez, C. M.; de Mello, C. J. B.; de Oliveira Carneval, J. R.; de Alcantara Bezerra, P. S.; de Azevedo, C.; Cardoso, C. M.; Mattos, O. R. In *Corrosion 2000*; NACE International, 2000; Paper 00102.
90. Rothwell, N. *Corrosion Monitoring Handbook*; Coxmoor Publishing, 2000.
91. Birch, N. N. In *Corrosion 2006*, NACE International, 2006; Paper 06642.
92. Crouzen, P. C. N.; Munns, I. J.; Verstijnen, W.; Hulsey, R. C. In *Corrosion 2006*, NACE International, 2006; Paper 06312.
93. Kane, R. D.; Eden, D. C.; Amidi, S.; Delve, D. In *Corrosion 2007*, NACE International, 2007; Paper 07268.
94. Ohtsu, T.; Miyazawa, M. In *Corrosion 2007*, NACE International, 2007; Paper 07266.
95. Hermse, C.; Kempen, A.; van Wortel, H. *Corrosion 2007*; NACE International, 2007Paper 07416.
96. Hamley, P. A.; Ilkenhans, T.; Webster, J. M.; Garcia-Vedugo, E.; Venardou, E.; Clarke, M. J.; Auerbach, R.; Thomas, W. B.; Whiston, K.; Poliakoff, M. *Green Chem.* **2002**, *4*, 235–238.
97. Latanision, R.; Mitton, D. B. In *ASM Handbook – Corrosion: Environments and Industries*; ASM International, 2006; Vol. 13C, pp 229–235.
98. www.imm-mainz.de
99. www.fzk.de

4.41 Management of Corrosion in the Oil and Gas Industry

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Glossary

Barrel A (depreciated) unit of volume, used for measuring production (1 barrel $\approx$ 0.159 m^3).

Consequence of failure The impact of components/equipment failure on health and safety, production, and environmental parameters.

Corrosion management (1) Defined as that part of the overall operation management program aiming at the implementation of the Corrosion Policy (2) Organization set-up and operational process to ensure corrosion control, inspection, monitoring, and assessment plans are implemented to optimize asset integrity.

Corrosion risk assessment A formalized process in which the combination of the consequences of failure and the likelihood of failure is assessed to identify the level of risk of ongoing operations. A corrosion risk assessment is used to (1) identify items in which design and/or corrosion control plans should be readdressed to reduce risk (2) to assist in defining the maintenance and monitoring tasks that should be implemented (see RBI).

Direct assessment Formalized method for reviewing information relating to the possible degradation of a pipeline due to corrosion (internal or external) to identify areas for excavation and physical direct assessment as part of fitness-for-service study.

Fitness-for-service Engineering assessment to determine the ability of a component to perform its function as designed in a safe manner and in accordance with the relevant regulations (also referred to as fitness-for-purpose or fitness-for-use).

Key point indicator An operational process or management parameter that can be measured and tracked during operations to assess the high level performance of critical items/activities.

Latent condition An undiagnosed or unrecognized flaw or defect in data, data management systems, documents, procedures, and guidance/standards that gives rise to human errors.

Likelihood of failure A method used to prioritize components/facilities that are subject to possible failure. Normally used in qualitative or semiquantitative risk assessments (some times used interchangeably with Probability of Failure).

Probability of failure A method used to prioritize components/facilities that are subject to possible failure. Normally used in as part of a fully quantitative risk assessment (sometimes used interchangeably with Likelihood of Failure).

Risk-based inspection A method for prioritizing and defining inspection activities to focus on items that are considered to have the highest risk of degradation, as defined by the combination of consequence and likelihood.

Safety, health and environment A formal process for defining policy and implementing strategy associated with the management of the safety and health of people in the vicinity of the facility, and the impact on the environment surrounding the facility.

Total quality management Is a business management strategy aimed at embedding awareness of quality in all organizational processes.

Abbreviations

ACVG AC voltage gradient
AIM Asset Integrity Management
API American Petroleum Institute
ASME American Society of Mechanical Engineers
ASTM American Society of Testing and Materials
bpd Barrel per day, unit of flow rate (1 bpd = 0.159 m^3 day^{-1})
CAPEX Capital Expenditure
CIPS Close Interval Potential Survey
CoF Consequence of failure
COMAH Control of major accident hazard
CP Cathodic protection
CRA Corrosion-resistant alloy
CRA Corrosion risk assessment
CSCC Chloride stress corrosion cracking
CUI Corrosion under insulation
DA Direct assessment
DCS Distributed control system
DCVG DC voltage gradient
DG Dry gas
DnV Det Norsk Veritas
EAC Environmentally assisted cracking
ECDA External corrosion direct assessment
EN Euronorm (European Standard)
EOR End of reservoir
ER Electrical resistance
FEED Front end engineering design
FEL Front end loading
FFS Fitness-for-service
FPO Floating, production, and offloading
FPSO Floating, production, storage, and offloading
GIS Graphical information system
GOR Gas–oil ratio
GRP Glass reinforced polymer
HAZOP Hazard and operability
HE Hydrogen embrittlement
HIC Hydrogen induced cracking
HSE Health and safety executive
ICDA Internal corrosion direct assessment
ILI In-line inspection
IP Intelligent pig
IT Information Technology
ISO International Standards Organization
KPI Key performance indicator
LoF Likelihood of failure
LP Liquid petroleum
LPR Linear polarization resistance
MFI Magnetic flux inspection
MFL Magnetic flux leakage
MIC Microbiologically influenced corrosion
mil A (depreciated) unit of length equal to one thousandth of an inch (1 mil = 25.4 μm)
mmscf Million standard cubic feet (1 mmscf = 28 316 sm^3)
mpy A (depreciated) unit of metal loss rate (corrosion rate) = 1 mil $year^{-1}$ (0.025 mm $year^{-1}$)
MR Materials recommendation
MSD Material selection diagram
NACE National Association of Corrosion Engineers
NDE Nondestructive examination
NDT Nondestructive testing
NUI Normally unattended installation
OPEX Operational Expenditure
P&ID Piping and instrumentation diagram
PEC Pulsed eddy current
PFD Process flow diagram
PI Point indicator/ plant information
PoF Probability of failure
ppb A unit of concentration, parts per billion (1 ppb = 1 μg dm^{-3}, or 1 μg kg^{-1})
ppm A unit of concentration, parts per million (ppm = 1 mg dm^{-3}, or 1 mg kg^{-1})
psi A (depreciated) unit of pressure, pounds force per square inch (1 psi = 6895 Pa or 0.069 bar)
PVT Pressure volume temperature
PWHT Post weld heat treatment
QA Quality assurance
RAMS Reliability and maintenance systems
RBA Risk based assessment
RBI Risk based inspection
RP Recommended practice
SAP Systems, applications, and products in data processing
SCADA Supervisory control and data acquisition
SCC Stress corrosion cracking
scf Standard cubic feet, unit of volume of gas at 15°C and 101 325 Pa (1 scf = 0.0283 sm^3)
scf/bbl A (depreciated) unit of gas to liquids ratio, standard cubic foot per barrel (1 scf/bbl = 0.181 sm^3/m^3)

SHE	Safety, health, and environment
sm^3	Standard cubic meter, unit of volume of gas at 15°C and 101 325 Pa
SOHIC	Stress oriented hydrogen induced cracking
SP	Standard practice
SRB	Sulfate reducing bacteria
SSCC	Sulfide stress corrosion cracking
TM	Test method
TOFD	Time of flight diffraction
TQM	Total quality management
TR	Technical report
TR	Transformer rectifier
TSA	Technical safety audits
UNS	Unified numbering system
UT	Ultrasonic testing
WG	Wet gas

4.41.1 Introduction

4.41.1.1 Outline

This chapter addresses issues concerned specifically with the management of corrosion in oil and gas production equipment both onshore and offshore and from subsurface, through pipeline systems and process plant to storage and export facilities. The industry covers a wide range of assets of differing ages and designs that operate with varying internal and external environments. Such infrastructures also reflect particular company cultures and the equipment designs/operations must meet different legislative requirements around the world. It is not possible to cover every aspect in this review, but the aim is to provide a general approach to corrosion risk mitigation and management of typical issues encountered in the field. The message is that 'one size does not fit all' and each case must be treated individually with appropriate assessments, reviews, and audits throughout the project life.

Corrosion management in the oil and gas industry follows the same requirements as outlined in the corrosion management overview chapter in this book. In fact, modern corrosion management across all industries evolved out of procedures and systems developed specifically for oil and gas production facilities, where the emphasis has been on 'managing assets constructed from carbon steels that are inherently at risk of corrosion deterioration.'[1]

Corrosion management for oil and gas operations has been the subject of considerable discussion in the industry. In 2001, the UK Health and Safety Executive (HSE) published a general guidance document aimed at UK offshore production facilities and focused on internal corrosion threats.[2] This has recently been updated by the UK Energy Institute[3] and expanded to cover all aspects of oil and gas processing, including onshore and external corrosion. Elsewhere, particularly North America, there have been developments in the requirements for corrosion management of pipeline systems, which has resulted in the development of *direct assessment systems*, which are described in Section 4.41.6.8.

The introduction to this chapter outlines the causes of corrosion damage found in equipment items, including the location, type, related problems, and mitigation measures. Aspects of corrosion management specific to oil and gas production are introduced in Section 4.41.2 and then the main focus is on the various project phases where specific concerns are addressed from the front end engineering design (FEED) in Section 4.41.3 and the requirements for design and detailed design in Section 4.41.4 to fabrication, construction, and commissioning in Section 4.41.5 and operations in Section 4.41.6. The objective is to provide a logical structure based on typical project timeliness that is useful to both specialists and nonspecialists.

4.41.1.2 Overview of Oil and Gas Industry Corrosion

The primary objective of oil and gas production is the cost-effective and safe abstraction of hydrocarbons from fields, reservoirs, and local wells into flow lines and gathering lines, separate oil and gas from any produced water and then export, usually through pipelines, to storage prior to refining or transfer to a tanker or export pipeline. All these facilities pose a potential risk for health and safety, environmental and commercial concerns. Secondary facilities, including water injection, firewater, produced water disposal, etc. are also subject to corrosion threats and while failure of these systems may not present a safety health and environmental (SHE) risk, it could result in the reduction/cessation of production with consequential commercial implications.

The industry covers a wide range of assets, both onshore and offshore, and it is not possible to address every design in this review nor to cover macroeconomics, seismic, and political risk. Also each field, facility, and asset will have its own specific corrosion issues that result from local produced fluid compositions, water cuts and changing chemistries, CO_2 and H_2S content, flow conditions and possible microbiological contamination during drilling and production. In many cases, external environments also provide a major threat, ranging from subsea, offshore processing, and onshore conditions with conditions ranging from cold arctic to hot dessert. In practice, all these issues have to be considered if the effects of corrosion damage are to be mitigated and managed effectively.

Other factors that influence the management of corrosion include the age, design, operation, organizational structure, and culture and maintenance philosophies, as well as local and corporate SHE obligations. Key concerns for installations are the prevention of incidents resulting from sudden or catastrophic failure and the prevention of hydrocarbon releases. Hydrocarbon fluids are flammable and produced fluids that contain hydrogen sulfide, a toxic and corrosive gas, are major hazards. There has always been an emphasis to design, construct, operate, and maintain the facilities in a safe manner, but what has changed over the past 15–20 years is that SHE issues now require that any procedures that are adopted need to be increasingly risk based and auditable, while the manner in which activities are conducted requires clearly defined reporting routes and appropriate actions from identified and responsible personnel.

For economic reasons, the majority of oil and gas facilities are constructed from carbon and low-alloy steels that are susceptible to both internal corrosion from the acidic process conditions and external corrosion from the environment. Hence, standard corrosion mitigation procedures are employed by the industry, such as chemical injection into produced fluids and the application of corrosion-resistant coatings plus cathodic protection to the outside of buried or immersed pipelines, as will be outlined below. Industry emphasis is on production deliverability and reliability and the efficiency of the overall process by the elimination of pinch points or poor practices that limit any specific areas of activity. A concern is that the experience and benefits from one field cannot be transferred automatically to a new development or existing facility without a management assessment of the risks arising from the changes and an understanding of the differences between locations, conditions and staff experience. A properly developed and well-functioning corrosion management system should be able to address such issues by highlighting the areas of varying risk, having in place suitable monitoring systems that are able to convert data into reports that trigger appropriate and timely management decisions.

Thus, although general principles are addressed in this chapter, it is essential that in practice each case is assessed on an individual basis. Corrosion risks can be identified, mitigated and managed effectively but require appropriate tools and practices, agreed procedures, clear processes with logical sequential steps, suitable organizational structures and adequate resources.

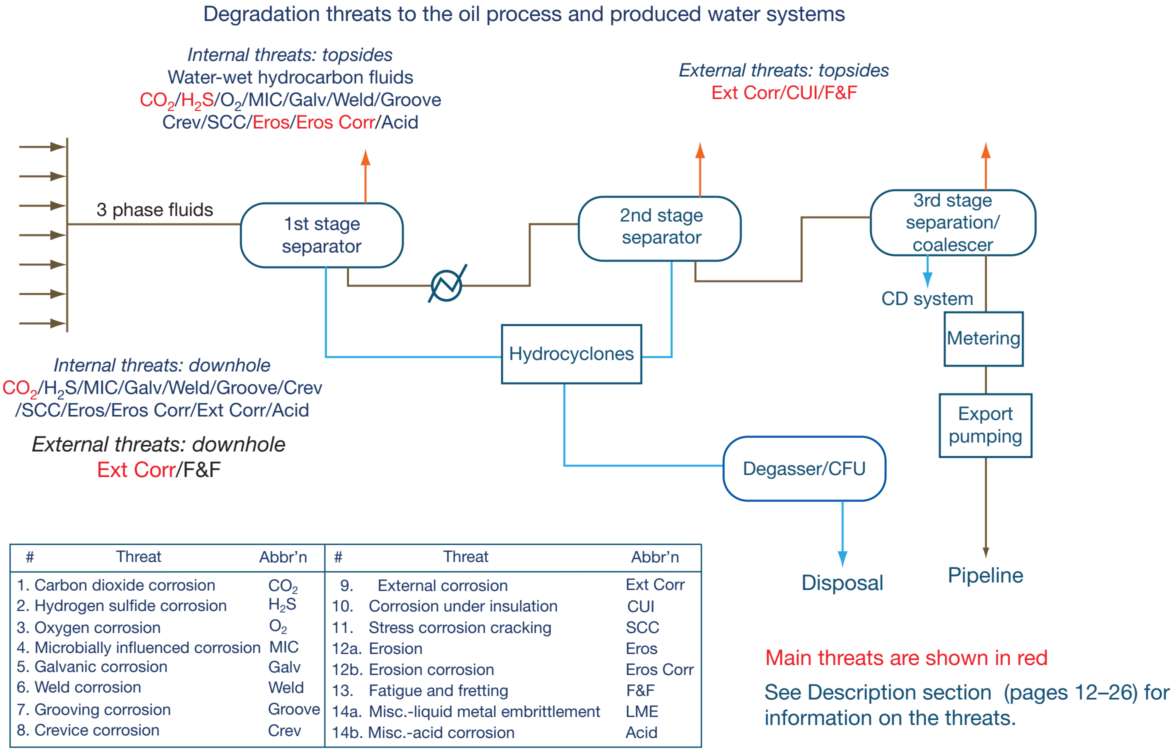
The different corrosion threats (internal and external) applicable to oil and gas production facilities are given in the *Corrosion Threats Handbook – Upstream Oil and Gas Production.*[4] Those relating to main production facilities are summarized in Figure 1. Other corrosion threats, associated with storage, transportation, and various utility services necessary for oil and gas production, are also applicable.[4]

Details of the different corrosion mechanisms are described in other chapters elsewhere in this book and include:

a. **Internal corrosion/degradation:**
   - ‘Sweet’ corrosion due to the formation of carbonic acid in produced waters from dissolved CO_2.
   - ‘Sour’ corrosion due to the formation of acidic conditions from dissolved H_2S.
   - Microbiologically influence corrosion (MIC) due principally to the presence of sulfate reducing bacteria (SRB).
   - Oxygen corrosion in water injection facilities due to an inadequate removal of oxygen and associated with high flow rates.
   - Galvanic corrosion caused by direct electrical connection of different materials/alloys to the same conductive environment.
   - Erosion and erosion corrosion, due to particulates, mainly sand, in the production stream.
   - Flow-assisted corrosion associated with effect of surface shear on the stability of protective films on the steel surface.
   - Environmentally assisted cracking (EAC), in particular:
     - ○ chloride stress corrosion cracking (CSCC) of austenitic stainless steels and corrosion-resistant alloys;
     - ○ sulfide stress corrosion cracking (SSCC) of carbon steels, austenitic stainless steels, and corrosion-resistant alloys (CRA);
     - ○ hydrogen induced cracking (HIC) of carbon steels

b. **External corrosion/degradation**
   - Atmospheric corrosion.
   - Corrosion under insulation(CUI).
   - Corrosion in seawater/fresh water.
   - Corrosion in soils.

A range of different corrosion control methods is adopted that are described in detail in other chapters, including:



#	Threat	Abbr'n	#	Threat	Abbr'n
1.	Carbon dioxide corrosion	CO_2	9.	External corrosion	Ext Corr
2.	Hydrogen sulfide corrosion	H_2S	10.	Corrosion under insulation	CUI
3.	Oxygen corrosion	O_2	11.	Stress corrosion cracking	SCC
4.	Microbially influenced corrosion	MIC	12a.	Erosion	Eros
5.	Galvanic corrosion	Galv	12b.	Erosion corrosion	Eros Corr
6.	Weld corrosion	Weld	13.	Fatigue and fretting	F&F
7.	Grooving corrosion	Groove	14a.	Misc.-liquid metal embrittlement	LME
8.	Crevice corrosion	Crev	14b.	Misc.-acid corrosion	Acid

Figure 1 Example of corrosion threats in oil/gas processing units. Reproduced from Corrosion Threats Handbook – Upstream Oil and Gas Production; Energy Institute and Oil and Gas UK: London, 2008.

- use of corrosion resistant alloy (CRA);
- use of chemical treatments, including use of corrosion inhibitors and biocides;
- use of protective coatings (external and internal organic and metallic);
- use of cathodic protection (CP), external and internal;
- process modification such as deoxygenation and dehydration.

4.41.1.3 Areas of Corrosion Risk and Industry Mitigation Approach

The following section provides a background to the different components/facilities used in oil and gas production and processing, and the different corrosion issues relating to them.

4.41.1.3.1 Corrosion subsurface

Wells typically comprise

- **casing** – carbon steel sections, that may be precoated, cemented to the formation;
- **bottom hole perforations** – explosively formed holes to allow reservoir fluids in the strata to enter the well bottom;
- **production tubulars** – sections of drawn pipe screwed together to form a continuous string for transport of produced fluids;
- **down-hole safety valve**;
- **annulus fluid and packer** – high-density fluid between the tubular string and the casing that helps to balance the well to surface pressure;
- **well head valve** and equipment;
- **cellar** – surface platform/foundations that holds well equipment in position;
- **gas injection valves** – enable low-pressure oil wells to maintain production;
- **inhibitor injection valve** – provides a continuous feed of corrosion inhibitor into the produced fluids via a thin 'spaghetti' tube inserted down the annulus.

4.41.1.3.1.1 Corrosion issues

Drilling a well could introduce SRB down-hole into the reservoir unless the monitoring and biocide treating of the aqueous drilling mud is carefully controlled. Well casings may be in contact with corrosive aquifers above the reservoir. Wells with high multiphase flow are subject to impingement and 'mesa' type elongated erosion–corrosion pits. Wellhead equipment, valves, and choke bodies are susceptible to erosion corrosion and severe localized corrosion especially with high temperature, high chloride content fluids and high-pressure gas wells. Maintenance of flow through the reservoir strata and removal of scale deposits from tubular goods may require chemical cleaning with corrosive chemicals (acids and acidic solutions of complexing reagent). These fracing/cleaning fluids, introduced as a 'squeeze' treatment, can cause significant corrosion when returned up the well. Materials must be specifically selected for their mechanical and corrosion resistance properties, particularly safety critical items.

Typical corrosion related problems include:

- uniform/general corrosion caused by carbon dioxide and hydrogen sulfide in reservoir fluids and acids/chemicals in treating fluids;
- pitting due to chlorides and sour environments under conditions of high chloride content and temperature;
- hydrogen damage of susceptible steels in sour systems;
- erosion corrosion due to high velocities of fluids (gas slugs);
- introduction of corrosive gas during gas lift operation;
- SRB contamination of annular fluids and injection waters.

Corrosion mitigation includes:

- CP of external well casing;
- selection of 'fit-for-service' tubular steel goods/CRAs/nonmetallic linings;
- down-hole inspection (wireline tools);
- use of corrosion inhibitors – squeeze/continuous injection;
- use of biocides;
- topside monitoring of produced fluids.

4.41.1.3.2 *Corrosion in pipeline systems*

Flow-lines, gathering lines, interfield trunk and export lines are typically constructed from rolled low-alloy steels, the wall thickness of which is determined by the design/operating pressure, the service duty (sweet or sour) and the required corrosion allowance. Internal corrosion is typically mitigated by chemical treating and/or pH control together with regular maintenance pigging, and effectiveness is confirmed by inspection (including intelligent pigs) and online monitoring. In some cases internal coatings or use of linings (with either CRA or non-metallic systems). External corrosion mitigation depends on the location. Above ground lines may be uncoated in dry dessert regions but coated in more humid/coastal areas. Buried/immersed lines have a primary protection from a barrier coating plus CP. Associated equipment includes manifolds, pumps/compressors, and valves, all of which may be susceptible to corrosion attack and hydrogen damage.

4.41.1.3.2.1 *Corrosion issues*

Multiphase lines are normally designed to operate under turbulent stratified flow conditions (liquid at the bottom, gas phase at the top) but slugging flow or gas/sand impingement may occur depending on the relative gas/liquid velocities and particle content. Some lines have a significant temperature profile that, together with the topography and bends/elbows/changes of diameter, can influence areas of water drop out, hold-up, and slugging. Bottom-of-the-line-corrosion generally occurs as water cuts increase and the fluid is no longer a water-in-oil emulsion, but local grooves ($<6\,\mathrm{mm}$ wide) may occur at the bottom of lines with low water cuts ($<10\%$). Such conditions may occur under low fluid velocities or when enhanced water coalescence causes water-in-oil emulsions to break down. A minimum flow (typically $>1\,\mathrm{m\,s^{-1}}$) is required to maintain particles in suspension and prevent sludge build-up. Fluid flow is often restricted to minimize erosion problems that is, $<15\,\mathrm{m\,s^{-1}}$ for liquids and $<20\,\mathrm{m\,s^{-1}}$ for gas.

Flow lines have a relatively small diameter and are not usually provided with launch/retrieval facilities for the deployment of cleaning pigs; hence, corrosion is often associated with water drop-out, deposits, and microbiologically contaminated sludge. Scale deposition can be a considerable problem in some fields. Scale control chemicals can limit the deposition but may lead to precipitates in the bulk fluid, these small crystals may form a sludge deposit if the flow conditions are not maintained at a high enough value ($>1\,\mathrm{m\,s^{-1}}$).

Internal corrosion in lines carrying produced/separated fluids results from CO_2/H_2S and in the lines carrying water for injection, fire mains, wash down, etc. from dissolved oxygen and MIC. Corrosion damage includes:

- metal wastage due to fluid corrosivity;
- localized pitting, especially in sour systems;
- grooving corrosion, especially where moderate water cuts result in a thin free water phase at the bottom of the pipeline;
- erosion corrosion at elbows, bends, riser sections or downstream of restrictions and when slugging flow is present;

- pitting/crevice type corrosion under deposits, debris and scales;
- local areas of attack due to water-drop out at low spots;
- microbiologically induced corrosion due to contamination through water injection and hydro test fluids;
- pipe-wall delamination and cracks due to hydrogen damage (HIC, SOHIC) and through-wall cracks due to SSCC.

External corrosion results from exposure to natural environments such as soils, immersion in or contact with seawater, etc. and local atmospheres. Corrosion damage takes many forms and includes:

- wastage and pitting that will be particularly severe for unprotected pipes that are buried in deaerated wet clay soils or in estuarine environments due to anaerobic SRB;
- stress corrosion cracking (SCC) due to carbonate/bicarbonate environments that may develop over time and/or hydrogen generated by excessive CP current;
- stray current effects from other CP systems, DC railways and welding; and
- telluric currents due to the Earth's magnetic field.

Corrosion mitigation options for pipelines include:

- selection of appropriate steels and weld procedures for either sweet (CO_2) or sour (CO_2/H_2S) service; this may require use of CRAs (either as solid pipe or as lined pipe) or use of nonmetallic pipe materials;
- inspections (pigging) to detect thinning, pitting and cracks;
- use of corrosion inhibitors by continuous injection and/or batch treatment;
- online monitoring to identify changes and control chemical treatments;
- use of biocides in batch treatments;
- control of process fluid compositions for example, dehydration of gases, removal of H_2S, pH control of wet gas (WG) lines, etc.;
- use of internal coatings, subject to concerns as to pinholes and crevice corrosion;
- use of internal linings, either non-metallic or CRA clad systems;
- coating of external walls;
- CP of buried and immersed lines and monitoring of CP systems and coating defect location, using techniques such as close interval potential survey (CIPS) and DC voltage gradient (DCVG) surveys.

4.41.1.3.3 Corrosion in process plant

Equipment such as separation vessels/trains are used to separate comingled produced fluids into oil and gas/condensate to aid transportation and downstream processing. Associated items include vessel internals, electrostatic precipitators, piping between separators, desalters, knockout drums, valves, pumps, and compressors. Other areas include produced water plant, utility systems for steam generation, cooling systems and storage tanks for separated products and chemicals.

Main concerns center on:

- wet gas streams that are cleaned up in gas separation vessels, compressed, cooled, often dried and exported via a gas line, and/or used for gas reinjection;
- wet crude handling streams comprising dehydrators, desalters and a crude oil pump and export-line;
- brine phase streams with water–oil separation or stripping sections to remove oil residues, after which the water is discharged/disposed of downhole via injection pumps used to maintain reservoir pressures.

4.41.1.3.3.1 Corrosion issues

Corrosion and pitting usually occur at water-wet surfaces in the system. High-risk areas are vessel bottoms (in contact with produced water), wet gas lines down stream of compressors, water lines, and tanks containing oil, from which water droplets may coalesce and drop-out. Three phase separators/vessels, constructed from low-alloy steel materials, and containing wet gases are usually completely coated internally with high build coatings (epoxy reinforced with glass flake, $>300\ \mu m$) in water immersed regions and 200–300 μm in water splash/condensation/water carry over regions in gas spaces. CP may also be installed in the water-containing vessel bottoms. Where conditions are particularly aggressive internal lining using CRA is some-times used. Separation of gases followed by compression increases the partial pressures of carbon dioxide and hydrogen sulfide that then increases the corrosivity. Weld corrosion may also be found on pipework that contains wet condensate saturated with carbon dioxide. Internals of thin section are normally fabricated from CRAs. Water lines and water processing equipment contain lower pressures and materials selection may allow the use of plastics. Specific concerns are 'dead legs,' areas of unused pipework that do not receive corrosion inhibitors/biocides, galvanic corrosion from mixed metal fabrications and external crevices/under insulation areas subject to wetting. Typical plant areas at risk from corrosion damage are given in *Corrosion Threats Handbook – Upstream Oil and Gas Production*.[4]

Corrosion in gas/oil separation equipment typically includes:

- uniform/general corrosion caused by carbon dioxide and hydrogen sulfide;
- pitting due to chloride containing brines and sour environments;
- hydrogen damage of susceptible steels;
- CRA internal lining, either as weld overlay or a sheet clad.;
- erosion corrosion due to high velocities of produced fluids at elbows and bends;
- water drop-out at low spots in low velocity regions;
- areas at the bottom of vessels that collect debris (under deposit corrosion, pitting and SRB contamination);
- microbiologically induced corrosion;
- weldment corrosion.

Corrosion mitigation includes:

- selection of 'fit-for-purpose' steels/CRAs and weldments;
- use of coatings for both internal and external corrosion control;
- CP for water immersed vessel internals;
- inspection for corrosion damage;
- monitoring of CP systems;
- use of chemical treatments:
  - corrosion inhibitors
  - scale control
  - demulsifirers
  - biocides;
- on-line monitoring to identify changes and control chemical treating.

4.41.1.4 Industry Drivers and Changes

Oil and gas production has derived significant economic benefits over the past 25 years from the use of asset management strategies that have been a major industry driver in eras of rising demand and fluctuating prices with operations in more severe environments, often with squeezed budgets. The asset manager in an organization essentially fulfils the traditional role of a process site managing director in balancing the requirements of stakeholders to achieve overall benefit. Asset managers have budget decision-making responsibility for resources and services to achieve defined objectives. Multi-disciplined teams are tasked with improvement of performance, optimization of costs and minimization of risks. This asset-centered approach has increasingly replaced traditional activity-centered groups and organizations based on functions such as design, engineering, production, operations, maintenance, and materials/purchasing, each with individual budgets. Client 'assets' now fund technology developments with contributions from the design, SHE, IT and financial specialists from both in-house, central, shared sources and external providers. Delivery of services such as corrosion mitigation requires development of strategic models that may well include input from both in-house and third party specialists. Provision of improved quality and value is what counts rather than whether the service provider is in-house or a contractor. Asset strategies and objectives are typically encompassed in the Asset Management Policy that cascades down into local asset business goals with intentions converted into plans and actions.[5]

Developments in asset management cannot be ignored in the delivery of corrosion management services and will continue to drive technical and management changes. In this context, the definition first adopted in the mid-90s is still appropriate:

***Corrosion Management** is that part of the overall asset management system that is concerned with development, implementation, review and maintenance of the corrosion policy.*[6]

*A **corrosion policy** includes establishment of organizational structures with defined responsibilities, reporting routes, practices, procedures, processes and resources. This requires the demonstration of responsibility and accountability for corrosion performance, managing risks, decreasing costs, controlling compliance and motivating personnel.*

A written corrosion policy, agreed by senior personnel, defines the corrosion mitigation objectives and provides a focus for various interdisciplinary and multidepartmental inputs and control of operational, day-to-day activities. Most corrosion related activities are undertaken by asset management team members with limited training in corrosion mitigation and difficulties arise from an industry shortage of experienced corrosion engineers.

Major changes during the 90s centered on safety and environmental issues following the Piper Alpha Report[7] and a number of high-profile oil leaks. Industry centered documentation has focused on engineering/safety procedures to identify failure modes likely to affect integrity and includes the *US Pipeline Safety Act*[8] with emphasis on risk management and cost benefit, *API 580 Risk-Based Inspection*[9] plus the accompanying resource document *API* 581[10] and DnV RP G101 *Risk Based Inspection of Offshore Topsides Static Mechanical Equipment*.[11] UK oil and gas regulations mirror EU requirements such that assets require development of a safety case,[12] that continues into design and construction.[13] This general risk-based approach continued in the '*Pipeline Standard*',[14] control of major hazard sites[15] and pressure systems.[16]

A framework for management process employed by the UK HSE[17] identifies six basic steps:

1. policy;
2. organizing;
3. planning and implementation;
4. measuring performance;
5. reviewing performance;
6. auditing.

The Norwegian regularity authorities have adopted similar requirements. For example, contractors working for offshore operators are subjected to a SHE evaluation[18] where the system elements addressed include:

1. leadership and commitment;
2. policy and strategic objectives;
3. organization, resources and documentation;
4. evaluation and risk management;
5. planning and procedures;
6. implementation and monitoring;
7. auditing and reviewing.

A matrix is also used to address consequence versus increasing probability that classifies activities into three categories – (low) 'manage for continuous improvement,' (medium) 'incorporate risk reduction methods' and (high) 'intolerable.' Similar requirements are found in the ISO standard for management of environmental issues.[19]

A general acceptance in industry of a risk-based approach, particularly RBI, by most international organizations means that information from benchmark standards has been incorporated into in-house guidelines as part of the input into industry changes. However, risk management is only one tool employed to mitigate corrosion and, for example, adoption of a risk-based inspection system must be backed up with *management of change procedures* and *end of life strategies.*

In many countries, there has also been a cultural shift from a rules-based regulatory system to a principles-based system with emphasis on defined objectives (i.e., *framework rules with guidelines – How it must be managed by first identifying hazards and risks and then prioritize actions accordingly*) rather than traditional/prescriptive rules based practice (i.e., *detailed rules and regulations – Defines what must be done, i.e., prescriptive, not always appropriate but do it anyway*). This change in emphasis is also reflected in the development of recent EN, ISO, and NACE standards for corrosion control such as materials for sour service,[20] CP and protective coatings that provide outline guidance for experienced engineers but should not to be used on their own for certification purposes. In principle, the implementation of these changes in an organization and their implication for the management of corrosion mitigation may be summarized by the following steps:

1. hazard identification;
2. assessment of associated risks;
3. consider alternative ways of managing the risks;
4. conduct a cost benefit evaluation of alternative risk management options;
5. decide which option(s) to select.

In practice, corrosion related incidents/accidents still occur as shown by the South Humberside Refinery explosion/fire[21] and the recent Alaska pipeline leakage,[22] that highlight an underlying organizational concern in relation to what appear to be human errors. Management of SHE hazards, and by inference corrosion risks, can be visualized as concentric defensive barriers designed to prevent failures and catastrophic incidents by containment of hazards and limitation of their effect.

John Reason[23] described such barriers as either physical (hard) or procedural (soft) but each barrier has weaknesses/holes (the *Swiss Cheese Model* as described in **Chapter 4.30, Corrosion Management Overview** in this book). Holes may be caused by active failures, such as unsafe actions, and latent conditions that are an inevitable feature of organizational life. The rare conjunction of a set of holes in successive defenses, allowing hazards to come into damaging contact with people and assets (the accident trajectory) is a necessary condition for an organizational accident. Unsafe actions are errors or violations that have an immediate effect on a system, usually a direct accident at the individual level. Reason also considered *latent conditions* as arising from strategic/top-level decisions made by regulators, designers, manufacturers and managers that may be present for many years, and include poor design, gaps in supervision, undetected manufacturing defects, maintenance failures, unworkable procedures and training shortfalls. Latent conditions promote the likelihood of active failures by the creation of local factors that promote errors and violations and aggravate the consequences of unsafe acts and their effects on a system's defenses, barriers, and safeguards, as indicated by the refinery fire and pipeline leak examples cited earlier.

The cultural shift toward principles-based legislation and industry ISO standards with an emphasis on a risk-based approach for assessment and mitigation is aimed at overcoming engineering shortfalls associated with latent conditions. This approach is also seen in hazard and operability studies (HAZOPS), technical safety audits (TSA), reliability and maintainability studies (RAMS), the control and use of databases, and the application of decision support systems that are essentially engineering applications to the control of hazards. However, the wider organizational approach proposed by Reason views human errors more as consequences than causes and as such symptomatic of latent conditions in the management system that adversely affect integrity defenses. The organizational model has therefore some similarities to TQM, that is, it uses continuous assessment to reform a system, but also combines quality-determining and safety-related factors. This organizational model approach also has many of the attributes of crisis management.

This resume highlights some relevant management philosophies on the basis of which corrosion management systems should be organized and operated. Successful management of corrosion is often achieved by being asset specific and is dependant on factors such as the design, life cycle stage, process conditions, operational history and organizational culture. There are however some basic and common requirements for management systems as first outlined in 1999[6] and 2001[2] to address continuing concerns of hydrocarbon emissions from offshore processing facilities. The aim was to develop a template based on the UK regularity authority's approach to safety management[17] and encourage the industry to adopt a common approach to the assessment of corrosion management systems already in place. This has been encompassed and extended in *Guidance for Corrosion Management in Oil and Gas Production and Processing* published in 2008,[3] a document considered *normative* for UK operators.

The document refers to the *barrier* concept to corrosion risk management without any details, but in particular highlights the importance of *key performance indicators* (KPIs) to assess the various stages and activities of the management process and provides an extensive checklist for the assessment of corrosion management. In general, the use of performance measurement/KPIs is normal practice in most quality and safety systems and these provide a basis for planning and measuring achievement. The setting of agreed performance criteria is crucial for the effective implementation of policies, checks on the performance of management systems and individual, day-to-day actions that are judged against acceptable criteria defined by in-house standards and/or industry benchmarks. Failure to achieve a performance standard may indicate latent conditions within a management system but should also trigger a review to identify reasons for the under-performance of the system.

4.41.2 Management of Corrosion

Corrosion is a risk to both structures and production processes and as such should be treated within a risk management framework with corrosion mitigation addressed early in the project and not considered as a series of procedures introduced at a later stage. As with safety and environmental management it is a live, continuous process that starts during the concept and grows and is modified throughout the project. Management of corrosion is also a multidisciplinary team effort with input from various in-house personnel, contractors, specialists, and groups, including exploration, design, construction, operation and maintenance, as well as materials specialists and corrosion engineers. The composition and size of the 'corrosion team' and its relationship with the 'integrity team' will depend on the project stage and the asset management boundaries. Equipment integrity is a key issue from an asset management perspective and much of the equipment damage sustained throughout a project is corrosion related. For example, corrosion produces sludges (detached mill scale/corrosion products/deposits), which affect operations resulting in significant chemical treatment costs and expensive downtime for cleaning and maintenance. Secondary risks also arise with corrosion mitigation strategies such as risk-based inspection that have as their basis a rate of deterioration based on the use of cost-effective corrosion inhibitors, in which case failure of the inhibition process has implications for integrity trending.

In principle, corrosion mitigation should be an easy task, the major tactics are well established and summarized as follows:

1. **Materials selection** – carbon steels/low-alloy steel (usual to include a corrosion allowance during design), CRAs (stainless steel, nickel alloys, titanium), nonmetallic materials (polymers, glass reinforced plastic (GRP), elastomers, ceramics).

2. **Chemical treatments** – typically corrosion inhibitors, biocides and scale control chemicals but packages also include surfactants and antifoaming chemicals. Treatment may include the use of glycol to control hydrate formation combined with pH control to lower corrosion in WG lines.
3. **Use of coatings** – metallic, nonmetallic, and organic/paints, used in external and internal environments. Major factors are cost, availability, ease of surface preparation, application, and life expectancy. It is important to ensure adequate inspection of field applications.
4. **CP** – applied to immersed and buried structures, jetties, pipelines, tanks and concrete and inside water containing vessels, separators, tanks, and the water boxes of heat exchangers.
5. **Process and environmental control** – modification of moisture/humidity levels, lowering of oxygen concentrations and changes of throughput and decreases in flow and/or heat transfer rate.
6. **Design** – use of codes/standards to produce specifications and drawings. During the detailing phase, assessment of factors associated with stress, shape, compatibility and surface condition, for example, eliminate stress raisers, crevices and consider increased wall thickness on some bends.
7. **Inspection and monitoring** – trending of deterioration rates, chemical dosages and changes in process chemistries.

The first six options seen earlier are corrosion control methods that are used either singly or in combination, the choice depending on the specific application. In practice the difficulty is ensuring that long-term strategies are adopted and operational day-to-day activities are conducted effectively and efficiently.

Management of corrosion is an interactive process comprising a series of steps that aim to ensure corrosion risk mitigation procedures are applied cost effectively, commensurate with safety, heath and environmental requirements. Figure 2 shows typical steps in a corrosion mitigation process based on those presented in the management of project risks.[24] The inputs are corrosion and SHE issues and the outputs are cost-effective corrosion mitigation, that is able to provide integrity and environmental assurance for the asset, and a continuously improving management system that is able to respond to both changing technical and worldwide economic conditions. In the UK, it would also meet the requirements for the review and audit of management systems conducted as part of a HSE assessment.

The steps are summarized as:

1. **Aims/objectives/policies.** An initial step in developing a corrosion management system is to define the aims and objectives of the corrosion input to a project. These then form the basis of the corrosion policy/strategy.
2. **Individuals/teams/organizations.** Identification of individuals and teams with ownership of corrosion management processes also helps to define roles, responsibilities and accountabilities of managers, staff and contracted bodies concerned with corrosion issues.
3. **Corrosion risk evaluations and assessment of mitigation options.** These are fundamental steps conducted throughout project life as conditions and the facility operational requirements and procedures change. The study would typically employ information as found in industry corrosion rate models[25–27] and guidance, including probabilistic assessments as in DnV RP G101[11] and API 581.[10] Evaluation of corrosion mitigation options, including their relative life cycle costs and required monitoring and inspection, is a basic step. The cost of preferred options must be compared using net present value/discounting procedures to obtain estimates of project life cycle costs. A useful assessment tool in the decision-making process is probabilistic analysis that enables various scenarios to be displayed as *S*-curves of anticipated life versus time.[28,29]
4. **Corrosion risk treatment planning and implementation.** These are vital to ensure that strategic, tactical, and operational/day-to-day activities designed to mitigate corrosion are employed effectively. The planning and implementation of the risk treatment process include strategic activities to meet optimal life cycle costs, SHE and other mandatory requirements, corporate corrosion practice and integrity requirements, and business concerns including development of condition-based maintenance and equipment reliability/uptime needs. The planning also includes assessment and development of chemical treating, inspection and maintenance specifications and protocols.
5. **Database development and maintenance.** The requirement for suitable databases for the storage of system documentation, the equipment design and as-constructed diagrams, commissioning information and field data generated during operation, inspection, and maintenance is given for any corrosion management system to have a chance of success. Corrosion mitigation and management

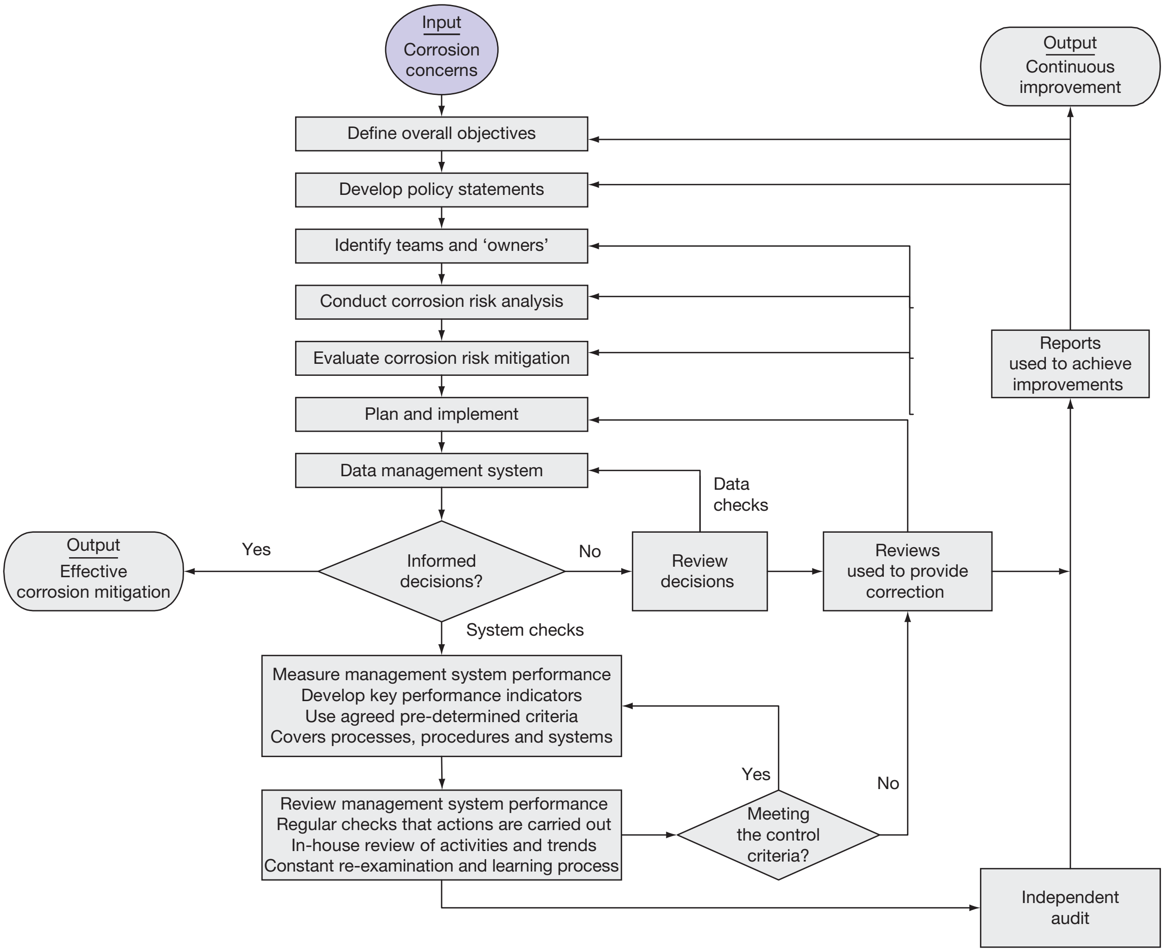


Figure 2 Basic steps in a corrosion management system.

often falls behind other disciplines in the management and use of data, for example, compared with predictive maintenance and energy control of processing in some industry sectors. An effective management tool is a transparent database that correlates field data to provide a regular weekly/monthly breakdown of corrosion mitigation costs.

6. **Informed decisions and actions.** These are key processes; many management systems fail because of a lack of a clear decision-making step even though adequate protocols and procedures are in place. Informed decisions are based on adequate data to instigate corrective actions from investigative studies, the issuing and following up of warnings or even shut down actions when required. Operational, day-to-day actions include the rescheduling of inspections, changes to chemical treating or CP levels and predictive maintenance work or recoating that involve other teams. Recommendations must either be followed up or rejected in a positive manner on the basis of other acceptable factors but not on a default 'do nothing' basis.
7. **Performance measurement of the management system**. Regular checks on the operating system should be conducted against agreed predetermined criteria – the performance standards or KPIs.
8. **Regular reviews**. These are normal in-house checks of overall corrosion management system performance. They ensure that management procedures and processes are consistent with any changing business plans, changing production requirements and changing legislation.
9. **Periodic audits.** Management and monitoring system audits provide evidence that the corrosion management system is efficient, effective, and reliable, and that processes and procedures are being implemented in accordance with agreed procedures. Regulations typically require owners to

> ensure that adequate arrangements are established for audit report making. Any dynamic corrosion mitigation process is also reliant for acceptable or improved performance on feedback from continuous, daily checks, regular reviews and scheduled audits to modify or improve the various processing steps. These require the development and use of performance indicators and form a key part of control of the corrosion management process. The use of KPIs is normal practice in most quality or safety systems and examples in corrosion management can be found in various publications.[2,3,30] They can be applied at various management levels and the aim is to ensure that the management system is operating effectively so that the required actions are carried out as scheduled and appropriate decisions are made on noncompliance.

Any management system relies on feedback for review and audit of the processes within the various steps. As shown in Figure 2 the emphasis is on assessment of the management process, first by regular/daily/weekly/monthly use of appropriate performance indicators with the review (quarterly/half yearly/yearly) and audit processes (every few years) used to not only identify areas of activity that are conforming to previously agreed criteria but also those areas needing improvement.

The left-hand output in Figure 2 (Effective Corrosion Mitigation) has usually been the major concern of corrosion teams, especially with regards to the impact on reliable operation and asset integrity. Effective corrosion management encompasses other issues as indicated by the feedback needed for review and audits. Hence, there are two outputs from modern corrosion management process: effective corrosion mitigation (as before) and also continuous improvement in performance (top right output in Figure 2). That is business related and safety, health and environmental outcomes, such as increased throughput at lower costs, less hazards from corrosion, fouling, fracture, wear, and better control over asset integrity with less leakages.

4.41.3 Front End Engineering Design (FEED)

4.41.3.1 Introduction

FEED is the process for conceptual development of process industry projects and is sometimes referred to as Front-End Loading (FEL) or Pre-Project Planning (PPP). FEED covers robust planning and design early (the ‘front end’) in a project’s life-cycle at a time when the ability to influence changes in design is relatively high and the cost to make those changes is relatively low, as described in the chapter on design in this book. The extra time and cost to make changes in the early stages of a project are minor compared with the costs and effort required to make changes at a later stage of the project. The influence of design stage decisions on life cycle costs is illustrated in the chapter on economics in this book.

For the oil and gas industry the FEED process is often split into pre-FEED and FEED. In pre-FEED the basic definitions of the project are identified that will cover material and energy balance, and basic economic evaluations. The basis of design is the data available on the likely produced fluid compositions and associated information on production rates, water cuts, etc. plus any specified requirements of the proponent. The main activities within the FEED itself include:

- preliminary equipment design;
- preliminary layout;
- preliminary schedule;
- preliminary and definitive budget estimate;
- identify critical/major equipment requirements;
- develop preliminary equipment specifications;
- develop project execution plan;
- preliminary 3D model;
- electrical equipment list;
- line list;
- instrument index.

Developments of new fields, especially in deeper, more aggressive conditions are pushing the boundaries of conventional carbon steel materials and hence there is an increasing focus on corrosion management at the FEED stage, where critical decisions are taken that will affect not only the fabrication/construction cost but also the long term operation and maintenance costs since these influence the corrosion mitigation strategies adopted.

Fields that have a potentially high corrosion rate are typically high-pressure, high temperature, high-CO_2 fields, with high levels of H_2S and chloride. Development of these fields even 10–15 years ago would have been considered technically and economically prohibitive.

Traditionally, the first part of any corrosion management consideration during pre-FEED and FEED would be to determine the estimated corrosion rate for carbon steel under the expected operating conditions throughout the expected life of the facility. This is normally carried out using industry standard models, most of which are based on the work of de Waard *et al.*[25] for pipelines containing CO_2. There are numerous versions of these models available that have been developed and expanded by major operators, academic/research centers and consulting organizations based on the same or similar databases and the same chemical equilibria constants. The model has been extended by de Ward and Smith[31] to include the effect of H_2S. A calculation using a standard corrosion model would be carried out to determine the likely corrosion rate of the produced fluids. Provided the estimated corrosion rates are within acceptable limits, the FEED would continue with the carbon steel option, usually with additional corrosion protection measures, as the preferred material of construction for the various components making up the development (tubulars, main flowlines, vessels) apart from specific safety critical items (down-hole completions, safety valves, choke valves, etc.).

However, because of the trend to more challenging field development it is not unusual for predicted corrosion rates of >10 or even $>20\,\text{mm year}^{-1}$ for unprotected carbon steel to be encountered in designs, which create major challenges for traditional oil and gas production corrosion control methods. Consequently such high corrosion risk fields require a more rigorous analysis at this early stage in the field development to determine a cost-effective design from a corrosion/durability stand-point.

4.41.3.2 Data Availability

A pressure/volume/temperature (PVT) report is typically the only item of data that is available at the FEED stage of a project. There are uncertainties associated with these data, particularly with regard to sampling techniques, and this has to be considered when considering suitable materials of construction.

Assessment of fluid corrosivity can be carried out by the following methods:

- theoretical calculation;
- laboratory test data;
- comparison with operational experience in a similar field.

The operational implications of any corrosion management strategy should also be considered at this stage for example

- For corrosion inhibitors:
  - Is the likely supply chain stable enough to ensure quality and delivery of any chemicals required for corrosion control?
  - Is the required inhibitor availability realistic? In particular, would an availability of 98% to 99.9% be required to achieve the necessary levels of protection?
  - Is it realistic to expect regular and routine pigging of pipelines, for cleaning purposes?
- If CRAs are to be specified:
  - Is there sufficient experience of fabrication available locally and/or within the fabrication contractor?
  - Has the likely effect of chlorides and sulfates been assessed, particularly where down-hole temperatures are high?

4.41.3.2.1 *Theoretical calculations*

As noted earlier, the first step in the FEED is the estimate of likely corrosion rates for carbon steel under the predicted range of operating conditions. When carrying out corrosion rate predictions the following factors would normally be considered when using standard CO_2 models to predict corrosion rate:

- Fluid composition:
  - Propensity to hold water.
  - Scaling/wax deposition propensity.
- Water composition:
  - Chloride, bicarbonate and acetate concentration.
- Water profile over field life:
  - Water cut in early, mid and late life.
- H_2S and CO_2 concentrations.
- Flow rates.
- Temperature:
  - Variation over field life and pipeline diameter.

The effects of flow can be complex, as described in the chapter on the effects of flow on corrosion in this book, and a number of flow models are available (such as NACE ICDA,[32] PIPESIMS®,[33] PIPEFLO®,[34] OLGA®,[35] HYSYS®,[36] and others) that will allow an assessment as to whether the likely flow conditions in tubulars, flowlines and pipelines are stratified, bubbly, or slugging. This then allows the likely corrosion rates to be determined for water lines and multiphase lines that have water wet walls under stratified flow. Maximum corrosion rates in CO_2 systems typically occur ~75 °C to 95 °C, depending on temperature, pressure and CO_2 content, as shown in **Figure 3**. At higher temperatures the corrosion rates fall due to increased

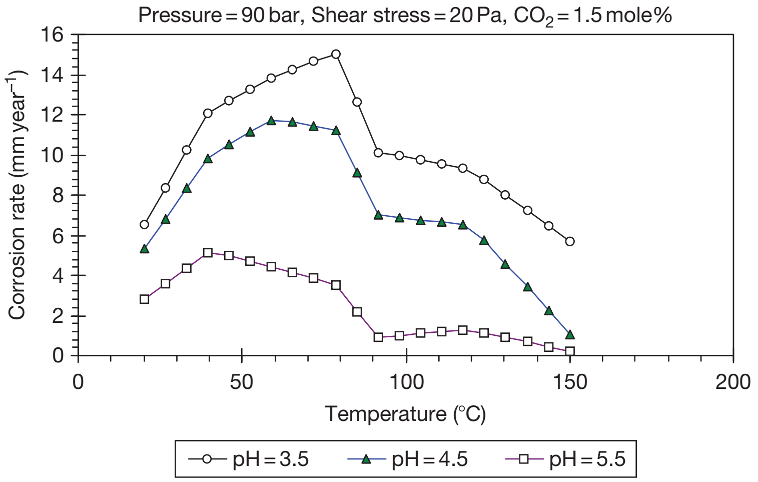


Figure 3 Typical estimated CO_2 corrosion rates obtained from the Norsok M506 model. Adapted from NORSOK M-506: Rev. 2, June 2005, CO2 Corrosion Rate Calcuation Model; Norwegian Technology Standards Instiution (Norsk Sokkels) www.standard.no/petroleum.

$FeCO_3$ scaling. Loss of protective scale obviously gives high local corrosion rates that can be significantly mitigated by selection of an effective inhibitor. Inhibited rates will depend on the inhibitor efficiency. The pH also influences CO_2 corrosion rates and this observation is employed in the use of pH control of methanol/glycol (hydrate control) injected into wet gas lines.

Standard corrosion rate models do not typically assess erosion or flow-assisted localized corrosion. The Norsok model[26] is limited to a fluid to wall shear stress maximum of 150 Pa and the de Waard (ECE) model[27] is limited to below the API RP 14E erosional velocity[37]; which is dependent on alloy. Other studies show that the arbitrary erosional velocity determined by API RP 14E, can be very conservative, since basic hydrodynamics, which considers the shear stress of the flow across the surface, is determined, indicate that the force created by normal flow patterns is several orders of magnitude lower than that required to damage protective iron carbonate layers, and that the effect of flow appear to be the result of 'freak energy density' or energy densities perpendicular to the wall.[38] This ties in with observations of areas of turbulence intensity (ratio of velocity fluctuations to the average velocity) that appear to be a key parameter in erosion corrosion in flowlines and pipes.[39,40] High turbulence intensity also means a high fluctuating wall shear stress and high mass transfer conditions with flow separation downstream of protrusions, bends, expansions restrictions, etc. can give rise to localized areas of erosion corrosion.

Particularly useful are corrosion models that allow for the water wetting of walls[41,42] and enable the ability of the fluid to hold water to be incorporated, that is a function of oil density and flow rate. Generally light oils can only hold a limited amount of water before a conductive phase is formed and condensates can only hold up to 200 ppm of water. Low flow conditions ($<1\ \mathrm{m\,s^{-1}}$) in most oil–water systems will result in water dropout. The assessment of what is essentially the emulsion tendency of the oil is not an accurate science, and therefore in some cases basic testing is applicable.[43] The effect of likely step change in conditions as water content changes is seen in **Figure 4**, where an increase from 3% to 4% results in a rapid increase in corrosion rate as water dropout occurs.[44]

As an alternative to assuming 'worst case' situations, the predicted or measured corrosion rate data can be expressed as graphs of probable life for different scenarios, as illustrated for a particular field development[45] where the options under consideration were:

a. do nothing;
b. wait for water breakthrough to occur;
c. install monitoring facilities and chemical treatment facilities now.

Option (a) has obviously the lowest capital expenditure (CAPEX), but has the highest risk relating to repair works and/or premature abandonment of wells. Options (b) and (c) have the same CAPEX costs, but option (b) has the advantage that the work can be delayed and/or phased to optimize expenditure, but runs the risk of unforeseen delays, which could result in unacceptable metal loss and some failures. Option (c) would be expected to provide the lowest risk option.

Baseline (uninhibited) corrosion rates for tubulars, flowlines and gathering lines were predicted to be between 0.3 and 0.9 mm year^{-1} using standard industry models. These could be controlled by the installation of chemical treatment facilities and the injection of corrosion inhibitors. Additional parameters taken into account were:

1. time after water breakthrough before water detected;
2. time to procure chemical injection components and install (For option (c), assumed to be already in place);
3. inhibitor availability, that is, reliability of supply;
4. inhibitor efficiency, that is, effectiveness of inhibitor once applied.

The analysis gave the results shown in **Figure 5** with the corresponding financial projections indicated in **Figure 6**, that justify the development of a mitigation and monitoring strategy for the field development.

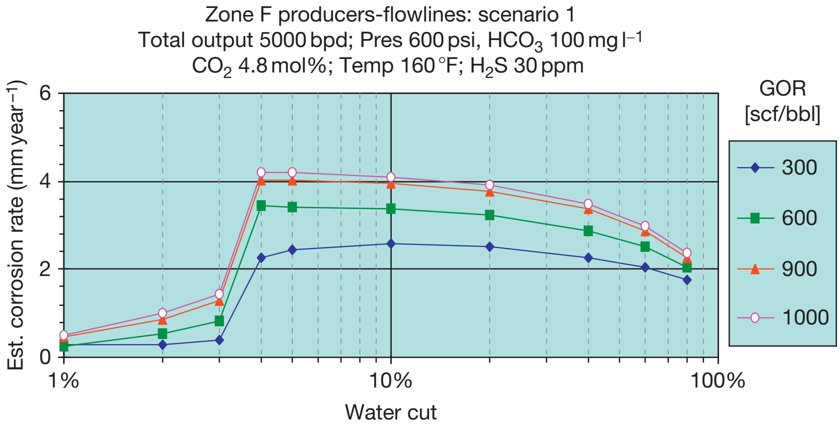


Figure 4 Part of a corrosion assessment for a field development showing the influence of water cut on the predicted corrosion rates. Reproduced from Moosavi, A. N.; John, D. G. In Corrosion/2002; NACE: Denver, CO, 2002; Paper No 02225.

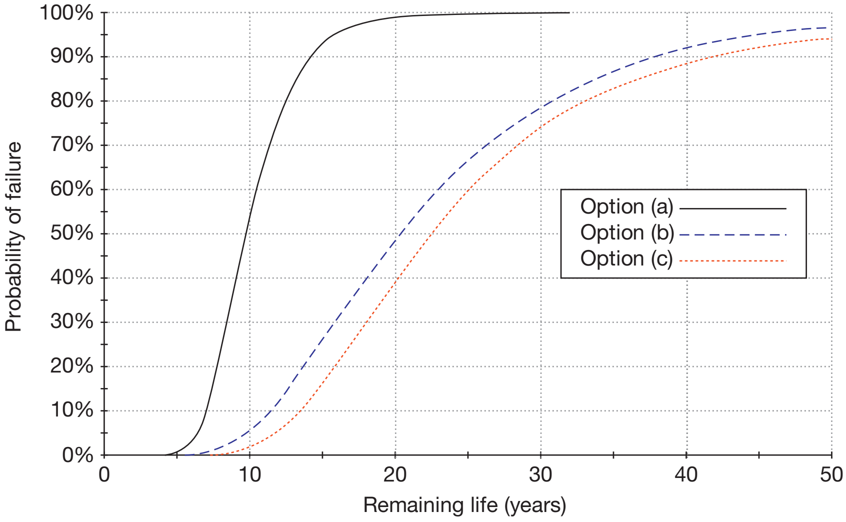


Figure 5 Probabilistic predictions of field corrosion rates. Reproduced from John, D. G.; Stokes, P.; McIntosh, P. *Risk assessments as part of a pipeline integrity determination for subsea oil and gas pipelines*, paper 03163, presented at NACE CORROSION'2003, San Diego, CA, March 2003.

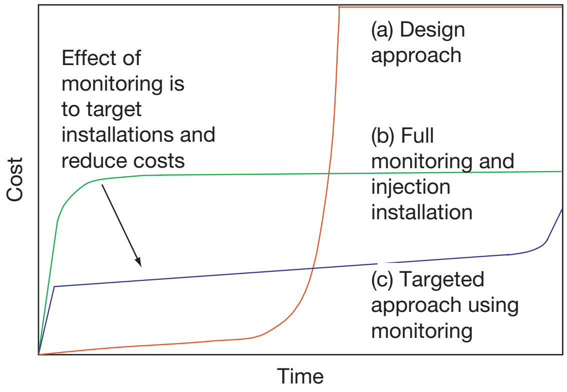
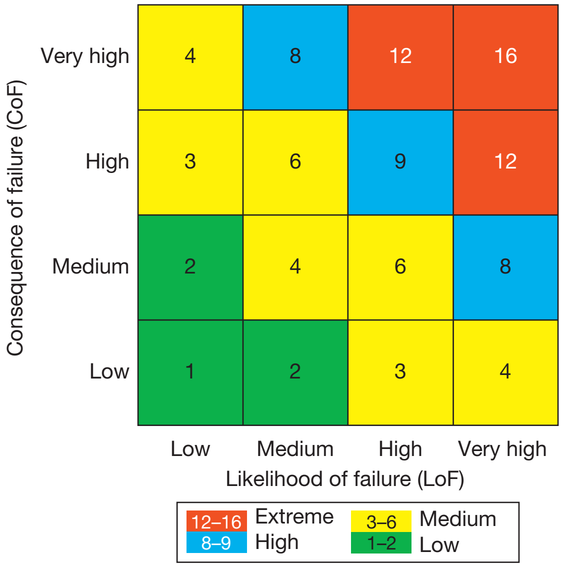


Figure 6 Cost versus time implications of different scenarios. Reproduced from John, D. G.; Stokes, P.; McIntosh, P. *Risk assessments as part of a pipeline integrity determination for subsea oil and gas pipelines*, paper 03163, presented at NACE CORROSION'2003, San Diego, CA, March 2003.



Consequence of failure (CoF)	Low	Medium	High	Very high
Very high	4	8	12	16
High	3	6	9	12
Medium	2	4	6	8
Low	1	2	3	4
	Likelihood of failure (LoF)			

12–16	Extreme	3–6	Medium
8–9	High	1–2	Low

Figure 7 Example of a typical risk matrix.

4.41.3.2.2 Corrosion risk analysis (CRA)

Corrosion rate data, from models or field information, can be used to assess corrosion risk across an asset or with individual equipment items (RBI). A common approach is the use of matrices, with linear or logarithmic scales, to prioritize risks and then to focus efforts on the most influential by evaluation of options. Important aspects for design teams or asset management teams are that a formal assessment of threats/risks is conducted using preagreed 'rules' or criteria are employed to define the likelihood of corrosion, the effect of corrosion and a ranking of the severity. The assessment report provides documentation for the next steps in the mitigation/management process and demonstrates the rationale employed by the corrosion engineer and replaces for other team members what often appears to be reliance on a subjective corrosion judgment.

Risk matrices provide a simple visual way of assigning risk where the consequences and likelihood of a failure are assigned to rows and columns of a matrix. Any combination can be used, the most common being based on four or five rows and columns; however, up to 10×10 matrices have been used by some operators. A typical 4×4 risk matrix is shown in Figure 7. Using this type of risk matrix identifies items where the risk is 'extreme' (i.e., where failure is both likely and of major concern), which should have immediate action taken (e.g., change of design, material selection, change in operations, etc.) to reduce the risk to an acceptable level. Items that are 'high' or 'medium' should be monitored during operations via a combination of inspection, corrosion monitoring and fluid sampling. However, items where the risk is identified as 'low' (i.e., where failure is both unlikely and would be of little concern) require less attention.

Data collected during operations should be fed back to enable the risk assessment to be reevaluated. While the consequence of failure is unlikely to change during operations (with some exceptions, e.g., pressure reduction), the uncertainty in the data used to assess likelihood will normally be reduced by the collection of operational data, and where justified, the likelihood of failure can be reduced (or in some cases increased) as appropriate.

It should be noted that in other publications and operational systems 'likelihood of failure' and 'probability of failure' may be used interchangeably. The authors preference is to use 'Likelihood' for qualitative and semiquantitative risk assessments, and 'Probability' for full quantitative assessments. Further details of corrosion risk assessments, and use of corrosion risk matrices are given in **Chapter 4.30, Corrosion Management Overview** in this book and elsewhere.[3,11]

4.41.3.2.3 Laboratory testing

While predictive modeling as described earlier is being used increasingly as part of the preliminary assessment approach, there remains a need for laboratory tests to confirm the likely corrosion conditions that will occur. This is especially so for systems with high CO_2/H_2S content, where many models will predict very high corrosion rates (often >20 mm year^{-1}) but where practical experience indicates that corrosion of carbon steel is negligible. For example, a review was carried out of production facilities in Oman[43] where performance in service of carbon steel components was compared with laboratory tests,[46] which showed that a stable FeS film is formed, giving *natural* corrosion rates (i.e., in the absence of corrosion inhibitor and not taking into account any oil wetting) of:

- gas phase 0.02–0.05 mm year^{-1};
- liquid phase 0.08–0.18 mm year^{-1}.

As part of the study, the water cut point at which a water/oil emulsion will release the water, thus switching from being an oil-wetting to a water-wetting mixture, was measured by determining the change in polarization resistance. The results for two different crude types showed that with one up to 20% water addition was required to affect the polarization resistance, while only 5% water addition was required for the other crude to have the same effect. These results were consistent with standard oil–water emulsion stability tests, ASTM D1401,[47] where emulsion stability is determined by the time required for the emulsion to separate after controlled agitation. The emulsion stability tests showed that the first crude formed a stable emulsion (stable for more than 24 h), while emulsions formed with the second crude broke down within 2 min. Data that are consistent with published experience.[41,42]

This evidence that the combination of a stable FeS scale formation and absence of a conductive phase in low water cut conditions provides acceptable levels of natural protection, making the use of carbon steel was viable, despite high theoretical corrosion rates, which is also supported by field experience led one operator to now require laboratory testing be carried out to assess the corrosivity of the fluids, and in particular the degree to which light crudes/condensates to hold water, for all future projects and not to solely rely on predictive rates.[43]

Even in areas where natural protective scales are not formed, where predicted field conditions are aggressive, such that carbon steel with corrosion inhibition with an efficacy of >95–98% is required and specified, it is often appropriate to carry out chemical screening tests at the FEED stage to ensure that a product is available in the market for the field conditions at a reasonable cost that can achieve the required corrosion efficacy for the life of the field.

Another key aspect that also has to be considered in any laboratory test program relates to presence of organic acids, and in particular, acetates in the oil, as described by Hedges.[48]

4.41.3.3 Procurement, Installation, and Operational Practicalities

Construction of oil and gas facilities worldwide comes up against a number of issues that differ from region to region and product to product including availability in specified thicknesses or line pipe grades, fitness for service (FFS) in sour service ISO 15156, shipping and storage costs as well as issues associated with basic materials selection considerations, i.e.:

- functional requirements;
- performance specification;
- design/redesign configuration;
- total life cycle in design;
- product availability and durability;
- inspection and QA testing;
- handling, packaging, shipping, and storage.

Procurement of raw materials is an issue as a vast proportion of the world supply of steel for equipment fabrication and pipelines comes from mills in the Far East where, unfortunately, there have been problems ensuring that the steel quality always meet the high stringent requirements of the oil industry, including the availability of compatible fittings (although it is recognized that European and North American mills have also been found wanting with regard to material quality in some instances).

Quality Assurance (QA) of manufacture must be considered at the FEED stage of a project. An understanding of these factors is essential for cost-effective materials selection and corrosion management during operations. The tolerances on standards and codes may be affected due to availability of source material. In some cases this can be an advantage from a corrosion perspective as often the higher specification of materials is purchased on grounds of availability. The cost of materials will vary from mill to mill and transport costs should also be considered during the lifecycle cost estimate.

The consideration of government legislation in terms of import and export of goods may also have to be considered. The level of tax imposed and the requirement for certificates of origin are both dependant on the local government regulations and are liable to change.

For example, if the government of a developing country requires the inspection of all ‘key’ components that are imported to be carried out by a government appointed agency at the operator's cost, then the definition of 'key' components could be crucial to the viability of the project. If, for example, 'key' was defined as any pipeline, valve or fitting over 4″ in diameter, that would have a major impact on the project economics. However if, through negotiation, key components are reclassified as those that are 6″ diameter and above then the imposed QA cost can be significantly reduced and this will influence the life cycle cost analysis.

Fabrication of topside modules are often carried out in a completely different location to the pipelines and interlinking pipework and therefore compatibility of materials (selected by different design teams/ fabricators) must also be considered. The supply of piping specifications, codes, schedules, etc. should be available irrespective of the manufacturing route, and the language of documentation should be clearly specified.

Consideration should be given to the locally available resource for fabrication of equipment. Handling and welding procedures for CRAs require much more stringent controls and may also require prequalification testing in H_2S containing fluids, than normally employed for carbon steel products and incorrect procedures can lead to failures during commissioning and operations.

Specification of chemical injection facilities should be clearly understood at the FEED stage. If a high level of chemical availability is required, the quality of equipment, redundancy and availability of spares should be considered, particularly with high-risk inhibition systems.[30] The local supply chain should be investigated to ensure that, if required, a continuous supply of product is feasible.

For example, in many remote parts of Russia the present chemical injection philosophy is to periodically top up gravity fed chemical storage systems to feed into well head systems. However, during the summer periods, wellpads that are situated in swamp areas become inaccessible, resulting in no delivery of chemical and hence lack of protection. Consequently for critical well heads consideration is given to providing continuous injection via large capacity well head storage tanks that only require restocking twice a year (i.e., when reliable access to the wellpad is available). Similarly for small scale offshore applications, where well head platforms are unmanned, an umbilical supplying chemical to the platform may be required. Where the platform is manned or easily accessible, regular top up and monitoring of the offshore tanks can be carried out; however, in these cases local storage facilities should be sized to ensure continuing availability of chemical if supply boats are delayed due to bad weather. Temperature differences between winter and summer operation in many dessert areas mean that viscosity changes in inhibitor packages result in a change of injection pump operation and hence a change in dosage and/or selecting injection pumping facility that is reliable in varying conditions.

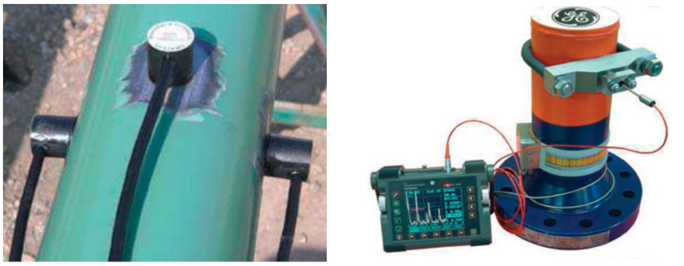
Another area that should be considered at the FEED stage is for necessary inspection and monitoring requirement to achieve the longer term objectives/ corrosion strategies, including the type and location of appropriate monitoring devices. There are a wide number of techniques (corrosion coupons, electrical resistance (ER), linear polarization resistance (LPR), etc. as described in **Chapter 4.36, Corrosion Monitoring and Inspection** in this book and also later in this chapter) and commercially available products that assess the condition of equipment or the corrosivity, chemistry or biochemistry of the fluids. Consideration should be given to the technical and economic feasibility of their use and the FEED should not assume that these will be specified at a later design stage. In particular, it must be noted that the use of insert probes or coupons is now subject to more stringent control in many areas, including the required use of a double block system. The use of instrumented spool pieces, permanently installed devices such as UT mats, or similar systems, as shown in Figure 8, are increasingly being adopted as standard practice. Consideration should also be given to having at least two or three complementary methods to ensure reliance of field data.

Retrieval of data from corrosion monitoring devises should also be considered. For remote facilities, automated systems may be required, while for easily accessible systems where labor is readily available, daily retrieval of data is normally considered adequate, except for very high-risk systems where inhibitor availability is more than 98%.

A preliminary assessment of design requirements for the specification of external corrosion mitigation should also be undertaken to identify any specific requirements. In some cases it may appropriate for a design for the CP system to be carried out for pipelines, and structures at the FEED stage, along with consideration of coatings for external protection. There is also a need to identify the supply of materials and local training requirements to ensure a system is designed, delivered and maintained to meet the long term objectives in a straightforward and easy-to-implement manner.

Cieon Subsea Spool®
Photograph courtesy of Cormon Ltd.

FSM® Subsea Spool,
Photograph courtesy of Rozar AS, Norway



Ultracorr® Permanent UT Sensors
Photograph courtesy of Rohrback Cosasco Systems

Rightrax® Permanent UT sensor
Photograph courtesy of General Electric Co Company.

Figure 8 Examples of spool pieces and permanently installed devices.

Key questions that need to be considered for materials and monitoring equipment are whether the supplier has local representation in the region where the system is going to be installed if servicing is required and whether suppliers have the experience of supplying material and equipment to similar fields.

4.41.4 Design Stage

At the design stage of the project the detail drawings and specifications are prepared for construction and this is the opportunity to get it right or, unfortunately as still happens, to really get it wrong! Modifications beyond the design stage are costly and inconvenient.

For example, in a case known to the authors, an onshore field designed on the basis of using aquifer water for downhole injection suddenly found that the injection waters contained SRB, which required a change in operating philosophy with implementation of significant monitoring and biocide treating facilities.

Depending on the size of a project, the design stage may be divided into two stages of *Engineering Design* and *Detailed Design*. Corrosion related activities undertaken during the engineering design phase include:

- detailed materials selection, including the use of design codes, standards, and procedures for construction, fabrication, and assembly;
- assessment of proposed corrosion control options.

During the detailed engineering design, detailed specification and drafting of procedure are undertaken to produce the finalized design specifications and engineering details that are required for construction.

The following is an example of documents that require some level of corrosion input during the engineering design and detailed design phases of the project:

Engineering design	*Detailed design*
Basis of design Material specification External coating specification Insulation specification Material selection philosophy statement Corrosion monitoring philosophy statement Chemical management philosophy statement	CP design Pipeline, vessels, tubulars, valve specifications/testing Welding procedures/testing Corrosion monitoring designs/specifications Equipment specification/inhibitor testing/data management specification

4.41.4.1 Documentation

4.41.4.1.1 Material selection report

The material selection philosophy would normally be developed by materials specialists and should be written into the project at the engineering design stage. It would typically contain details of materials for each system based on the fluids and operational conditions, plus details on materials specifications and properties. For example, for pipelines basic requirements would include standard dimensions, adequate strength for operational pressures, material to be identifiable and traceable, weldable under site conditions, free from defects that would cause leakage, and adequate fracture toughness to resist brittle fracture and resist propagation. Most requirements for linepipe are covered in API 5L[49]/ISO 3183,[50] but other requirements must also be specified including testing for weldability, fracture toughness tests, sour service tests to ISO 15156/NACE MR0175[20] (including testing for SSCC susceptibility to ASTM G39[51] and NACE TM0177[52]) restrictions on manufacturing process, limitations on chemical composition, element ranges, wall tolerances, and marking requirements. Budget costs are an output from the materials selection process.

One approach typically adopted in many projects would be the development of material selection diagrams (MSDs), that are based on the process flow diagrams (PFDs). They show the generic materials type, applicable corrosion allowance, internal coating requirements, and any other corrosion control requirement for pipelines, vessels, and piping, for example, as shown in **Figure 9**.

At the detailed design stage the detailed materials specifications would then be developed with reference to appropriate standards. Piping schedules are produced that detail the appropriate material grade, wall thickness, operating pressure and temperature for each specific service in addition to insulation and welding specification and post weld heat treatment (PWHT) requirements. This information forms the basis of the line identifier on the process and instrument diagrams (P&IDs).

4.41.4.1.2 Corrosion management philosophy

This document should contain high level details of the monitoring and mitigation measures that are required for the installation, plus important information that needs to be carried forward to detailing, specifications, fabrication and construction and operation, for example:

- injection of corrosion inhibitor to mitigate CO_2 pitting/general corrosion and H_2S pitting corrosion;
- injection of biocide to mitigate MIC corrosion;
- injection scale control chemicals;
- injection of chemicals for pH/hydrate control;
- deoxygenation/treatment of injection water;
- CP of pipelines, structures, internals of vessel and tanks;
- corrosion/erosion (sand) monitoring;
- specification of pipe internals to remove mill scale during external blasting for coating application, which minimizes sludge formation during the first few years of operation as CO_2/H_2S corrosion products replace air formed films;
- routine cleaning of pipelines using cleaning pigs;
- routine flushing of sand from vessels and procedures for removing sand deposits from lines/manifolds following sand breakout in a well.

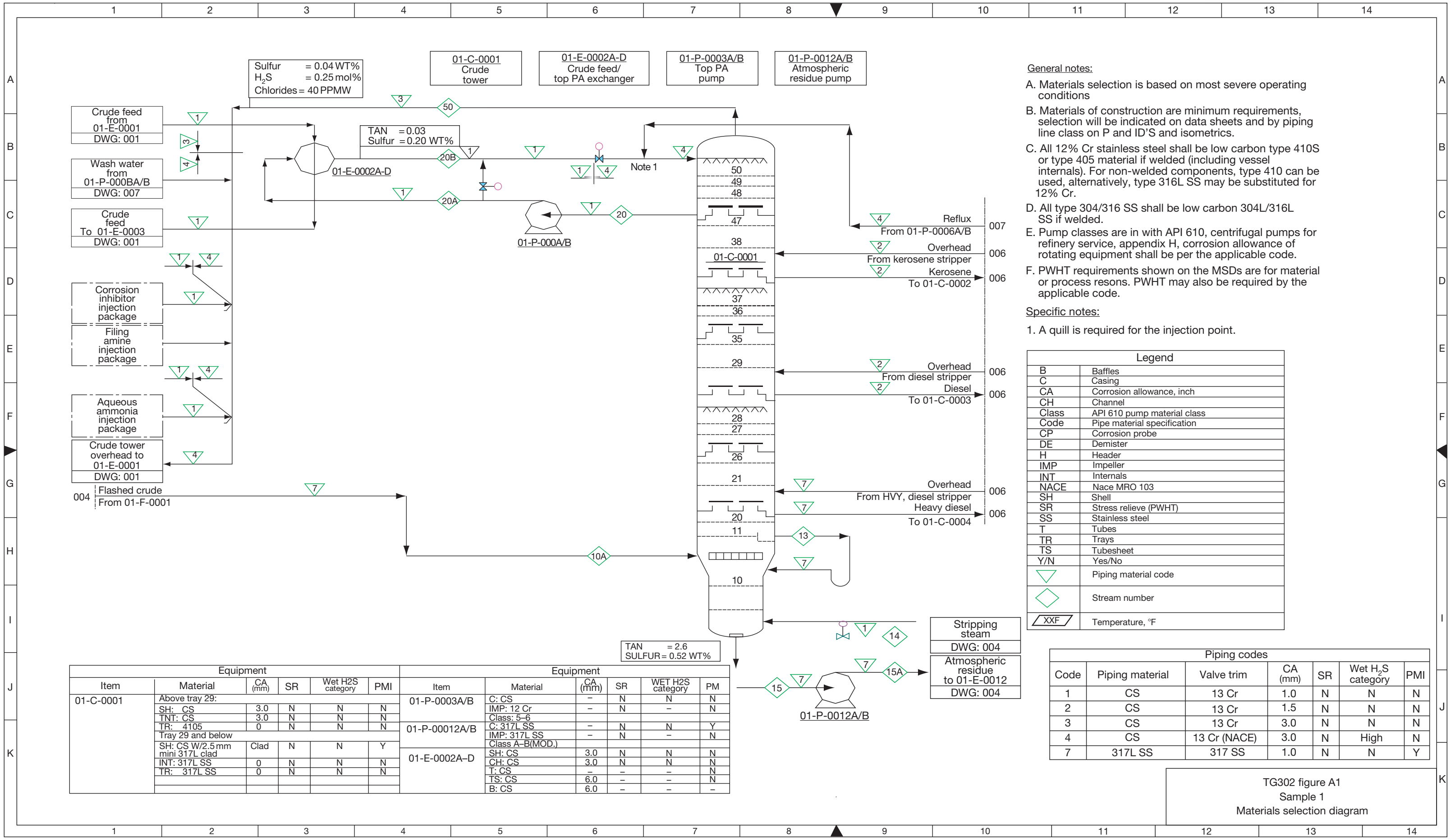
This will enable the equipment to be designed to deliver these various requirements.

4.41.4.1.3 Chemical injection systems

Where chemical injection of corrosion inhibitors, biocides, scale inhibitors, emulsifiers/deemulsifiers, etc. is required it is important that the injection location and injection facilities are correctly identified. The injection must take place sufficiently far upstream of where the chemical is expected to provide benefit to ensure adequate mixing. Typically, this mixing distance will be defined as at least 2 m or 10 pipe diameters upstream. Where more than one chemical is required at nominally the same point they should be injected separately and not via the same injection point to avoid the risk of clogging. The injection nozzle should also be designed to provide the optimum distribution into the stream.

The method of injection, that is, the use of mechanical or electrical pumps, and local storage also have to be taken into account in relation to factors such as protection from solar heating, the use of plastic or stainless steel tanks, etc. In the concentrated form corrosion inhibitors and other chemicals can be very corrosive and/or toxic and hence suitable precautions, including the use of austenitic stainless steels for injection equipment and lines, will be needed to prevent leakage.

The pumps will also need to be sized so that sufficient chemicals can be injected into the stream to ensure the necessary dosage levels. Most corrosion inhibitors are formulated to be typically present at levels of 10–20 ppm (in the range 5–100 ppm) and, depending on the production rates, the actual amount of chemical injected could range from 2 $dm^3\ day^{-1}$ for production facilities of 167 $m^3\ day^{-1}$ (1000 bpd)



General notes:

A. Materials selection is based on most severe operating conditions

B. Materials of construction are minimum requirements, selection will be indicated on data sheets and by piping line class on P and ID'S and isometrics.

C. All 12% Cr stainless steel shall be low carbon type 410S or type 405 material if welded (including vessel internals). For non-welded components, type 410 can be used, alternatively, type 316L SS may be substituted for 12% Cr.

D. All type 304/316 SS shall be low carbon 304L/316L SS if welded.

E. Pump classes are in with API 610, centrifugal pumps for refinery service, appendix H, corrosion allowance of rotating equipment shall be per the applicable code.

F. PWHT requirements shown on the MSDs are for material or process resons. PWHT may also be required by the applicable code.

Specific notes:

1. A quill is required for the injection point.

Legend	
B	Baffles
C	Casing
CA	Corrosion allowance, inch
CH	Channel
Class	API 610 pump material class
Code	Pipe material specification
CP	Corrosion probe
DE	Demister
H	Header
IMP	Impeller
INT	Internals
NACE	Nace MRO 103
SH	Shell
SR	Stress relieve (PWHT)
SS	Stainless steel
T	Tubes
TR	Trays
TS	Tubesheet
Y/N	Yes/No
▽	Piping material code
◇	Stream number
XXF	Temperature, °F

Equipment					
Item	Material	CA (mm)	SR	Wet H2S category	PMI
01-C-0001	Above tray 29:				
	SH: CS	3.0	N	N	N
	TNT: CS	3.0	N	N	N
	TR: 4105	0	N	N	N
	Tray 29 and below				
	SH: CS W/2.5 mm mini 317L clad	Clad	N	N	Y
	INT: 317L SS	0	N	N	N
	TR: 317L SS	0	N	N	N

Equipment					
Item	Material	CA (mm)	SR	WET H2S category	PM
01-P-0003A/B	C: CS	–	N	N	N
	IMP: 12 Cr	–	N	–	N
	Class: 5–6				
01-P-00012A/B	C: 317L SS	–	N	N	Y
	IMP: 317L SS	–	N	–	N
	Class A–B(MOD.)				
01-E-0002A–D	SH: CS	3.0	N	N	N
	CH: CS	3.0	N	N	N
	T: CS	–	–	–	N
	TS: CS	6.0	–	–	N
	B: CS	6.0	–	–	–

Piping codes						
Code	Piping material	Valve trim	CA (mm)	SR	Wet H_2S category	PMI
1	CS	13 Cr	1.0	N	N	N
2	CS	13 Cr	1.5	N	N	N
3	CS	13 Cr	3.0	N	N	N
4	CS	13 Cr (NACE)	3.0	N	High	N
7	317L SS	317 SS	1.0	N	N	Y

TG302 figure A1
Sample 1
Materials selection diagram

Figure 9 Example of material selection diagram (taken from NACE SP0407). Reproduced from NACE Standard Practice SP0407-2007 'Format, Content and Guidelines for Developing a Materials Selection Diagram'.

up to 30 $dm^3 day^{-1}$ for production of 1670 $m^3 day^{-1}$ (10 000 bpd). A description on the use of inhibitors in oil and gas operations are given in **Chapter 4.26, Chemical Treating in Oil and Gas Production** in this book and elsewhere.[30]

4.41.4.1.4 CP systems

The majority of CP systems will be aimed at the external protection of offshore production facilities such as fixed platforms, floating platforms and FPSOs, onshore and offshore pipelines, and onshore storage tank bottoms. However, CP can also be applied to the internals of oil and gas process equipment, including separators, filters, heat exchanger water boxes and storage tanks.

The selection decision for pipelines and storage tanks at the design stage will be between the use of galvanic anodes and/or impressed current systems, and the extent or otherwise that different components are electrically isolated or deliberately bonded together. Note that CP will protect against crevice corrosion if applied as soon as the component is immersed but, will not necessarily protect crevices after the corrosion has initiated. For offshore applications, and in particular subsea developments, the compatibility of CP systems required for carbon steel pipelines and other structures also has to be assessed, specifically for the effects of over protection on either high strength carbon steel components or components fabricated from other materials such as duplex stainless steels and titanium. While CRAs may not require external CP, they will receive it, because they are connected to carbon steel pipelines that have CP applied, and this has led to failures of subsea manifolds in the past.[53]

Internal CP can also be applied to process equipment and the main concerns relate to the low pH/elevated temperatures in the process, which in turn leads to higher current demand and low anode performance and hence more challenging CP design. Most internal CP systems are galvanic[54,55]; however, impressed current CP systems have also been installed.[56]

If internal CP is to be incorporated it is important that ease of anode installation/replacement is taken into account as part of the overall design. Methods for determining performance are also more complex, and include the use of ER probes.

4.41.4.2 Engineering Considerations

4.41.4.2.1 Minimizing corrosion threats

Variations in pipeline and pipework geometry, such as the presence of dead-legs and low points, create areas where water and debris can settle and accelerate a number of different corrosion threats, including CO_2 corrosion, under deposit corrosion and microbial corrosion, as illustrated in **Figure 10**. Similarly, sections of pipeline that cannot be pigged increase the chance of build-up of deposits. While low points and dead legs cannot be fully eliminated in any design, they can be minimized. The awareness of corrosion should be raised with the piping designers at the design stage of a project and, where possible, a review of the piping design should be carried out to challenge any excessive use deadlegs and low points.

4.41.4.2.2 Corrosion allowances

Most carbon-steel components selected for use in oil and gas facilities will incorporate a corrosion allowance. The wall thickness for the component (pipeline, pipework, vessel, tank, etc.) will be increased above the minimum allowable wall thickness as determined by the appropriate design code, to allow for metal loss due to corrosion or erosion. This is separate from the inclusion of a fabrication tolerance for the component.

The corrosion allowance will be selected based on the expected corrosion rate that will occur with the planned corrosion control procedures in place and allowing for the design life of the facility. The inhibitor availability concept provides the procedure that should be used in practice.

During operation, provided that the actual metal loss, as determined by inspection and trend monitoring according to API 570,[57] API 580,[10] or other RBI system, is less than the corrosion allowance then the component will be operating within the design code requirements and is considered fit for service. Only when the actual or estimated metal loss exceeds the corrosion allowance would a more detailed assessment as to the continued fitness for service (FFS) be required (see **Section 4.41.6.9** later in this chapter).

Typically, corrosion allowance would be 2 or 3 mm, and while most projects try and limit corrosion allowance to 6 or 8 mm, in some cases a corrosion allowance of up to 12 mm have been considered, especially where there is a risk that the corrosion control program may not be fully effective. However, other projects choose not to include any corrosion allowance, normally this is when there is a high confidence in the effectiveness of the corrosion control program (for example for commercial quality dry gas pipelines).

4.41.4.2.3 Inaccessible pipework

While some piping, especially for offshore installation, will not be easily accessible, it is important to consider that corrosion monitoring equipment needs

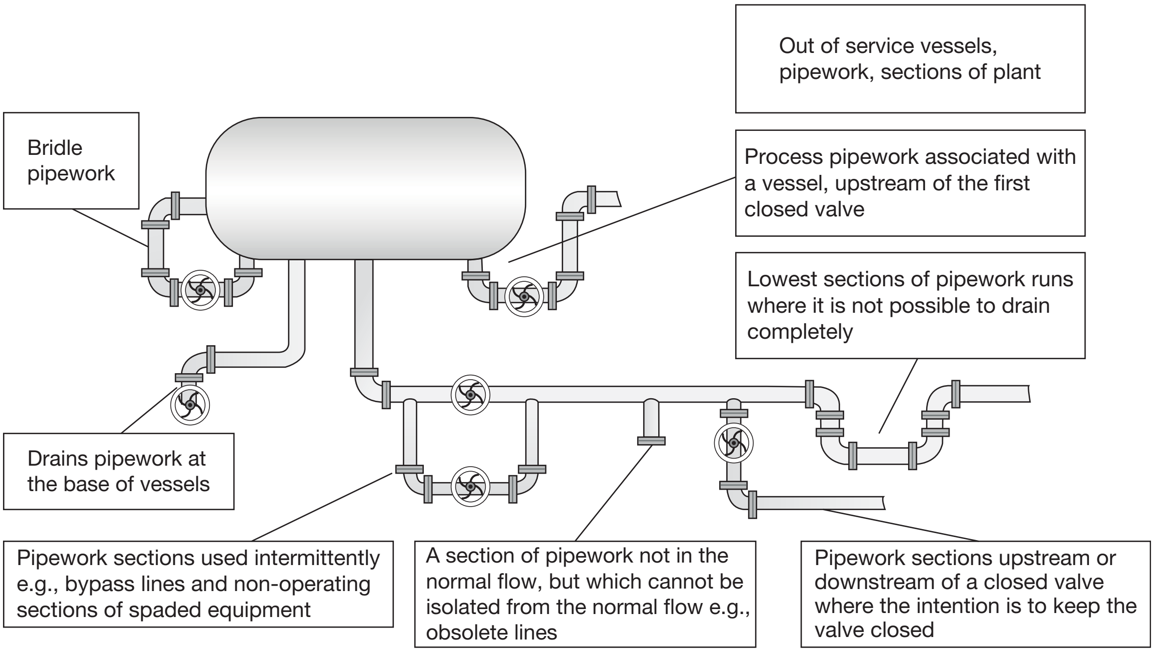


Figure 10 Schematic of 'dead-legs,' from the Energy Institute 'Guidance for corrosion management in oil and gas production and processing.' Reproduced from Guidance for Corrosion Management in Oil and Gas Production and Processing; Energy Institute: London, May 2008. ISBN 978 0 85293 497 5.

to be accessed by retrieval tools and that the external surface of piping will need to be inspected.

For subsea pipelines, direct access is almost impossible and therefore the design should be robust enough to deliver a 'fit and forget' solution. There should be a high level of confidence in any monitoring equipment that is to be located in inaccessible locations.

4.41.4.2.4 Insulation

A major problem with external corrosion of oil and gas production facilities is corrosion under insulation (CUI), where excessive corrosion and/or SCC can occur where water (rain water, seawater, deluge water, etc.) enters the insulation. In many cases, the insulation is necessary for process control and hence steps need to be taken to ensure that that system is correctly designed to reduce the threat of water ingress and also to minimize any subsequent corrosion by use of protective coatings on the metal piping.[58,59] Where insulation is not necessary, for example, when solely used for personnel protection, it should be removed and alternative methods to prevent harm, such as the use of open mesh guards, applied.

4.41.4.2.5 Pigging facilities

The installation and design of temporary or permanent pigging facilities should be considered and will be dependant on the expected frequency of pigging and the availability of labor. Consideration should be given at the design stage to the requirement to pig individual pipelines, which can impact on detailed materials selection philosophy. Normally unmanned installation (NUI's) that require regular launching of cleaning pigs to protect the export pipeline will require a robust automated launching system that is capable of storing the number of cleaning pigs that are required between visits to the facility.

In the case of an onshore facility with an extensive pipeline and flowline network that has the need to run cleaning pigs on a monthly basis in the flowlines, the installation of permanent pigging facilities at each wellhead may be considered prohibitively expensive and the design of mobile pigging facilities for each region of the field may be considered. The number of temporary pig launchers needs to be balanced with the number of teams that will be available to carry out the pig launching and receiving activities. Alternatively the pipeline network can be designed with pigging loops to enable launch and reception to be carried out in similar locations.

It should be recognized that one of the major hurdles for many existing pipelines world wide are pipelines that are not piggable, either because the lines include bends that are too tight or more often because the internal diameter (bore) of the pipeline is not constant, such that pigs (whether used for cleaning or inspection) cannot travel along the line reliably. In general the less a pipeline is cleaned the higher the possible corrosion threat.

4.41.4.3 Design of Data Management Systems

At the design stage, the type of data management system that is required for the facility should be considered[60] and the selected system will normally be set up during the construction phase in order to input inspection information such as 'as built' wall thickness measurements. The choice of corrosion management system may influence, or be influenced by, the corrosion monitoring and materials of construction. If the corrosion monitoring is linked into an online measurement system (e.g., PI, SCADA) then a real time corrosion data management system can be used.[61] If a high level of manual inspection is to be carried out then a comprehensive inspection management database should be considered, particularly if RBI is to be adopted.

Methods and procedures for all activities will be required, including specifications, procurement of materials, testing, fabrication and welding, coatings, CP equipment applications, corrosion monitoring and inspection instrumentation, field data collection and analysis, required databases and means of achieving their population, specification of reporting by appropriate routes and development of corrective action procedures to be carried out when necessary.

The development and maintenance of corrosion databases, usually electronic, could include provision for storage of system documentation including facility design documents, as-constructed diagrams, commissioning information and field data during operation, inspection and maintenance. These should cover information on the basis of the design, design drawings, modifications, testing requirements and construction so that relevant information data are transferred through to the operational phase database.

The means by which field data such as visual inspections, coating surveys, hand held/permanently wired instrumentation, DCS/SCADA downloads are to be collected, analyzed, and used for trending and correlations must be agreed and specified, including post fabrication inspection data that provide the initial field data point for trending as in RBI.

An effective management tool is a transparent database that correlates field data to provide a regular weekly/monthly breakdown of corrosion mitigation costs. Ideally, field databases should be live documents where measurements are inputted as soon as possible and analyzed/trended/correlated to provide virtually continuous management information for the corrosion team leader/supervisor. The use of a web page approach is becoming more accepted with simple traffic light schemes (red, yellow, green) providing easy to identify out-of-condition processes.

4.41.4.4 Commissioning Procedures

During the detailed design phase, commission procedures should be written for each area. Procedures that have particular emphasis on corrosion are:

- commissioning procedure for chemicals management system;
- pressure testing and preservation procedure (in particular water treatment for hydrotest systems).

4.41.5 Fabrication, Construction, and Commissioning

4.41.5.1 QA and Quality Control

An integral part of maintaining technical integrity of a new facility is to ensure that the materials selected in the FEED/Design Phase are manufactured, procured, and constructed as envisaged and in a way that they maintain their degradation resistant properties for the intended use. Normally the responsibility of ensuring that materials meet required specification will fall to the QA teams within the design project team. Their role is to ensure that the minimum compliance checks and nondestructive examination requirements are fully adhered to and that the construction materials retain their original specified properties.

A main issue that needs to be addressed during fabrication and construction is that where special properties for a material are required, in particular with respect to sour service in accordance with ISO 15156/NACE MR 0175,[20] they are delivered as specified. Note this should not just rely on material certificates unless supported by internationally recognized standards/quality control organizations. Many problems have arisen where materials have been supplied as being of a particular grade and in accordance with specification, only for them to be eventually discovered as being out of specification, for example, austenitic stainless steel grade SS316L (UNS S31603/EN 1.4919) piping specified, but grade SS304 (UNS 31400/EN 1.4841) supplied, or forged valves specified as being compliant to MR 0175[20] found subsequently to have unacceptable hardness, resulting in cracking and failure after only a few weeks operation.[62]

Any deviation or other changes to the original design should only occur after review and approval by the design team and should always be fully documented and the responsible material and corrosion engineers notified in order to ensure that the relevant information is incorporated into the corrosion management manuals.

During fabrication and construction, items of equipment will be subjected to a range of routine inspection to confirm fabrication in accordance with specification and code requirements. In addition it is increasingly used to ensure that as delivered wall thickness checks (using nondestructive inspection systems, such as ultrasonic wall thickness systems) are carried out to confirm the original wall thickness prior to operations. This then becomes the baseline value used in assessing performance during ongoing operations, and eliminates the uncertainty associated with actual versus nominal wall thicknesses.

4.41.5.2 Development of Integrity Management Systems

During this phase, the integrity management systems are normally set up. This should comprise a suite of documentation that enables a structured framework for integrity management to be delivered and should cover integrity policy, strategy, codes of practice procedures, specifications, and guidelines. Some of the typical documentation required includes:

- integrity management policy and strategy;
- sand management strategy;
- corrosion management manual;
- hydrotest and preservation procedures;
- chemical management strategy;
- RBI strategy;
- corrosion monitoring manual;
- inspection procedures.

Risk assessments and the generation of RBI plans require PFDs, piping and instrumentation diagrams (P&IDs), MSDs, pipework isometric drawings, vessel data sheets and process and operations manuals to be available. Development of the integrity management system during the construction and commissioning phase enables the systems to be implemented from day one of operations. This ensures that all operational data are collected and fed back into the system.

Corrosion and materials consulting engineers typically act in an advisory capacity during the construction and commissioning phase to assist in the following activities:

- Define requirements for integrity management systems.;
- Reassess design decisions related to integrity monitoring and mitigation.
- Advise on materials approvals, quality control and QA checks.

During commissioning it is important that the detailed hydrotest and preservation procedures are followed, the chemical injection packages are commissioned and the dose rates and logistics associated with chemical supply are confirmed. Vibration screening should also be carried out during commissioning of susceptible components.

Following fabrication and construction, the facilities will be tested and commission in different phases. Even at this stage, full attention to corrosion management requirements is vital, since major damage and/or problems for future operation can be created during this stage.

A significant issue relates to hydro-testing of pipelines, pipework, and vessels, which, unless carried out correctly, can lead to major problems. This includes problems associated with leaving inadequately treated hydrotest water in the line allowing oxygen corrosion or MIC due to introduction of bacteria, that can lead to severe metal loss prior to operation or, if the line is not fully cleaned and dried, can leave water in place that then allows corrosion to proceed once production starts.

Most problems associated with external corrosion of pipelines are also caused during pipe laying, either due to damage to the coating, in particular the field joints, either due to 'roller damage' for offshore or mechanical damage from slings, stones, etc. during trench placement onshore.

4.41.5.3 Handover to Operations

Following successful commissioning the fabrication and construction team will disperse. Before this occurs all historical records developed during the fabrication, construction and commissioning phase that could be useful for ongoing operational corrosion management should be handed over to the operational team responsible for ongoing corrosion management.

The extent of this information should not be underestimated (see compliance with ISO 9001: 2008[63]) and the key documents and information are summarized in the following section. It should be recognized that this is not an exhaustive list, but intended to give guidance on the type of information that is not only useful for corrosion, inspection and integrity engineers during operations but identifies the means by which risk mitigation is transferred from design to operations.

Handover documents:

- Basis of design.
- Corrosion management premise.
- Material selections and peer review.
- Corrosion management manual (including preliminary inspection/monitoring plans, reporting plans, KPIs, etc.).
- RBI plan.
- PFDs marked with corrosion circuits.
- Maintenance reference plan.
- Preservation procedures.
- Hydrotest procedures.
- Chemical injection procedures.
- Piping and instrumentation diagrams (P&IDs).
- Process flow diagrams (PFDs).
- Operations manuals.
- Corrosion barriers spreadsheet.
- Process simulation/heat and mass balance data.
- Hydrotest procedure.
- Chemical dosing manuals/procedures.

4.41.6 Operations Phase

4.41.6.1 Corrosion Management Strategy Implementation

Implementation of the corrosion management strategy involves the correct execution of the mitigation, monitoring and inspection activities that ensure the facility remains fit for purpose. Examples of these activities are corrosion rate monitoring, process monitoring and inspection, data collection, analysis, reporting and corrective action.

The requirements for implementation are:

- The strategy should be translated into practical instructions, for example, planned maintenance routines, operating instructions and work packs. There should also be a means for implementation of the strategy.
- Written procedures, work instructions and guides to performing the implementation tasks should be provided. Responsibility for implementation should be identified.
- Adequate manpower, material and equipment resources need to be allocated to undertake the plan. Permanent physical facilities should be installed.
- The locations for monitoring and inspection activities should be defined.
- Procedures and instructions should include criteria of nonconformance.
- A corrosion damage reporting process should be continuously in place to capture information regarding failures that occur unconnected to the planned activity.
- A procedure should be in place to allow for opportunity based inspection, separate to the plans, of items that are not normally accessible for operational reasons.

An important point to realize in any corrosion management implementation is that '*no plan survives contact with the enemy*'[64] and, as a consequence, it is unlikely that all the original plans and procedures will be able to run smoothly thought the operational life of a facility. Hence, as either process conditions change (e.g., due to increase in water cut, incorporation of new production wells, changes in oil lift methods, etc.) or where unforeseen events occur (e.g., failure of chemical injection facilities) then alternative methods of detection may be required to be used and incorporated into the corrosion management 'tool kit,' either in place of, or in conjunction with, existing methods. Any new inspection and monitoring technologies should also be evaluated and considered as part of an ongoing system improvement process.

4.41.6.2 Routine Inspection and Monitoring

Corrosion inspection and monitoring are key activities in ensuring asset integrity and control of corrosion. It is important to monitor appropriate parameters that indicate the performance of a corrosion barrier to check whether the performance limit has been exceeded.

Monitoring can comprise inline, online and offline systems and provide rate of corrosion degradation data and information on the effectiveness and performance of the corrosion mitigation techniques (e.g., corrosion inhibition, process treatment, etc.). Analyses of the results from these systems allow steps to be taken to prevent failure, if necessary.

In-line systems are devices installed directly into the process that need to be extracted for analysis or sampling of process fluids for analysis, for example, corrosion weight loss coupons, biostuds, fluid sampling, etc.

Online corrosion monitoring techniques, that is techniques that use fixed probes or sensors that can be integrated without the need to remove them from the system (insert probes or externally mounted probes), include:

- electrical resistance (ER) probes;
- linear polarization resistance (LPR) probes;
- fixed ultrasonic (UT) probes;
- acoustic emission;
- electrochemical noise;
- monitoring of process conditions;
- magnetic flux leakage (MFL) or UT in line inspection (intelligent pigging) of pipelines;
- field signature method (FSM) monitoring spools.

Offline techniques retrospectively identify corrosion degradation and quantify the onset and causes, and the extent and degree to which it has occurred. Offline monitoring or inspection mainly utilize the following inspection and nondestructive testing/evaluation (NDT/NDE) techniques:

- visual;
- manual/automatic ultrasonic;
- radiography;
- pulsed eddy current (PEC);
- magnetic flux leakage (MFL);
- time of flight diffraction (TOFD).

Detailed descriptions of the different inspection and monitoring systems, together with their advantages and disadvantages, are described in **Chapter 2.04, Pitting Corrosion** in this book and in various standards, technical reports and other publications.[65–71] New inspection and monitoring technologies should always be evaluated and considered as part of a continuous improvement process, for example, a combination of new development methods (FSM and electrochemical noise) were used successfully to identify corrosion problems in an aging sour gas system.[72]

Regular proactive and reactive monitoring should be undertaken to measure the degree to which the policy objectives of the corrosion management plan are being achieved. There are two measurements of success: (1) meeting the performance limits for the effectiveness of the corrosion barriers, that is, the FFP of the facility and (2) meeting the targets in terms of the effectiveness of identifying the barriers and organizing, planning and implementation, that is, the success of the management system itself.

Routine inspection provides a key input into corrosion management activities. This is mainly aimed at nondestructive inspection to determine the wall thickness of pipelines, pipework and vessels, but also includes NDT/NDE to identify cracking or other forms of deterioration. The most common form of inspection utilizes wall thickness measurements obtained using compression ultrasonic probes (UT). Various types of UT systems are available, including simple 'all-in-one' probe and digital meter, digital wall thickness gauges and full screen systems, which allow measurement at points on the surface. With these units the operator manually moves the sensor around the area to locate the point with the lowest wall thickness. Fully automatic scanning systems are also available that can travel around/along the component providing a 3-D image of the wall thickness allowing clear identification of localized corrosion.

While simple digital only UT meters can give quick measurements, they are not fully reliable. The readings can be affected by inclusions or defects within the pipe/vessel wall, which can give a false low thickness reading and also by tightly adherent scales, which can give a false high thickness reading. Wherever possible full screen UT meters should be used to ensure that such features do not affect the reading, since the ultrasonic echo is displayed allowing an experienced operator to distinguish the interface formed at inclusions (false – low) and adherent scale (false – high).

When using manual meters, the reading will normally be collected from around a section of pipe (typically 100–300 mm long) or a marked out section of vessel, typically 100×100 mm to 300×300 mm in size, recording the minimum wall thickness observed within the area. For larger diameters of pipe the section may be split into four subsections (typically top, right side, bottom, and left side for horizontal pipe).

By repeating wall thickness measurements at intervals, an estimate of the corrosion rate can be obtained. In all cases, UT equipment should always be operated in accordance with manufacturer's instructions, including calibration for the specific metal/alloy and operating temperature of the facility.

Wall thickness measurements, should be trended over a period to identify changes in condition and rate of metal loss. A typical example is shown in Figure 11; here data are initially collected at nominally three yearly intervals (period 1) and shows an estimated corrosion rate of 0.05 mm year^{-1}. At the time of the next inspection a significant change is noticed with an increase in corrosion rate to 0.3 mm year^{-1}, as a consequence the inspection frequency was changed to annually and this rate is seen to continue for a few years, until corrosion control is reestablished (period 3) with corrosion rate back to 0.05 mm year^{-1}.

This also shows the advantage of obtaining both 'short' and 'long' corrosion rates from inspection data. 'Short' corrosion rates are taken at the penultimate and ultimate (i.e. most recent) readings, while 'long' corrosion rate is based on the first reading and last reading; in the example in Figure 11 this is 0.1 mm year^{-1}.

When using UT inspection as part of corrosion monitoring activity particular attention should always be given to identification and measurement of localized corrosion (pitting), especially in sour systems.

Increasing use is being made of long-line UT, where a series of sensors are fixed around a pipe sending signals along the pipe transversely identifying possible defects up to 20–50 m in either direction from the sensors. The distance that the long range UT can effectively scan is a function of pipe geometry, number of fixings/supports (that provide 'false' echoes) and whether the pipe is buried or not. When buried the acoustic impedance is lost such that the signal 'leaks' into the ground, limiting the effective distance. Once possible defects are located then they should be confirmed using standard UT inspection.

Other methods for providing a rapid inspection of pipework are also used and continue to be developed. These include magnetic and hall-effect (eddy current) systems and pulse eddy current, that is used to detect metal loss under insulation.

For pipelines the most common inspection method is inline inspection (ILI), also referred to as intelligent pigging or smart pig (notwithstanding the problem of nonpiggable pipelines as highlighted earlier). Today ILI is a routine method of assessing FFP of pipelines and it can be applied to a wide range of sizes (6″ up to 36″ diameter) and can be deployed in any type of pipeline (i.e., oil, gas, water) and for long distances. The actual distance that can be surveyed in one deployment is dependent on the memory capacity of the tool but typically up to 100 km per deployment can be accommodated.

There are two different types of ILI tool deployed, the most common type utilizes MFL that measures wall thickness by the distortion of the magnetic signal generated by the tool caused variations in thickness of the pipeline wall. The second type is an ultrasonic tool that measures wall thickness in the same way as normal UT inspection. MFI tools can be used in any media, liquid or gas, but UT tools can only be used in a liquid media to allow acoustic coupling between the sensors and the pipe wall, and hence are not normally used gas lines.

Both MFI and UT tools detect and quantify metal loss and can identify whether the loss is internal or external. The requirements for ILI surveys are governed by International Standards, including NACE RP0102,[73] NACE TR 35100[74] and API STD 1163.[75]

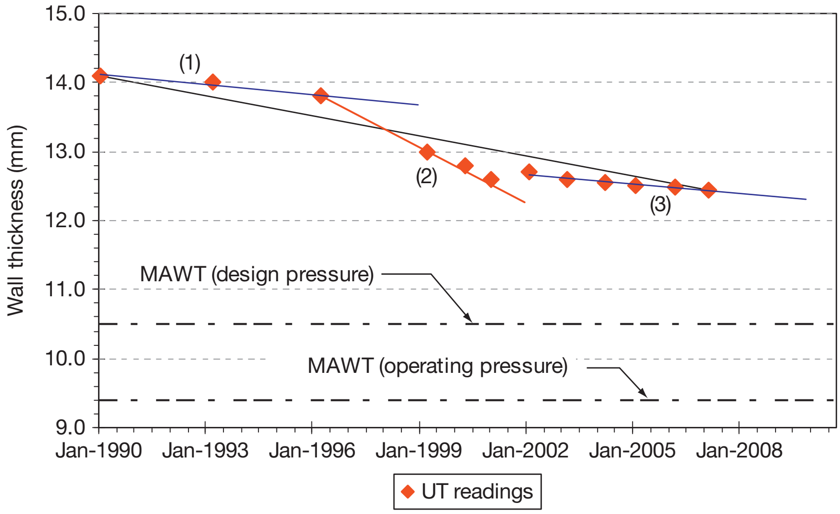


Figure 11 Example of UT Inspection data with time (indicative).

4.41.6.3 External Protection

Performance assessment of the external corrosion control system, typically coatings and/or CP will also be required. For operating plants, this will normally be limited to visual inspection, but for items that are insulated a more detailed inspection plan will be required, which will be based on risk assessment for CUI and may also include specialist NDT/NDE systems such as pulse eddy current, long range UT, radiography or thermal imaging systems.[58,59]

For buried and submerged pipelines, in addition to use of ILI surveys, the condition of the protective coating and effectiveness of the CP system will also be determined by one or more specialist pipeline surveys. For subsea pipelines inspection will normally be by a remote operated vehicle (ROV) carrying out both visual inspection but also potential measurements to determine the performance of the CP system.

For onshore (buried) pipelines a number of different surveys are carried out,[76] covering:

- close interval potential surveys (CIPS);
- pearson surveys;
- DC voltage gradient (DCVG);
- AC voltage gradient (ACVG).

Often a pipeline survey will combine two of the methods, in particular CIPS and DCVG, the aim being to identify areas where either the protection potential is less than required (typically a polarized or 'instant-off' potential more negative than −850 mV versus Cu/$CuSO_4$ reference electrode), and/or where there is evidence of significant coating damage.

Pipeline survey data, together with information from fixed monitoring points, will be used to assess overall performance of the pipeline protection and to identify areas where excavations of the pipeline may be required for direct assessment of the condition. In particular for buried pipelines a growing concern relating to buried pipelines is the risk of EAC, typically associated with specific local ground conditions/chemistry, damage to protective coatings and poor/inadequate CP. EAC is described in other chapters in this book and direct assessment issues are described in more detail in Section 4.41.6.8.

The management of external corrosion and maintenance of coatings on structures, piping, handrails, walkways, and gratings has been addressed using a risk based assessment (RBA) to prioritize work based on inspection of coatings condition linked to performance monitoring on a visible KPI reporting system[3,77] (see also Section 4.41.6.10.4).

4.41.6.4 Chemical Treatment

Chemical treatment of process and service fluids is widely used in oil and gas production and processing in order to manage corrosion. Commonly used chemical treatments are:

- corrosion inhibitors;
- methanol;
- H_2S scavenger;
- glycol;
- wax inhibitor;
- biocide;
- O_2 scavenger;
- sodium hypochlorite;
- scale inhibitor;
- pH buffer;
- antifoulant.

The purpose of each of these treatments may not necessarily be for corrosion management, but they do contribute toward corrosion mitigation and control.

Chemical selection should include performance and compatibility testing and feasibility studies prior to implementation. Part of the ongoing corrosion management process is ensuring that the correct chemical is fed at the correct dose rate/concentration at the correct location at the correct time and that there is always stock available. This is the key to the production process running efficiently and effectively.

The background to some of the different analysis issues is summarized in the following section.

4.41.6.4.1 Temperature, pressure, CO_2/H_2S content

Temperature and pressure measurements will be routinely recorded by the plant DCS. These values, together with CO_2/H_2S content, can then be used to provide an estimate of the system corrosivity using any of the standard corrosion modeling software packages, for example, De Waard and Milliams,[25] ECE4,[27] Norsok M506,[26] etc.

There are methods for measuring dissolved CO_2/H_2S in water samples taken from the process. However, dissolved CO_2/H_2S content is highly dependent on pressure and temperature (since gas flashes off from solution when samples are depressurized and H_2S is rapidly lost by air oxidation) and therefore results can be erroneous. Measured values in water are always lower than true values in the case of pressurized samples, unless elaborate sampling procedures are followed.

Hence, in the authors opinion, the preferred method would normally be to measure CO_2 and H_2S content in associated gas (ppmv values) using sampling tubes, and then use a PVT model (e.g., Multiflash™) in conjunction with known pressure and temperature data to back calculate the dissolved CO_2/H_2S content of the aqueous and oil phase(s) *in situ*, throughout the system. In addition to providing a more accurate assessment it also means that only one measurement per fluid stream is required as opposed to multi-measurements at different points in the stream.

4.41.6.4.2 pH measurements

The corrosivity of a solution is directly related to the solution pH, hence a measure of pH can be used to monitor changes in system corrosivity. In oil field systems pH measurement is normally carried out on fluid samples, with measurement either in the field shortly after taking the sample, or later in the laboratory. On-line pH measurements, while possible, are unreliable in oil field systems due to contamination of pH electrodes by oil and/or H_2S.

The biggest problem with on-site measurements is the massive and rapid rise in pH almost immediately on depressurization of a sample, due to flashing-off of gas. *In situ* pH is almost always dominated by the CO_2/bicarbonate buffer system, so the concentration of dissolved CO_2 greatly influences the pH and it changes greatly from downhole to wellhead to separators to export system. Laboratory measurements of pH on degassed or partly degassed samples are of no value.

Hence, the optimum procedure is to calculate pH throughout all stages of fluid handling from pressure and temperature data, gas phase CO_2 and water composition (salinity and mineral bicarbonate content), using standard software packages, such as NORSOK M506[26] or others.

4.41.6.4.3 Oxygen monitoring

For seawater injection systems the principle method of corrosion control is deoxygenation, typically to < 10 ppb. Hence, a measure of oxygen content provides a direct measure of the effectiveness of the corrosion control system. Oxygen measurement can be carried out on-line or on liquid samples.

On-line measurements can use either specialist oxygen monitors or galvanic probes.[78] Oxygen monitors give a direct measure of the oxygen content and, provided that they are correctly serviced/calibrated (to prevent fouling of the electrode).

Galvanic probes (with elements of carbon steel and copper) can be more robust for some field applications. Although they do not give a direct measure of the oxygen content, the measured galvanic current is directly proportional to the oxygen concentration in the process stream.

4.41.6.4.4 Iron count

A common and relativity straightforward method for assessing corrosion in water (e.g., seawater injection, process water, etc.) is *iron counts*, that is the measure of soluble iron ion (Fe^{2+}).[66] If the corrosion is occurring the Fe^{2+} concentration will increase. Hence, ideally, iron content at the both start and end of the system/pipeline is needed to provide an estimate of the corrosion occurring; however, in most cases simple changes in Fe^{2+} content are used to assess increasing/decreasing corrosion conditions.

However, iron counts are only viable where the corrosion product is soluble. Hence, they are not suitable for use in sour environments (where the corrosion product is insoluble iron sulfide, FeS) or in sweet systems with a high bicarbonate content (once the process becomes $FeCO_3$ saturated, any increase in corrosion rate cannot add extra iron to solution, instead more insoluble iron carbonate scale forms). In both cases misleading information will be obtained.

4.41.6.4.5 Inhibitor residuals

Inhibitor residuals are an important measurement to check that sufficient corrosion inhibitor is injected into the system. In most cases, the method of testing will be provided by the chemical vendor and will be targeted for the specific active component of the inhibitor package. However, experience has shown that some methods used are subject to interference and hence can be unreliable. Generic methods are available that can provide a reliable result, provided that they are calibrated for the specific chemical. Further details on corrosion inhibitors is given elsewhere in this book and in EFC publication.[30]

4.41.6.5 Data Management

Is it essential that data collected as part of the corrosion management process are stored in an efficient manner that enables easy retrieval and trending of data.

A large number of commercially availably systems are available that offer a varying level of interaction with process monitoring systems (e.g., PI® and SCADA®) and planning systems (e.g., Maximo® and SAP®) as well as various GIS systems and web interfaces to enable user remote access. The level of support from the suppliers of commercially available systems can vary from a simple software sale to a fully supported service agreement. In addition a bespoke system can be developed that increase the level of flexibility required.

Stand alone systems can easily be developed for activities such as Corrosion Risk Assessment (CRA), RBA, Inspection Planning, storing Inspection Data, storing Corrosion Monitoring/CP Data, storing fluid data, and monitoring KPI's. There can be advantages when using a simple system compared with a large multifunctional database and the merits of each should be assessed.

When selecting a data management system for a facility consideration should be given to

- Type of asset:
  - Pipeline networks have a limited number of 'data locations' but a large number of data measurements and therefore require a system that can enable easy trending of data (e.g., CP data, Corrosion probe data).
  - Process plant typically has a large number of 'data locations' and a limited number of data measurements (e.g., NDT inspection data).
  - Consideration must be given to how manually generated data (e.g., Corrosion Coupon analysis and fluids analysis) are to be integrated into the data management system.
  - Is the database expected to be a complete asset register, or just consider key high-risk areas?
- Expected degradation mechanism/type of data to be collected:
  - For time-dependent degradation trending of inspection and monitoring data is appropriate.
  - For cracking mechanisms, trending of inspection data has a limited value and recording of fluid and operating parameters are of more significance.
  - Is trending of fluid monitoring data essential? What parameters are key?
  - Is the system to be used to monitor, trend and report KPIs
- National legislation:
  - If the national legislation defines a prescriptive inspection approach there is little point in trying to implement a data management system that calculates RBI frequencies.
- Level of IT infrastructure in place:
  - Where IT infrastructure is limited there is little point in trying to implement a fully automated system. A fit for purpose procedure driven system is sometime far more appropriate.
- Roles and responsibilities:
  - Clearly defined roles and responsibilities are required for data collection, data input and data review/analysis.
  - All data systems should have a level of security that enables competency levels to be assessed better access to the system.

While data management systems are an essential tool as part of a Corrosion Management system, user intervention, audits and continuous improvement process are essential to maintain a database that is truly representative of the facility in terms of physical and operational information and perceived degradation threats. Any database that is not maintained as a live system cannot be considered an effective Corrosion Management tool.

4.41.6.6 Change in Process Conditions

The original corrosion risk assessment carried out at the FEED and/or design stage will have taken a range of operating conditions from the basis of design for the particular field/facility. This in turn will have driven the material selection, corrosion control, and planning inspection/monitoring for the system once in operation. However, as highlighted at the start of this section, there is always the chance that the actual operating conditions will be different to those envisaged. This is often due to change in conditions as the facility ages/expands.

Many operators handle possible changes in process conditions by predefining the corrosion 'window' or 'envelope' (that is the range of conditions to which the original assumptions remain valid) as part of the original risk assessment carried out during FEED or Design stage. Then if any of the parameters change sufficiently with time such that they are no longer in the 'corrosion window' then they will automatically trigger a reassessment of the corrosion risk. In fact most ongoing corrosion risk assessments simply start with checking whether the operating conditions are within the original design assumptions ('window') and if they are and the performance has also been demonstrated to be in line with predictions then this is taken as sufficient to keep the existing corrosion risk assessment in place.

If the conditions have changed then the likely effect, for example, increase water cut, gas lift resulting in increase in CO_2 content, reduction in flow rates, etc., on the expected corrosion rate, location and morphology should be determined and, where necessary, a change in the inspection/monitoring/ corrosion control plans put in place.

4.41.6.7 Risk Based Inspection (RBI)

RBI schemes are a key component of corrosion management schemes and provide a planning tool to develop the optimum plan for the execution of inspection activities. RBI uses the findings from formal risk analyses, including corrosion risk assessments, to guide the direction and emphasis of the inspection planning and the physical inspection procedures.

A risk-based approach to inspection planning is used to:

- ensure risk is reduced to as low as reasonably practicable;
- optimize the inspection schedule;
- focus inspection effort onto the most critical areas;
- identify and use the most appropriate methods of inspection.

RBI methodologies are well described in published documents such as API 581[10] and DnV RP G-101[11] and have been adopted by many operators, further details on this topic are also given in the chapter on **Risk Based Inspection** in this book.

Where RBI schemes are used, it should be noted that the determination of future inspection requirements, by extrapolation of historical trends, is based on an assumption that the conditions in the future are similar to those in the past and that there is no change in degradation mechanism(s). Any significant change in operating conditions (for example, water break-through, increase in CO_2 content, change in wax or scaling tendency, etc.), could result in significant changes in corrosion rate and/or corrosion damage, which could in turn lead to different inspection requirements. It is therefore appropriate for the model that is driving the RBI scheme to be rerun either at specific time intervals, or when a process variable exceeds a previously agreed boundary condition.

On new assets or in the absence of good quality historic data on mature assets, it is normally considered good practice to carry out a baseline survey to establish a known condition from which to monitor.

Many RBI schemes are operated as part of a major inspection software database and analysis tool and are normally applied to process plant and facilities. However, many standard RBI software systems can be very 'data hungry,' that is unless the majority (if not all) of critical information is available standard software systems will not run. To overcome this limitation, 'high level' assessment schemes are being developed that allow engineering judgment to be used to where data is sparse.[79] High-level risk assessment for pipeline operations have also been developed.[28,45,80]

4.41.6.8 Direct Assessment Procedures

For onshore pipelines, a major change in operational corrosion management has occurred over recent years, where the methods of '*direct assessment*' are now routinely used, and in some countries have become mandated. Here *direct assessment methodology*, actually covers a wide ranging assessment of the likely pipeline condition as determined by a review of the design, installation, geographic, operational and ILI data to identify the sections of the line that are most at risk of corrosion degradation, both internal and external, that should be selected for excavation and physical confirmation of condition (i.e., *direct assessment*).

At this time, direct assessment procedures have been developed and adopted as a number of NACE Standard Practices for:

- Pipeline External Corrosion Direct Assessment Methodology (EC-ECDA); NACE SP0502–2008.
- Stress Corrosion Cracking (SCC) Direct Assessment Methodology (SCC-ECDA); NACE SP0204–2008.
- Internal Corrosion Direct Assessment Methodology for Pipelines Carrying Normally Dry Natural Gas (DG-ICDA); NACE SP0206–2006.
- Internal Corrosion Direct Assessment Methodology for Liquid Petroleum Pipelines (LP-ICDA); NACE SP0208–2008.

A further NACE standard, for internal corrosion due to wet gas operation (WG-ICDA) is currently under-development and is expected to be published by 2010.

In all cases the direct assessment methodology requires a detailed analysis of existing data to determine whether or not there is sufficiant information so that the methodology can be applied and provides guidance for what critical information needs to be obtained.

Once sufficient data have been collected, the methodology provides a structured procedure to analyze the data to highlight areas of specific corrosion risk. This normally requires dividing the pipeline into different sections (lengths) where the conditions are likely to be similar.

- For internal corrosion assessment, sections will be defined by significant changes in operating pressure/temperature/flow rates, and especially angle of inclination, since this will define where water drop out and collection will occur and hence the most likely place for corrosion to occur.;
- For external corrosion assessment, sections will be defined by changes in ground (soil) condition, CP systems, etc.

The comparison of the analysis of theoretical conditions together with pipeline inspection data, such as ILI surveys (to identify both internal and external features) and external surveys (CIPS, DCVG – to identify areas of coating damage and/or under protection), is used to prioritize areas to be excavated and examined, usually by UT inspection.

The whole process provides a transparent method of assessment and ensures that high-risk areas are correctly identified and actions taken in a timely manner, and is essentially a pipeline equivalent to process facility RBI schemes.

4.41.6.9 Fitness for Service (FFS)

As highlighted previously, the main objective of corrosion management is to ensure that plant and facilities are operated in a safe and reliable manner and the principle challenge for corrosion management in the oil and gas industry is that the preferred material of construction (low-alloy carbon steel) can, and is, subject to both internal and external corrosion, especially where the corrosion control plans do not operate as intended.

Hence, an important aspect of corrosion management is assessing the condition and FFS for items of equipment (pipeline, pipework, vessels, tanks, etc.) where corrosion has been found. FFS assessment (also referred to as FFP) can be simple to the complex, depending on the component, the extent and type of deterioration, and regular requirements. API 579[81] defines three levels of assessment, as:

- **Level 1** FFS assessments provide conservative screening criteria that require the least amount of inspection and component information. Level 1 assessments usually do not require extensive calculations. Either inspectors or plant engineers will conduct a Level 1 assessment.
- **Level 2** FFS assessments involve a more detailed evaluation of components and usually require an accurate measurement of flaws or damage. Most Level 2 FFS assessments require calculation of the required component thickness or of component stress. Either plant engineers or engineering specialists will conduct Level 2 assessments.
- **Level 3** FFS assessments require detailed evaluation of components. Component flaws or damage must be accurately determined, and calculation methods often involve numerical analysis such as the finite element method. Level 3 assessments often require the services of engineering specialists experienced in advanced stress analysis, fracture mechanics, etc.

A Level 1 assessment could be as simple as confirming whether any metal loss is within the design corrosion allowance (i.e., based on the original design pressure). If metal loss exceeds this limit, then the item may still be suitable for service, but only at a reduced maximum operating pressure (as described in API 570[57] and ASME B31G[82]), this would form part of a Level 2 assessment.

Level 3 assessments apply to more complex conditions, in particular localized corrosion and/or EAC, where alternative methods of assessment may be required. The specific method/procedure to be used will be dependent on component type, original design code and nature of damage, for example, API 579,[81] ASME B31G,[82] DnV RP F-101,[83] BS 7910,[84] and others.

4.41.6.10 Communication and Management Structure

4.41.6.10.1 *Corrosion management team*

The corrosion management team is the main vehicle for communication between the key players. Communication within the operator's organization and its relevant contractors is also important in order to achieve understanding and obtain support in meeting objectives:

- Appropriate information should be disseminated to the correct people.
- Written information on hazards, risks and preventative measures should be provided.
- Procedures, work instructions, and guidelines should be published and shared.
- Corrosion awareness information should be distributed to those who need to be aware of the importance of corrosion management to assist those directly involved. Training and information to develop corrosion awareness should be provided.
- Key players in the organization and their contracted bodies that comprise the corrosion management team should be identified.

- Regular meetings of the corrosion management team on implementation status, trends in deterioration and failure, status of corrective action, and planning and budgetary issues should be undertaken.
- Managers, technical specialists, authorities, supervisors, and wherever appropriate, contractor personnel should be visible through the publication of charts and guides.
- Experiences should be shared with other facilities, other operators and with appropriate external bodies.

4.41.6.10.2 Management of change

Management of change is an important part of corrosion management activity. As described previously, it is vital that changes in operating conditions are identified and their impact on the corrosion risk and effectiveness of the corrosion control program including the inspection/monitoring plans are assessed.

Most oil and gas operating companies will have a management of change procedure, so that as new developments are planned and existing facilities are phased out the engineering impact is fully considered and implications for fabrication, maintenance and operations are put in place. The corrosion management team should be included within the management of change process ensuring that implications to operational windows, and effects on corrosion risk are identified early in the change process so, as was the case during initial design, cost-effective procedures can be developed in a timely manner.

In the case of new development/tie-ins, etc., a policy should be adopted regarding the required life of the facility. The materials and corrosion control aims at providing that life. To maintain design intent and operate within the design limits, the plan should identify the elements to be built into the design, the performance limits on which it is based and the actions required during operation. If there is a choice of suitable materials then life cycle costing can be used to identify the final materials. The development plan should consider that the design should make provision for monitoring equipment such as corrosion probes, access fittings, instruments and the provision for data gathering. Also, design to enable inspection such as pig traps suitable for online inspection tools should be considered.

In the case of field extension, as technology advances, asset life expectancy is increasingly being extended beyond the original design life. Therefore, it is important to be able to accurately gauge the control status of the asset if field life extension is required. This might require a reappraisal of corrosion risks and introduction of major changes to current activities. The individuals responsible for setting and implementing the corrosion management strategy and strategic plan should be made aware of the future business and operational requirements of the asset.

4.41.6.10.3 Contracting structure

There are many different operational and contractual structures adopted by operators world-wide. These range from all staff (management, engineering, operating, inspection and maintenance) being employed directly by the operator to fully out-sourced conditions, where with the exception of management and senior engineering functions, all other roles are let on a contract basis to either a main operation/maintenance contractor or as a series of contracts for specific roles.

In all cases, the roles and responsibilities for the different disciplines/contractors/subcontractors relating to corrosion management should be clearly identified. Reporting routes should also ensure that relevant information/data pasted sideways to other corrosion management team members allow timely review and action. There are many cases where information relating to problems with, for example, corrosion inhibitors, high measured corrosion rates, changes in operating conditions, etc. are not identified or not passed to the responsible person/department until it is too late to provide cost-effective intervention.

4.41.6.10.4 Key point indicators (KPI)

KPIs are used as a measure of the integrity of the facility and the corrosion management system. KPIs should be:

- Relevant, practicable, and meaningful to the corrosion threats and the policy and plan in place.
- Quantifiable to avoid subjective judgments.
- Intended primarily at demonstrating success or identifying trends that enable corrective action.
- Determined with reference to the engineering design of the facility in terms of performance limits for corrosion barriers. Target values should be set for all indicators.
- Selected so that they indicate how successfully the plan is being implemented linked to corrosion – proactive measurement and leading indicators.
- Selected so that they indicate trends toward the achievement the desired outcomes linked to

corrosion – reactive measurement and lagging indicators.

KPI's allow quick indication of where corrosion management schemes are working and, more importantly, where they are failing, either due to failure to meet specific objective (e.g., delays in the retrieval of corrosion coupons, delays to planned inspection, insufficient dosing of chemicals, etc.) or where corrosion control is compromised (e.g., increased in measured corrosion rate above critical limits). There are various ways of presenting KPI information, increasing so-called '*traffic light*' systems (with KPIs reported as 'red,' 'amber,' or 'green') are used,[3] for example, as shown in Table 1.

In addition to using KPIs for assessing the performance of the management system as a whole, technical KPIs can also be used to highlight the performance of the corrosion control plans. Here, similar arrangements would apply but criteria based on acceptable/expected corrosion rates, bacteria counts, inhibitor residual concentrations, etc. would be used.

4.41.6.10.5 Audit/compliance

An important aspect of modern corrosion management systems is that they should provide a clear and transparent approach to the decision-making process, the overall performance of the corrosion monitoring plan, and the performances of the corrosion control procedures adopted.

Part of this process is that the system should be subjected to regular audits (internal and external) to determine whether the corrosion management system effectively conforms to the requirements. They are an essential check on the performance of the system and are normally carried out by an independent party (i.e., somebody not directly involved in the operation of the corrosion system). Audits cover the following aspects:

- implementation of procedures and processes;
- competency;
- checks in place;
- compliance.

An audit reviews the processes and procedures that are aimed at achieving the performance targets and determines if the procedures for ensuring that they are achieved are being properly implemented. If activities are found to be not in accordance with the procedures and processes it is called a noncompliance.

Audits can be performed in two ways. A complete audit can be undertaken in one exercise or individual elements can be audited separately on a rolling basis. An audit cycle duration is generally 2 to 3 years. In addition to independent audits, internal audits should be carried out more frequently in specific procedures or functions.

The procedures of contractors will be audited on award of contract if not covered by prequalification and then periodically in the same manner as for the operator.

4.41.6.10.6 Ongoing improvements

As identified in the corrosion management overview chapter in this book, an important aspect of any

Table 1 Examples of corrosion management key performance indicators for an offshore facility (partial extract from Guidance for Corrosion Management in Oil and Gas Production and Processing[3])

Activity	*Target*	*Green*	*Amber*	*Red*
Plan				
RBI reviews up to date	None outstanding	None	2 or less	3 or more
Annual pipework inspection scope	Completed by year end	Yes		No
Annual vessel inspection scope	By end of Jan	Jan	Feb	Mar or later
Implement				
% pipework inspections on target	$>$90% of planned cumulative completion	$>$90% complete	75–90% complete	$<$ 75%
Safety critical vessel inspections on target as per RBI due date	On target or above	All on target (0)	2 below target (1–2)	$>$2 below target ($\geq$3)
Measure				
No of leaks (safety or production critical)	No leaks	0		$\geq$1
No of unexpected leaks (noncritical)	No leaks	0	$\leq$4	$\geq$5
Review				
Bi-monthly pipework integrity summary been updated	100% complete	Yes		No
Annual report completed (1Q)	Complete report within Q1	Yes		No

system is its ability to develop and improve with experience. Hence, the system should regularly review its performance and determine where it is meeting and nonmeeting its targets. This is often referred to as '*do and improve loops*.'

4.41.7 Summary/Conclusions

The management of corrosion in oil and gas production has a long history of pioneering developments and has been instrumental in progressing many successful field applications that would have been unthinkable 25 years ago. In particular, the 'FFS' of materials for sour service is increasingly allowing more aggressive conditions to be handled, while improvements in corrosion inhibitors has enabled multiphase lines to have increased throughput even under erosive conditions. Hand in hand with these technical developments has been an increased awareness of the need to manage SHE issues, hence corrosion mitigation activities are increasingly seen as having an important impact on integrity and loss containment.

The aim of the chapter was to identify some of the basic corrosion inputs into projects during the main development phases. Much of the detail can be found in industry and international standards quoted throughout the text (NACE, API, DnV, ISO) and industry relevant publications such as the *Corrosion Threats Handbook – Upstream Oil and Gas Production*[5] and *Guidance for Corrosion Management in Oil and Gas Production and Processing*.[3] These publications provide good examples of the corrosion damage sustained by process equipment during operational life and the detailed requirements and performance indicators needed to ensure that corrosion is managed effectively to maintain asset integrity.

The increasing demand for improvements in all aspects of asset management will impact on the delivery of corrosion services as more aggressive environments are exploited. Although driven primarily by SHE concerns, a continuous improvement in management systems, involving the use of performance indicators, reviews and audits of activities should also result in improvements in operational and day to day activities to deliver less unscheduled downtime and improved performance. The importance of a good record keeping/data management system cannot be over emphasized as field data are vital to provide the information needed for good decision making.

References

1. Milliams, D. Corrosion Management, 12th International Corrosion Congress on Corrosion Control for Low Cost Reliability, Sep 1993; NACE International: Houston, TX; vol 4, p 2420.
2. Review of Corrosion Management for Offshore Oil and Gas Processing; Offshore Technology Report 2001/044, UK Health and Safety Executive, 2001www.hse.gov.uk/research/otopdf/2001/oto01044.pdf
3. Guidance for Corrosion Management in Oil and Gas Production and Processing; Energy Institute: London, May 2008. ISBN 978 0 85293 497 5.
4. Corrosion Threats Handbook – Upstream Oil and Gas Production; Energy Institute and Oil and Gas UK: London, 2008.
5. BSI PAS 55–1: 2003, Asset management, Specification for the optimised management of physical infrastructure assets, and BSI PAS 55–2: 2008, Asset management: Guidelines for the application of PA 55–1–British Standards Institute.
6. Dawson, J. L.; Bruce, K.; John, D. G. Corrosion Risk Assessment and Safety Management for Offshore Processing Facilities; Offshore Technology Report 1999/064, UK Health and Safety Executive, 1999.
7. The Public Inquiry into the Piper Alpha Disaster Report by the Hon. Lord Cullen; HMSO: London, Nov. 1990. ISBN 0 10 113102.
8. US Pipeline Safety Act 1995.
9. API Recommended Practice RP580, Risk Based Inspection American Petroleum Institute, 2000.
10. API Publication 581 Risk Based Inspection Resource Document; 2002, American Petroleum Institute, 2002.
11. DnV RP G101 Risk Based Inspection of Offshore Topsides Static Mechanical Equipment; DnV, 2002.
12. The Offshore Installations (Safety Case) Regulations, SI 1992/2885; The Stationery Office Limited: London, 1992. ISBN 011025869X.
13. The Offshore Installations and Wells (Design and Construction, etc.) Regulations 1996 SI 1996/913; The Stationery Office Limited: London, 1996. ISBN 011054451X.
14. The Pipelines Safety Regulations, SI 1996/825; The Stationery Office Limited: London. ISBN 0110543734.
15. The Control of Major Accident Hazard Regulations, SI 1999/743; The Stationery Office Limited: London. ISBN 0 11 082192 0.
16. Pressure Systems Safety Regulations, SI 2000/128; The Stationery Office Limited: London. ISBN 0 11 085836 0.
17. Successful Health and Safety Management, UK HSE HS(G) 65 1991. ISBN 0–11–882055–9.
18. NORSOK Standard S-006, Rev. 2 December 2003, HSE evaluation of contractors.
19. ISO 14001:1996, Environmental management systems – Specification with guidance for use.
20. ISO 15156: 2001/NACE MR 0175–2001 Petroleum and natural gas industries – Materials for use in H2S-containing environments in oil and gas production,
21. Public Report of the Fire and Explosion at the ConocoPhillips Humber Refinery on 16th April 2001; UK Health and Safety Executive, www.hse.gov.uk/comah/conocophillips.pdf.
22. Congressional Report Services, Library of Congress, BP Alaska North Slope Pipeline Shutdowns, Regularity Policy Issues, October 2006, www.cnie.org/NLE/CRSreports/06Oct/RL33629.pdf.
23. Reason, J. T. *Managing the Risks of Organizational Accidents*; Ashgate Publishing Ltd: England, 1997.

24. BS 6079–3:2000 Project Management – Part 3: Guide to the Management of Business Related Project Risk; BSI Standards, 2000.
25. de Waard, C.; Lotz, U.; Milliams, D. *Corrosion* **1991**, *47*, 976; de Waard, C.; Lotz, U. In Corrosion'93; NACE International: Houston, TX, 1993; Paper No 69.; de Waard, C.; Lotz, U.; Lugstad, A. In Corrosion'95; NACE International: Houston, TX, 1995; Paper No 128.
26. NORSOK M-506: Rev. 2, June 2005, CO2 Corrosion Rate Calculation Model; Norwegian Technology Standards Institution (Norsk Sokkels) www.standard.no/petroleum.
27. Electronic Corrosion Engineer (ECE®) Smith, L. M. Intetech, Waverton, Chester, UK
28. Oliver, K. E.; John, D. G. In Corrosion 2007, NACE, Nashville, TN, March 2007, paper on 07124.
29. Kolovich, K.; Kiefner, J. F. In Corrosion 2007; NACE: Nashville, TN, 2007; Paper no 07120.
30. Palmer, J. W.; Hedges, W.; Dawson, J. L. *The Use of Corrosion Inhibitors in Oil and Gas Production; European Federation of Corrosion Document Number 39*; Institute of Materials: London, 2004.
31. Smith, L. M.; de Waard, K. In Corrosion 2005; NACE: Houston, TX, 2005; Paper No 05468.
32. NACE SP0208–2008 Internal Corrosion Direct Assessment Methodology for Liquid Petroleum Pipelines.
33. PIPESIMS®. Copyright Schlumberger plc; www.slb.com/content/services/software/production/pipesim/index.asp.
34. PIPEFLO®. Copyright Engineered Software; http://www.eng-software.com.
35. OLGA®, http://www.sptgroup.com/en/Products/olga.
36. HYSYS® http://www.aspentech.com/core/aspen-hysys.cfm.
37. API RP 14E Recommended Practice for Design and Installation of Offshore Production Piping Systems; API: Washington, DC, 1991.
38. Schmidt, G.; Gudde, T.; Strobel-Effertz, E. In Corrosion'96; NACE, Houston TX, 1996, Paper no 9.
39. Johnson, B. V.; Choi, H. J.; Green, A. S. In Corrosion'91; NACE: Cincinnati, OH, 1991; Paper No 573.
40. Green, A. S.; Johnson, B. V.; Choi, H. J. *Flow-Related Corrosion in Large-Diameter Multiphase Flowlines*; SPE Production and Facilities, May 1993; pp 97–100.
41. Craig, B. *Corrosion* **1998**, *54*(8), 657.
42. de Waard, C.; Smith, L. M.; Craig, B. D. In Corrosion'2003; NACE International: Houston, TX, 2003; Paper No. 03629.
43. Johnson, B. V.; Al-Ghafri, M.; Harthy, A.; John, D. G.; Schofield, M. J. In Corrosion 2009; NACE: Atlanta, GA, 2009; Paper No 093549.
44. Moosavi, A. N.; John, D. G. In Corrosion/2002; NACE: Denver, CO, 2002; Paper No 02225.
45. John, D. G.; Stokes, P.; McIntosh, P. In Corrosion 2003, NACE: New Orleans, April 1984, paper no 343.
46. Johnson, B. V.; Al-Ghafri, M. J. H; Al-Harthy, A. S. M; Kompally, S. N.; Dicken, G.; Schofield, M. J.; Bruce, K.; John, D. G. Paper SPE 114140, presented at '*2008 SPE International Oilfield Scale Conference*', Aberdeen, Scotland May 2008.
47. ASTM D1401– 02 'Standard Test Method for Water Separability of Petroleum Oils and Synthetic Fluids.'
48. Hedges, B.; McVeigh, L. In Corrosion '99; NACE: San Antonio, TX, 1999; Paper No 99021.
49. API Spec 5L, Specification for Line Pipe, 42nd ed.; American Petroleum Institute, Jan- 2000.
50. ISO 3183:2007 Petroleum and natural gas industries – Steel pipe for pipeline transportation systems.
51. ASTM G39 – 99(2005) Standard Practice for Preparation and Use of Bent-Beam Stress-Corrosion Test Specimens.
52. NACE TM0177–2005, Laboratory Testing of Metals for Resistance to Sulfide Stress Cracking and Stress Corrosion Cracking in H_2S Environments.
53. Taylor, T. S.; Pendlington, T.; Bird, R. Foinaven super duplex materials cracking investigation, Paper presented at Annual Offshore Technology Conference; Houston: TX 1999.
54. J. de Nouyer, J.; J. Slining, J.; and V. Ashworth, V. In Corrosion'84, NACE: New Orleans, April 1984; Paper No 343.
55. Turnipseed, S. P. In Corrosion/91; NACE: Cincinnati, 1991; Paper No 234.
56. John, G.; Rosbrook, T.; Robinson, J.; Munro, I. In Corrosion 2000; NACE: Orlando, FL, 2000; Paper No 00011.
57. API Document 570 Inspection, Repair, Alteration, and Rerating of In-Service Piping Systems American Petroleum Institute, 1998.
58. NACE RP0198–2004 The control of corrosion under thermal insulation and fireproofing materials – As systems approach.
59. European Federation of Corrosion Publications Number 55, Corrosion under insulation (CUI) guidelines (EFC 55); Winnik, S., Ed.; Woodhead Publishing Ltd., Cambridge, 2008. ISBN 13 978–1–84569–423–4.
60. John, D. G.; Attwood, P.; Rothwell, A. N. In Corrosion/99; NACE International: Houston, TX, 1999; Paper 249.
61. Khlefa, A. Esaklul In Corrosion 2007; NACE: Nashville, TN, 2007; Paper No 07264.
62. Turissini, R. L.; Hingoraney, R. Paper presented at 4th Middle East Corrosion Conference: 11–13 January 1988; NACE/The Society of Engineers Bahrain.
63. ISO 9000: 2008, Quality management systems. Fundamentals and vocabulary.
64. Moltke, Helmuth, Graf Von, Militarische Werke. vol. 2, part 2, pp 33–40. Found in Hughes, Daniel J. (ed.) Moltke on the Art of War: Selected Writings. (1993). Presidio Press: New York, NY, ISBN 0-89141-575-0. p. 45
65. NACE RP 0775–2005 Recommended Practice: Preparation and Installation of Corrosion Coupons and Interpretation of test data in Oilfield Operations.
66. NACE RP 0192–98 Recommended Practice: Monitoring Corrosion in Oil and Gas Production with Iron Counts.
67. NACE SP 0499–2007 (formerly TM0299–99) Standard Practice: Corrosion Control and Monitoring in Seawater Injection Systems.
68. NACE TM 0194–2004 Test Method: Field Monitoring of Bacterial Growth in Oil Field Systems.
69. ASTM G96–90(2008) Standard Guide for Online Monitoring of Corrosion in Plant Equipment (Electrical and Electrochemical Methods).
70. NACE Technical Report 3T199, Techniques For Monitoring Corrosion and Related Parameters In Field Applications, December, 1999.
71. Rothwell, N. *Corrosion Monitoring Handbook*, Coxmoor Publishers: UK, 2000. ISBN: 1 901892 03 4.
72. Thomas, J.; Barr, E. E. In Corrosion 2004; NACE: New Orleans, LA, 2004; Paper No 04171.
73. NACE RP 0102–2002 Recommended Practice. In-Line Inspection of Pipelines.
74. NACE Technical Report 35100. In-Line Nondestructive Inspection of Pipelines, 2000.
75. API STD 1163 In-line Inspection Systems Qualification Standard 2005.
76. NACE TM0109–2009 Aboveground Survey Techniques for the Evaluation of Underground Pipeline Coating Condition.

77. Paterson, S. External Corrosion Management in Shell; presentation at UK Oil and Gas and Energy Institute Workshop, Aberdeen 18 Jun 2008. (available online at http://www.oilandgas.org.uk/downloadabledocs/358/f.Steve_Paterson_Presentation.pdf).
78. NACE Technical Report 1C187, Use of Galvanic Probe Corrosion Monitors in Oil and Gas Drilling and Production Operations (2005ed.).
79. Hodges, S.; Oliver, K.; Tipton, E.; Spicer, K.; Adams, R.; John, G. In Corrosion 2010; NACE: San Antonio, TX, 2010.
80. Chevrot, T. C.; Bonis, M.; Stroe, M. In Corrosion 2009; NACE: Atlanta, GA, 2009; Paper No 09113.
81. API 579–1/ASME FFS-1 (2007) Fitness-For-Service.
82. ANSI/ASME B31G-1991 (R2004) Manual for Determining the Remaining Strength of Corroded Pipelines: a Supplement to B31, Code for Pressure Piping.
83. DNV-RP-F101, Recommended Practice Pipelines Corroded Oct 2004.
84. BS 7910: 2005, Guide to methods for assessing the acceptability of flaws in metallic structures.

4.42 Management of Corrosion of Onshore Pipelines

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Glossary

Drip A drip is a leg located underneath the pipeline that collects liquids and solids that can be transported down the pipeline with the product. Drips are usually equipped with a siphoning arrangement so that the collected materials can be removed.

Electric resistance welding Electric resistance welding is a process used to weld the longitudinal seam. The heat required for welding is produced by the resistance of the steel to the passage of an electric current. The heated plate edges are then forced together under pressure to produce the weld.

Groundbed A groundbed is one or more anodes installed in the earth to provide a low-resistance electrical path to ground in cathodic protection systems.

Lack of fusion A lack of fusion defect is a region of the weld where full fusion has not been achieved. This could be due, for example, to mill scale on the plate edges or a lack of adequate heat or pressure during the welding process.

Linepipe An individual length of pipe (sometimes also referred to as a spool or joint), typically 12m in length.

Town gas Town gas is a type of manufactured gas that is principally made from coal. Town gas was used extensively in homes in the UK until the discovery of natural gas.

Abbreviations

In-line Inspection (ILI) Pipeline inspection conducted using an instrumented vehicle that travels inside the pipeline usually propelled by the fluid in the pipe.

Symbols

V_{IR} Potential drop associated with the flow of Cathodic Protection current through the soil of finite resistance (mV)

V_p Actual potential on the pipe surface (mV)

V_s Cathodic protection potential measured on the surface (mV)

4.42.1 Introduction to Pipelines and Pipeline Engineering

The first recorded use of pipelines for the transportation of natural gas was ~400 BC when the Chinese used bamboo pipe to transport natural gas to Peking to be used for lighting. Since then pipelines have become the principle method for the transportation of natural gas and hazardous liquids, and currently, it is estimated that there are over 3.5 million kilometers of pipelines installed worldwide.[1]

Pipelines can be categorized according to their location (onshore or offshore), the product carried (liquids, gases or multiphase, that is, mixtures of gases and liquids), or the purpose of the pipeline. To explain this last category, consider the schematic of Figure 1, which shows a typical pipeline network for oil or gas transportation. This network starts with the gathering system, which transports the product from the wells to a processing station or a transmission line. The transmission pipeline network links the gathering system to the distribution system. Finally, the distribution system transports the product from a distribution point to the point of end use or storage and typically consists of low-pressure gas pipelines for domestic and industrial use.

The relative size of each of these pipeline systems is illustrated in Table 1 for the US pipeline network.[2] These figures show that the distribution system is by far the largest part of the network. However, the focus of this chapter is to investigate the effects of corrosion on the high-pressure onshore gathering and transmission pipelines that transport natural gas and hazardous liquids. Over 98% of the world's pipelines are buried and therefore emphasis is placed on the management of both internal and external corrosion and stress corrosion cracking (SCC) in these types of pipelines.

Having defined the scope, it is important to first investigate the scale of the corrosion problem, both in terms of the cost of corrosion and the impact of corrosion on pipeline safety.

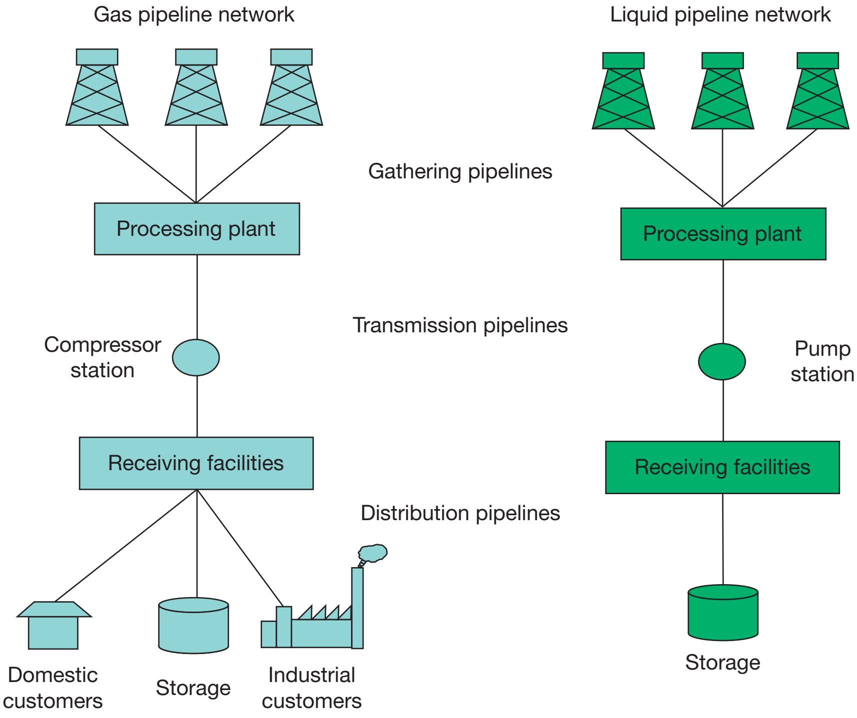

Figure 1 Schematic representation of a typical pipeline network.

Table 1 Distribution of US pipelines by usage (Statistics for 2006)[2]

Pipeline category	*Total length (miles)*	*Total length (km)*
Onshore gas gathering	13 056	21 012
Offshore gas gathering	7331	11 798
Onshore gas transmission	293 622	472 539
Offshore gas transmission	6699	10 781
Distribution	1 182 534	1 903 102
Liquid transmission	166 481	267 925

4.42.2 Introduction: The Scale of the Corrosion Problem

In 2002, the Federal Highway Administration (FHWA) in the US published the results of a two-year study to determine the cost of corrosion to the US economy.[3] One of the 26 sectors investigated in the study was gas and liquid transmission pipelines. (It should be noted that in this report the term transmission pipelines included the gathering system.) In this sector, the cost of corrosion was estimated at between $5.4 and $8.6 billion every year.[4] This cost was reported in three areas: the cost of failures (10%); the capital costs related to installing a corrosion control system and the replacement or repair of pipelines (38%); and operations and maintenance costs related to controlling corrosion on the pipeline and ensuring that the control systems remain effective (52%). Included in the cost of failure is the loss of throughput, and therefore revenue, and also estimates for fatality and injury compensation and legal costs for liability.

Corrosion is therefore a significant cost to the pipeline operator in the operation and maintenance of a transmission pipeline; however, it is important to understand the threat of corrosion in relation to other threats on the pipeline. One of the most rigorous means of achieving this perspective is through the analysis of pipeline failure statistics.

4.42.2.1 Pipeline Failure Statistics

A number of organizations worldwide collect statistics on the frequency and causes of pipeline failures. In the United States, the Office of Pipeline Safety (OPS) within the Department of Transportation (DOT) regulates the safety aspects of pipelines. Natural gas and hazardous liquid transmission, distribution, and gathering companies are required by law to report to the DOT all serious and significant incidents involving a release from their pipelines, which involves either:

- a death or injury requiring in-patient hospitalization;
- total costs of $50 000 or more measured in 1984 dollars (including, for example, lost product and repair costs);
- highly volatile liquid releases of five barrels or more or other liquid releases of fifty barrels or more; or
- liquid releases resulting in an unintentional fire or explosion.

The statistics are available from the DOT website from 1986.[5] However, the reporting categories for transmission pipelines changed in 2002, and therefore, it is difficult to compare statistics for some failure types.

CONCAWE, a group of European oil companies committed to environmental research, has systematically collected information on oil spills since 1971 and has reported the outcome annually ever since. In 2004, the database included over 35 000 km of onshore oil pipelines.[6] The CONCAWE statistics record any spill of greater than 1 m^3, which is more rigorous than the requirement in the US and therefore care has to be taken when comparing data from these sources. Equivalent data for the European gas transmission system are collected by EGIG (European Gas Pipeline Incident Data Group). EGIG has collected data since 1970 on unintentional releases of gas from onshore steel pipelines with a design pressure greater than 15 bar. Over 122 000 km of the European gas pipeline network was included in the 2004 EGIG incident report.[7]

In the UK, the UK Onshore Pipeline Association (UKOPA) has also compiled a database of product loss incidents for nearly 22 000 km of Major Accident Hazard Pipelines (MAHP) as specified by the UK Pipeline Safety Regulations,[8] which includes natural gas, ethylene, and crude oil.[9] The database records all unintentional releases from pipelines in the public domain (i.e., outside the fences of installations) but does not include releases from ancillary equipment such as valves and compressors.

4.42.2.2 Causes of Pipeline Failures

Using data from the failure statistics, it is possible to build up a picture of the role of corrosion in pipeline incidents, although it is highlighted that direct comparisons between data sets should be treated with caution as the categories under which failures are reported differ between the databases.

One immediate conclusion that can be drawn from the analysis of the pipeline failure data for the years reviewed is that corrosion does not pose the most severe threat to pipeline integrity. In fact, in the OPS, CONCAWE, and EGIG databases, the majority of pipeline incidents result from external interference, that is, an outside force, such as an excavator striking the pipeline, whether intentionally or unintentionally. Corrosion accounts for the second largest number of spills in the CONCAWE (Table 2)[6] and OPS databases and the third largest number of incidents in the EGIG database (Table 3). The UKOPA database presents a slightly different picture in that the data are skewed by historical failures that occurred due to internal cracking when the system was transporting wet town gas. However, the data do show that external interference accounts for more failures than corrosion (Table 4).[9]

Table 2 Summary of failure statistics from the CONCAWE database of incidents on oil pipelines (1971–2004)[6]

	Number of incidents		*Percentage gross volume spilled (m^3/year)*
	Average per year (1971–2004)	*Percentage (1971–2004)*	*1971–2004*
Mechanical failure	3.0	23.8	31.4
Operational	0.9	6.8	3.6
Corrosion	3.6	28.9	18.8
Natural hazard	0.4	3.5	4.1
Third party activity	4.6	36.9	42.1

Table 3 Summary of failure incidents by cause from the EGIG database of incidents on gas pipelines (1970–2004)[7]

Failure cause	*Percentage of incidents*
External interference	49.7
Construction defect/material failure	16.7
Corrosion	15.1
Ground movement	7.1
Hot-tap made by error	4.6
Other and unknown	6.7

The failure data also allow an investigation into the dominant failure location for different categories of pipeline, that is, whether corrosion occurs predominantly on the external or internal surface of the pipeline. Table 5 provides a summary of the statistics for corrosion failures by location for transmission pipelines (natural gas and hazardous liquids) from the OPS statistics.[5] It is interesting to note that for hazardous liquid pipelines, the corrosion incidents in the US are primarily attributable to external corrosion, a trend that has also been observed in the CONCAWE database.[10] For natural gas pipelines, the OPS data show that internal corrosion accounts for the majority of corrosion failures, which is contrary to the experience in Europe. The EGIG data indicate that external corrosion is responsible for nearly 80% of all corrosion failures

Table 4 Summary of failure incidents by cause from the UKOPA database (1962–2004)[9]

Failure cause	*Number of incidents*	*Percentage of incidents*
Girth weld defect	33	19.2
External interference	37	21.5
Internal corrosion	2	1.2
External corrosion	31	18.0
Unknown	8	4.7
Other[a]	40	23.3
Pipe defect	13	7.6
Ground movement	5	2.9
Seam weld defect	3	1.7

[a] Includes 30 failures of internal cracking due to wet town gas.

Table 5 Summary of failure statistics from the DOT database of incidents on natural gas and hazardous liquid pipelines (1986–2005)[5]

	Gas transmission	*Hazardous liquid*
Total number of incidents	1025	2646
Total number of corrosion incidents	254	718
Percentage of total incidents due to corrosion	24.8	27.1
Percentage of corrosion incidents due to external corrosion	41.3	68.0
Percentage of corrosion incidents due to internal corrosion	58.3	30.8
Percentage corrosion incidents not specified	0.4	2.1

on the European gas system.[7] Even then, these statistics may be misleading as the internal corrosion failures were caused by manufactured gas and not natural gas. The dominance of external corrosion is similarly observed in the UKOPA data, which include both gas and liquid pipelines (Table 4).[9]

One of the issues that both CONCAWE and EGIG wanted to investigate from their statistics was whether there was any evidence that older pipelines were more likely to fail as a result of corrosion. Although the majority of oil pipelines in Europe were built more than 25 years ago, the CONCAWE statistics show that the failure rate from corrosion (i.e., the most likely failure mode with increasing age) has not significantly increased with age for pipelines up to 45 years old (Figure 2).[10] The statistics from the EGIG database also lead to the conclusion that there is no evidence of an ageing effect, that is, there is no increase in the corrosion failure frequency as a pipeline gets older. In fact the data show that the failure frequencies are actually decreasing with time. These conclusions demonstrate that corrosion failure on pipelines can be successfully managed through preventative inspection and maintenance measures.

The CONCAWE and EGIG databases also record information about the percentage of product volume spilt by cause. The figures for oil pipelines are reported in Table 2. In both databases, external interference results in larger releases or volumes spilled than corrosion. Data in the EGIG database indicate that this observation can be attributed to the fact that the pipeline is more likely to rupture as a result of external interference, resulting in a large hole from which product can escape, whereas corrosion is more likely to result in a leak from a small defect or pinhole.

It can therefore be concluded that although external interference accounts for the highest number of pipeline failures and a greater volume of product lost, corrosion, predominantly external, remains one of the main threats to pipeline safety. However, the statistics indicate that the corrosion threat can be successfully managed and measures put in place to detect and prevent corrosion on pipelines as part of a pipeline integrity management plan. Specific to that integrity management plan will be a corrosion management strategy in which the pipeline operator will have to optimize the cost of corrosion from an economic, environmental, and safety point of view.

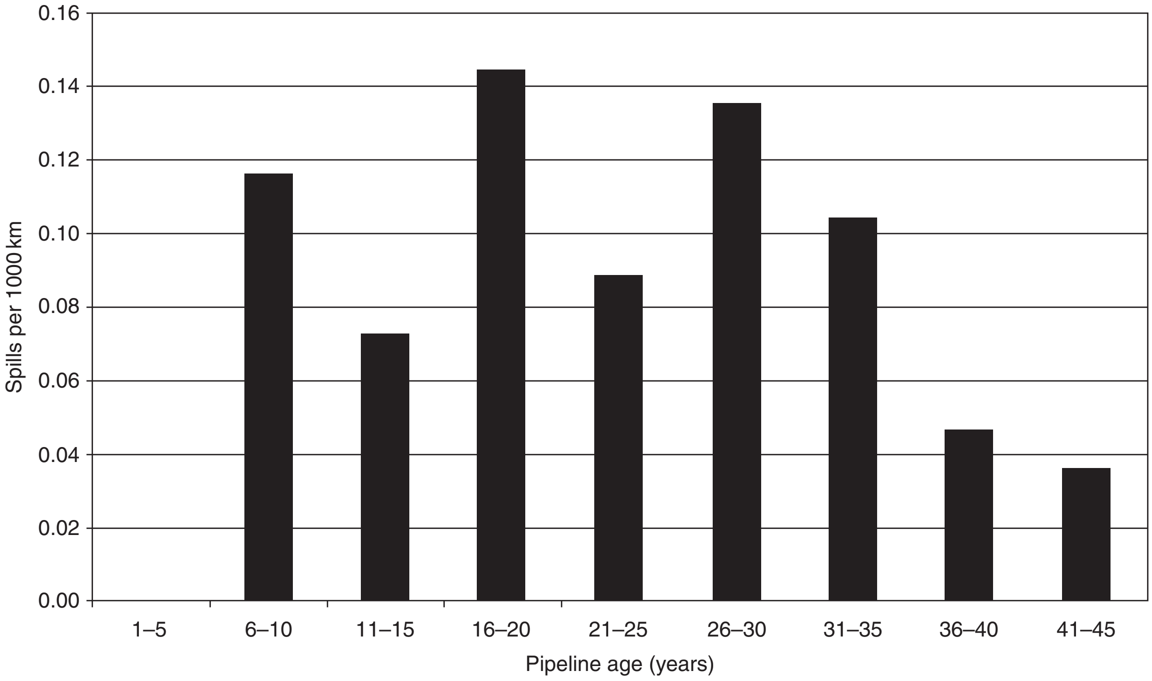

Figure 2 Relationship between corrosion spill frequency and age in the CONCAWE database.

4.42.2.3 Pipeline Safety

Although the requirement to collect failure statistics may, in some cases, be regulatory, in others it is voluntary among the pipeline operators to demonstrate the inherent safety of pipeline transmission systems and also to identify the main causes of pipeline failure in order that safety improvements can be made. Indeed, one of the conclusions that can be drawn from the incident data is that pipelines are one of the safest modes of transport for hazardous liquid and gas products over long distances. A study conducted in the US, comparing incident data for pipeline transportation of oil products relative to other modes of oil transport, confirms that pipeline transport has the best overall safety record[11,12] (**Table 6**). In particular, based on this normalized data, road transport of oil resulted in 103 times more deaths and 32 times more injuries in the US over the five-year period between 1997 and 2001 than pipeline transport and this figure is increasing when compared with the previous 5 years (1992–1997). A similar trend is inherent in the statistics from Western Europe, which has caused CONCAWE to conclude that "unlike marine and road traffic accidents, so far in Western Europe nothing of large enough scale or frequency has occurred with oil pipelines to draw them to the attention of the general public."[10]

Notwithstanding, in the US in the past few years there have been a number of high-profile pipeline failures, which have refocused public attention on pipeline safety. One corrosion-related failure in particular is highlighted here, which illustrates not only the severe consequences of pipeline failure but also the requirement to understand the threats to a pipeline system and to put adequate procedures in place to address the threats before incidents occur.

In August 2000, a 30″ natural gas pipeline ruptured in New Mexico. The escaping gas ignited and killed twelve members of an extended family who were camping near the rupture site. Property and other damages totaled $998 296. The pipeline accident report concluded that the probable cause of the failure was "a significant reduction in wall thickness due to severe internal corrosion."[13] The corrosion had occurred at a low point, caused by a bend in the pipeline, where water had been allowed to accumulate.

The internal corrosion control program that was employed by the operator was to monitor the quality of gas entering the pipeline, to visually inspect the inside of the pipeline when it was exposed, to run cleaning tools through the pipeline and to maintain the pipeline drips by ensuring that they functioned properly and liquids were regularly removed. However, the company procedures for gas monitoring were not rigorous enough to be able to identify whether internal corrosion could be occurring. In addition, due to the design of the drip assembly for the pipeline that ruptured, cleaning and in-line inspection and cleaning (ILI) tools could not be run in this section. As a result, the drip upstream of the rupture location became blocked, allowing liquids to bypass the drip and continue down the pipeline. Although this section of the pipeline could not be inspected using ILI, the corrosion control program did not specify additional inspection, such as ultrasonic thickness measurements at low points or the installation of corrosion-monitoring devices to determine whether corrosion was occurring. The National Transport Safety Board concluded that the corrosion had occurred because the "corrosion control program failed to prevent, detect, or control internal corrosion within the company's pipeline."[13]

Incidents such as this have resulted in the introduction of new regulations regarding pipeline integrity management in the US.[14,15] Many of the approaches that have been used to draw up integrity management plans have been based on risk assessment methods to ensure that the major threats are identified, prevented, detected, and controlled. The remainder of this chapter will examine the causes of corrosion, risk-based inspection and maintenance

Table 6 Comparison of safety data for oil transport per ton mile transported (1992–2001)[11,12]

	Pipeline	*Trucks*		*Barge*		*Ship*		*Rail*	
		1992–1997	*1997–2001*	*1992–1997*	*1997–2001*	*1992–1997*	*1997–2001*	*1992–1997*	*1997–2001*
Deaths	1.0	87.3	103	10.2	10	4.0	10	2.7	0
Injuries	1.0	2.3	32	0.9	14	0.7	14	2.6	11
Fire/explosion	1.0	34.7	46	4.0	3	1.2	2	8.6	2

The data is presented based on a multiplier of the pipeline rate, which is given a value of one. Therefore, a value of less than one indicates a better safety record.

strategies and integrity assessments that are used in the pipeline industry to identify, manage, and control pipeline corrosion.

4.42.3 Pipeline Integrity Management

The role of pipeline integrity management is to increase public safety by minimizing or eliminating pipeline failures. Integrity management planning requires an operator to identify the major threats to the integrity of the pipeline and then to plan and implement inspection, maintenance, and control strategies to ensure that these threats are appropriately managed. The basic principle of pipeline integrity management planning is outlined in Figure 3.

Risk assessment procedures are now being widely used in the pipeline industry as a tool to enable operators to rigorously identify the critical pipeline threats and to determine whether particular sections of a pipeline or particular pipelines in a network are at increased risk of failure. These critical areas can then be prioritized for appropriate inspection and mitigation actions implemented to address the identified threats. Risk assessment methods also allow the operators to run risk reduction scenarios in order that effort and resources can be concentrated on those activities that have the greatest impact on reducing the risk. In many countries, risk assessment forms part of the pipeline integrity management codes and regulations.[8,14–16]

The risk assessment approach that is adopted by the pipeline operator can be qualitative, semiquantitative, or fully quantitative. A qualitative approach is the simplest method and will provide a coarse (high, medium, low) assessment of the risk on the pipeline, although it tends to be very subjective. A fully quantitative method may be the most rigorous approach; however, there is often not enough pipeline data and associated information available to conduct such an assessment. Therefore, most operators adopt semiquantitative methods that use scoring models to determine a relative risk score for each of the threats on a pipeline. These methods consist of a series of algorithms for each of the threats that identify the key parameters contributing to that threat and then weight the relative importance of those parameters and their contribution to the overall risk.[17] The benefit of semiquantitative methods is that nonsubjective data, such as pipeline inspection results, can be used in the threat analysis.

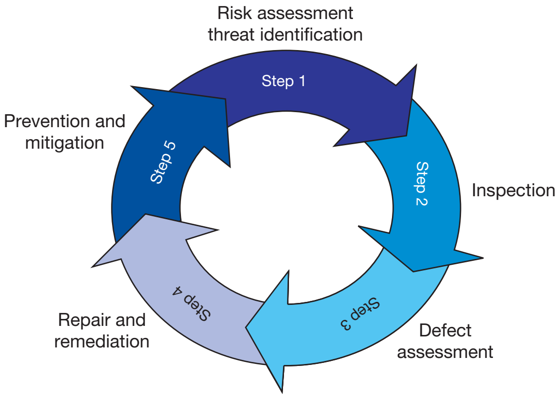

Figure 3 Pipeline integrity management process.

The first stage in the process illustrated in Figure 3 is therefore to identify the potential threats to the pipeline and to collect the appropriate data to allow the threat to be assessed. The ASME B31.8S code supplement [18] provides guidance for the implementation of integrity management plans on gas pipelines and identifies 22 root causes of pipeline failure that have to be addressed as part of a risk assessment. Three of these relate to corrosion: external corrosion, internal corrosion, and SCC. In order to understand the risk assessment process as it pertains to these corrosion related threats, a review of the factors that contribute to the mechanisms and control of pipeline corrosion is required.

4.42.4 External Pipeline Corrosion Risks

The majority of the onshore pipeline networks are constructed from plain carbon–manganese steel that is alloyed and processed to produce the required strength, toughness, and weldability properties. One of the consequences of using plain carbon steel for onshore pipelines is that it is not inherently resistant to corrosion, either from the soil environment or from potential corrodents in the product.

4.42.4.1 External Corrosion: Mechanisms

In the presence of water from the external environment, either the atmosphere or the soil, unprotected carbon steel will corrode. Corrosion defects reduce the load-carrying capability of the pipeline, and if they are allowed to continue to grow, may result in leak or rupture failures. In conducting pipeline corrosion management programs, it is therefore essential to understand the type of corrosion to which the pipeline is susceptible and the rate at which that corrosion could grow. The following sections describe the main types of external pipeline corrosion and highlight the risk factors for each type.

4.42.4.1.1 Soil corrosion

As with all corrosion reactions, for external corrosion to occur on a pipeline, there must be anodic and cathodic areas on the pipe surface that are electrically connected by the pipe material and are immersed in a conducting electrolyte, the soil. For buried pipelines in a wet, oxygenated soil environment, the half-cell corrosion reactions are:

$$\text{Anodic(oxidation)reaction: Fe} \rightarrow \text{Fe}^{2+} + 2\text{e}^-$$

$$\text{Cathodic(reduction)reaction:}$$

$$\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow 2(\text{OH})^-$$

The rusting of carbon steel in the soil environment can therefore be described by the general equation:

$$2\text{Fe} + 2\text{H}_2\text{O} + \text{O}_2 \rightarrow 2\text{Fe(OH)}_2$$

In the simplest form of corrosion, the anodes and cathodes are distributed evenly over the metal surface and the result is uniform wastage or general corrosion. However, at times, distinct anodic and cathodic zones are formed and this results in localized pitting corrosion. Whether a particular area of the pipe becomes anodic or cathodic can be dependent on local variations in steel chemistry or soil constituents, particularly oxygen. The nature of the soil is therefore very important in the determination of the likelihood and severity of external corrosion.

In general, soils that are good conductors will produce higher corrosion rates, that is, soils with low pH values, high soluble salt content, and high moisture content. The conductivity and therefore the corrosivity of the soil are measured by its resistivity, that is, the higher the resistivity value, the lower the corrosion rate, as there is more resistance to the flow of current. ASME B31.8S[18] contains guidance on estimating corrosion rates based on soil resistivity measurements and site observations. Similar correlations between corrosion rate and soil type and resistivity have also been published by Simon-Thomas *et al.*[19] and Peabody.[20] All of these correlations are compared in **Figure 4**.[21] From these data, it can be seen that corrosion rates for soil corrosion are in the

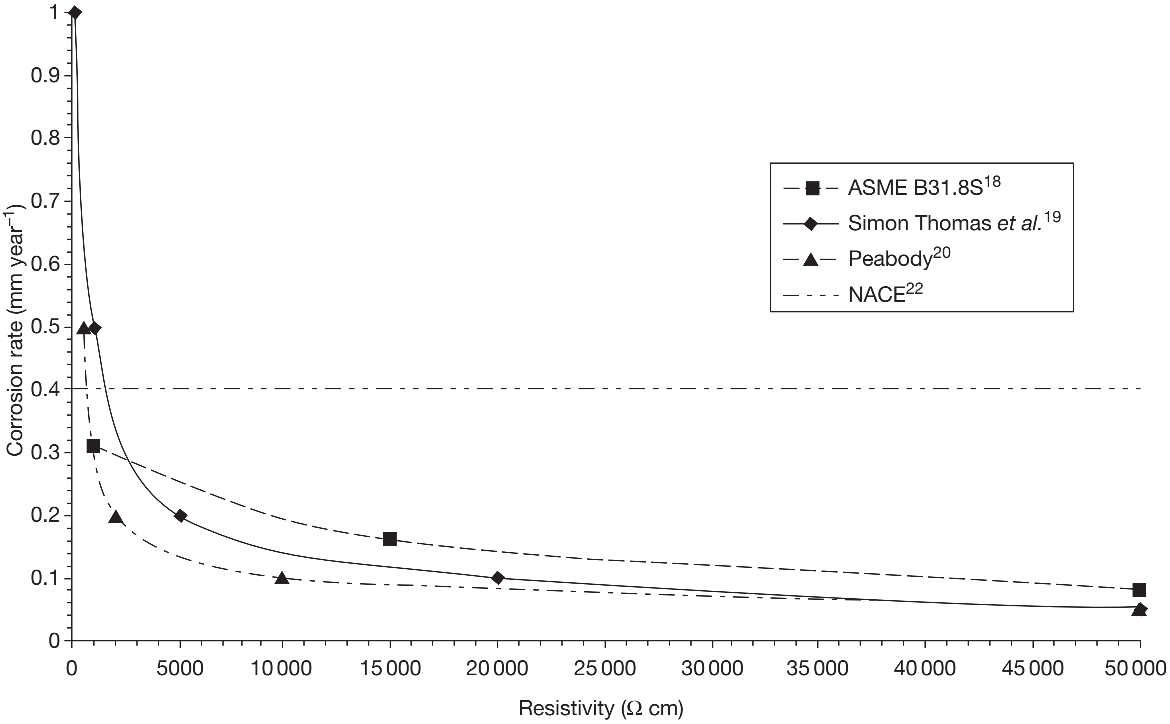

Figure 4 Comparison of external corrosion rate prediction models. Reproduced with permission from Race, J. M.; Dawson, S. J.; Stanley, L. M.; Kariyawasam, S. *J. Pipeline Eng.* **2007**, *6*(1), 13–29.

range 0.05–0.5 mm year^{-1} depending on soil resistivity. At the lower end of the range, corrosion rates of 0.05 mm year^{-1} would be associated with soils such as limestone, sands, or gravels, which typically have resistivity readings greater than 10 000–20 000 Ω cm. At the upper end, corrosion rates of 0.5 mm year^{-1} are typical for steel in peat or swamp-like terrain and correlate to resistivity readings in the range 100–1000 Ω cm. It is possible that even higher corrosion rates could be observed if the backfill material contains industrial waste, particularly conductive materials such as coke. The National Association of Corrosion Engineers (NACE) has conducted long-term underground corrosion tests of unprotected steel in a variety of soils. The upper 80% confidence level of these exposure tests indicates that a rate of 0.4 mm year^{-1} may be typical for soil corrosion.[22] It should be noted that soil conditions will change along the length of a pipeline and therefore the severity of corrosion will also change. It should also be remembered that pipelines are generally buried and therefore soil conditions at the surface may not reflect those in the vicinity of the pipeline.

Although typical rates for external corrosion of pipeline steel are in the range 0.05–0.5 mm year^{-1}, there are particular types of corrosion that can occur in pipelines where much higher corrosion rates can be achieved. These types of corrosion are of particular concern from a pipeline integrity management viewpoint, as they have to be identified quickly in order that mitigative measures can be implemented. These mechanisms are discussed in the following sections.

4.42.4.1.2 External microbiologically influenced corrosion (MIC)

With reference to pipeline corrosion, MIC can be defined as corrosion that is initiated and/or accelerated by the physical presence and metabolic activities of microorganisms in the soil. Although the bacteria themselves do not directly attack the steel surface, they can initiate and maintain conditions for corrosion by interacting with the electrochemical corrosion process.

Different types of bacteria found in soil have been shown to be responsible for pipeline steel corrosion. One of the key groups of microbes in this respect is sulfate-reducing bacteria (SRB). SRB are known as obligate anaerobic bacteria, which means that they become active in the absence of oxygen and thrive in waterlogged soils such as clays. One theory regarding the role of SRB in promoting corrosion is that sulfate is reduced to sulfide during the metabolic process. The sulfide can then react with hydrogen, produced either as a result of the cathodic corrosion reaction or by further metabolic processes, to produce hydrogen sulfide. A corrosion reaction between hydrogen sulfide and iron produces an iron sulfide corrosion deposit on the surface and further corrosion of the steel occurs through a galvanic couple established between the iron sulfide deposit and the surrounding iron. Corrosion rates of between 0.2 and 0.7 mm year^{-1} have been measured for this mechanism on pipelines in the field, although rates above 5 mm year^{-1} have been cited.[23]

Another important microorganism in the microbiological corrosion of steel is acid-producing bacteria (APB). This type of bacteria is classed as facultative aerobic bacteria, which means that, although they prefer aerobic conditions, such as sandy soils, they can survive in an anaerobic environment, such as clay soils. APB are capable of forming organic acids, such as acetic acids, which concentrate under the biofilm and as a result are very corrosive to carbon steel. There are other forms of APB that produce organic acids, such as sulfuric acid, or that produce carbon dioxide, which reacts with the water in the soil to produce carbonic acid.

However, the most aggressive attack of pipeline steels occurs when bacteria act cooperatively in communities to form complicated biofilms on the steel surface. Under these circumstances, anaerobic bacteria can survive in aerobic conditions if they are present in biofilms in which aerobic bacteria consume the oxygen.

Although the potential for MIC, to a large extent, is governed by the type of soil and the available nutrients, it has been suggested that even the process of trenching a pipeline can increase the levels of bacteria in the soil around the pipeline.[20] There are also other factors that will increase the susceptibility of a pipeline to MIC; indeed even measures designed to protect a pipeline from external corrosion can make it more susceptible to MIC if these measures fail. For example, the disbonding of the protective pipeline coating can produce an ideal microbial habitat, which is isolated from the effects of cathodic protection (CP). In fact, it has been shown that almost all cases of external MIC are associated with disbonded coating.[24] Some coatings are more prone to disbonding than others and therefore pipelines coated with these types of coating can be more at risk from MIC.[23] Coating types and failure mechanisms are discussed in detail in Section 4.42.4.2.2.

4.42.4.1.3 Preferential corrosion

Preferential (or selective) corrosion is predominantly found in pipelines manufactured prior to 1970, using a welding technique called low-frequency electrical resistance welding (LF-ERW). LF-ERW pipe is manufactured by forming a steel strip into a pipe and then simultaneously heating the edges of the strip using a low frequency alternating current and forcing the edges together under pressure. There are two problems associated with this type of pipe material: firstly, the pipe steel of the era could contain large amounts of nonmetallic inclusions due to high sulfur contents and secondly, the weld area was not always heat-treated and therefore could have inferior corrosion resistance and mechanical properties to the parent. As a result, the weld corrodes at a higher rate than the parent plate resulting in a V-shaped crack-like groove along the weld line in a region that tends to have properties inferior to those of the parent pipe material. There are two potential mechanisms by which preferential corrosion can occur in LF-ERW: by crevice corrosion at a lack of fusion defect and by dissimilar metal corrosion cells.

- *Crevice corrosion*

Surface-breaking lack of fusion defects in the weld are tight crevices that are open to the corrosive environment. Moisture becomes retained within the crevice and a local corrosion cell is formed. As a result, the crevice will corrode preferentially resulting in a groove-like defect at the weld line.

- *Dissimilar metal corrosion cell*

The other mechanism by which preferential corrosion can occur is the formation of a dissimilar metal corrosion cell at the surface. In ERW welds, the corrosion cell is set up between the weld material and the pipe body material due to chemical and physical property differences within the weld. The result is that the weld material becomes the anode in the corrosion cell and will corrode preferentially, again resulting in sharp groove defects at the weld line.

4.42.4.1.4 Stray-current corrosion

Another mechanism by which accelerated corrosion rates might be experienced on pipelines is stray-current corrosion. NACE defines stray-current corrosion as “corrosion resulting from the current through paths other than the intended circuit, for example, by any extraneous current in the earth.”[22] Direct currents can be present in the soil from electrified transport systems (e.g., railways or trams), CP systems for other pipelines, mining operations, high-voltage electricity transmissions systems, or even telluric currents caused by changes in the earth’s magnetic field. For an explanation of CP refer to Section 4.42.4.2.8. In these systems, the earth provides part of the return path for the current to the source. However, any buried metallic structure in the vicinity, such as a pipeline, provides a favored, low-resistance path along which the currents can travel.

The mechanism for stray-current corrosion with reference to an electrified traction system is illustrated in Figure 5. The return path for this system is provided by the rails; however, if the rails are not adequately insulated from the earth, some of the current will enter the ground and return via an earth path, unless a pipeline can provide a lower resistance return path. Where the current flows onto the pipe, the pipeline is cathodic and therefore protected as a result of the same process that applies in a CP system (see Section 4.42.4.2.8). The current travels along the pipeline and is discharged close to the source. At this point, the pipe is anodic and corrosion will occur at a rate that is dependent on the magnitude of the current flow, but may be many times greater than the soil corrosion rates.[20]

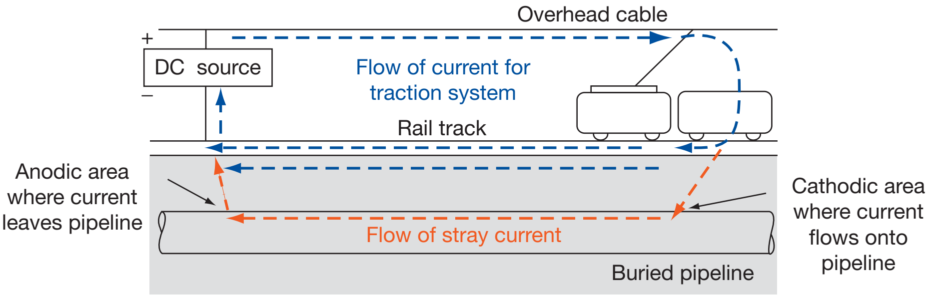

Figure 5 Schematic of stray current corrosion from a railway system.

As a result, it is important that locations of suspected stray-current activity are identified and appropriate corrective actions implemented.

One of the problems with stray-current corrosion from electrified transport systems is that the current is dynamic or fluctuating, because the load varies with every train that passes. It is therefore important to identify the locations on a pipeline that may be at risk, that is, where the pipeline runs close to traction systems or where there may be locations of low track to earth resistance. In these areas, continuous monitoring for stray-current corrosion should be conducted over a 24-hour period to ensure that the time periods when the pipeline is at risk are identified. Stray currents from CP systems for other pipelines are termed static as they do not vary with time.

4.42.4.1.5 AC corrosion

The occurrence of pipeline corrosion as a result of direct current discharge (i.e., stray-current corrosion) is well recognized and accepted. However, there have also been reports of pipeline corrosion as a result of induced alternating current discharge. Although, the phenomenon of AC corrosion in soils is not fully understood and there is no agreement in the literature on the mechanism, it is possible to draw conclusions regarding the factors that make a pipeline susceptible to AC corrosion.

Pipelines at highest risk are those that run parallel to overhead AC power lines. The flow of current in the power lines produces an alternating magnetic field around the power line. If a pipeline is running within the magnetic field, then it is possible that an AC potential may be induced in the pipeline resulting in current flow. At points where the pipeline enters or leaves the magnetic field, the induced voltages are greatest. It is interesting to note that pipelines that cross at right angles to AC power lines do not have AC currents or voltages induced in them.

When a pipeline suffers from induced AC voltages, it has also been found that coatings with high dielectric strength, and therefore good insulators, will make the pipeline more susceptible to AC corrosion. The AC corrosion has been found to occur at small pinhole holidays in an otherwise good condition, adherent pipe coating. Another factor that makes a pipeline more susceptible is the resistivity of the soil. Low-resistivity soils in particular provide a more favorable route to earth for the current.

Corrosion caused by AC discharge occurs in the form of a small, deep hemispherical pits covered by a hard corrosion product. The current density at a coating defect is one of the major factors influencing corrosion rate and is affected by the size of the defect, the soil resistivity, and the AC voltage on the pipeline. Initial work suggested that corrosion rates associated with AC corrosion were significantly lower than those caused by a direct current of a similar magnitude. However, corrosion rates of up to 10 mm year^{-1} have been reported by pipeline operators.[25]

4.42.4.2 External Corrosion: Prevention

As described in previous sections, plain carbon steel is not resistant to corrosion from the external environment and therefore pipelines must be protected to prevent corrosion in the soil environment and a resulting loss of integrity. In general, underground pipelines are protected by the application of both an external coating and a CP system. These systems act synergistically to prevent external corrosion, the primary protection mechanism being the coating with the CP system designed to protect areas of the pipe where the coating becomes damaged. The next sections describe the features of the coatings and CP systems used to protect onshore pipelines.

4.42.4.2.1 Requirements of pipeline coatings

As described in Section 4.42.4.1.1, for external corrosion to occur, two of the conditions that must be met are that the pipeline steel is immersed in a conducting electrolyte and that electrical current flow is permitted between the steel and the electrolyte. To prevent external corrosion therefore, the role of the pipeline coating is to provide a barrier between the soil and the steel to prevent moisture and oxygen contact with the pipe surface and also to act as an electrical insulator.

The construction of onshore pipelines involves welding together sections of pipe, generally 12 meters in length, in the field before lowering the completed pipeline section into the ditch. Historically the pipe spools were coated on site, ‘over-the-ditch,’ and although this practice is still used, the spools are more usually precoated in the pipe mill leaving a cutback area at the end of each spool to allow the field or girth weld to be made on site. This cutback area and the completed girth weld are then coated in the ditch. Two types of coating have therefore to be specified for the pipeline, the mill-applied main line coating and the field-applied girth weld coating.

In order for a material to be suitable as a pipeline coating, it must meet certain requirements, which are outlined in detail in the NACE recommended practice RP0169.[22] The more critical requirements for the specification and selection of a pipeline coating can be summarized under the following general headings:

- *Adhesion*

As a primary role of the coating is to prevent water contact with the pipe surface, one of the critical requirements of a coating is that it should remain adherent to the steel for the design life of the pipeline. When a pipeline coating loses adhesion, water can enter beneath the coating and migrate along the pipeline between the pipe and the coating. One particular form of disbonding, termed 'tenting,' can occur along irregularities on the pipe surface, especially at long seam or girth welds. Coating disbonding is one of the most damaging modes of coating failure because, as will be described later, the area under the disbonded coating cannot be protected by the CP system. Although adhesion to the steel surface is dependent in part on the prolonged strength of the bond between the coating and the steel, it is also critically dependent on the surface preparation prior to the application of the coating. The surface of the steel must be adequately prepared to remove contaminants and also provide a suitable surface profile onto which the coating can attach.

- *Electrical resistivity*

Besides providing a barrier between the soil and the pipe steel, another critical function of the coating is that it should be an effective electrical insulator to prevent the flow of any corrosion current between the pipe and the soil. It is therefore important that the coating has a high electrical resistance (ER) that does not vary over time or with exposure to the environment as this will cause variation in the demand from the CP system.

- *Resistance to handling and construction damage*

If the coating is applied in the mill, then, before the pipeline is commissioned, there is the potential for the coating to be damaged at a number of stages, for example, during the handling and transportation of the linepipe to site, during manipulation for welding and laying operations, during the fabrication of cold field bends on site, and as a result of impact from rocks in the trench and backfill material. In order to minimize the extent of the coating damage, it is important that the coating has adequate flexibility as well as abrasion and impact resistance.

- *Compatibility with the pipeline environment*

For a buried pipeline, the coating selected for a particular application must be compatible with the soil environment, and in particular, should not allow water to penetrate through the coating onto the steel surface. The coating must also be resistant to any other chemicals, for example, acids and alkalis, or microorganisms that may be found in the soil in which the pipeline is buried.

Another important factor associated with the pipeline environment is the operating temperature. If a coating is subject to temperatures outside the recommended maximum operating temperature, then this can result in disbonding, melting, creep, sagging, embrittlement, or softening of the coating. Ultimately, this will lead to the degradation of the coating and compromise the ability of the coating to protect the pipeline for the design life.

- *Compatibility with the CP system*

As the coating and CP system are acting together to protect the pipeline, it is important that the coating is not degraded by the CP system. One of the mechanisms by which this can happen is cathodic disbonding, a phenomenon by which accelerated disbonding can occur at the edge of a coating defect due to the action of the CP. Although the mechanism has not been fully characterized or understood, the major cause is thought to be chemical attack on the coating–steel bond by alkali generated by the cathodic electrochemical reaction:

$$O_2 + 2H_2O + 4e^- \rightarrow 4(OH)^-$$

Another effect of CP is that it can promote the permeation of water at the edge of a coating defect, which can also contribute to accelerated disbonding.

- *Resistance to in-service loads*

Once the pipe coating has been installed, the coating should be able to withstand any loads imposed during service. For example, it must be flexible enough to remain adherent to the pipe particularly during changes in internal pressure. However, the main external loading on the coating in service is as a result of soil loading and soil movement. Settlement of the backfill can create a tensile load on the pipe and cause creep of the coating. In addition, particularly in clay-type soils, the action of seasonal wetting and drying can lead to the expansion and contraction of the soil around the pipeline. As the soil moves, it can cause the coating to wrinkle and lose adhesion with the pipe. Soil movement around the pipe can also result from the creep of soil on slopes. In these types of soil environments, it is important to specify a coating with a high creep or shear resistance.

- *Compatibility with other coating systems*

Particularly for field joint or girth weld coatings, compatibility and adherence to the main line coating are especially important to prevent loss of adhesion around the girth welds. It is also essential that the coating is easy to repair if it becomes damaged.

Prior to specifying a coating for a pipeline, it is important that all of these factors are taken into account, and in particular, that the operating conditions of the pipeline, the location, that is, the local terrain and soil conditions, and the CP requirements are fully quantified and understood to ensure that the most appropriate pipeline coating is selected. NACE RP0169[22] identifies a series of tests that can be used to evaluate the suitability of a coating in the operating conditions.

4.42.4.2.2 Types of pipeline coatings

The principal types of coating that are used for onshore pipelines are outlined in Table 7.

Enamel-type coatings have been applied to pipelines for over 80 years, and consequently, they have been used to protect more pipelines around the world than any other coating. Coal tar coating systems consist of coal tar enamels, reinforced with felt or fiberglass wraps, which are applied hot over a primer of either chlorinated rubber or a two-component epoxy, depending on the service temperature requirements. One of the issues with the older coal tar systems was concern over the toxicity of the coal tar when heated. This led to the use of bitumen or asphalt coating systems, which are applied in a similar way to coal tar systems but do not have the same health concerns.

In the 1950s, tape-wrap coating systems started to be used on pipelines and they remain a popular selection as they are readily available and easy to apply, either in the pipe mill or on site, and they tend to be a lower cost option. The first tape coatings were fabric reinforced petrolatum-based systems, but now there are a variety of systems available that can be applied either hot or cold. In general, a tape coating is a laminate system consisting of an outer backing material (e.g., polyethylene (PE), PVC, woven polyolefin) and an inner adhesive mastic (e.g., petrolatum grease, rubber-based compounds) that are spirally wrapped around the pipe ensuring a high degree of overlap between turns. Additional outer layers may be included for enhanced mechanical protection.

Mill-applied extruded polyolefin coatings were first introduced as pipeline coatings in the mid-1950s when PE was hot extruded onto small-diameter pipes over an asphalt mastic adhesive using a cross-head extruder. The process involved extruding a PE sheath onto a heated pipe coated in mastic, which shrank onto the pipe as it cooled. These two-layer PE-mastic adhesive systems were subsequently improved by replacing the asphalt mastic with butyl rubber or bitumen to provide better adhesion. Since the first extruded PE systems were used on pipelines, the number of layers, method of extrusion, type of mastic, and type of polyolefin have varied to improve the coating properties and the

Table 7 Types of external pipeline coating and their application

		Mill applied	*Field applied*	*Joint coating*	*Repair coating*
Enamel systems	Coal tar enamel	✓	✓	✓	
	Asphalt/bitumen	✓	✓	✓	
Polyolefin systems	Two-layer PE – mastic adhesive	✓			
	Two-layer PE – hard adhesive	✓			
	Three-layer PE – two-pack epoxy primer	✓			
	Three-layer PE – FBE primer	✓			
	Three-layer Polypropylene – FBE primer	✓			
Fusion bonded epoxy powder (FBE)		✓		✓	
Liquid coating systems		✓		✓	✓
Heat shrinkable materials				✓	✓
Tape systems		✓	✓	✓	✓

range of pipeline sizes that may be coated with this system. The most recent developments were introduced in the 1980s with the use of three-layer PE and three-layer polypropylene (PP) systems with a fusion bonded epoxy (FBE) first layer. In these systems, the first layer of the coating is FBE, which is sprayed onto the heated pipe. The second layer is required to form either a mechanical or chemical bond between the FBE and the polyolefin and is either a copolymer or an adhesive-based material. The final layer is the extruded polyolefin; either PE (low, medium, or high density) or PP (for higher temperature operations). Although not the cheapest coating systems available, due to their enhanced properties, three-layer polyolefin FBE systems are one of the most widely used coating systems in Europe.

Besides its use in multilayer polyolefin systems, FBE is also applied on its own as a coating system. The coating consists of a partially reacted mixture of epoxy resin, curing agent, fillers, and pigments, which are dry-sprayed as a powder onto a heated pipe. The mixture then fuses and reacts to form a continuous epoxy film that cures under the action of heat. The system was first introduced in the mid-1950s but has only found application on large-diameter pipes since the mid-1970s. The superior properties of this type of coating, particularly with respect to soil stress and cathodic disbonding, make FBE one of the most popular pipeline coatings.

4.42.4.2.3 Types of field joint coatings

All of the coatings described in Section 4.42.4.2.2, except the extruded polyolefin systems, can also be applied in the field to the girth weld joints. However, there are also some coating systems that were specifically designed for the field joint.

One of the field joint systems that has been in use since the 1960s is heat-shrinkable sleeves. As the name implies, these coatings consist of a polymer sleeve that is shrunk onto the pipe joint, either over a mastic adhesive or an epoxy primer, by the application of heat. It is important that the coating is heated correctly when applying heat-shrinkable materials as too little heat can mean that the adhesive fails to flow and therefore the coating loses adhesion, although too much heat can damage the sleeve and main pipe coating.

Liquid coating systems, such as two-pack epoxies or two-pack urethanes, were developed to be compatible with FBE coatings, both for field joints and for repair. The systems consist of two components, a base resin and a hardener, which are combined together before application either by brush, trowel, or spray. It is critical that the components are correctly mixed as otherwise the coating will not cure properly.

4.42.4.2.4 Coating failure

Even after specifying the requirements of a coating for a particular service, conducting laboratory or field testing and selecting the most appropriate coating for the pipeline and field joints, coating damage must still be expected on buried pipeline systems and it is impossible to maintain the coating in a damage-free condition. Some of the damage mechanisms have been discussed in Section 4.42.4.2.1 and include the disbonding of the coating, rock damage during installation and service, handling and construction damage, soil loading, and degradation due to environmental and temperature effects. However, many pipeline coating failures can often be attributed to either incorrect application of the coating or incorrect specification.

- *Incorrect specification*

There is no standard method for selecting a coating for a particular service, and although laboratory or field test results are useful, they will not fully predict the long-term performance of a particular coating system. Therefore, the decision on which coating system to choose is not straightforward. It has also to be recognized that the cost of the coating system is not an insignificant factor in coating selection and can be particularly significant when coating a pipeline of hundreds of kilometers. Selection can therefore be a balance between long-term performance of the coating and cost.

- *Incorrect application*

Even if the most suitable coating material is selected, poor preparation and application will lead to premature failure. It is therefore essential that rigorous procedures are specified for each stage of the pipeline coating process, not only for surface preparation and application but also for repair and testing of the coating. As mentioned previously, adhesion to the steel substrate is one of the most important factors in the performance of pipeline coatings. Most coating systems rely on a clean, properly prepared surface to develop and maintain maximum adhesion to the pipeline. Poor surface preparation can either lead to contamination being left on the pipe surface or the incorrect surface finish being achieved to promote a good bond between the pipe surface and coating. This can result in a rapid loss of adhesion and coating deterioration during service.

Once the surface has been prepared, the coating needs to be applied in accordance with appropriate specifications and the process monitored with quality standards that are regularly checked. Poor coating application often results when the specification program is inadequate or the applicator does not adhere to the correct procedures in the program. It cannot therefore be overemphasized that it is only through attention to the whole coating process that maximum coating performance can be maintained throughout the design life of the pipeline.

4.42.4.2.5 Coating condition monitoring

It is recognized that the coating system on buried pipelines cannot be maintained in a 100% defect-free condition. Not only can handling during construction cause damage to coatings but also soil movements and soil stresses may cause subsequent damage to coating systems after they are installed. It is a fact that all coating systems will eventually show some degradation with time. Although defects in a coating are intended to be protected by the CP system, if a coating holiday is large enough or if there are too many coating holidays on the pipeline, the current required to protect the total bare area of steel may exceed the capacity of the CP system. Therefore, understanding the condition of the coating during pipeline operation is an important part of maintaining corrosion protection on the pipeline. There are a number of techniques that can be used to evaluate the condition of the coating that do not require random excavation and visual inspection. These coating defect survey techniques can identify the location of holidays, and in ideal conditions, can give an indication of relative coating size. The measurements are taken through the soil layer by walking above the pipeline and are therefore referred to as above-ground surveys.

One of the property requirements of the pipeline coating that was discussed in Section 4.42.4.2.1 was good electrical insulation. Therefore, if the coating is maintained in a defect-free condition and an electrical current is applied onto the pipe, no leakage of that current should occur unless there is a hole in the coating. Where there is a hole in the coating, any applied current will leak out into the surrounding soil. This is the principle on which the coating defect inspection techniques that are used on pipelines are based; the detection of the effects of an applied current leakage is either achieved through measuring the reduction in current flow ahead of the holiday or by measuring the potential gradient in the soil caused by the flowing current.

The above-ground survey techniques can be grouped on the basis of the type of current that is applied to the pipeline to detect the holiday, that is, AC or DC. In this chapter, a brief description is given of some of the main methods in these categories. However, more information on different survey techniques can be found in Appendix A of NACE RP0502.[44] It should be emphasized that the above-ground survey techniques will not find disbonded coatings. In this situation, the hole in the coating may be very small and does not relate to the size of the corroding area under the disbonded coating.

4.42.4.2.6 Coating condition monitoring: DC methods

The current required for DC methods is already available on the pipeline from the CP system, although the current may have to be increased in order to ensure that the potential gradients created at coating defects are more measurable. If the CP current cannot be changed or interrupted, the current can be obtained from a temporary supply. Although the ability to use the CP current is an advantage, it also means that these survey techniques cannot be conducted at the same time as a CP monitoring survey, as the enhanced current requirements will not represent the normal working conditions of the CP system.

- *Analog Direct Current Voltage Gradient (DCVG)*

In a DCVG survey, the CP current is switched on and off at a frequency of ~1 Hz and the resulting voltage gradient created at coating defects is measured between two earth contact probes that are carried by a single operator. The two probes are calibrated at the start of the survey by ensuring that no difference in potential is registered when the probes lie on the same equipotential line. To understand how the survey is conducted, imagine lines of potential around a coating defect (Figure 6). As the operator approaches the defect, a potential difference will be recorded between the two probes. The direction of voltage swing will indicate the location of the defect center. When the operator is directly above the defect, no swing in potential is recorded and therefore the location of the defect is identified.

One of the advantages of DCVG is that it is also able to give an indication of the size of the coating defect. To do this, one probe is positioned directly above the defect and the other is moved out to one side at right angles to the flow direction of the pipeline. The operator records the potential difference between the probes and continues to move away from

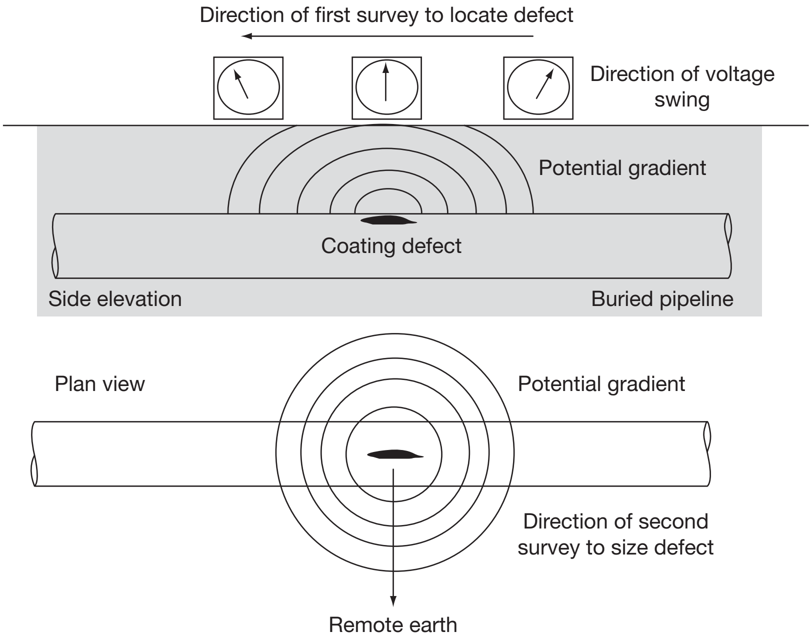

Figure 6 Potential fields surrounding a coating defect in the analog DCVG technique.

the pipeline until no further detectable potential shift is noted. At this point, the probes are considered to be outside the field of significant current flow and in a remote earth potential zone where there is no significant current flow through the earth. The total potential gradient to remote earth is a measure of the size of the defect at that location. This value is usually divided by the difference between the pipe-to-soil ON and OFF potentials (for an explanation of these terms refer to Section 4.42.4.2.14) at that point to provide a benchmark measure of the size of the defect. This is referred to as the %IR reading and the larger the %IR value the larger the coating defect. DCVG survey readings are reported in four categories depending on the magnitude of the measured %IR, and the recommendations regarding remediation requirements are based on the %IR reading.

The main disadvantage of the DCVG method is that electric fields can be distorted by adjacent uncoated foreign structures, which can make data interpretation very difficult. In addition, it should be emphasized that the size of the coating defect is not an indication of the potential size of the underlying corrosion defect, that is, deep pits could be located under small coating holidays. In addition, a good contact with the soil has to be maintained with this technique. Consequently the DCVG survey method is not easy to use in built-up areas where the pipeline route may be surfaced.

4.42.4.2.7 Coating condition monitoring: AC methods

In AC methods, the current is applied via a transmitter. The advantage of an AC method is that, as the method does not use the CP current, it can be conducted at the same time as a CP survey (see Section 4.42.4.2.15.) However, AC signals can also be generated from other sources in the vicinity of the pipeline, such as overhead power cables, a phenomenon that was discussed in Section 4.42.4.1.5. The effect of these AC signals on the readings can be overcome by using filters and by selecting an appropriate signal frequency for the survey.

- *Pearson surveys*

Pearson testing was one of the first types of holiday testing developed for buried pipelines. The technique employs two operators who are connected together by a wire and make an earth contact with the ground either using boots with metal cleats on them or with metal-spiked poles. The change in potential difference between the operators as they pass over a defect locates the defect on the pipeline and this is recorded by a receiver/data logger that is carried by the lead operator. As with DCVG, one of the problems with Pearson testing is that a good contact with the soil must be maintained. In addition, detection can be difficult in high-resistivity soils as the current leakage detectable at the surface will be small.

- *AC current attenuation*

In this method, an AC current is applied to the pipeline via a signal generator that is generally connected at a CP rectifier. The resultant electromagnetic field generated around the pipeline is measured by an operator carrying a receiving unit. The principle of operation is that when a signal is applied to a coated buried pipeline, it will gradually decay away from the point of application. The rate of decline (attenuation) is a measure of the average coating condition between two given points. In general, the survey is first conducted on a macro scale (e.g., every kilometer) to identify sections of poor coating and then on a finer scale in specific areas (e.g., every meter) to pinpoint larger coating defects. One of the advantages of this method is that it does not require soil contact and can be conducted over any surface that will allow transmission of the electromagnetic field, for example, ice, water, or concrete. It is also possible to use the same equipment to locate the pipeline and provide a reading of the depth of burial of the pipeline in the same survey.

4.42.4.2.8 Cathodic protection (CP)

Although a pipeline coating is specified to last for the design life of the pipeline, it has been shown that it is impossible to maintain a coating in a defect-free condition. Where there are defects in the coating, and therefore where there are areas where the steel is exposed to the soil environment and current can flow, the pipeline can corrode. To protect these areas from corrosion, a CP system is also installed on the pipeline.

Remembering the half-cell reactions for the corrosion of steel in the soil environment from Section 4.42.4.1.1, corrosion, or the dissolution of iron, occurs at the anode where current leaves the pipe surface. The principle of CP is therefore to reduce the current flow away from the pipeline at these points by imposing a direct current onto the pipeline so that it becomes the cathode in the corrosion cell and does not corrode. Of course, in principle, it is possible to protect a pipeline using CP alone. However, the current required to achieve protection makes this unfeasible, which is why the combination of coatings and CP is the most practical method for protecting a pipeline from external corrosion. Two main methods of CP are used in onshore pipelines: the galvanic, sacrificial anode method and the impressed current method.

4.42.4.2.9 CP: Sacrificial anode systems

The principle of the sacrificial anode method is to make the pipeline the cathode in the corrosion cell by connecting it to an anode material that is more electronegative than steel in the electromotive series. Thus, current will flow from the corroding 'anode,' typically magnesium, zinc, aluminum, or alloys of these materials, to the pipeline 'cathode' through the soil. At locations where there are holidays in the coating, the current can flow onto the pipeline and repress the anodic reaction. The return path is provided by thermit welding a cable connection to the pipeline (Figure 7).

The advantage of the sacrificial anode system is that no external power source is required and therefore the system is easy to install and requires minimal maintenance. However, one of the main disadvantages of this type of CP system is that the available current is fixed and the driving potential between the steel and the anode material is limited by their separation in the electromotive series. In order to maximize the available current, these systems are therefore most effective in low-resistance soil environments. The limited current availability of this system also means that to protect long lengths of pipe, particularly poorly coated or bare pipe, requires large numbers of anodes to ensure that sufficient current is provided to the pipeline. The sacrificial anode system is therefore often used onshore to protect small areas of pipeline at specific critical locations. Another main disadvantage of a sacrificial anode system is that the anodes are consumed over time and therefore have a finite life after which they have to be replaced.

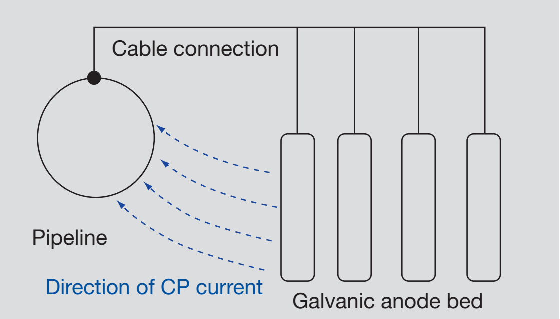

Figure 7 Schematic of the sacrificial anode cathodic protection system.

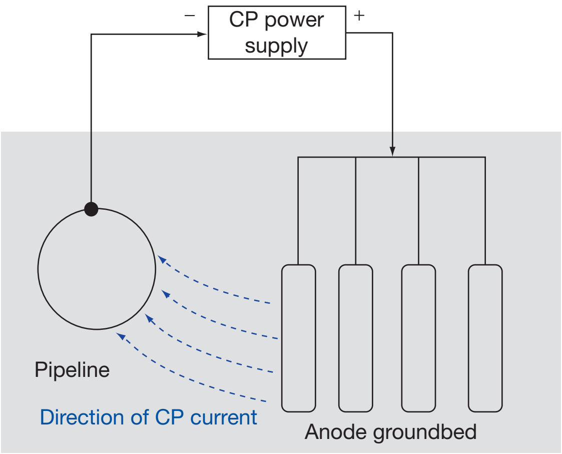

Figure 8 Schematic of the impressed current cathodic protection system.

4.42.4.2.10 CP: Impressed current systems

In an impressed current system, the protection current is supplied by connecting the negative terminal of an external power supply to the pipeline and the positive terminal to an inert anode (Figure 8). The system therefore consists of an AC source, which is rectified to produce a DC output, a groundbed of anodes, and wires connecting the anodes and the pipeline to the rectifier. Current flows from the anode groundbed through the soil to the pipeline and returns via the thermit-welded CP connection. The anodes that are used for the protection of pipelines are generally high-silicon chromium cast iron or mixed metal oxide coated titanium, buried in a coke-filled groundbed, to provide a low-resistance path for the current into the soil.

The main advantage of the impressed current system over the sacrificial anode system is that a larger driving potential is available and the voltage and current can be controlled. This makes the system more adaptable to the changing current levels required to protect the pipeline as it ages and the coating deteriorates and also more adaptable for use in high-resistivity soils. However, this system does require an external power supply and therefore has an associated ongoing through-life cost, and in addition, also requires more frequent maintenance and inspection than a sacrificial anode system.

4.42.4.2.11 Basic CP design

Although the subject of CP design is addressed in international standards and guidance, several key factors need to be considered when installing a CP system to ensure that the pipeline is adequately protected from external corrosion.

One of the critical requirements is ensuring that enough current is supplied to the pipeline to protect areas of coating damage. The larger the area of coating damage, the larger the current required to achieve a sufficiently high current density to ensure that the pipeline is protected. Other factors that need to be addressed are the type of CP system to be used (i.e., sacrificial anode or impressed current) and the spacing of the anodes along the pipeline to ensure that the required current levels are achieved at locations remote from the anode or power supply. These decisions will require knowledge of the pipeline environment including the soil resistivity, the coating type, the location of other metallic structures that could interfere with the CP current, and the presence of sources of stray current. In this respect, one of the features of the CP design includes the location of isolation joints. These joints are used to insulate the pipeline from current paths that could take current away from the pipeline and therefore reduce the level of protection. Isolation joints are therefore located at above-ground facilities such as terminals, pumping stations, offtakes, and instrument lines. They can also be used to control stray currents by electrically separating sections of pipeline.

The CP system must also be designed in such a way that it can be easily monitored and therefore test points are installed along the pipeline at intervals that are dependent on the location of the pipeline. An ideal spacing is every one to two kilometers, although often test points are located close to road crossings for ease of access and convenience. The test point consists of a wire connection from the pipeline to a test box that is usually located above ground so that measurements of current and voltage can be made to confirm that the pipeline is adequately protected. Additional test points are also located at other critical locations, for example, crossings, sources of external current (i.e., traction systems), and isolation joints.

4.42.4.2.12 CP requirements

In order for CP to be effective, the current supplied to the pipeline must shift the potential at that pipe surface sufficiently negative such that the surface becomes the cathode in the corrosion cell and the anodic reactions are reduced or suppressed. Therefore, in order to ensure that the pipeline is protected to a level that will stop significant corrosion, it is necessary to set criteria for monitoring a pipeline to ensure that the protection levels are achieved. In this respect, the current supplied is not a reliable measure of protection, as it can change with time and therefore protection criteria are based on a measure of the potential difference between the pipe and the soil as measured against a copper–copper sulfate reference electrode.

Both ISO 15589[26] and prEN 14919–1[27] state that for onshore buried pipelines, all parts of the pipeline should be polarized to a potential more negative than −850 mV. This is the most widely accepted and common criterion and indicates that protection is achieved if the potential of the structure is more negative than −850 mV when measured with a copper–copper sulfate reference electrode. The criterion is increased to –950 mV if active bacterial or anaerobic conditions are suspected and can also be adjusted to account for low resistivity-soils or high temperature operation.

Another criterion that can be applied, typically to pipelines that have poor or aging coating systems, is the 100 mV polarization shift criterion. This criterion states that protection is achieved if the polarized potential is shifted at least 100 mV in the cathodic direction below the natural corrosion potential as illustrated in the schematic Evans Diagram of Figure 9. Although this criterion may be easier and cheaper to achieve than the −850 mV criterion for some pipeline systems, in order to apply the criterion successfully, a detailed characterization of the environment around the pipeline is required. In particular, this criterion should be avoided in anaerobic soils, where SRB activity is expected, or in regions affected by interference currents or stray currents. In these types of environments, the 100 mV shift may not be sufficient to reduce the corrosion rate to acceptable levels and could result in the pipeline being in the critical range for high-pH SCC (see Section 4.42.6.1.1).

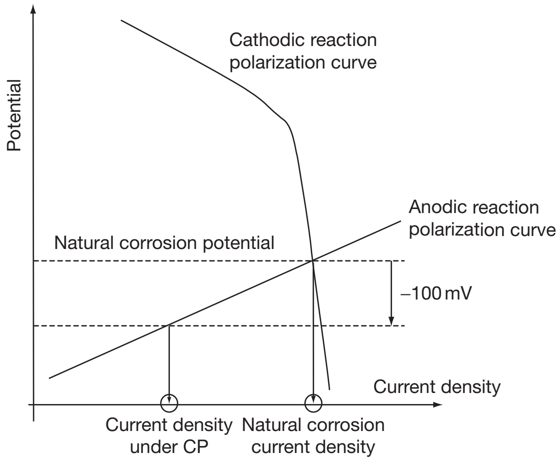

Figure 9 Schematic Evans diagram illustrating the principle of the 100 mV CP criterion.

4.42.4.2.13 CP shielding

In a discussion on CP effectiveness on pipelines, the subject of CP shielding should be included, as this phenomenon reduces the effectiveness of the CP and can cause a serious problem with respect to the detection of corrosion. Shielding in effect reduces the current flow to the pipeline, although measurements taken above the surface will indicate that the pipeline is still protected. The most common shielding situations are pipelines installed within a bare steel casing with the casing short-circuited to the pipe and pipelines under a disbonded coating. The latter situation was introduced in Section 4.42.4.2.1 when coating adhesion was highlighted as a major requirement for a pipeline coating. When the coating becomes disbonded, sufficient CP may not be able to penetrate to the area of corrosion under the coating and protect the pipeline from corrosion.

4.42.4.2.14 CP monitoring

To make sure that cathodic protection is achieved and continues to be achieved, the CP system should be regularly monitored. There are two levels of monitoring: regular equipment checks to ensure that the systems are operating and less regular surveys at fixed test points to ensure that protection is being achieved. These surveys involve measuring the pipe potential at every test point and then carrying out further surveys between test points and remedial action if the readings show inadequate protection.

However, before looking at the survey techniques, an initial explanation of pipeline potential measurements is required. There are essentially three potential measurements that can be made on a pipeline; the natural potential, the ON potential, and the OFF potential.

- *Natural potential*

The natural potential of the pipeline is the potential of the corroding pipeline with no protection current applied. Ideally, the natural potential should be measured before any current is applied to the pipeline either from a CP system or by the action of stray currents as these alter the natural current balance, which can then take weeks or months to recover. A reading of natural potential is required if the pipeline is going to be protected using the 100 mV shift criterion (see **Section 4.42.4.2.12**).

- *ON potential*

An ON potential reading is the potential measured on a pipeline at the above-ground surface once a CP current has been applied. The reading does not necessarily imply that CP has been achieved because of the errors that occur in the readings of CP and how they are taken. In effect, the measurement of potential on the surface above the pipeline with the CP system on is made up of two components as shown in the following equation:

$$V_s = V_p + V_{IR}$$

Where V_s is the measured potential at the surface, V_p is the actual potential at the pipe, and V_{IR}, sometimes termed the IR drop, is the potential drop associated with the flow of CP current through the soil of finite resistance and onto the pipeline. Therefore, although V_p is the reading that is required to determine whether CP criteria have been achieved on a pipeline, an ON potential reading is measuring V_s, which includes the IR drop. Therefore an ON potential reading will overestimate the level of CP on a pipeline, but if IR drops are known to be low, then it can provide an estimate of the amount of protection.

- *Instant OFF potentials*

One method adopted for assessing the true potential without the IR component is what is termed the Instant OFF polarized potential. This test is carried out by switching the CP system off and monitoring the potential of the structure before the potential has begun to decay significantly. There is no current flowing through the soil to the defect and thus the IR component or error in the potential reading will, for practical purposes, be almost eliminated.

4.42.4.2.15 CP Monitoring: Close interval potential (CIPS or CIS) surveys

This technique involves measuring ON and OFF potentials at close intervals over a pipeline, and hence, the method is often called a CIPS survey or close interval survey (CIS). The CP current is switched ON and OFF by inserting a timer switch at the rectifier and the switching cycle is set up so that the ON cycle is longer than the OFF cycle, by a typical ratio of 5:1, to avoid significant decay of the potential. The survey is conducted by attaching a spool of very fine insulated wire to a pipeline test point terminal and connecting this to a test meter and a copper/copper sulfate half-cell, which is located in a pole that is carried by the operator. The survey operator then walks along the pipeline route taking ON and OFF potential readings with the half-cell, approximately every meter along the pipeline. Often two half-cells are used so that one is always in contact with the ground. Although ON and OFF potentials may be routinely measured at test posts, this type of survey allows the potential to be measured between test posts and can determine whether the pipeline is adequately protected along its length.

A CIPS or CIS survey is generally used to measure the effectiveness of the CP system, although it can also be used to locate coating defects using the same principle as the DC methods described in **Section 4.42.4.2.6**. The basis of this technique is that a dip in the ON and OFF potential profiles along the pipeline provides an indication of the presence of a coating defect due to the loss of protection at that point.

4.42.4.3 Assessing the External Corrosion Risk

The preceding sections have served to outline the causes of external corrosion on buried pipelines and to describe how external corrosion is prevented and controlled. The knowledge of how and why external corrosion occurs also aids in identifying the key factors that are used in risk assessment strategies for external corrosion. On the basis of this review, a summary list of typical data that are required to assess the threat of external corrosion is presented in **Table 8.** It can be seen that this list includes not only information about the environment of the pipeline but also information about how the pipeline is maintained in terms of the coating condition and the effectiveness of the CP. All these factors are then fed into the types of algorithms described in **Section 4.42.3** to rank the relative risk of external corrosion on the pipeline.

4.42.5 Internal Pipeline Corrosion Risks

The scope of this chapter has been limited to an investigation of corrosion in onshore gas and liquid transmission and gathering pipelines. For external corrosion, the type of pipeline, that is, transmission or gathering, is less relevant in determining whether

Table 8 Summary of typical information required to assess the external corrosion threat

	Data required to assess threat	*Comment*
Pipeline characteristics	Age of pipeline Type of pipe	Could highlight a susceptibility to certain forms of corrosion (e.g., preferential corrosion).
Coating information	Coating type	Indicates the likely modes of coating failure and corrosion damage, for example, disbonding.
	Coating condition	Could either be a subjective view (i.e., good, average, poor, etc.) or a more quantitative measure gathered from coating monitoring surveys.
CP information	CP availability CP protection levels	Indicates the likelihood that damaged areas of coating are not protected. Could be subjective or determined from CP monitoring surveys.
Pipeline environment	Soil characteristics	Indicates the corrosivity of the soil and would include the type of soil as a minimum but could also include more detailed resistivity data, pH, bacterial levels.
	Evidence of MIC	Usually evidence gathered during direct inspection although could also be implied from soil conditions.
	Potential sources of stray currents	Would include data such as proximity of other pipelines, structures, rail crossings
	Potential sources of AC corrosion	For example, proximity of overhead power lines
Pipeline history	Leak history Previous inspection reports	Provides more quantitative evidence of a corrosion threat

the pipeline will be susceptible to external corrosion. However, the type of pipeline becomes more significant when considering the threat of internal corrosion. Gathering systems are generally collecting product from a wellhead and transporting it to a processing plant or transmission pipeline. The fluid is not processed before it enters the gathering system and therefore the product can contain contaminants that increase the susceptibility to internal corrosion. However, the product in a transmission pipeline will have undergone basic or full product processing and therefore the internal corrosion threat is more controllable.

It should be highlighted at this stage that dry natural gas and moisture-free oil and petroleum products are not corrosive to carbon steel. It is only in the presence of water and contaminants such as chlorides, CO_2, H_2S, organic acids, bacteria, and oxygen that corrosion will occur. Internal corrosion of pipelines is generally classified as either sweet or sour depending on the level of H_2S in the product.

4.42.5.1 Sweet or CO_2 Corrosion

Sweet corrosion of carbon steel occurs in the presence of free water that has been acidified by carbon dioxide present in the oil or gas. It is therefore important to note that sweet corrosion will not occur in the pipeline if free water is not present in the product, that is, dry CO_2 gas does not pose a corrosion threat to pipeline steel. Water in the pipeline can be present from different sources, depending on whether the pipeline is in the gathering or transmission system and what processing has been carried out.

In the gathering system, the pipeline is transporting product directly from the reservoir generally without any pretreatment. Therefore, water that is naturally present in the gas phase or water present in the rock pores, which is then mobilized with the oil or gas (formation water), can be present in the pipeline. Once the product has been processed, it is still possible for water to enter the transmission pipeline either as a result of water carryover from the separators or due to water dropping out or condensing from the product. Water drop out occurs in oil pipelines if water is entrained in the oil as an emulsion. During transport through the pipeline, the water can separate out of the emulsion as a distinct phase at the bottom of the pipeline. In gas pipelines, water can condense out of the gas phase (condensed water) if the temperature of the steel surface falls below the dew point of the gas. This type of corrosion is sometimes termed top-of-line (TOL) corrosion and tends to be a particular issue for subsea pipelines where exposed sections of the pipeline can be cooled by the sea.

The mechanism of CO_2 corrosion is complicated,[28] but initially the CO_2 gas dissolves in water to form carbonic acid according to the equation:

$$CO_{2(g)} \Leftrightarrow CO_{2(aq)}$$
$$CO_{2(aq)} + H_2O \rightarrow H_2CO_3$$

The carbonic acid then reacts with the steel according to the following reaction to produce iron carbonate and hydrogen.

$$Fe + H_2CO_3 \rightarrow FeCO_3 + H_2$$

Under favorable conditions, the iron carbonate can form a protective or semiprotective scale on the pipeline surface. It is the presence and stability of this film that determines the rate of general corrosion and can also dictate the susceptibility to localized attack by mechanisms such as pitting corrosion, preferential weld corrosion, and flow-induced localized corrosion (FILC).

Schmitt and Hörstemeier[29] have reviewed the parameters that influence the CO_2 corrosion mechanism and have concluded that the factors affecting the rate and nature of the CO_2 corrosion reaction can be divided into three categories: interface-related parameters (temperature, flow rate, condensation, and presence of scales), materials-related parameters (alloy composition, microstructure, and heat treatment) and medium-related parameters (pH, CO_2 partial pressure, solution chemistry, and oxygen content). The key parameters in this list are worthy of further discussion in relation to the factors that affect internal pipeline corrosion.

4.42.5.1.1 Effect of temperature

Below 60 °C and at low levels of pH, the solubility of iron carbonate is high and the formation of a stable $FeCO_3$ film on the pipe surface is difficult. The rate of the reaction is controlled by the dissolution of iron and increases with increasing temperature. Above 60–80 °C, the solubility of iron carbonate decreases, allowing the formation of a more adherent, semiprotective scale of $FeCO_3$ on the surface and an overall reduction in the corrosion rate. It should be noted, however, that in order for the $FeCO_3$ scale to be effective in reducing corrosion rates, it must be adherent and cover the whole pipe surface. If the scale becomes damaged, for example, as a result of turbulent flow, then corrosion of the unprotected steel can occur at high rates. This gives rise to a particular type of localized corrosion called mesa corrosion, which is described in more detail in Section 4.42.5.2.2.

4.42.5.1.2 Effect of flow rate

As already mentioned, the corrosion rate for CO_2 corrosion is dependent on the ability of the system to establish and maintain a stable iron carbonate scale on the steel surface. If the flow velocity is greater than a certain critical value, then it is possible that the scale can be eroded by the turbulent conditions near the pipe wall. Under such flow conditions, the scale is unable to reform, resulting in unprotected areas of the pipe and therefore increased corrosion rates.

The flow rate can also affect the distribution of corrosion. As discussed previously, in oil pipelines it is possible that water is carried over into the pipeline entrained in an emulsion. In low-velocity or nonturbulent flow, the water will separate out of the emulsion and collect in pools, particularly at low points in the pipeline.

4.42.5.1.3 Effect of pH

In general, the corrosion rate for CO_2 corrosion decreases as the pH increases. The pH is dependent on the type of free water present in the pipeline, that is, whether it is condensed water or formation water. Condensed water is relatively pure and therefore the pH is determined by the partial pressure of CO_2; the higher the CO_2 concentration, the more acidic the water and the lower the pH. However, as the pipeline corrodes, the condensed water will become saturated with carbonate from the corrosion product and the pH will rise with a consequent reduction in the corrosion rate. Although the concentration of CO_2 in the product will also affect the pH of formation water, ionic species present in the rocks, (e.g., bicarbonate, chlorides, sulfates, etc.), which are in solution in the water, also influence the pH.

Another impact of the pH on sweet corrosion is that, as the pH of the water is increased, the solubility of iron carbonate is reduced and therefore the deposition of the protective scale on the steel surface becomes more favorable. This effect also reduces the corrosion rate.

4.42.5.1.4 Effect of partial pressure of CO_2

As the sweet corrosion reaction involves the dissolution of CO_2 in water to produce carbonic acid, the concentration of the acid produced is directly related to the concentration of CO_2 in the gas and therefore to the partial pressure of CO_2. Consequently, the reaction rate will increase as the CO_2 partial pressure increases producing higher concentrations of carbonic acid and reducing the solution pH.

4.42.5.1.5 Effect of H_2S content

H_2S can be present naturally in the reservoir or can be produced during the extraction process. The influence of small amounts of H_2S (i.e., <0.0035 bar partial pressure H_2S) on CO_2 corrosion is dependent on the concentration of H_2S and whether iron sulfide can precipitate as a protective surface scale. At low concentrations of H_2S and low values of pH, when iron sulfide precipitation does not occur, the experimental evidence is confusing and the mechanism by which H_2S affects the corrosion rate is not well understood. For example, some studies indicate that the corrosion rate is increased compared with an equivalent H_2S-free CO_2 corrosion environment,[30] while others suggest that small amounts of H_2S could reduce the corrosion rate.[31]

As the H_2S concentration increases the formation of the iron sulfide surface film becomes more favorable. The exact composition of the surface scale in slightly sour conditions is dependent on the CO_2–H_2S ratio. Iron sulfide scales are conductive and therefore make very efficient cathodes. However, if the scale becomes damaged, then small anodic areas can form, which can result in high pitting corrosion rates. At higher concentrations of H_2S, that is, greater than 0.0035 bar partial pressure H_2S, the mechanism of corrosion changes from one of general or pitting corrosion to cracking, and the product is termed sour. Sour cracking is discussed in more detail in Section 4.42.5.3.

4.42.5.2 CO_2 Corrosion – Localized Effects

The general corrosion rate for sweet corrosion is principally determined by the establishment of a scale of either iron carbonate or iron sulfide (depending on the H_2S content) on the surface of the pipe. If this scale is not uniform or becomes damaged (e.g., due to erosion, shear stresses in the scale, scratching, or mechanical damage), then the underlying steel is locally unprotected and the pipeline becomes susceptible to localized attack. Particular forms of localized attack that are found in pipelines include pitting corrosion, mesa corrosion, FILC, and preferential corrosion.

4.42.5.2.1 Pitting corrosion

The susceptibility of the pipeline steel to pitting corrosion increases with increasing temperature. As discussed previously, below 60 °C, the iron carbonate scale is thin and the protection that it provides to the steel is low. However, the scale becomes more stable and adherent above 60 °C, and therefore, a reduction in corrosion rate is observed for general corrosion. However, if the scale becomes locally damaged, the steel is unprotected and CO_2 corrosion can occur at high rates, due to the increased temperature. It is therefore possible to observe localized pitting damage in pipelines operating above 60 °C.

4.42.5.2.2 Mesa corrosion

Mesa corrosion is a form of CO_2 corrosion that occurs under conditions of high temperature (above 60–80 °C) and under enhanced flow rates. The morphology of the attack is characterized by steep-sided transitions from uncorroded to corroded areas similar to mesa formations in rocks. Mesa corrosion results from flow-induced spalling of the carbonate film due to internal stresses developed in the scale during its formation. The underlying, unprotected metal is then exposed and corrosion occurs at rates of up to several $\mathrm{mm\,year^{-1}}$, resulting in the formation of deep flat-bottomed, sharp-edged pits.[29] As a higher temperature is required than is normal for transmission pipelines, mesa corrosion is mainly found in gathering systems.

4.42.5.2.3 Flow-induced localized corrosion (FILC)

FILC occurs in pipelines under conditions of local turbulence where the carbonate scale cannot reform. FILC is normally initiated at locations where the scale becomes cracked or spalled by the action of hydrodynamic forces induced by the local flow conditions. In order to fracture the scale, the hydrodynamic force must exceed the fracture stress of the scale. There is still debate in the literature with regard to the best way to quantify the hydrodynamic forces and therefore to determine the critical parameters under which FILC occurs.[29]

4.42.5.2.4 Preferential weld corrosion

Another localized corrosion effect that has been observed in pipelines is preferential weld corrosion. It can occur at welded joints if a galvanic couple is established between the parent pipe and the weld heatly-affected zone (HAZ) or weld metal due to local differences in composition. The susceptibility of a pipeline to preferential weld corrosion and the location and morphology of the corrosion are dependent on the environment (in terms of the nature of the scale that is formed); the microstructure and composition of the steel and the weld (in terms of the establishment of the galvanic couple and the general corrosion resistance of the material); and local geometry effects (in terms of the establishment of regions of local turbulence). In terms of the corrosion theory, preferential weld corrosion occurs because the weld or HAZ material becomes anodic with respect to the parent material. Solutions to prevent this form of corrosion are therefore aimed at adding elements such at Cr, Ni, and Cu to the weld metal to make the weld more cathodic with respect to the parent.

4.42.5.3 Sour Corrosion

The effect of low levels of H_2S on internal pipeline corrosion was described in **Section 4.42.5.1.5**. In this section, a partial pressure of H_2S of 0.003 5 bar was defined as a threshold above which sour corrosion cracking mechanisms would dominate over sweet corrosion mechanisms. This limit has been defined in the standard NACE MR0175/ISO15156–2[32] and is presented in the form of a domain diagram that indicates the susceptibility to sour cracking on the basis of the local pH and partial pressure of H_2S. The diagram is divided into four domain areas; in domain zero, there is low risk from sour corrosion. However, as the partial pressure increases above 0.003 5 bar, decreasing the pH and/or increasing the pressure increases the severity of sour service damage from domain one (mild sour service) to domain three (severe sour service). It is critical that the susceptibility of a pipeline to sour service cracking is understood and quantified at the design stage as material choices have to be made to prevent rapid pipeline failure. Failure times as short as days or hours have been observed for sour corrosion mechanisms under test conditions. Material selection for sour service is discussed in **Section 4.42.5.4**.

The principal mechanism of sour corrosion is hydrogen damage and the role of H_2S is to promote the penetration of atomic hydrogen, produced at the cathode, into the steel. As with sweet corrosion, sour corrosion mechanisms also require a source of water. When hydrogen diffuses into the steel matrix, it can either remain in solution in the steel lattice (hydrogen embrittlement) or recombine to form hydrogen gas (internal hydrogen pressure). The defects that are characteristic of sour service result from one of these two mechanisms; hydrogen embrittlement results in sulfide stress corrosion cracking (SSCC), whereas internal hydrogen pressure can result in hydrogen-induced cracking (HIC). Stress-orientated hydrogen-induced cracking (SOHIC) is thought to occur by a combination of the two mechanisms.

4.42.5.3.1 Sulfide stress corrosion cracking (SSCC)

When atomic hydrogen diffuses into a steel matrix, it embrittles the material, reducing the ductility and the toughness of the material. Embrittled steel is less tolerant to defects and can readily crack, either under the action of an applied tensile stress (e.g., due to the internal pressure in the pipeline) or as a result of residual stresses in the pipe wall (e.g., as a result of welding). In a sour environment, this cracking is called SSCC. Weld areas are particularly susceptible to SSCC, as the welding can produce hard zones that embrittle more easily in a hydrogen environment.

Under test conditions, SSCC has been shown to cause failure within hours of exposure to the sour environment and therefore it is imperative that materials used in the pipeline construction have been selected appropriately and that welding procedures are designed to limit the hardness in the HAZ. Although postweld heat treatment may be applied to reduce the residual stress and temper any hard microstructures in the steel, this is not feasible for pipelines.

4.42.5.3.2 Hydrogen-induced cracking (HIC)

Although there are differing theories in the literature, one mechanism for the formation of HIC is that atomic hydrogen diffuses into the steel and collects around nonmetallic inclusions, particularly sulfide laminations in the pipe wall. At these locations, the hydrogen atoms can recombine to form hydrogen gas. As hydrogen gas is unable to diffuse in steel, the hydrogen gas pressure in the internal voids builds up to such a high level that the steel can crack. This process is represented in **Figure 10**. The cracks propagate away from the voids and the crack path is influenced by microstructure, particularly in rolled plate where the cracks run along the banded rolling microstructure, parallel to the pipe wall.

If HIC is initiated at different locations in the pipe wall, it is possible for the cracks to link up by growing at right angles to the pipe wall (i.e., in a radial direction). For this reason, HIC is sometimes referred to as stepwise cracking. In addition, if the inclusion is close to the pipe wall, the pressure of the hydrogen gas may be sufficient to cause local yielding and can result in visible blistering on the pipe surface.

As with SSCC, failure by HIC can be very rapid, and under test conditions, has been found to occur within days of exposure to a wet, sour environment.

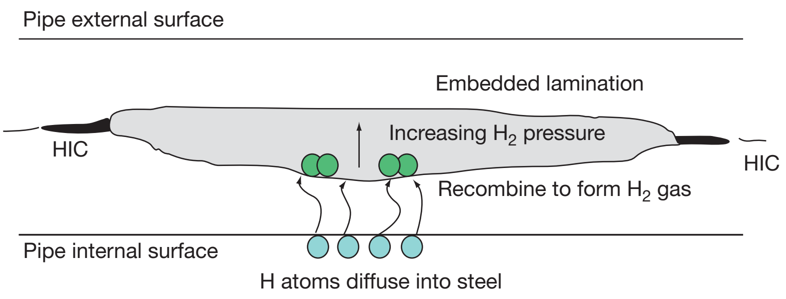

Figure 10 Mechanism of HIC in pipeline steels.

4.42.5.3.3 Stress-oriented HIC (SOHIC)

HIC is not influenced by the stress state of the pipeline. However, under the influence of either the operating stress or a residual stress, the HIC cracks can become aligned perpendicular to the principal stress direction in a characteristic array of small, staggered cracks. This type of cracking is known as Stress-oriented HIC (SOHIC).

4.42.5.4 Material Selection for Sour Service

High-strength steels are more susceptible to hydrogen embrittlement and therefore cracking in a sour environment and consequently steels have to be selected to comply with maximum hardness levels to avoid cracking in both the parent and the weld material. The risk of sour service cracking such as HIC is also reduced by producing steels with the minimum of inclusions. This is achieved by using steel with very low sulfide concentrations to avoid the formation of MnS inclusions. In addition, the surface area of the inclusions is reduced by the addition of Rare Earth Metals (REMs) and calcium, which form spherical inclusions rather than elongated inclusions and therefore there is less inclusion area on which hydrogen can accumulate. Suitable pipeline materials for use in sour service are specified in the International Standard NACE MR0175/ISO15156–2:2003.[32]

4.42.5.5 Microbiologically Induced Corrosion

The final type of internal pipeline corrosion to be considered here is MIC. This type of corrosion was described earlier with respect to microbe activity in soil resulting in external MIC (**Section 4.42.4.1.2**). However, SRBs can also be present in the reservoir and can be carried over into the pipeline if the system is not properly treated with an appropriate biocide. SRBs can cause MIC and can also increase the H_2S content in the product. SRBs that appear in reservoirs over time are usually due to the contamination of the reservoir during completion or water injection.

4.42.5.6 Internal Corrosion: Prevention

In the control of external corrosion, the principle of protection is based on the combination of a pipeline coating, to prevent the electrolyte from contacting the pipe wall and to restrict the flow of the corrosion current, and CP, to make the pipeline the cathode in the corrosion cell. The rationale for corrosion protection of pipelines from internal corrosion is principally to accept that corrosion is going to occur if water cannot be removed from the system but to take steps to reduce the corrosion rate or to allow for corrosion within the pipeline design. The latter step is provided by the use of a corrosion allowance or by using more corrosion-resistant alloys and the former could include such measures as product treatment, inhibition, and internal coating. These strategies are discussed in more detail in the following sections.

4.42.5.6.1 Corrosion allowance

A corrosion allowance is additional material that is added to the pipe wall thickness to allow for predictable, in-service corrosion. The corrosion allowance in pipeline design is calculated by predicting the corrosion rate in the pipeline, taking into account the anticipated effectiveness of other corrosion control strategies, and allowing for that amount of controlled, uniform wastage of the pipe wall over the design life of the pipeline. In practice, typical corrosion allowances for carbon steel are between 3 and 5 mm.[33] However, in situations where the corrosion rate is predicted to be high, the use of a corrosion allowance may not be viable due to the cost of the extra material required.

Strictly speaking, providing a corrosion allowance is not a corrosion prevention method as corrosion is still assumed to continue, but it can increase the design life of a pipeline that is susceptible to internal corrosion.

4.42.5.6.2 Corrosion-resistant alloys

For pipelines that are transporting unprocessed product over short distances, the use of a corrosion-resistant alloy may be feasible. Chromium is the most commonly used alloying element for steel to improve the corrosion resistance in wet CO_2 environments. Even at low levels (0.5 – 1%Cr), there have been reports of improvements in corrosion resistance, an observation that is thought to be due to the fact that Cr acts to stabilize the iron carbonate film. Higher additions of Cr and Ni, as in stainless steels, can make the steel resistant to CO_2 corrosion and the improved corrosion resistance in these cases is due to the formation of a chromium oxide scale on the surface. However, as with all surface scales, if the scale becomes damaged and is not reformed, the pipeline becomes susceptible to pitting corrosion. For stainless steels, the presence of high levels of chloride can result in pitting corrosion.

Although the use of more corrosion-resistant alloys may be viable for short lengths of pipeline, for transmission pipelines, it is not an economical solution to internal corrosion, and carbon steel is the construction material that is used. However, for transmission pipelines, there is the opportunity to process the fluid and to add chemical inhibitors to reduce the corrosion rate.

4.42.5.6.3 Coatings

Internal coatings are used particularly in gas pipelines to improve pipeline flow efficiency by reducing frictional losses. However, it is also possible to use internal coatings to protect the pipeline if it is going to be transporting a highly corrosive product. Either the coating can be applied in the mill with the girth welds coated after construction or the entire pipeline can be coated *in situ* by introducing the coating medium between cleaning tools after the pipeline has been constructed.

It is recalled that for external corrosion protection, both pipeline coating and CP are applied to control corrosion, as it is impossible to maintain a coating in a defect-free condition. The problem with relying on a coating to provide internal corrosion protection is that, where the coating becomes damaged, corrosion could occur very rapidly and therefore these areas of damage have to be protected. Coatings should therefore be used in conjunction with inhibitors to reduce the corrosion rate at the sites of damaged coating.

4.42.5.6.4 Product treatment

Based on the descriptions of both sweet and sour corrosion, it can be stated that pipeline internal corrosion will not occur if water is not present. Therefore, one of the key corrosion prevention strategies is to remove water from the product prior to pipeline transportation. The decision to use dehydration obviously carries a cost penalty and provision must also be made for upsets in the water separation and dehydration systems to prevent significant internal corrosion under these conditions.

Another treatment that can be applied to the product is pH control. It was mentioned in Section 4.42.5.1.3 that the corrosion rate decreases as the pH increases, and therefore, the addition of alkaline additives to raise the pH can be used to control corrosion.

Large quantities of glycol or methanol are often introduced into wet gas-producing systems to prevent and control hydrate formation, which can cause plugging problems. Both of these chemicals, if present in sufficient concentrations, can also reduce CO_2 corrosion rates.

4.42.5.6.5 Inhibitors

Inhibitors are principally used for the control of general corrosion in sweet environments. However, there are packages available for the control of mesa type corrosion and pitting corrosion in both sweet and sour environments. The selection of an inhibitor to adequately protect a pipeline requires consideration of a number of interrelated factors. Detailed information on the use of inhibitors can be found in texts such as the European Federation of Corrosion publication.[33] However, the key factors and considerations with respect to pipelines are discussed in the following sections.

Corrosion inhibitors used in hydrocarbon pipelines are generally long-chain nitrogen-based compounds (e.g., amines, amides), but they can also be organophosphates. These compounds have a charged surface-active group and a hydrocarbon chain. The surface-active groups are attracted to the pipe wall where they become physically adsorbed and then chemisorbed onto the surface as charge transfer with the pipe wall occurs and a chemical bond is formed. In oil pipelines, the hydrocarbon chains in the inhibitor molecules mean that the inhibitor becomes partially oil soluble and therefore forms a hydrophobic barrier between the steel and the water phase. The principle of inhibition is therefore twofold: the removal of water from the pipe surface through the formation of a stable film and the modification of the surface potential, inhibiting both the anodic and cathodic reactions. In addition to the active species, the inhibitor will also include a solvent carrier fluid and other additives, such as surfactants to optimize the delivery and storage properties of the inhibitor.

It is highlighted that inhibitors do not stop corrosion but the aim of inhibition is to reduce the corrosion rates to manageable levels. The effectiveness of the inhibitor regime is measured by the efficiency, which is defined as:

$$\%\text{Inhibitor Efficiency} = \left[1.00 - \frac{\text{Weight loss (with inhibitor)}}{\text{Weight loss (without inhibitor)}}\right] \times 100$$

Although laboratory tests have shown that efficiencies of more than 95% can be achieved, in practice, most operators achieve an inhibitor efficiency of 80–90%,[33] although higher efficiencies may be expected if the inhibitor has been carefully selected.

In order for an inhibitor to be effective, it must be dispersed to those surfaces that are wet by water and must be able to establish and maintain a protective film at that location. The transport of the inhibitor to all corroding sections along the full length of the pipeline is therefore important, whether the corrosion is at the bottom of the pipeline due to water drop out or at the top of the pipeline due to condensation (Section 4.42.5.1), at the start of the line or toward the end of the line. There are two main methods for introducing inhibitor into the pipeline: continuous injection and batching.

In continuous injection, the inhibitor is dispersed by the flowing product. For gas pipelines, this requires the inhibitor to be injected either as a separate liquid phase or as droplets entrained within the gas phase. However, the distance of travel of the inhibitor is limited using this method and therefore inhibition is not really a viable corrosion control option for gas pipelines. Continuous injection is more generally used for multiphase pipelines or pipelines containing crude oil and condensate where the transport of the inhibitor is in the liquid phase. In this situation, the inhibitor type has to be specified depending on the particular conditions and whether the inhibitor is required to be soluble in the oil or water phases in the carrier fluid.

In batch treatment, the inhibitor is introduced into the pipeline as a slug between two cleaning tools and is used in situations where continuous injection may not be an option or where TOL corrosion is expected and the flow regime does not allow the transport of inhibitor to this location by continuous injection. The frequency of batching is dependent on the inhibitor and the flow conditions in the pipeline.

Another important factor that has to be considered in the specification of an inhibitor is the dosing rate. The dose rate has to be monitored continuously to ensure that sufficient inhibitor is being injected to account for changes in water concentration in the pipeline. The dose rate is also dependent on how the inhibitor partitions between the oil and water phases. The aim is to obtain a sufficient concentration of the inhibitor in the water phase at the location of the corrosion and it is this concentration that must remain constant through the adjustment of the amount of inhibitor injected into the pipeline.

The performance and effectiveness of an inhibitor is also dependent on other factors such as the flow rate (turbulent flow can prevent the inhibitor film from forming or can strip the film from the pipe wall), temperature, composition of the product, interaction with other chemical additions, and pressure. These factors can change throughout the life of the pipeline and particularly during upset conditions, and therefore, it is important that continuous monitoring is employed to ensure that adequate inhibition is being achieved.

4.42.5.7 Internal Corrosion Monitoring

Internal corrosion monitoring can either be used to determine the effectiveness of the corrosion prevention strategies and to detect any upset conditions that could increase the corrosion rate in the pipeline, or to take measurements of corrosion rate. In practice, it is recommended that more than one technique is used and that monitoring is not reliant on only one type of measurement.

The types of monitoring used to determine whether corrosion prevention is being achieved include measurements of water content and chemistry, inhibitor availability, inhibitor dose rate, and inhibitor residuals (i.e., estimates of the concentration of inhibitor in the water phase). However, while these techniques may indicate that the pipeline is corroding, they will give no information on the rate of corrosion or location of that corrosion. Iron counts (i.e., measurements of the amount of iron entering the water phase as a result of corrosion) can also be used to indicate the effectiveness of the inhibitor program but it is not possible to determine whether the increased iron content is as a result of localized pitting or general corrosion, and therefore, calculating realistic corrosion rates using this method is difficult.

There are therefore alternative monitoring techniques that can be used to provide an indication of corrosion rate. These include weight loss corrosion coupons and probes that are inserted into the pipeline through hot tap fittings or through valves and access points. Immediately, this highlights one of the limitations of this type of monitoring: a measurement is only available at the location of the probe and this location is often selected due to ease of access rather than corrosion risk. The selection of appropriate locations for monitoring equipment should be made through evaluation of the pipeline operation and route and considering such factors as low points, flow regimes, temperature, and potential localized corrosion effects.

Coupons are the oldest method of monitoring corrosion. They are strip or disk-shaped coupons manufactured from the same steel as the pipe wall. The coupon is weighed and inserted into the process stream. At regular intervals, the coupon is then removed and weighed to determine the amount of weight loss since the last measurement, which will determine the average corrosion rate over that time period. The coupon can also provide useful information regarding deposits, fouling, and localized corrosion that may be occurring in the pipeline.

There are several types of insert probes that are available, that are based on measurements of changing ER probes or linear polarization resistance measurements (LPR probes). ER probes can provide a measurement of the average corrosion resistance, whereas LPR probes have the advantage of providing instantaneous data. The disadvantage of LPR probes is that they need to be immersed in a conductive medium, which in practice means the water phase.

Other monitoring techniques that can be used include specially instrumented pipeline spools and ultrasonic mats. However, with these techniques, it is critical that the equipment is placed in the locations at highest risk of internal corrosion to ensure that relevant readings are taken.

4.42.5.8 Assessing the Internal Corrosion Risk

The preceding sections have identified the types of data that are required to assess the risk of sweet and sour internal corrosion in pipelines, both from the point of view of the factors that contribute to the threat and also in respect of the prevention and monitoring activities that are conducted by the pipeline operator. A summary table of the type of data required is presented in Table 9. As with the external

Table 9 Summary of typical information required to assess the internal corrosion threat

	Data required to assess threat	*Comment*
Pipeline characteristics	Pipe and weld material	Could highlight a susceptibility to certain forms of corrosion (e.g., preferential weld corrosion) and is also required to determine suitability for sour service.
	Pipeline type	For example, whether the pipeline is a gathering or transmission line could indicate how much preprocessing has been conducted on the product.
Pipeline operation	Flow regime	Indicates the susceptibility to mesa or FILC corrosion.
	Upset conditions	Indicates how likely water is to enter into the pipeline.
Product data	Product analysis	Indicates susceptibility to sweet or sour corrosion and likely corrosion rates. Could include such information as water content, pH, CO_2 partial pressure, H_2S partial pressure, O_2 content.
	Temperature	With product analysis data, indicates typical corrosion rate and also the likelihood of scale formation and therefore susceptibility to certain types of corrosion.
Monitoring information	Inhibitor efficiency Inhibitor availability	Indicates whether the inhibitor is likely to have been adequately protecting the pipeline and therefore the period over which corrosion could occur.
	Coupon and probe data	Provides information on the likely corrosion rates in the pipeline.
Pipeline history	Leak history Previous inspection reports	Provides more quantitative evidence of a corrosion threat.

corrosion threat, this information can be used in semiquantitative risk assessment algorithms to determine how susceptible a pipeline may be to internal corrosion.

4.42.6 External SCC Risks

Although pipeline failures due to external SCC are relatively rare, it is worth including a brief description of this threat in a discussion of pipeline corrosion. OPS statistics indicate that only 1% of reported incidents in North American transmission and gathering pipelines (natural gas and hazardous liquids) between 1985 and 1996[34,35] have resulted from SCC. However, for specific pipelines, SCC can be the dominant failure mechanism and the consequences can be extremely serious. Although many of the reportable incidents of SCC have occurred in gas pipelines, failures have also been reported on liquid pipelines[36] and almost all cases of SCC have been encountered in pipe installed for more than 10 years with no failures reported to date for pipe that is less than 5 years old.

Two forms of external SCC have been identified on high-pressure gas transmission pipelines; high-pH SCC and near-neutral pH SCC. High-pH SCC was responsible for the first recognized failure due to SCC, in Louisiana in 1965, and incidents of this form of cracking have since been reported in Australia, Iran, Iraq, Italy, Pakistan, and Saudi Arabia. Near-neutral pH SCC was first identified in 1985 and has typically been associated with incidents in northern climates such as northern United States, Canada, and Russia.

For either form of SCC to occur in a pipeline, a complex array of conditions must be met including a critical combination of operating stress and stress cycling, faults in both the protective coating and the applied CP, a susceptible steel, and moisture at the pipe surface.

4.42.6.1 Nature and Occurrence of SCC

SCC is a corrosion process in which the form or geometry of the corrosion is strongly influenced by stress. As a result, the corrosion process creates linear, crack-like defects rather than rounded corrosion pits or general metal wastage. The stress corrosion cracks grow at right angles to the principal stress, and hence, on an operational pipeline, where the principal stress is generated by internal pressure, it is most usual for the cracks to be aligned parallel to the axis of the pipeline. However, a number of instances of circumferential SCC have also occurred where high axial stresses have been developed due to geotechnical instabilities.[37]

4.42.6.1.1 High-pH SCC

High-pH SCC is the most common mode of SCC and is characterized by intergranular cracking, following the grain boundaries within the steel microstructure. Weak points or areas of damage of the protective magnetite iron oxide film (Fe_3O_4) that forms on the steel surface, particularly at grain boundaries, are preferential sites for corrosion and crack-like features are formed at these locations. One theory for the mechanism of grain boundary cracking is that the grain boundaries act as stress raisers causing the oxide film to crack at these locations under the influence of a cyclic stress. In the alkaline environment of high-pH SCC, active dissolution will then occur at grain boundaries where the steel may also be less corrosion resistant due to grain boundary segregation. The water in the region of the crack is generally found to be alkaline with a pH above 10.

In order for SCC to occur, three conditions must be satisfied concurrently: there must be a tensile stress, a cracking environment, and a material that is susceptible to cracking in that environment. The factors that affect these conditions are discussed under these three headings:

- *Effect of stress*

It is generally accepted that there is a threshold stress, below which stress corrosion cracks will not occur. In the absence of a sustained cyclic stress, the threshold stress approaches yield. However, incidents of high-pH SCC in the US have generally been observed in pipelines where the combined stress level (i.e., from internal pressure and secondary loading) is above 60% of the minimum yield stress of the material.

An alternating stress on the pipeline has two effects in contributing to high-pH SCC failure: first, it reduces the threshold stress for crack initiation, and second, it damages the protective oxide film, preventing it from reforming and allowing the SCC to propagate.

- *Effect of environment*

High-pH SCC is generally found in areas where the CP is working and occurs in otherwise unaffected pipe with little or no associated corrosion. This is principally due to the formation of the magnetite film under the high pH conditions. However, there is a critical potential for high-pH SCC cracking, which is dependent both on the temperature and on the pH level. Typically, cracking occurs at potentials

~−750 mV with respect to a standard copper/copper sulfate electrode and the range over which cracking will occur is ~100 mV. This means that the critical potentials are less negative than the generally accepted requirement of −850 mV for effective CP of a pipeline (see Section 4.42.4.2.12). It is therefore important that the CP protection criteria selected do not allow the potential to drop into the cracking region. It was highlighted in Section 4.42.4.2.12 that this is of particular concern if the 100 mV shift criterion is used. In addition, the coating should be well maintained to prevent areas of disbonding, which could partially shield the pipe and lower the potential.

Although there has been no reported correlation between soil chemistry and the occurrence of high-pH SCC, it has been observed that pipelines that are located in soils that are alternately wet and dry are more susceptible. Areas that are continually wet, such as in rivers or lakes, have not experienced SCC to the same extent as has occurred on the edges of streams or lakes.

Temperature has an effect on the growth rate of high-pH SCC and also influences the range of potentials over which cracking will occur. There is also an observed relationship between the occurrence of high-pH SCC and the distance from a compressor station. Most severe cracking is generally found within ~5 km of compressor outlets and falls to a low level at ~16 km. Although there are other factors that could contribute to this observation, such as alternating stresses, one of the contributors could be temperature as the temperature of the product is raised as it passes through the compressor station.

Although the pipe coating does not have a direct influence on high-pH SCC initiation and growth, the coating properties do influence the formation of an environment and a potential conducive to cracking. High-pH SCC will only occur in pipelines where the coating has failed in some manner. The likelihood of coating failure and disbondment is increased at higher temperatures, which could also be a contributing factor to the observed increase in cracking incidences close to compressor stations. It is highlighted that no SCC has been found to date under undamaged FBE coatings.[38] However, further experience with the use of FBE may be required before it can be concluded that this coating provides resistance to SCC.

- *Effect of material*

There is no apparent correlation between pipe grade or manufacturing process and the risk of high-pH SCC. However, grit blasting of the surface to remove surface scale has been shown to avoid or delay the onset of cracking. Firstly, this relates to the cracking potential; if the steel is clean, then it is difficult to maintain the potential in the cracking range. Secondly, if the surface is grit blasted, then the coating will also adhere more easily, and finally, grit blasting will leave the surface in a state of compression and therefore more resistant to crack initiation.

4.42.6.1.2 Near-neutral pH SCC

Near-neutral pH SCC is characterized by a transgranular mode of cracking, where the cracks grow through the grain structure without following boundaries. These cracks also initiate at the pipe wall and form in clusters, often more closely spaced than is the case for high-pH SCC. However, in contrast to the tight nature of high-pH SCC, near-neutral cracking tends to be wider and more open and is often filled with corrosion product. The water surrounding the crack appears to be neutral with a pH ~7. The mechanism of near-neutral pH SCC is still a subject of research but is thought to involve both the dissolution of oxide films and hydrogen embrittlement. Near-neutral pH SCC is often associated with general pitting or metal loss and the cracks can sometimes be embedded within corrosion pits, which can make detection difficult. It is also often, but not always, associated with welds.

As with high-pH SCC, the cracking requires a combination of stress, environment, and material.

- *Effect of stress*

Near-neutral pH SCC requires a tensile stress acting on the pipeline. In addition, stress raisers and residual stresses are also thought to play a significant role in the initiation of near-neutral pH SCC. Pressure cycling has also been shown to influence both the rate of crack growth and the threshold stress for near-neutral pH.

- *Effect of environment*

Laboratory tests indicate that near-neutral SCC occurs at or near the free corrosion potential for steel. Cracking only occurs therefore in pipelines where there is inadequate CP or where the pipe is shielded from the CP, for example, by a disbonded coating.

As with high-pH SCC therefore, the role of the coating is to enable the cracking environment to be developed at the pipe surface. The majority of failures have occurred on pipelines with field-applied PE tape. The coating failure mode is thought to influence the crack development. For example, tenting of the coating over the long seam creates a long narrow zone in which cracks can easily coalesce and link up. Disbonding of coal tar coating tends to be localized around a defect and any resulting crack cluster is shorter and broader.

The composition of the soil does not seem to be critical to this type of cracking, although the amount of carbon dioxide in solution does appear to be important. For this reason, cracking generally occurs in colder climates where the carbon dioxide levels are higher. High levels of carbon dioxide are particularly found in winter under frozen surfaces.

There does not appear to be any relationship between temperature and the initiation and growth of near-neutral SCC. Therefore, with respect to temperature, there is no equivalent correlation between the incidence of cracking and the distance from compressor station as there is with high-pH SCC. It is possible, however, that the increased stresses close to compressor stations may be a contributing factor in near-neutral SCC.

- *Effect of material*

Near-neutral pH SCC has been identified in a range of steel grades and manufacturing routes. Research has shown that important material factors that correlated with the incidence of near-neutral pH SCC were residual stress, local increases in microhardness, and increased surface roughness. However, no correlation was reported with chemical composition, inclusions, and stress strain behavior. Surface preparation prior to coating application is less critical to near-neutral pH SCC than for high-pH SCC.

4.42.6.2 Assessing the SCC Risk

The preceding sections have described the critical risk factors that render a pipeline susceptible to high-pH SCC. On the basis of these criteria, ASME B31.8S[18] Appendix A3.3 has defined the areas of a pipeline at greatest risk as

- the pipeline operating stress is greater than 60% of the minimum yield stress of the steel;
- the operating temperature is greater than 37 °C;
- the distance from a compressor station is <32 km;
- the pipeline is older than 10 years; and
- the pipeline coating is not FBE.

These criteria have also been adopted by the NACE Recommended Practice NACE RP0204[38] to identify areas of greatest risk from near-neutral pH SCC, although the temperature criterion has been removed. In addition, if there has been one or more service incidents or hydrotest leaks that were attributable to SCC, then a SCC integrity management plan has to be put in place.

4.42.7 Corrosion Inspection Techniques

In **Section 4.42.3**, the concept of using risk assessment procedures to identify the critical pipeline threats was introduced. The following sections then detailed the principal internal and external corrosion mechanisms that can be present on onshore pipelines and detailed some of the risk factors that are used in risk assessments.

Once the risk of a particular corrosion mechanism or threat has been highlighted, the next stage in the process (**Figure 3**) is to inspect the pipeline to confirm or otherwise the existence of the threat, locate the damage and, if possible, identify the extent of the damage. The type of inspection method that is used is dependent on the type of corrosion or cracking and the accessibility of the pipeline for that inspection technique.

Three inspection methods that can be used for the inspection of corrosion-related threats in onshore pipelines are discussed in the following sections. It is highlighted that more than one inspection technique may be required to identify all the corrosion threats on a pipeline and when a particular inspection method has identified the location of damage, further nondestructive evaluation may be required to fully categorize the damage.

4.42.7.1 In-Line Inspection

In-line inspection (ILI) is an inspection method that can locate and size defects on a pipeline, not only corrosion defects but also defects arising from manufacturing, construction, and mechanical damage. There are two basic technologies that are used for the detection of corrosion on pipelines using ILI tools: magnetic flux leakage (MFL) and ultrasonics (UT). The ILI tools are inserted into the pipeline through specially designed traps and the majority are free-swimming tools that are propelled by the flow of the product in the pipeline. This is one of the advantages of ILI over some other inspection methods in that the product flow does not have to be interrupted to conduct the assessment.

4.42.7.1.1 MFL for corrosion

MFL tools detect defects by the application of a magnetic field in either the longitudinal or circumferential direction. As the tool travels through the pipeline, powerful permanent magnets magnetize the surrounding metal via wire brushes that contact the pipe wall. Sensors surrounding the circumference of the tool record the change in the magnetic field. This change in magnetic field can then be related to metal loss defect dimensions, using algorithms developed from test runs in pipes with machined defects of known dimensions. It is important to note therefore that the tools using MFL technology do not make direct measurements of remaining wall thickness.

As already mentioned, the magnetic field can be orientated either in the axial direction, to detect corrosion with a larger circumferential aspect ratio, or in the circumferential direction, to detect corrosion with more of a longitudinal extent. Examples of longitudinal corrosion would include internal sweet corrosion caused by water drop out or external axially extended corrosion caused by loss of coating adhesion around the longitudinal seam weld.

MFL tools can be used to inspect both liquid and gas pipelines and can discriminate between internal and external corrosion. The accuracy of sizing of the defects is dependent on the geometry of the features and the resolution of the tool.

4.42.7.1.2 Ultrasonic wall thickness measurement (USWM)

USWM tools are based on a system that uses the ultrasound echo time technique to measure the remaining wall thickness of pipes by sending an ultrasonic beam at 90° through the pipe wall. The inspection tool has a number of ultrasonic sensors mounted in a carrier and orientated such that they provide maximum coverage of the pipe wall. The sensors act as both transmitters and receivers of the ultrasound. Once the ultrasound leaves the sensor, it is reflected from both the inner and outer surfaces of the pipe wall (Figure 11). If there is a defect in the pipeline, then the ultrasound will be reflected from the defect and the time between the sound leaving and returning to the sensor is a direct measurement of the remaining wall thickness at that location. The difference in the stand-off distance (i.e., the distance between the sensor and the pipe wall) at the location of the defect indicates whether the corrosion is internal or external. USWM can also detect HIC cracking in pipelines where the HIC is running parallel to the pipe wall. For example, in the illustration in Figure 10, ultrasound traveling at 90° to the pipe wall will be reflected by the HIC.

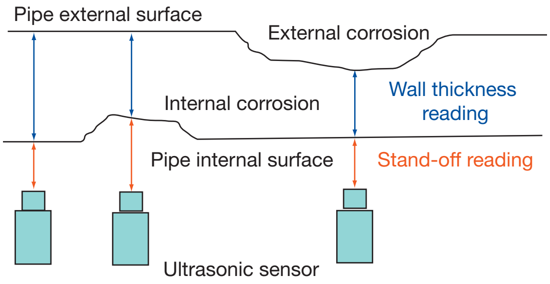

Figure 11 Principle of operation of USWM.

One of the main limitations of ultrasonic inspection tools is that that they can only be used in liquid pipelines as a liquid couplant is required between the sensor and the pipe wall to allow the ultrasound to travel into the pipe wall. If ultrasonic ILI is to be conducted in a gas pipeline, then the tool must be run in a liquid slug.

4.42.7.1.3 ILI for crack detection

Although the ILI tools described earlier can detect metal loss features and a limited amount of cracking, in order to identify SCC and certain types of sour cracking, a separate crack detection inspection must be undertaken.

For liquid pipelines, ultrasonic crack detection (USCD) is the most appropriate tool. The principle of the inspection is similar to USWM except that the pulses of ultrasound emitted by the tool are directed circumferentially into the pipe wall at an angle that generates 45° shear-waves within the metal. The angle of incidence means that the beam is reflected and diffracted from axially aligned cracking.

For gas pipelines, using the USCD tool would require the inspection tool to be run in a liquid slug. Therefore, the most appropriate inspection tool for gas pipelines uses electromagnetic acoustic technology (EMAT). EMAT allows ultrasound to be generated in a steel pipe wall without the requirement for a liquid couplant to transfer the ultrasound into the steel. A magnetic field is established in the pipe wall using magnets. A coil carrying AC current at 90° to the magnetic field produces eddy currents in the pipe wall. A force normal to the pipe wall is exerted on the eddy currents, which generates ultrasound traveling through the pipe wall.

4.42.7.1.4 Benefits of in-line inspection

The main benefit of ILI is that no interruption to the flow of product is required to inspect the pipeline and it is possible to obtain data for the entire length of the pipeline. Besides providing information on the defect sizes, an ILI inspection will also allow patterns of corrosion activity to be identified that assist in the diagnosis of the corrosion problem. For example, a clustering of external corrosion features around girth welds could highlight a problem with the girth weld coating. If this information was combined with above-ground survey data that indicated that there were no defects in the coating and that the CP was adequately protecting the pipeline, then this pattern could further indicate that there was a potential disbonding problem with the coating. Another benefit of ILI is that corrosion growth studies can be conducted using the data from two inspection runs and comparing the sizes of defects between the two data sets. This type of analysis allows corrosion rates to be calculated for internal and external corrosion features at different locations along the pipeline.

4.42.7.2 Hydrotesting

It is a requirement of commissioning that all pipelines undergo a hydrotest at a pressure above the maximum allowable operating pressure prior to entering service. The major aim of the pressure test is to prove the integrity of the pipeline by deliberately testing to a pressure higher than the operating pressure. As a result, all defects large enough to cause failure during service are removed. The test pressure and the duration of the test are specified in pipeline design codes and are dependent on the product and the location of the pipeline. It is also possible to conduct a hydrotest during the operating life of the pipeline with the same aim, to remove defects that would fail at the operating pressure.

There are several factors that have to be considered before selecting a hydrotest as the optimum method for assessing the integrity of the pipeline. Firstly, the pipeline has to be taken out of service and filled with water, which can be a time-consuming and costly process. If not properly removed, the hydrotest water can also cause internal corrosion and therefore it is imperative that the pipeline is properly dried following the test. Another drawback of this test is that the criterion for determining whether the pipeline is safe is pipeline failure. For buried onshore pipelines, locating the leaking defect and repairing it is not an inexpensive or trivial task. Finally, the hydrotest will only identify those defects that were unacceptable on the day of the test. For time-dependent defects, such as corrosion or SCC, the test interval has to be selected such that defects that pass the test will not grow to an unacceptable size prior to the next test.

4.42.7.3 Direct Assessment

Direct assessment is defined in ASME B31.8S[18] as “an integrity assessment method utilizing a structured process through which the operator is able to integrate knowledge of the physical characteristics and operating history of a pipeline system or segment with the results of inspection, examination, and evaluation in order to determine the integrity.” Currently, this standard allows direct assessment methods to be used to assess the pipeline integrity with respect to external corrosion (ECDA), internal corrosion (ICDA), or stress corrosion cracking (SCCDA).

In practice, direct assessment involves remotely identifying or predicting the locations along the pipeline where the risk of damage from a particular threat is high. Depending on the threat, this identification can utilize techniques such as above-ground corrosion monitoring (see Sections 4.42.4.2.5 and 4.42.4.2.15), hydraulic analysis, predictive models, and operator experience. Direct field measurements are then made at the high-risk locations by excavating the pipeline at these sites and using standard non-destructive inspection techniques such as visual examination, magnetic particle flaw detection, and ultrasonic inspection to size and assess the damage. These results are then fed back into the assessment procedure to determine whether further sites require excavation, to assess the integrity of the pipeline and to set the reinspection interval for the next direct assessment.

If an operator is to apply the direct assessment process, he/she has to develop a direct assessment plan, the requirements of which are dependent on the threat being addressed. Obviously, the highest resolution direct assessment that can be achieved is to excavate an entire pipeline segment and apply direct examination techniques, but this would also be extremely costly and in some cases impractical. However, direct assessment approaches do allow the pipeline operator to draw conclusions regarding the integrity of the pipeline from a limited number of excavations and supporting data (e.g., above-ground survey data, predictive models) for the remainder of the pipeline that is not excavated.

Direct assessment principally finds application for both liquid and gas pipelines that are uninspectable by ILI or where the supply of product cannot be interrupted to conduct a hydrotest or to allow pipeline modification for internal inspection.

4.42.7.3.1 External corrosion direct assessment (ECDA)

The objective of direct assessment for external corrosion is to locate areas along the pipeline where the coating has become damaged and the CP system is not effective, that is, areas where active external corrosion could be occurring. The process is conducted in four stages: preassessment, indirect examination, direct examination, and postassessment.

The first stage is essentially confirming that ECDA is feasible for the pipeline and selecting appropriate above-ground methods for locating areas of corrosion damage. For example, it was described in **Section 4.42.4.2.13** how above-ground methods cannot be used in locations where disbonded coatings result in electrical shielding of the pipeline. In these locations, alternative methods of pipeline assessment must be used and these must be defined in the preassessment stage. In the indirect examination, the pipeline is inspected at least twice using two above-ground survey techniques, for example, a CIPS survey can be used to locate regions of underprotection in the CP and a DCVG survey could locate regions of coating damage. The reason that two complementary techniques are used is to ensure that the strengths of one tool compensate for the limitations of another. The results of these two surveys are then aligned to identify regions where the CP and/or the coating are failing. These areas would then be classified and the most severe areas would be subjected to direct examination by exposing the pipeline.

During the direct examination stage, measurements are taken of the pipeline environment and CP, the coating, the corrosion dimensions, and the extent of cracking (if any). These measurements allow assessments to be made regarding the corrosion cause, the fitness-for-purpose of the defect, and the corrosion rate. One of the key requirements of this stage is to validate the classification that has been given on the basis of the indirect examination (i.e., minor, moderate or severe). The number of digs required by the standard is dependent on the results of the direct examinations relative to the initial classification. Finally the postassessment stage defines the reassessment intervals and assesses the overall effectiveness of the ECDA process, particularly with respect to the predictions made in the preassessment stage.

4.42.7.3.2 Internal corrosion direct assessment (ICDA)

Similar to ECDA, the purpose of ICDA is to identify areas where internal corrosion is occurring or has occurred along a pipeline. Currently, the procedure as defined in ASME B31.8S[18] is only applicable to gas pipelines that normally operate dry but may suffer from an upset that allows water to enter the pipeline. The principle of ICDA is based on the assumption that water will first settle at the low points in the pipeline or at locations where the angle of inclination is exceeded for specific gas flow velocities. If examinations are made at these points and no corrosion is detected, then it can be assumed that the remaining lengths of the pipeline will not be corroded.

As with ECDA, there is a preassessment that determines whether the method is appropriate for the pipeline. The identification of the direct examination sites is achieved by conducting flow calculations taking into account information on the route topography of the pipeline. At points where internal corrosion could occur, ultrasonic measurements are taken on the excavated pipe to determine the remaining wall thickness. The requirement for conducting further examinations is based on the results of the direct examinations.

4.42.7.3.3 Stress corrosion cracking direct assessment (SCCDA)

The procedure for conducting SCCDA is outlined in the NACE document RP0204[38] and follows a similar methodology to that previously described for ECDA, that is, preassessment, indirect examination, direct examination, and postassessment.

The preassessment stage of the SCCDA procedure determines whether the whole pipeline or a section of a pipeline is susceptible to SCC using the factors described in **Section 4.42.6.2** for high-pH SCC and removing the temperature criterion for the assessment of near-neutral pH SCC. NACE RP0204[38] also contains guidance regarding more detailed information that could be collected about the pipe material, the construction of the pipeline, the environment, corrosion control, and operation of the pipeline that could indicate an increased susceptibility to SCC. If a section of a pipeline is found to be susceptible, then further investigation has to be made, by hydrotesting, ILI, or by direct assessment.

In this respect, SCCDA may act as complimentary methodology to ILI or hydrotesting rather than as a replacement for these techniques. The indirect examination step involves many of the techniques used in ECDA such as CIPS and DCVG as well as additional surveys (e.g., soil characterization) to provide supplementary information and to identify sites for direct examination.

Direct examination not only allows the relevant data to be collected to assess the SCC threat but also provides an opportunity for the external and internal corrosion threats to be investigated at the same time. It is therefore good practice, not only to conduct nondestructive examination to determine the size, type, and extent of cracking, but also to collect data on, for example, the coating condition, the nature of deposits on the pipe surface, the presence of microbes, the remaining wall thickness, etc., which will also inform the evaluation of the internal and external corrosion threat. The information collected during the direct examination stage is used to assess the integrity of the pipeline at the excavated sites and also to determine whether further sites require excavation, or whether an alternative inspection methodology, such as ILI, may be more appropriate. As with ECDA, the final step is a postassessment stage where the success of the process is reviewed and appropriate reinspection intervals are set.

4.42.8 Pipeline Corrosion Management: Overview

Returning to the pipeline integrity management process introduced in Figure 3, the focus of this chapter has principally been on Steps 1 and 2 in this process, the threat identification and inspection processes. This has included a description of the factors that contribute to the threats of external and internal corrosion and SCC on land-based transmission and gathering pipelines and the appropriate inspection techniques to locate and size these defects. However, reference to Figure 3 indicates that this is only part of the continuing process of pipeline integrity management.

Once corrosion or cracking defects have been located and sized on a pipeline, whether by an in-line inspection or by direct assessment technique, the defects need to be assessed to determine whether they pose a threat to the continued operation of the pipeline under the operating stresses. The factors that control how and when a pipeline failure will occur due to corrosion are the size, shape and orientation of the corrosion, the applied stress, and the properties of the pipe material (strength and toughness). Corrosion and crack assessment techniques for pipelines are included in codes such as ASME B31.G[39] modified ASME B31.G and RSTRENG[40] and DNV-RP-F101,[41] BS7910,[42] and API 579.[43] As with all assessment methods, care must be taken to ensure that the method being used is appropriate and within the validated limits of the data and the readers are referred to the code document for specific application.

If the defect is assessed as being unacceptable for continued operation, then either the pressure in the pipeline can be reduced to attain a stress level in the pipe where the defect is acceptable or the defect can be repaired. There are a number of permanent pipeline repair solutions available in the market that can be applied while the pipeline is still operational. However, in severe situations, the pipeline operator may choose to replace the section of pipe containing the defect. Obviously this is one of the most expensive pipeline repair options.

The next stage in the management cycle of Figure 3 is prevention and mitigation. This is an extremely important step in the control of corrosion and requires the corrosion engineer to be able to accurately diagnose the type of corrosion that is occurring in order that the correct mitigation actions can be implemented. Inspection data, particularly from ILI tools, can play a very important role in this diagnosis as the location and pattern of corrosion will indicate the likely mechanism of corrosion damage.

Once all the data from the risk assessment, inspection, assessment, and analysis has been collected and recorded, the cycle begins again. This illustrates the final critical point regarding pipeline corrosion management; it is not a once-for-all activity. In order to ensure that pipelines remain protected from the threat of corrosion and continue to be one of the safest modes of transport for hazardous liquid and gas products, corrosion management must be conducted on a regular and ongoing basis.

References

1. Mohitpour, M.; McManus, M.; Trefanenko, B. In *IPC2002*, Proceedings of the 4th International Pipeline Conference, Calgary, Canada, Sept 30–Oct 3 2002; American Society of Mechanical Engineers: New York, 2002; pp 1493–1501.
2. *PHMSA Pipeline Safety Program: Distribution and Transmission Annual Mileage Totals*, Pipeline and Hazard Materials Safety Administration, 2007; Available from http://www.phmsa.dot.gov/.

3. Koch, G. H.; Brongers, M. P. H.; Thompson, N. G.; Virmani, Y. P.; Payer, J. H. Corrosion Cost & Prevention Strategies in the US, Report No. FHWA-RD-01–156, Federal Highway Administration, September 30, 2001.
4. Thompson, N. G. Corrosion Cost & Prevention Strategies in the US – Appendix E – Gas and Liquid Transmission Pipelines, Report No. FHWA-RD-01–156, Federal Highway Administration, September 30, 2001.
5. *PHMSA Pipeline Safety Program: Pipeline Safety Incident Reports*, Pipeline and Hazard Materials Safety Administration, 2007, Available from http://www.phmsa.dot.gov/.
6. Davis, P. M.; Dubois, J.; Olcese, A.; Uhlig, F.; Larivé, J.-F.; Martin, D. E. Performance of European Cross-Country Oil Pipelines: Statistical summary of reported spillages – 2004, CONCAWE, 2006.
7. EGIG Gas Pipeline Incidents: 6th Report of the European Gas Incident Data Group, 2005.
8. PSR 1996 The Pipelines Safety Regulations 1996 – Statutory Instrument 1996 No. 825, The Stationery Office Limited, 1996.
9. Browne, D.; Hicks, R. UKOPA Pipeline Fault Database – Pipeline Product Loss Incidents (1962–2004), UKOPA Fault Database Management Group, 2005.
10. Lyons, D. Western European Cross Country Oil Pipelines 30 Year Performance Statistics, CONCAWE, Report No. 01/02 2002.
11. Trench, C. J. The U.S. Oil Pipeline Industry's Safety Performance; Allegro Energy Consulting, 2003.
12. Pipeline Safety: The Office of Pipeline Safety is changing how it oversees the pipeline industry, United States General Accounting Office GAO/RCED-00–128, 2000.
13. Pipeline Accident Report NTSB/PAR-03/01 Natural Gas Pipeline Rupture and Fire Near Carlsbad, New Mexico, August 19, 2000, National Transport Safety Board, 2003.
14. 49CFR192 Pipeline Safety: Pipeline Integrity Management in High Consequence Areas (Gas Transmission Pipeline), Final Rule, Department of Transportation, December 15 2003.
15. 49CFR195 Pipeline Safety: Pipeline Integrity Management in High Consequence Areas (Hazardous Liquid Operators With 500 or More Miles of Pipeline), Final Rule, Department of Transportation, December 1 2000.
16. IGE/TD1/1. *Steel Pipelines for High Pressure Gas Transmission*, 4th ed.; Institute of Gas Engineers, 2001.
17. Muhlbauer, W. K. *Pipeline Risk Management Manual – Ideas, Techniques and Resources*, 3rd ed.; Elsevier: Burlington, 2004.
18. ASME B31.8S. *Managing System Integrity of Gas Pipelines*; American Society of Mechanical Engineers: New York , 2004.
19. Simon-Thomas, M. J. J.; Prager, L. H.; Voermans, C. V. M.; Pots, B. P.; Rippon, I. J. In Corrosion 2002, Denver, Colorado, April 7–12 2002; NACE International: Houston, Texas, 2002, Paper no. 02075.
20. Peabody, A. W. *Control of Pipeline Corrosion*, 2nd ed.; NACE International: Houston, Texas, 2001.
21. Race, J. M.; Dawson, S. J.; Stanley, L. M.; Kariyawasam, S. *J. Pipeline Eng.* **2007**, *6*(1), 13–29.
22. NACE RP0169:2002 Control of External Corrosion on Underground or Submerged Metallic Piping Systems; NACE: Houston, Texas, 2002, Item no. 21001.
23. Jack, T. R.; Wilmott, M. J.; Sutherby, R. L.; Worthingham, R. G. *Mater. Perf.* **1996**, *35*(3), 18–24.
24. Pope, D. H.; Morris, E. A., III *Mater. Perf.* **1995**, *34*(5), 23–28.
25. Hanson, H. R.; Smart, J. In Corrosion 2004, New Orleans, Louisiana, December 7–9 2004; NACE International: Houston, Texas, 2004, Paper no. 04209.
26. ISO 15589–1:2003 Petroleum and Natural Gas Industries – Cathodic Protection of Pipeline Transportation Systems – Part 1: On Land Pipelines, International Organization for Standardization, 2003.
27. prEN 14919–1:2004 Petroleum and Natural Gas Industries – Cathodic Protection of Pipeline Transportation Systems - Part 1: On-land pipelines (ISO 15589–1:2003 modified), European Committee for Standardization, 2004.
28. De Waard, C.; Milliams, D. E. *Corrosion* **1975**, *31*(5), 177–181.
29. Schmitt, G.; Hörstemeier, M. In Corrosion 2006, San Diego, California, March 12–16 2006; NACE International: Houston, Texas, 2006, Paper no. 06112.
30. Ikeda, A.; Ueda, M.; Mukai, S. In Corrosion 85, Boston, USA, March 25–29 1985. NACE International: Houston, Texas, 1985; pp 1–29.
31. Brown, B.; Lee, K.-L.; Nesic, S. In Corrosion 2003, San Diego, USA, March 16–21 2003; NACE International: Houston, Texas, 2003, Paper no. 03341.
32. NACE MR0175/ISO 15156–2 Petroleum and natural gas industries – Materials for use in H_2S-containing environments in oil and gas production – Part 2: Cracking-resistant carbon and low alloy steels, and the use of cast irons; NACE/ANSI/ISO: Houston, Texas, 2003.
33. EFC 3. *The Use of Corrosion Inhibitors in Oil and Gas Production*, Palmer, J. W., Hedges, W., Dawson, J. L., Eds.; European Federation of Corrosion Publications: Maney, London, 2004.
34. Vieth, P. H.; Roytman, I.; Mesloh, R. E.; Kiefner, J. F. In Analysis of DOT Reportable Incidents for Gas Transmissions and Gathering Pipelines 1985 through 1994, PRC International Catalog No. L51745, May 31, 1996.
35. Kiefner, J. F.; Kiefner, B. A.; Vieth, P. H. In Analysis of DOT Reportable Incidents for Hazardous Liquid Pipelines – 1986 through 1996; The American Petroleum Institute: Washington, January 7, 1999.
36. Krishnamurthy, R. M.; MacDonald, R. W.; Marreck, P. M. In IPC-96, Proceedings of the First International Pipeline Conference, Calgary, Canada, June 9–13 1996; American Society of Mechanical Engineers: New York, 1996; pp 495–506.
37. Sutherby, R. L. In *IPC-98*, Proceedings of Second International Pipeline Conference, Calgary, Canada, June 7–11 1998; American Society of Mechanical Engineers, 1998; pp 493–503.
38. NACE RP0204–2004. Stress Corrosion Cracking (SCC) Direct Assessment Methodology, ANSI/NACE Standard; NACE: Houston, Texas, 2004, Item no. 21104.
39. ASME B31.G. Manual for Determining the Remaining Strength of Corroded Pipelines, Supplement to ASME B31 Code for Pressure Piping, ANSI/ASME B31G-1991; American Society of Mechanical Engineers: New York, USA, 1991.
40. Kiefner, J. F.; Vieth, P. H. A Modified Criterion for Evaluating the Remaining Strength of Corroded Pipe (with RStreng), AGA Catalog No. L51609, PR3–805; American Gas Association, 1989.
41. DNV-RP-F101 Corroded Pipelines; Det Norske Veritas, October, 2006.
42. BS 7910:2005. Guide to methods for assessing the acceptability of flaws in metallic structures, BS 7910:2005; British Standards Institute, 2005.
43. API Recommended Practice 579. *Fitness for Service*, 1st ed.; American Petroleum Institute, January 2000.
44. NACE RP0502. Standard Recommended Practice, Pipeline External Corrosion Direct Assessment Methodology; NACE: Houston, Texas, 2002, Item no. 21097.

Tables

This list of tables has been reproduced from the previous edition of Shreir's Corrosion but has not been checked for accuracy against current data sources.

Table 21.2 Physical Properties of some metals and alloys

	Thermal conductivity ($W\,m^{-1}\,K^{-1}$; 273–373 K)	*Thermal expansion per kelvin (K^{-1})*	*Elect. resistivity ($\mu\Omega\,m$)[a]*	*Temp. coef. of res. per kelvin (in range 273–373 K) (K^{-1})*	*Mean specific heat in range 273–373 K ($J\,kg^{-1}\,K^{-1}$)*	*Young's modulus ($MN\,m^{-2}$ or MPa)[b]*
Ag	418.400	18.9×10^{-6}	0.016	4.1×10^{-3}	225.936	0.07584×10^{6}
Al	221.752	23.5×10^{-6}	0.0269	4.2×10^{-3}	916.296	0.06894×10^{6}
Be	221.752	13.0×10^{-6}	0.04–0.06	6.0×10^{-3}	2012.504	0.29647×10^{6}
Co	69.036	12.3×10^{-6}	0.0624	6.0×10^{-3}	435.136	0.20684×10^{6}
Cu	393.296	16.5×10^{-6}	0.01673	4.3×10^{-3}	384.928	0.11031×10^{6}
Mg	153.553	27.0×10^{-6}	0.0440	4.2×10^{-3}	1037.632	0.04481×10^{6}
Mn	–	22.0×10^{-6}	1.60(α)	–	489.528	0.15857×10^{6}
Mo	142.256	5.1×10^{-6}	0.0570	4.6×10^{-3}	259.408	0.29647×10^{6}
Nb	52.300	7.2×10^{-6}	0.169	3.95×10^{-3}	255.224	0.10342×10^{6}
Ni	92.048	12.8×10^{-6}	0.0684	6.8×10^{-3}	451.872	0.20684×10^{6}
Pb	34.309	29.0×10^{-6}	0.206	3.36×10^{-3}	129.704	0.01378×10^{6}
Pd	70.291	11.7×10^{-6}	0.108	3.8×10^{-3}	246.856	0.11721×10^{6}
Pt	69.036	9.0×10^{-6}	0.106	3.92×10^{-3}	133.888	0.15168×10^{6}
Sn (white)	62.760	23.5×10^{-6}	0.128	4.2×10^{-3}	225.936	0.04688×10^{6}
Ta	54.392	6.5×10^{-6}	0.145	3.8×10^{-3}	142.256	0.18615×10^{6}
Ti	17.029	8.4×10^{-6}	0.550	3.5×10^{-3}	527.184	0.11721×10^{6}
U	25.104–27.196	[c]	0.29(α)	3.4×10^{-3}	117.152	0.18960×10^{6}
V	30.962	8.3×10^{-6}	0.195	2.8×10^{-3}	497.896	0.13789×10^{6}
W	166.105	4.6×10^{-6}	0.055	4.6×10^{-3}	138.072	0.35852×10^{6}
Zn	110.876	31.0×10^{-6}	0.059	4.2×10^{-3}	393.296	0.09652×10^{6}
Zr	16.736	5.9×10^{-6}	0.446	4.4×10^{-3}	288.696	0.09307×10^{6}
Al alloys	167.360(±)	21.6×10^{-6}	0.035(+)	–	962.320	0.06895×10^{6}
Brass (70/30)	125.520	19.6×10^{-6}	0.062	1.5×10^{-3}	380.744	0.11032×10^{6}
Bronze (95/5)	86.680	18.0×10^{-6}	0.096	1.9×10^{-3}	376.560	0.11032×10^{6}
Monel (70/30)	25.104	14.4×10^{-6}	0.482	1.1×10^{-3}	543.920	0.17926×10^{6}
Fe-18Cr-8Ni stainless steel	14.644	9.5×10^{-6}	0.70	—	502.08	0.19305×10^{6}

[a] To convert into $\mu\Omega$cm multiply by 100.

[b] To convert into $KN\,cm^{-2}$ multiply by 10^{-1}.

[c] α-Uranium 23×10^{-6} parallel to *a*-axis; -3.5×10^{-6} parallel to *b*-axis; 17×10^{-6} parallel to *c*-axis; β-uranium 46×10^{-6} parallel to *c*-axis; 23×10^{-3} perpendicular to *c*-axis.

Table 21.6 Standard electrode potentials against the standard hydrogen electrode for inorganic systems at 25°C

Two tables:	Aqueous Acid solutions Aqueous Basic solutions

Table 21.7 Reference electrodes

Electrode	*Electrode equilibrium*	*Potential at 25°C (vs. S.H.E.; V)*			
Calomel (Hg/Hg_2Cl_2, Cl^-)	$Hg_2Cl_2 + 2e \rightleftharpoons 2Hg + 2Cl^-$	$E = 0.2677 - 0.0591 \log a_{Cl}^{-}$			
		Solution	$E_{calomel}$	$E_{calomel + liquid\ junction}$	Temp. coeff.
		0.1 mol dm^{-3} KCl	0.3337	0.336	-0.06 mV °C^{-1}
		1.0 mol dm^{-3} KCl	0.280	0.283	-0.24 mV °C^{-1}
		Sat. KCl	0.241	0.244	-0.65 mV °C^{-1}
Mercury/mercurous sulphate (Hg/$HgSO_4$, SO_4^{2-})	$HgSO_4 + 2e \rightleftharpoons Hg + SO_4^{2-}$	$E = 0.6151 - 0.0295 \log a_{NO_2}$			
Silver/silver chloride (Ag/AgCl, Cl^-)	$AgCl + e \rightleftharpoons Ag + Cl^-$	$E = 0.2224 - 0.0591 \log a_{Cl}$			
		Average temp. coeff. ≈ -0.6 mV °C^{-1}[a]			
		0.1 mol dm^{-3} KCl, $E = 0.2881$ V			
		1.0 mol dm^{-3} KCl, $E = 0.2224$ V			
		Sea-water $E = 0.250$ V			
Copper/copper sulphate (Cu/$CuSO_4$, Cu^{2+})	$Cu^{2+} + 2e \rightleftharpoons Cu$	$E = 0.340 + 0.0295 \log a_{Ca}^2$; for sat. $CuSO_4$, $E = 0.318$V; for practical electrodes $E = 0.30$V			
Quinhydrone	Quinone + H_2 $\rightleftharpoons$ hydroquinone	$E = E^* - 0.0591$ pH, and $E^* = 0.6990$ at 25 °C E^* contains a term due to diffusion potentials and is not a thermodynamic constant			
Antimony/antimony oxide (Sb/Sb_2O_3, H^+)	$Sb_2O_3 + 6H^+ + 6e \rightleftharpoons 2Sb + 3H_2O$	$E = 0.1445 - 0.0591$ pH			
Mercury/mercuric oxide (Hg/HgO, OH^-)	$HgO + 2H^+ + 2e \rightleftharpoons Hg + H_2O$	$E = 0.926 - 0.0591$ pH (for pH determinations in alkaline solution)			
Lead dioxide/lead sulphate (Pb/PbO_2/$PbSO_4$, SO_4^{2-})	$PbO_2 + 4H^+ + SO_4^{2-} + 2e \rightleftharpoons PbSO_4 + 2H_2O$	$E = 1.685 + 0.0295 \log 4m^3\gamma^3/\alpha^2$, where γ and α are the stoichiometric mean activity coefficient of sulphuric acid and the activity of water, respectively, at molality m of H_2SO_4			
		Solution	*E*		
		0.1 mol dm^{-3} H_2SO_4	+ 1.565		
		1.1 mol dm^{-3} H_2SO_4	+ 1.632		
		6.1 mol dm^{-3} H_2SO_4	+ 1.735		
Zn/$ZnSO_4$	$Zn^{2+} + 2e \rightleftharpoons Zn$	$E = -0.763 + 0.0295 \log a_{\gamma}^{2*}$			
Zn/sea-water	Mixed potentials approximating to $E^o_{M^{2+}/M}$	$E = -0.80$ V			
Zn/artificial sea-water	Mixed potentials approximating to $E^o_{M^{2+}/M}$	$E = -0.81$ V			
Cd/sea-water	Mixed potentials approximating to $E^o_{M^{2+}/M}$	$E = -0.52$ V			
Cd/artificial sea-water	Mixed potentials approximating to $E^o_{M^{2+}/M}$	$E = -0.54$ V			

[a] Variation of $E^o_{Ag/AgCl}$ with temperature:

Temp. (°C)	35	45	55	70	95	125	150	200
E'' (V)	0.21570	0.20828	0.20042	0.18782	0.1651	0.1330	0.1032	0.0348

Table 21.8 Galvanic series of some commercial metals and alloys in seawater

↑	Platinum
	Gold
	Graphite
Noble or cathodic	Titanium
	Silver
	Chlorimet 3 (62Ni–18Cr–18Mo) Hastelloy C (62Ni–17Cr–15Mo)
	18/8 Mo stainless steel (passive) 18/8 stainless steel (passive) Chromium stainless steel 11–30% Cr (passive)
	Inconel (passive) (Ni–13Cr–7Fe) Nickel (passive)
	Silver solder
	Monel (Ni–30Cu) Cupro-nickels (Cu–(10–40)Ni) Bronzes(Cu–Sn) Copper Brasses (Cu–Zn)
	Chlorimet 2 (66Ni–32Mo–1Fe) Hastelloy B (60Ni–30Mo–6Fe–1Mn)
	Inconel (active) Nickel (active)
	Tin
	Lead
	Lead–tin solders
	18/8 Mo stainless steel (active) 18/8 stainless steel (active)
	Ni-Resist (high nickel cast iron)
	Chromium stainless steel, 13% Cr (active)
	Cast iron Steel or iron
	2024 aluminum (Al–4.5Cu–1.5Mg–0.6Mn)
Active or anodic	Cadmium
↓	Commercially pure aluminum (1100)
	Zinc
	Magnesium and magnesium alloys

Table 21.11 Ionization constants of water and weak electrolytes and their variation with temperature

A. Ionization constants of water ($pK_w = -\log K_w$)

Temperature (°C)	$-\log K_w$	*Temperature (°C)*	$-\log K_w$
0	14.9435	35	13.6801
5	14.7338	40	13.5348
10	14.5346	45	13.3960
15	14.3463	50	13.2617
20	14.1669	55	13.1369
25	13.9965	60	13.0171
30	13.8330		

B. Ionization constants of weak electrolytes and their temperature variation $pK_\alpha = -\log K_\alpha = A_1/T - A_2 + A_3T$

Aqueous solution	pK_α *at 25°C*	A_1	A_2	A_3
Acetic acid	4.756	1170.48	3.1649	0.013399
Ammonium ion	9.245	2835.76	0.6322	0.001225
Benzoic acid	4.201	1590.2	6.394	0.01765
Boric acid	9.234	2237.94	3.305	0.016883
n-Butyric acid	4.820	1033.39	2.6215	0.013334
Carbonic acid K_1	6.352	3404.71	14.8435	0.032786
Carbonic acid K_2	10.329	2902.39	6.4980	0.02379
Chloroacetic acid	2.861	1049.05	5.0273	0.014654
Citric acid K_1	3.128	1255.6	4.5635	0.011673
Citric acid K_2	4.761	1585.2	5.4460	0.016399
Citric acid K_3	6.396	1814.9	6.3664	0.022389
Formic acid	3.752	1342.85	5.2743	0.015168
Glycine K_1	2.350	1332.17	5.8870	0.012643
Glycine K_2	9.780	2686.95	0.5103	0.004286
Lactic acid	3.860	1286.49	4.8607	0.014776
Malonic acid K_1	2.855	–	–	–
Malonic acid K_2	5.696	1703.31	6.5810	0.022014
Oxalic acid K_1	1.271	–	–	–
Oxalic acid K_2	4.266	1423.8	6.5007	0.020095
Phosphoric acid K_1	2.148	799.31	4.5535	0.013486
Phosphoric acid K_2	7.198	1979.5	5.3541	0.019840
o-Phthalic acid K_1	2.950	561.57	1.2843	0.007883
o-Phthalic acid K_2	5.408	2175.83	9.5508	0.025694
Succinic acid K_1	4.207	1206.25	3.3266	0.011697
Succinic acid K_2	5.638	1679.13	5.7043	0.019153
Sulphamic acid	0.988	3792.8	24.122	0.041544
Sulphanilic acid	3.227	1143.71	1.2979	0.002314
Tartaric acid K_1	3.033	1525.59	6.6558	0.015336
Tartaric acid K_2	4.366	1765.35	7.3015	0.019276
Trimethylammonium ion	9.800	541.4	−12.611	−0.015525

Note. All values are with reference to the molarity scale. Data for bases are expressed as acidic ionization constants, e.g. for ammonia we quote p*K* at 25°C = 9.245 for the ammonium ion

$$NH_4^+ + H_2O \rightarrow NH_3 + H_3O^+$$

The basic ionization constant of the reaction

$$NH_3 + H_2O \rightarrow NH_4^+ + OH$$

is obtained from the relation

$$pK_a(\text{acidic}) + pK_b(\text{basie}) = pK_w(\text{water})$$

pK_w (water) being 13.9965 at 25°C.

Table 21.12 Tafel constants for hydrogen evolution from aqueous solution. The Tafel equation for a cathodic reaction is $\eta_c = a - b \log_{10} i = b \log_{10} (i_0/i)$, where η_c is the overpotential (mV), i is the current density ($A\,cm^{-2}$) and i_0 is the exchange current density ($A\,cm^{-2}$)

Metal	*Electrolyte*		*Temp. (°C)*	*$-\log_{10} I$ range*	*$-a$ (mV)*	*b (mV)*	*$-\log_{10} i_0$ (i_0 in $A\,cm^{-2}$)*
Ag	0.001 N	HCl	20	6.0 to 2.0	810	125	6.5
	0.01 N	HCl	20	6.0 to 2.0	820	130	6.3
	0.1 N	HCl	20	6.0 to 3.3	570	90	6.3
	0.1 N	HCl	20	3.3 to 1.0	670	120	5.6
	1.0 N	HCl	20	6.0 to 2.3	320	60	5.4
	1.0 N	HCl	20	2.3 to 1.0	480	130	3.7
	5.0 N	HCl	20	6.0 to 2.8	470	70	6.7
	5.0 N	HCl	20	2.8 to −2	630	120	5.3
	7.0 N	HCl	20	6.0 to 3.4	640	90	7.1
	7.0 N	HCl	20	3.4 to 1.0	740	110	6.7
Al	2 N	H_2SO_4	25	3.0 to 0.7	1000	100	10.0
Au	0.001 N	HCl	20	7.0 to 2.0	524	72	7.32
	0.01 N	HCl	20	6.0 to 2.0	558	84	6.63
	0.1 N	HCl	20	6.6 to 3.0	468	71	6.59
	0.1 N	HCl	20	3.0 to 2.0	548	97	5.64
	0.001 N	NaOH	20	6.0 to 4.5	832	118	7.05
	0.01 N	NaOH	20	6.5 to 3.7	836	119	7.04
	0.1 N	NaOH	20	4.8 to 3.0	856	123	6.95
Be	1.0 N	HCl	20	3.0 to 1.3	1080	120	9.0
Bi	1.0 N	HCl	20	3.0 to 1.0	840	120	7.0
Cd	1.7 N	H_2SO_4	20	4.0 to 3.0	1450	120	12.1
	10 N	H_2SO_4	20	4.0 to 2.0	1400	120	11.7
Cu	0.001 N	HCl	20	5.0 to 3.3	802	122	6.61
	0.01 N	HCl	20	4.5 to 2.3	786	118	6.71
	0.1 N	HCl	20	5.0 to 2.5	790	117	6.76
	0.005 N	NaOH	16		890	139	6.40
	0.02 N	NaOH	16	6.0 to 3.7	710	114	6.29
	0.15 N	NaOH	16		690	117	5.99
Fe	0.001 N	HCl	20	4.0 to 3.8	787	127	6.19
	0.01 N	HCl	20	4.1 to 3.2	741	118	6.29
	1 N	HCl	16	3.0 to 0.0	770	130	5.9
	0.01 N	NaOH	20	4.5 to 3.8	776	117	6.62
	0.1 N	NaOH	20	4.1 to 3.2	726	120	6.06
	4.8 N	KOH	20	4.0 to 3.0	350	70	5.0
	10.5 N	KOH	20	4.0 to 3.0	340	70	4.9
Ga	0.2 N	H_2SO_4	87		800	120	6.7
Hg	0.001–0.1 N	HCl	20	7.0 to 1.0	1410	116	12.2
	1 N	HCl	20	6.0 to 2.5	1390	119	11.7
	3 N	HCl	20	6.0 to 2.5	1420	141	10.1
	5 N	HCl	20	6.0 to 2.5	1320	127	10.4
	7 N	HCl	20	6.0 to 2.5	1130	108	10.5
	10 N	HCl	20	6.0 to 2.5	1020	95	10.7
	0.1 N	H_2SO_4	20	6.0 to 2.5	1440	114	12.7
	0.25 N	H_2SO_4	20	6.5 to 3.0	1403	116	12.1
	5 N	H_2SO_4	20	6.5 to 3.0	1400	116	12.05
	0.1 N	LiOH	20	6.0 to 4.0	1598	102	15.7
Hg	0.2 N	LiOH	20	6.0 to 4.0	1545	100	15.5
	0.1 N	NaOH	20	6.0 to 4.0	1457	100	14.6
	0.2 N	NaOH	20	6.0 to 4.0	1405	97	14.5
	0.002 N	KOH	20	6.0 to 4.0	1682	98	17.1
	0.02 N	KOH	20	6.0 to 4.0	1545	90	17.3
	0.1 N	KOH	20	6.0 to 4.0	1430	93	15.4
	0.01 N	$Ba(OH)_2$	20	6.0 to 4.0	1170	45	26.0
	0.02 N	$Ba(OH)_2$	20	6.0 to 4.0	1220	65	18.8
	0.1 N DCl in D_2O		20	5.0 to 2.4	1485	119	12.19

Continued

Table 21.12 Continued

Metal	*Electrolyte*		*Temp. (°C)*	*$-\log_{10} I$ range*	*$-a$ (mV)*	*b (mV)*	*$-\log_{10} i_0$ (i_0 in $A\,cm^{-2}$)*
Mo	0.001 N	HCl	20	5.6 to 4.2	557	81	7.12
	0.01 N	HCl	20	5.2 to 3.7	543	76	7.19
	0.1 N	HCl	20	6.0 to 3.5	586	80	7.30
	0.1 N	HCl	20	3.5 to 2.0	671	104	6.45
	0.001 N	NaOH	20	5.9 to 4.4	667	92	7.27
	0.01 N	NaOH	20	4.9 to 3.6	664	103	6.42
	0.1 N	NaOH	20	4.7 to 3.7	641	87	7.35
	0.1 N	NaOH	20	3.6 to 2.1	739	116	6.37
Nb	1.0 N	HCl	20	3.0 to 1.0	900	80	11.0
Ni	0.000 04 N	HCl	20	6.0 to 5.0	650	100	6.5
	0.001 N	HCl	20	5.8 to 3.3	617	93	6.6
	0.01 N	HCl	20	5.5 to 3.3	611	91	6.7
	0.1 N	HCl	20	5.0 to 2.0	626	104	6.0
	1.0 N	HCl	20	4.3 to 2.0	594	109	5.4
	0.001 N	NaOH	20	6.8 to 4.8	720	103	7.0
	0.006 N	NaOH	20	6.3 to 3.8	660	101	6.6
	0.1 N	NaOH	20	6.0 to 3.0	650	101	6.4
Pb	0.1 N	HCl	20	5.8 to 2.5	1524	116	13.2
	1 N	HCl	20	5.8 to 2.5	1531	119	12.9
	3 N	HCl	20	5.1 to 2.5	1573	142	11.1
	5 N	HCl	20	4.9 to 2.5	1495	140	10.7
	7 N	HCl	20	4.7 to 2.5	1417	138	9.76
	10 N	HCl	20	4.6 to 2.0	1195	135	8.84
	0.1 N	H_2SO_4	20	7.0 to 2.5	1533	118	13.0
	1 N	H_2SO_4	20	6.5 to 2.0	1536	119	12.9
	8 N	H_2SO_4	20	5.9 to 2.0	1530	120	12.8
	15 N	H_2SO_4	20	5.3 to 2.0	1469	121	12.1
	20 N	H_2SO_4	20	5.0 to 2.0	1411	119	11.9
	1 N	HBr	20	5.3 to 2.3	1484	116	12.7
	3 N	HBr	20	5.1 to 2.3	1467	123	11.9
	6 N	HBr	20	4.7 to 2.3	1377	130	10.6
	8.5 N	HBr	20	4.3 to 2.3	1285	140	9.17
	1 N	$HClO_4$	20	4.8 to 1.6	1537	118	13.0
	3 N	$HClO_4$	20	4.8 to 1.6	1517	118	12.8
	7 N	$HClO_4$	20	4.8 to 1.6	1504	121	12.4
	9 N	$HClO_4$	20	4.8 to 1.6	1453	122	11.9
	11.6 N	$HClO_4$	20	4.8 to 1.6	1446	132	11.0
Pd	1.0 N	H_2SO_4	20	3.0 to 2.0	240	80	3.0
	0.01 N	HCl	20	3.9 to 3.1	447	107	4.18
	0.1 N	HCl	20	2.9 to 1.4	321	99	3.25
	0.001 N	NaOH	20	5.0 to 3.9	589	100	5.88
	0.01 N	NaOH	20	5.4 to 4.0	610	110	5.56
	0.1 N	NaOH	20	4.1 to 3.1	637	125	5.01
Pt	0.5 N	HCl	25	2.0 to 0.7	73	28	2.6
Rh	0.01 N	HCl	20	3.4 to 3.1	209	55	3.80
	0.01 N	NaOH	20	4.2 to 3.5	551	119	4.64
Sb	2 N	H_2SO_4	20	3.0 to 0	900	100	9.0
Sn	1 N	HCl	20	3.0 to 0	1100	140	8.0
Ta	1 N	HCl	20	3.0 to 1.0	550	120	4.6
W	5 N	HCl	20	2.0 to −2.0	550	110	5.0

Note that η will always be negative.

Table 21.13 Exchange current densities i_o for the hydrogen evolution reaction

Metal	*$-\log i_0$ (A cm^{-2}) in approx. 1 mol dm^{-3} H_2SO_4*
Palladium	3.0
Platinum	3.1
Rhodium	3.6
Iridium	3.7
Nickel	5.2
Gold	5.4
Tungsten	5.9
Niobium	6.8
Titanium	8.2
Cadmium	10.8
Manganese	10.9
Thallium	11.0
Lead	12.0
Mercury	12.3

After Bockris, J. O'M.; Reddy, A. K. N. *Modern Electochemisty*, Macdonald. 1970.

Table 21.14 Exchange current densities and transfer coefficients α for evolution of gases at 20–25 °C at different anodes

Gas	*Metal*	*Solution*[a]	α	*i_0 (A cm^{-2})*
O_2	Au	0.1 mol dm^{-3} NaOH	0.74–1.2	5×10^{-13}
	Pt	0.5 mol dm^{-3} H_2SO_4	0.45	$10^{-8} - 10^{-11}$
	Pt	HNO_3 + NaOH pH 0.5–14	0.51	$0.6\text{–}1 \times 10^{-10}$
	Pt	Phosphate buffer pH 6.8	0.29	
	Pt	0.1 mol dm^{-3} NaOH	0.81	4×10^{-13}
	PbO_2	0.5 mol dm^{-3} H_2SO_4	0.50	
		1.0 mol dm^{-3} KOH	0.50	
Cl_2	Pt	1.0 mol dm^{-3} HCl	0.48	5×10^{-3}
	Pt	Various solutions	0.5–0.7	10^{-3}
	Ir	1.0 mol dm^{-3}	0.73	4×10^{-5}
	PbO_2	0.5–2 mol dm^{-3} NaCl	0.17–0.27	10^{-7}
Br_2	Ir	1 mol dm^{-3} HBr	0.6	3×10^{-3}
	Pt	1 N KBr	0.5–0.7	3×10^{-3}
N_2	Pt	1.0 mol dm^{-3} NaN_3	0.98	10^{-76}
	Ir	1.0 mol dm^{-3} NaN_3	1.0	10^{-75}
	Pd	1.0 mol dm^{-3} NaN_3	1.1	10^{-81}

Data after Parsons *Handbook of Electrochemical Constants*; Butterworths: London, 1959.

Table 21.19 Solubility of gases in water

		Temperature of water (θ, °C)							
		0	*10*	*15*	*20*	*30*	*40*	*50*	*60*
Ammonia	S	1130	870	770	680	530	400	290	200
Argon	A	0.054	0.041	0.035	0.032	0.028	0.025	0.024	0.023
Carbon dioxide	A	1.676	1.163	0.988	0.848	0.652	0.518	0.424	0.360
Carbon monoxide	A	0.035	0.028	0.025	0.023	0.020	0.018	0.016	0.015
Chlorine	S	4.61	3.09	2.63	2.26	1.77	1.41	1.20	1.01
Helium	A	0.0098	0.0091	0.0089	0.0086	0.0084	0.0084	0.0086	0.0090
Hydrogen	A	0.0214	0.0195	0.0188	0.0182	0.0170	0.0164	0.0161	0.0160
Hydrogen sulfide	A	4.53	3.28	2.86	2.51	1.97	1.62	1.37	1.18
Hydrochloric acid	S	512	475	458	442	412	385	362	339
Nitrogen	A	0.0230	0.0183	0.0165	0.0152	0.0133	0.0119	0.0108	0.0100
Nitrous oxide	A	–	0.88	0.74	0.63	–	–	–	–
Nitric oxide	A	0.071	0.055	0.049	0.046	0.039	0.034	0.031	0.029
Oxygen	A	0.047	0.037	0.033	0.030	0.026	0.022	0.020	0.019
Sulfur oxide	S	79.8	56.6	47.3	39.4	27.2	18.8	–	–

Values of A for 20 °C for other rare gases are: Ne, 0.0101; Kr, 0.0594; Xe, 0.126. S indicates the number of m^3 of gas measured at 0 °C and 101.325 kN m^{-2} which dissolve in 1 m^3 of water at the temperature stated, and when the pressure of the gas plus that of the water vapor is 101.325 kN m^{-2}. A indicates the same quantity except that the gas itself is at the uniform pressure of 101.325 kN m^{-2} when in equilibrium with water.

Table 21.21 Oxygen dissolved in seawater (ppm) in equilibrium at 1 atm (101.325 kPa) of air saturated with water vapor

Parts per million					
Chlorinity (‰)	0	5	10	15	20
Salinity (‰)	0	9.06	18.08	27.11	36.11
Temperature (°C)					
0	14.62[a]	13.70	12.78	11.89	11.00
5	12.79	12.02	11.24	10.49	9.74
10	11.32	10.66	10.01	9.37	8.72
15	10.16	9.67	9.02	8.46	7.92
20	9.19	8.70	8.21	7.77	7.23
25	8.39	7.93	7.48	7.04	6.57
30	7.67	7.25	6.80	6.41	5.37

Note: the table gives the quantity of oxygen dissolved in sea-water at different temperatures and chlorinities when in equilibrium with a normal atmosphere saturated with water vapor. It thus represents the condition approached by the surface water when biological activity is not excessive.

[a] The values of solubility in water of zero chlorinity differ slightly from those for freshwater.

Table 21.22 Saturated solubilities of atmospheric gases in seawater at various temperatures

Gas	*Chlorinity (‰)*	*Temperature (°C)*	*Concentration*	
			ml l^{-1}	*ppm*
Oxygen	0	0	49.2[a]	70.4
		12	36.8	52.5
		24	29.4	42.1
	16	0	40.1	56.0
		12	30.6	42.9
		24	24.8	34.8
	20	0	38.0	52.8
		12	29.1	40.4
		24	23.6	32.9
Nitrogen	0	0	23.0[a]	28.8
		12	17.8	22.7
		24	14.6	18.3
	16	0	15.0	18.4
		12	11.6	14.2
		24	9.36	11.5
	20	0	14.2	17.3
		12	11.0	13.4
		24	8.96	10.9
Carbon dioxide[b]	0	0	1715[a]	3370
		12	1118	2198
		24	782	1541
	16	0	1489	2860
		12	980	1888
		24	695	1342
	20	0	1438	2746
		12	947	1814
		24	677	1299

[a] These values differ slightly from those for freshwater.
[b] Includes CO_2 present as H_2CO_3 but not as HCO_3^- or CO_3^{2-}.
Note: Atmospheric gases are present in seawater in approximately the following quantities:

	ml 1^{-1}	*Parts per million*
Oxygen	0–9	0–12
Nitrogen	8–15	10–18
Carbon dioxide[a]	33–56	64–107
Argon	0.2–0.4	0.4–0.7
Helium and neon	1.7×10^{-4}	0.3×10^{-4}[b]

[a] Includes CO_2 present as H_2CO_3, HCO_3^- and CO_3^{2-}
[b] Estimated as helium
Concentrations of oxygen, nitrogen and carbon dioxide in equilibrium with 1 atm (101.325 kPa) of designated gas.

Table 21.23 Properties of sea-water of different salinities

Salinity (‰)	*Freezing point (°C)*	*Temperature of maximum density*	*Osmotic pressure (atm)*	*Specific heat (J kg^{-1})*
0	0.00	3.95	0	4.184×10^3
5	−0.27	2.93	3.23	4.109×10^3
10	−0.53	1.86	6.44	4.050×10^3
15	−0.80	0.77	9.69	4.008×10^3
20	−1.07	−0.31	12.98	3.979×10^3
25	−1.35	−1.40	16.32	3.954×10^3
30	−1.63	−2.47	19.67	3.929×10^3
35	−1.91	−3.52	23.12	3.899×10^3
40	−2.20	−4.54	26.59	3.874×10^3

Table 21.25 Soil resistivities and corrosiveness

Range of resistivity (Ω cm)[a]	*Location*	*Soil type and classification*
10 000–100 000 and above	Perth, Scotland	Comparatively noncorrosive. Red sand-stone
8000–10 000	West Durham	Mildly corrosive. Sandstone and shale
Varying 1000–20 000	Staffordshire	Many built-up areas. Possibly very corrosive
1000–1500	Eastbourne, Sussex	Marshy ground. Very corrosive
15 000–20 000	Sussex Downs	Chalk. Non-corrosive
750–1500	Port Clarence, S.E. Durham	Salt marsh. Very corrosive
600–1500	S. Essex	Essex clay. Very corrosive
1400–3200	Newport, Gwent	Grey, yellow and blue clays, Corrosive
12 000–15 000	North Devon	Millstone grit. Comparatively non-corrosive
1000–2500	Gloucester	Generally clay. Corrosive
25 000–250 000	West Hampshire	Sandy gravel. Not generally corrosive

[a] To obtain Ω m divide by 100.

Table 21.27 Corrosion-rate conversion factors

Multiply	*by*	*To obtain*
Milligrams per square decimetre per day ($mg\,dm^{-2}\,day^{-1}$ or mdd)	10	Grams per square metre per day ($g\,m^{-2}\,day^{-1}$ or gmd)
Inches per year (in $year^{-1}$ or ipy)	25.4	Millimetres per year ($mm\,year^{-1}$ or mpy)
Milligrams per square decimetre per day (mdd)	$0.00144/\rho$ (ρ in $g\,cm^{-3}$)	Inches per year (ipy)
Milligrams per square decimetre per day (mdd)	$0.036\,52/\rho$ (ρ in $g\,cm^{-3}$)	Millimetres per year (mpy)
Grams per square metre per day (gmd)	$0.365\,25/\rho$ (ρ in $g\,cm^{-3}$)	Millimetres per year (mpy)
Grams per square inch per hour	372 000	Milligrams per square decimetre per day ($mg\,dm^{-2}\,day^{-1}$)
Grams per square metre per year	0.0274	Milligrams per square decimetre per day ($mg\,dm^{-2}\,day^{-1}$)
Milligrams per square decimetre	0.0003277	Ounces per square foot ($oz\,ft^{-2}$)
Milligrams per square decimetre per day	0.00000269	Grams per square inch per hour ($g\,in^{-2}\,h^{-1}$)
Milligrams per square decimetre per day	36.5	Grams per square metre per ($g\,m^{-2}\,year^{-1}$)
Milligrams per square decimetre per day	0.00748	Pounds per square foot per year ($lb\,ft^{-2}\,year^{-1}$)
Ounces per square foot	3052	Milligrams per square decimetre ($mg\,dm^{-2}$)
Pounds per square foot per year	133.8	Milligrams per square decimetre per day ($mg\,dm^{-2}\,day^{-1}$)
Grams per square metre per day	$0.36525/\rho$ (ρ in $g\,cm^{-3}$)	Millimetres per year ($mm\,year^{-1}$)
Grams per square metre per day	$365.25/\rho$ (ρ in $kg\,m^{-3}$)	Millimetres per year ($mm\,year^{-1}$)

Table 21.28 Calculation of Corrosion rates of metals

The corrosion rate of a metal in terms of weight loss per unit area ($\mathrm{g\,m^{-2}\,day^{-1}}$) or rate of penetration ($\mathrm{mm\,year^{-1}}$) can be calculated from Faraday's law if the current density is known. Conversely, the corrosion current density can be evaluated from the weight loss per unit area or from the rate of penetration. The following symbols and units have been adopted in deriving these relationships in which it is assumed that corrosion is uniform and the rate is linear:

m = Mass of metal corroded (g)
M = Molar mass ($\mathrm{g\,mol^{-1}}$)
z = Number of electrons involved in one act of the corrosion reaction
F = Faraday's constant, 96 487 C ($1\ \mathrm{A} = 1\ \mathrm{C\,s^{-1}}$)
I = Current (A)
i = Current density ($\mathrm{A\,cm^{-2}}$) and $i = I/S$
t = Time (s)
ρ = Density of metal ($\mathrm{g\,cm^{-3}}$)
S = Area of metal involved ($\mathrm{cm^2}$)
d = Thickness of metal removed (cm)

From Faraday's law the weight loss per unit area is

$$\frac{m}{S} = \frac{Mit}{zF}\,(\mathrm{g\,cm^{-2}}) \qquad [21.1]$$

Since $m = \rho Sd$, then from eqn [21.1]

$$\rho Sd = \frac{MiSt}{zF} \text{ or } \rho d = \frac{Mit}{zF} \qquad [21.2]$$

and from eqn [21.2] the rate of penetration d/t when I is in $\mathrm{A\,cm^{-2}}$ is given by

$$\frac{d}{t} = \frac{Mi}{\rho zF}\,(\mathrm{cm\,s^{-1}}) \qquad [21.3]$$

If the c.d. i' is in $\mathrm{mA\,cm^{-2}}$, d in mm, and t in years, then

$$\frac{d}{t} = \frac{10^{-1}}{365 \times 24 \times 60 \times 60} = \frac{Mi'}{\rho zF} \times 10^{-3}\,(\mathrm{mm\ year^{-1}})$$

$$\therefore \frac{\mathrm{d}}{\mathrm{t}} = 3.2706\,\frac{\mathrm{M}i'}{z\rho}\,(\mathrm{mm\ year^{-1}}) \qquad [21.4]$$

To convert rate of penetration into weight loss per unit area per unit time:

$$(\mathrm{gm^{-2}\ day^{-1}}) \times \frac{0.36525}{\rho} = (\mathrm{mm\ year^{-1}})$$

To convert c.d. ($\mathrm{mA\,cm^{-2}}$) into gmd:

$$(\mathrm{gm^{-2}\ day^{-1}}) = 3.2706\,\frac{Mi'}{z\rho} \times \frac{\rho}{0.36525} = 8.954\,\frac{Mi'}{z} \qquad [21.5]$$

If i'' is the current density in $\mathrm{\mu A\,cm^{-2}}$

$$(\mathrm{gm^{-2}\ d^{-1}}) = 8.954\,\frac{Mi''}{z} \times 10^{-3} \qquad [21.6]$$

Relevant Websites

Properties and Designations of Materials: www.matweb.com
Table of the Elements and Their Properties: www.webelements.com
International Standards Organisation: www.iso.org
National Institute for Standards and Technology: www.nist.gov

4.43 Preservation of Metallic Cultural Heritage

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Glossary

Conservation Preservation of cultural heritage.

Dense corrosion product layer (DPL) The corrosion layer on archaeological iron objects that approximates to the original shape of the metal lost.

Interventive conservation Preservation strategy that involves physical or chemical change to an object.

Marker layer The layer of corrosion that approximates to the original position of the metal surface.

Preventive conservation Preservation strategy that utilizes techniques that do not involve physical or chemical change to an object.

Abbreviations

BTA	Benzoriazole
CD	Current density
CSS	Confederate Southern States
DPL	Dense corrosion product layer
EDX	Energy dispersive X-ray analysis
EIS	Electrochemical impedance spectroscopy
HMS	Her Majesty's Ship
RH	Relative humidity
SEM	Scanning electron microscope
XRD	X-ray diffraction

Symbols

E_{corr}	Corrosion potential (volts)
w/w	Ratio of weights

4.43.1 Introduction to Conservation of Metals

4.43.1.1 Cultural Heritage Context

Cultural heritage is an industry that significantly contributes to the economy of nations via tourism, employment, and taxation. Whole communities rely on it for their economic welfare. Cultural objects and structures document developments and events within a society, offering a bridge to the past and providing important markers for individuals, religions, and cultures. To continue their contribution to the welfare, stability, development, and understanding of societies, cultural objects must be actively preserved. Age, origin, and use mean that historical, archaeological, industrial, and art objects are often decayed, corroded, and prone to further deterioration. The diversity of contexts from which cultural heritage metals originate presents a significant preservation challenge. This chapter briefly defines conservation and provides an insight into the goals and ethical constructs that underpin its decision-making rationale. This is followed by an overview of how corrosion processes relate to treatment design and assessment. Conservation strategies for metals are revealed using selected examples of treatments to illustrate conservation research and practice.

Metals conservation involves the preservation of cultural objects and conservators are its practitioners. Their goal is to preserve objects while retaining evidence of their cultural context and integrity. Ideally there should be minimum change to an object while achieving this and restoration to the former state is rarely carried out. Refinishing, replacement of parts and repairing of metal objects with new corrosion-resistant materials are not normally options within the conservation process. While preservation appears to be a straightforward material science problem, involving elucidation of the structure and corrosion of metals to develop conservation procedures that prevent or control corrosion, it is constrained by ethics, aesthetics, and cultural contexts that may complicate, constrain, and ultimately direct preservation strategies.[1] The goal of conservation is normally the preservation of an object using minimum intervention, although in some instances arguments for partial or total restoration are valid and professional guidelines aid rationalization here.[1]

Research into the corrosion and conservation of historic and archaeological metals is developing significantly due to the increasing contribution of dedicated specialists and funding of large collaborative research programs that have a specific focus[2,3] and the challenges of large complex objects. An influx of corrosion scientists has improved the methodology of research and the understanding of conservation methods by widespread introduction of electrochemistry into corrosion and treatment studies.[2–4] As conservation is a blend of art and science, it utilizes data and publications generated by many disciplines to devise its preservation strategies. Literature sources within conservation focus mainly on conference proceedings and research project publications dedicated to specific themes that provide discussion forums for developing, interpreting, and reporting metallic corrosion and the conservation process. Metals conferences are organized and published by national conservation groups, museums, universities, and the International

Council for Museums Committee for Conservation Metals Working Group (ICOM-CC Metals WG). The Triennial Conference Proceedings of the ICOM-CC Metals WG provide the main dissemination route for metals corrosion and treatment research. This is supplemented by a web-based newsletter Bulletin of Research on Metals Conservation (BROMEC).[5] There are few textbooks that either specifically address metals conservation or contain significant sections dedicated to it.[6–8] A number of conservation journals report metals conservation and amongst these are *Studies in Conservation* and *Reviews in Conservation* published by the International Institute of Conservation; *Journal of the American Institute for Conservation*; *The Conservator* (Journal of the Institute of Conservation); and the German *Arbeitsblater fur Restauraten.*

4.43.1.2 Conservation: Definitions and Rationale

4.43.1.2.1 Conservation rationale

Conservation of metals can be broadly split into interventive methods, which involve adding or removing something from an object in order to preserve it, and preventive techniques that aim to prevent corrosion by controlling the environment.[1,9] Both approaches require an understanding of the physical and chemical structure of metals, their interaction with environmental variables and the properties of their corrosion products. This information is used to design safe storage environments and to develop, implement, and assess interventive treatments. Conservation does not have its own universally defined preservation standards and generally works towards goals generated to satisfy prevailing situations.

4.43.1.2.2 Preservation goals

The ultimate conservation goal of indefinite preservation has driven conservation rationale for many years. Stabilization is a much used word in conservation literature and a reassessment of its meaning and context are long overdue. Since few metals are inherently stable in ambient conditions, corrosion prevention for metals and alloys requires some degree of environmental control.[9] Depending on the degree of control required, significant capital outlay and ongoing energy consumption may be called for. This will carry a carbon footprint and may be beyond the financial means of many museums. Qualitative and quantitative control of environmental parameters, backed by relevant research to identify the environmental needs of the metals in question, underpins the concept of preventive conservation. Unstable metals are merely prevented from corroding using environmental control and they remain inherently unstable. Since they have not been stabilized by an interventive treatment, any changes to the environment could once again favor their decay. This minimalist approach to preservation is now much favored in conservation practice. Previously, environmental control was normally employed as the end point of an interventive process focused on enhancing the chemical and physical stability of an object by attempts to remove corrosion accelerators and apply coatings and inhibitors. Interventive treatments should only be used where there is evidence that they enhance the stability and lifespan of an object without contravening ethical guidelines.[1]

Preservation strategies should be designed to support the role and function of the object in a society. This may involve public accessibility, which will require provision of oxygen, light, and heat. All of these are agencies of decay that can contribute to corrosion. Access to metal objects may mean it is necessary to accept the concept of limited lifespan, although this will depend on the metal in question and its condition. Alternatively, never viewing an unstable metal object while knowing it is preserved in deoxygenated storage may be an acceptable preservation strategy if the mere knowledge of its existence is sufficient for it to fulfill its cultural role. This may be the case for iconic objects that form cultural cornerstones within societies and history timelines.

4.43.1.2.3 Standards in conservation

Few defined preservation and test standards exist within conservation at the time of writing (2008). The concept of indefinite preservation still pervades conservation thinking for metals. A move towards a rationale that pragmatically measures conservation outcomes as a function of resources, treatment success, cost, and object context is required to facilitate the defining goals that can be used to create standards. To produce attainable standards requires research that provides quantitative evidence of the success of treatment. Within metals conservation there is currently limited quantitative data that could be translated into hard currencies of object longevity, stability, and survival.

Standards grow from attainable and reproducible quantified outcomes. Gaps in our understanding of corrosion processes, treatment mechanisms, and treatment success hinder the production of conservation standards. There is a need for more research that definitively identifies corrosion mechanisms, quantifies treatments and measures their success relative to defined goals. International agreement on what constitutes realistic treatment success is required, as is a recognized body that defines or approves standards with the support of the conservation profession. Thus, if a standard does not prevent decay there must be an indication as to the extent to which it protects from corrosion or prolongs lifespan. This requires a definition of lifespan reliant upon identifying the function of a cultural object and defining when it ceases to fulfill this function. These are difficult questions but until they are answered conservation cannot develop models that quantitatively define goals and offer a framework of standards to achieve them. There is a case for the conservation profession to devise its own standards for use in research and quality assurance, as ISO and ASTM standards are often inappropriate for use in conservation research and practice.

4.43.1.2.4 Ethics

Ethics both guide and constrain conservation practice. National guidelines define generic rules for good practice that include minimum intervention with objects, reversibility of conservation materials and of treatments applied to cultural objects, as well as retention of the cultural integrity of an object and the information it contains.[1] Situation ethics prevail when determining the level of intervention required to preserve objects. Within archaeological conservation, significant intervention is normally essential for understanding the technology and function of a metal object or for revealing its shape from a corroded metal conglomerate. Ethical dilemmas abound when devising treatment procedures. While a blistering paint surface on a working engine comprising cast iron and steel might be removed and the surface repainted to approved international standards, accessioning such an object into a museum changes this and the paint now constitutes part of the object history. An ethical preservation process for such an object might involve the local stabilization treatment of pits in the paint layer, followed by application of an unobtrusive protective coating and storage in a controlled relative humidity. This is more expensive to execute and offers a less predictive corrosion control strategy than stripping the metal to an SA standard and repainting.

4.43.2 Corrosion

4.43.2.1 The Influence of Corrosion on Conservation Strategies

The nature and extent of corrosion strongly influences conservation strategies. Understanding how metals corrode within specified environments such as museum interiors, enclosed storage boxes and the atmosphere is central to developing treatments and identifying realistic conservation goals. It may be necessary to understand more than one corrosion model to devise conservation procedures. For instance, understanding how archaeological metals corrode during burial is essential for developing a model of their corrosion in the atmosphere following excavation. Equally, elucidating the corrosion mechanisms on a historical pewter salt cellar facilitates an understanding of how this object corrodes in a museum environment. It may no longer contain salt, but the legacy of its original function influences its future survival. Corrosion models also contribute to understanding object aesthetics and developing conservation ethics. Research into corrosion mechanisms informs conservators about the stability of objects, their rate of decay and their conservation needs.[2]

4.43.2.2 Corrosion of Archaeological Metals

Although reviews of archaeological and historical metal corrosion exist,[10] aspects of corrosion relevant to the treatments discussed here are briefly outlined. Archaeological metals normally corrode extensively during burial to form corrosion products related to their burial environment and alloy composition.[2,6,7,9,10] Environment, alloy composition and the mechanisms of ionic and electron transfer during corrosion dictate the nature of the corrosion layer formed and whether corrosion products are passive or unstable. Smooth dense patinas or voluminous disfiguring corrosion layers may form. Some corrosion layers can retain good approximation of the shape of the object and surface details like wear marks or engraving[2,6,7,9,10] (see **Figure 1**). These layers have been loosely referred to as representing the original surface of the object[2,7] but are now more often called marker layers.[2] They are often hard and compact and may be overlaid with softer more voluminous corrosion.

Conservation is not just about preservation. Archaeological metals are subjected to investigative conservation that involves analysis designed to answer questions on technology, provenance, and trade.[1,7] Mechanical cleaning employing hand tools like scalpels and micro air abrasion techniques, which utilize powders such as aluminum oxide, are often employed to remove overlying corrosion to reveal the marker layer. Guidance in this process is helped by X-radiography. By detecting differences in density juxtaposition of differing corrosion products are shown, along with dissimilar metals, technological detail and evidence of residual metal[7] (see Figure 2). This information-sensitive marker layer may be physically weak and infused with soluble corrosion accelerators, but it must remain undamaged by any treatment, whether it has been revealed or is left covered with corrosion products. Chemical treatments that strip off all corrosion products to remove the soluble corrosion accelerators they contain cannot be used to treat archaeological metals, as the remaining metal rarely represents the original shape of the object[7] (see Figure 3).

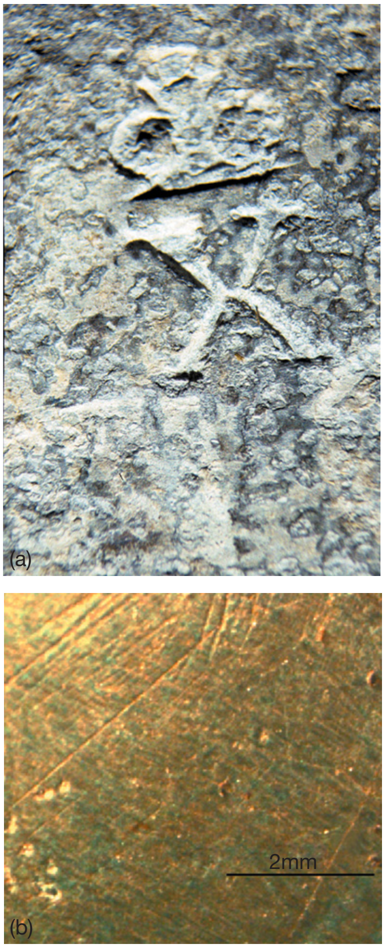

Figure 1 Corrosion products can sometimes retain significant surface detail. Lead and tin corrosion products record an assay mark in an archaeological pewter object (a) and a Roman copper alloy stud retains wear mark scratches in its fine smooth patina (b).

Post-excavation corrosion processes usually differ from those occurring in the burial environment, as the atmosphere contains more oxygen and is normally less damp than soil.[2,10] To develop a preservation plan it is essential to understand how the corrosion model changes, especially how corrosion products form in the burial environment, respond to the new environment and influence the metal they are associated with.

The instability of archaeological iron offers a clear example of how an understanding of corrosion mechanisms is essential to treatment design. It is used here to illustrate conservation thought processes for metals containing soluble corrosion accelerators. During burial, chloride is attracted to anodes as a counter ion to balance charge from Fe^{2+}.[2,10] In damp burial conditions it exists as a Fe^{2+}/Cl^- solution at the metal surface. Chloride content may be typically 0.1–1.5 wt % of object, but can be significantly greater for marine metals[7,10–12] Soluble chloride acts as an electrolyte making the iron inherently unstable. Overlying the corroding metal core is a dense corrosion product layer (DPL) identified as comprising a goethite (α-FeOOH) or sometimes a siderite ($FeCO_3$) matrix in which are embedded magnetite (Fe_3O_4) or maghemite (γ-Fe_2O_3) strips[2] (see Figure 3). This is effectively the marker layer for the surface of the object and is also present in totally mineralized objects, which present no ongoing corrosion problem, but remain a conservation problem due to their fragility and the need to reveal their original shape.

Moisture and oxygen in the post-excavation environment facilitates the formation of β-FeOOH

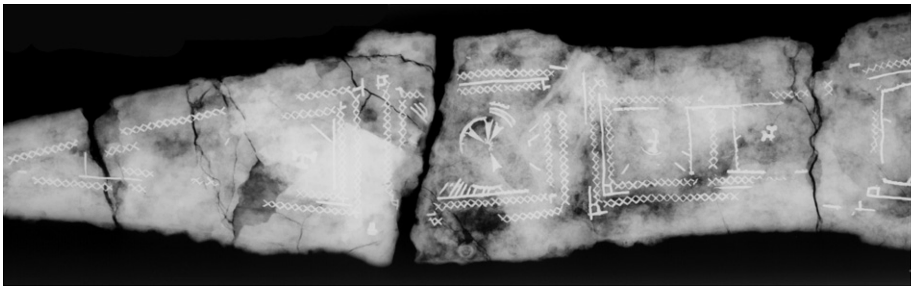

Figure 2 X-radiography records the presence of a dissimilar metal inlay (silver) hidden under corrosion of uneven density on this Roman Scabbard. The density distribution on the radiograph indicates that no metallic iron remains.

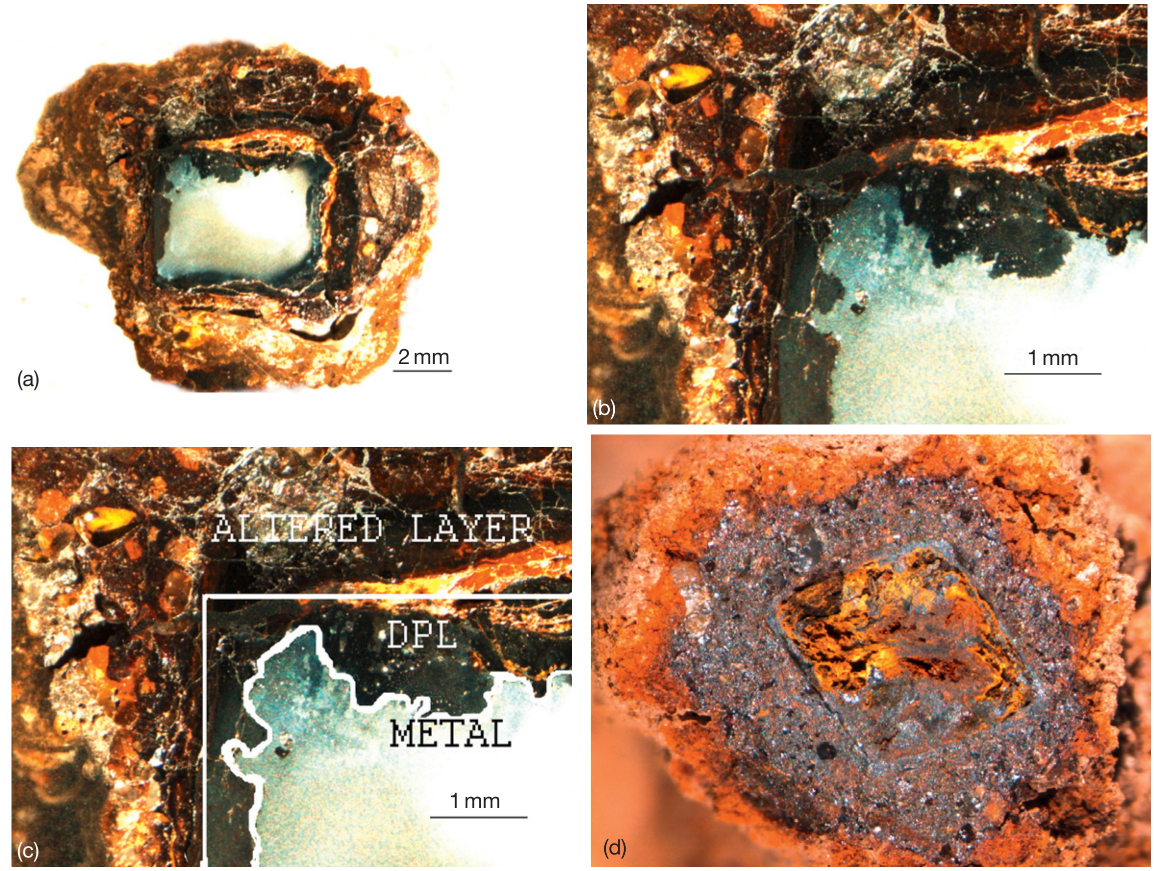

Figure 3 A cross section of a medieval nail shows it retains a substantial metal core and differing corrosion layers (a). Images (b) and (c) show how the dense corrosion product layer (DPL) retains the shape of the nail, which is overlaid with a corrosion matrix containing soil. Stripping the nail of all corrosion would lose the shape of the object and its surface detail. Totally mineralized iron retains the shape of the object as a corrosion layer, visible in this Roman nail (d).

(akaganeite) in the acidic chloride rich solution sited at anodes on the metal surface. Chloride is incorporated into tunnels within the hollandite-type β-FeOOH crystal structure and adsorbed onto its surface.[2,10] Growth of these voluminous tower-like β-FeOOH crystals pushes off the overlying DPL and is catastrophic for the object as an information resource, as it destroys evidence of the original surface and shape leaving only an unevenly corroded metal core (see Figure 4). While conservation strategies aim to reveal the shape of the object they must also prevent the corrosion of metallic iron, as the consequent formation of β-FeOOH would remove the information retaining DPL. Totally mineralized iron is stable, as there is no more metal to oxidize and this has allowed soluble anodically held chloride to diffuse out of the object.

Figure 4 Corrosion at the metal/DPL interface results in loss of overlying corrosion products and the information they contain.

Corrosion of nonferrous archaeological metals presents different conservation problems. Most are alloyed with other metals as; bronze (copper/tin sometimes with added lead); brass (copper/zinc); pewter (lead/tin); and precious metals (silver/gold, silver/copper, gold/copper). This facilitates preferential corrosion.[7,10] Thus, gold may lose the copper it is alloyed with and be covered in copper corrosion products. Chemically removing these copper corrosion products leaves a soft porous copper depleted layer of gold on the surface of the alloy. Mechanical removal of corrosion leaves copper corrosion products embedded in the metal surface alongside the gold, but produces a stronger surface.

Corrosion processes, products, and rates can vary according to the proportions of metal within alloys and the burial conditions. This can prove advantageous, although bronzes often decuprify the corrosion of alloyed tin, producing an insoluble and poorly mobile tin oxide to act as a marker layer for the original surface of the metal.[2] Lead forms very stable lead carbonates in neutral to alkaline burial conditions and insoluble chloride compounds that are stable following excavation.[9] Silver is also stable after excavation due to the highly insoluble silver chloride and silver sulfide formed on its surface.[10,13] Lead and tin have similar corrosion potentials and both corrode in pewter to produce a lamellar wart-infested surface with powdery corrosion products that are unlikely to form marker layers. Copper that forms sparingly soluble cuprous chloride (CuCl) next to the metal surface can be unstable following excavation if there is sufficient water to hydrolyze it to voluminous Cu_2OH_3Cl known as 'bronze disease.'[2,6,7,8,10] Conservation procedures will be dictated by the stability of the corroded metals, corrosion mechanisms, and the presence or absence of marker layers.

4.43.2.3 Corrosion of Historical and Modern Metals

Historical metals are found in outdoor and indoor environments and may be decorative objects d'art, functional artifacts, or large industrial items. Metals kept indoors since their fabrication may have very little corrosion and retain their original surface finish. Conservation aims to retain such surfaces. This can be achieved by monitoring environments, simple good housekeeping and environmental control in relation to corrosion threshold values for the metals in question.[1,9,14]

The context of the object is important and the nature of a corrosion patina (see Section 4.43.5.2) may be seen as an important aesthetic value of the object or part of its life history. This will dictate whether it is removed or retained during conservation and heavily influences the choice and success of treatments. Analysis aids decision making in conservation. Sometimes it may be necessary to replace metals if they are performing a structural function. Analysis detected dezincification of brass (70:30) in nails used to join the planks in the hull of the yacht Asgard (see Figure 5). Built in 1905 by Colin Archer the renowned Norwegian shipwright for Robert Erskine Chalders the yacht is now an important part of Irish history. The analysis provided information that aided conservation decisions for nails that otherwise appeared to have only surface corrosion.

Modern metals increasingly occur in museum collections and are the fabrication materials of many cultural icons and monuments. These include zinc, aluminum, magnesium, and their alloys.[15] Conservation of protective and technologically informative surface finishes on metals like aluminum may be equally as important as preserving the metal itself.[16] Air quality, relative humidity, and temperature are important for metal stability within museums. The Oddy test[17] was devised to determine if materials used to construct boxes and showcases give off gas pollutants that will cause metals within them to corrode over long-time periods. It can also be applied to show if metals and

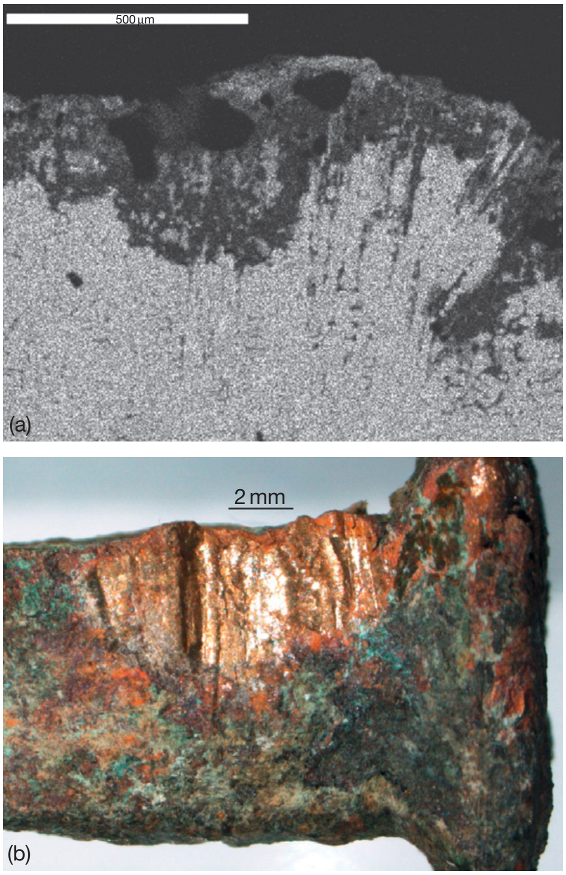

Figure 5 SEM/EDX mapping of zinc brass hull nails from the yacht Asgard revealed surface dezincification (a) which is not visible on the nail (b). This analysis contributed to designing the yacht's conservation plan carried out at the National Museum of Ireland. (SEM scale bar 500 μm).

alloys corrode in polluted environments, thus aluminum and Duralmin (Al/Cu) corrode in the presence of formic acid and magnesium and AZ31 (Mg/Al/Mn/Zn alloy) corrode in the presence of a wide range of materials that include oak, plywood, formic acid and wool, which may all be found in museum environments.[15] Lead and copper are also susceptible to corrosion from carbonyl pollutants.[2,9,10,18] Equally studies must examine what occurs when objects are handled, as chloride corrosion products on zinc coins and Indian Bidri ware (zinc alloy) in museum collections were attributed to handling.[15] The influence of handling on corrosion is evident for tarnishing of silver by sulfur compounds, where fingerprints can act as a focus for corrosion (**Figure 6**). Conservation has moved some way towards developing standards for showcase design and the use of corrosion-safe construction materials, but much more remains to be done.

Outdoor corrosion patterns on metals are predominantly influenced by alloy composition, environment, climate, and the object morphology.[19] Out of doors iron produces a corrosion layer mostly comprised of loose α FeOOH rather than form the shape retaining DPL that occurs on archaeological objects[2] (see **Figure 3**). Sulfurous gases can produce a $FeSO_4$ corrosion cycle that is humidity sensitive. While conservation of iron that has corroded in the atmosphere may involve removal of corrosion layers, rather than their retention, outdoor copper alloys may develop patinas considered to be aesthetically desirable and conservation planning takes account of this[2,6] (see **Section 4.43.5.2**). Humid air containing SO_2 will attack copper alloys dissolving passive layers and supporting electrochemical corrosion of the alloy,[19] which is problematic for statuary and architectural fittings. Establishing the precise role of patinas and corrosion product layers in the corrosion process is currently underway for many metals,[2] which will facilitate better long-term planning and improve treatment design.

Figure 6 The influence of a fingerprint on the pattern of sulfur tarnishing on this silver surface is clearly visible. A protective coating on the surface would have prevented this.

4.43.3 Environmental Control of Corrosion: Preventive Conservation

4.43.3.1 Desiccation

A common preservation strategy for cultural metals is to prevent their electrolytic corrosion by controlling one of the agencies essential for this process to occur. Normally, removal of moisture is used to prevent electrolyte formation, although in some instances the oxygen necessary to support cathodic processes and form corrosion products is removed. Removal of electrolyte ions from corroded metals involves interventive treatment. It is easier, cheaper, and more user friendly to control corrosion by desiccation than to remove oxygen. The degree of desiccation necessary to prevent corrosion differs according to the corrosion mechanism of the particular metal or alloy and dictates the cost of corrosion control as capital outlay on plant, fuel, and personnel. Despite the importance of understanding corrosion mechanisms for optimizing preventive conservation strategy, only chloride infested iron has been extensively researched to identify relative humidity (RH) no-corrosion thresholds for reactions within its corrosion mechanism.

4.43.3.1.1 Relative humidity – Threshold corrosion values

Ambient humidity can supply moisture to solvate ions within corroded metals and create electrolytes. Conservation of metals examines corrosion as a function of RH rather than absolute humidity.[6,8,10,14] It is well known that hygroscopic or deliquescent salts such as sodium chloride can lower the RH threshold for corrosion to occur.[10] The RH at which the formation of electrolytes begins is the threshold corrosion value.[20] On corroded iron the surface adsorbed chloride on hygroscopic β-FeOOH becomes mobile within atmospheric moisture and corrodes iron in contact with it at 15% RH[20] (see **Figure 7**). Additionally, ferrous chloride may form in the low pH and high Fe^{2+}/Cl^{-} environment created as damp chloride infested iron, dries[10] (see **Figure 8**). Any $FeCl_2 \cdot 4H_2O$ that forms contains enough water to corrode iron in contact with it, but once $FeCl_2 \cdot 2H_2O$ forms at 20%, RH corrosion ceases[20] (see **Figure 7**). Storage standards

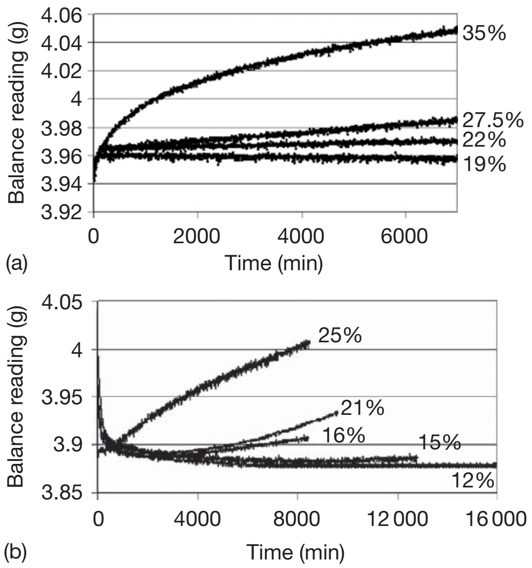

Figure 7 Relative humidity influences the corrosion of iron powder mixed with $FeCl_2 \cdot 2H_2O$ (image 1) and βFeOOH (image 2); with no-corrosion points at low humidity and significant corrosion as 30% relative humidity is approached, as shown by weight gain due to oxidation. Initial weight loss (b) is due to dehydration of βFeOOH as it equilibrates with its environment.

for chloride infested iron at 20 °C have been defined as: at 12% RH no corrosion; 15–20% RH β-FeOOH causes slow corrosion of iron; above 21% RH both β-FeOOH and $FeCl_2 \cdot 4H_2O$ contribute to corrosion[20] (see **Figure 7**). Corrosion increases significantly above 25%[19–21] and several times faster above 30% RH than at 25%.[20,21]

In contrast controlled storage of corroded iron from historical contexts has received scant attention in conservation research, as it will tolerate higher humidity values before incurring corrosion if it is chloride free. No conservation studies have examined how iron contaminated with sulfates from SO_2 pollution would respond to RH.

Corrosion of archaeological copper alloys can occur when cuprous chloride (CuCl) close to the metal surface hydrolyses to form basic cupric chloride (Cu_2OH_3Cl) polymorphs, usually clinoatacamite or atacamite with an accompanying molar volume increase.[6] This pressures or undermines the overlying hard and dense corrosion layers that predominantly comprise malachite ($CuCO_3 \cdot Cu(OH)_2$), breaking their contact with the $CuCl/Cu_2O$ mixture next to the metal and ultimately causing their exfoliation. Scott[6] observed no reaction over the relative humidity range 42–46% but rapid corrosion at 70%, leading him to recommend storage below 45% relative humidity in contrast to the anecdotal 39% commonly cited in conservation. The CuCl/Cu corrosion model merits closer scrutiny to define both the critical no-corrosion humidity and corrosion rates above this value.

Unless it has been already corroded by aggressive ions such as chloride and sulfate, aluminum offers minimal conservation challenges provided it is stored at around 55% relative humidity.[16] Reaction of chloride infested aluminum alloys to relative humidity has not been examined in relation to safe storage thresholds. Similarly, the role of soluble tin chlorides in the corrosion of tin and tin alloys merits detailed study, since tin chloride solutions are prone to hydrolysis.

4.43.3.1.2 Practical humidity control

Humidity control either employs active dehumidification using mechanical plant or passive desiccation using desiccants like silica gel to control environment in fixed storage or display areas.[9,14,21–23] A significant advantage of controlling corrosion of cultural metals by desiccation is that they remain easily accessible, especially if an entire store room is desiccated as opposed to individual storage boxes. Although maintaining low humidity using mechanical desiccation plant demands finance and energy, it is capable of controlling large spaces that will require only one or two telemetric sensors to monitor relative humidity. These can immediately and remotely detect any failure to maintain target relative humidity on a macroscale, which allows for rapid remedial response. Thus mechanical corrosion control is a low risk corrosion control strategy for cultural metals, provided resources exist to underpin its continuing operation and management.

In contrast the small scale control of climate by silica gel for storage within enclosed polyethylene boxes and for display in sealed showcases appears to offer a cheap conservation strategy for small metal objects. Gradual hydration of the desiccated silica gel will occur as a function of air exchange rate, external relative humidity and initial moisture content of the metals being desiccated.[21–24] This eventually raises internal humidity within the controlled space to values that support corrosion, which will speed up as internal relative humidity continues to rise until it equilibrates with the external environment. The metals now rest in a continually aggressive environment. Determining when to replace the silica gel relies upon knowing the threshold corrosion value of the metals in question and detecting when the interior of the box exceeds this value.

Research to evaluate the complex equation of storage, hardware performance, air exchange, monitoring, maintenance time, and human error is needed

Figure 8 Brunel's iconic SS Great Britain was the first ocean going screw driven iron hulled passenger liner and is now preserved by a mechanical desiccation system that maintains relative humidity to 20% and allows visitors to walk around the hull. Reproduced from Watkinson, D.; Tanner, M.; Turner, R.; Lewis, M. *The Conservator* **2005**, *29*, 73–86.[25]

to offer a realistic and practical assessment of this corrosion control strategy. Enclosure design largely controls air exchange rate which is the governing factor in passive desiccation systems.[24] Assessment of enclosure performance can produce predictive life spans for specified passive desiccation storage systems.[21,24,26] Showcases designed for desiccation maintained relative humidity below 20% for 1 year without a change of their silica gel desiccant, when external relative humidity fluctuated between 60% and 95%.[22,24] As telemetric monitoring of showcase performance is easy to initiate and financially viable, this system offers potentially reliable low energy consumption corrosion control for unstable metals on display. The major cost will be an initial outlay to meet the showcase specification. Further work could establish performance of the showcase with age and use. This requires real-time testing that may take several years. Attempting to define long-term effectiveness by extrapolating a one year study or short-term laboratory results cannot provide a definitive guide to performance.

The performance of polyethylene storage boxes as desiccated depositories for archaeological iron has been studied as functions of manufacturer, age, use, silica gel performance, and ambient relative humidity.[21] The study confirmed earlier studies on threshold corrosion values[20] and determined most air leakage was via lid seals, making storage protocols important in relation to the stacking of boxes compromising their seals. Storage in polythene boxes suffers from a reliance on the limited accuracy of moisture sensitive indicators to detect the internal relative humidity of boxes for gel regeneration cycles. Individual telemetric monitoring of the interior of the box is financially prohibitive for the several hundred polyethylene boxes normally housed in a storeroom. Good management is also necessary if the gel is to be changed as required. It is essentially a low cost, but high risk corrosion control strategy when the frailties of human nature are taken into account.

Relating corrosion rate to increasing relative humidity provides opportunity for pragmatic management decisions.[25] The degree of corrosion control implemented can be matched to resources available to produce a package that will reduce, but not prevent corrosion. This reasoning was used to control corrosion of Brunel's famous 1843 wrought iron steamship SS Great Britain, whose chloride-ridden lower hull is preserved in a mechanically desiccated dry dock maintained at 20% relative humidity with a goal of retaining its structural integrity for at least 100 years[25] (see **Figure 8**). This allowed public access to the hull and avoided employing costly and environmentally unfriendly alkaline washing methods (see **Section 4.43.4.2**) in attempts to remove chloride corrosion accelerators from the 324 ft long hull. The conservation challenge required a scientific investigation to identify the influence of RH on corrosion, followed by an engineering project to design an envelope to maintain the operating RH.

4.43.3.2 Deoxygenation

Ageless™ is a commercial oxygen absorber that has been used in conservation to deoxygenate enclosed spaces.[26] It is expensive to use and the exothermic reaction that expends oxygen produces water, which should offer no corrosion risk provided the storage environment remains oxygen free. Despite technical challenges, high cost, and reduced accessibility, archaeological iron has been stored in heat sealed low linear density polyethylene tube, with barrier properties 2000 times better than polypropylene, deoxygenated with oxygen scavenging RP-A™ (mordenite/CaO/PE/activated carbon).[27] This study showed that iron objects, which had been pretreated in aqueous NaOH to wash out chloride (see **Section 4.43.4.2**), remained visibly unchanged over a 5-month period but untreated iron had a 12% failure rate attributed to poor seals and bag punctures. Although the researchers predict a storage lifespan of 4–6 years, the high initial cost of materials and labor and a one-shot storage system make it unlikely that it will displace desiccation in popularity. A long-term quantitative testing program comparing its effectiveness, ease of use and global cost with desiccation techniques would define the relative merits of these two treatments. Using a flow of nitrogen gas through an enclosed container offers a no-corrosion environment for damp high status archaeological objects prior to their conservation.

4.43.4 Interventive Treatments

4.43.4.1 Removing Ions that Act as Corrosion Accelerators

Interventive treatments aimed at reducing or preventing corrosion of unstable metals mostly focus on removing chloride and other soluble ions that are capable of acting as electrolytes in high humidity environments. Entirely removing soluble ions should prevent corrosion, while their partial removal enhances the stability of the object by reducing electrolyte availability. Additionally, some washing treatments may aim to remove or modify sparingly soluble or insoluble corrosion products that promote corrosion.[11,28]

From an ethical standpoint, merely enhancing stability without controlling environment to prevent corrosion may not be considered an appropriate corrosion control strategy. Even a small amount of corrosion occurring at anode sites on the metal can interfere with adhesion of important overlying corrosion layers, whose loss destroys the object as an information resource despite the survival of the metal core (see **Figures 2–4**). Delaying this for a short time by reducing corrosion rate could be viewed as a very limited goal, when measured against the ideal of indefinite preservation. Equally, treatments that partially remove corrosion accelerators could be seen as unnecessary, since post treatment storage must be similar to that provided for untreated metals. Why bother trying to remove electrolytes if the objects still need to be subjected to the same stringent storage conditions? One possible advantage is that failure to maintain the controlled environment will lead to a slower corrosion rate, as compared to untreated iron objects. Quantitative understanding of treatment efficiency and effectiveness is essential for facilitating informed decisions about their use.

To optimize treatments designed to remove corrosion accelerators that are normally predominantly comprised of chlorides, it is necessary to: identify the corrosion mechanism; devise appropriate chloride removal procedures; quantify the removal of chloride as an absolute value of chloride contained in the metal; use this value to calculate extraction efficiency; determine the extent to which the metal is stabilised.[11] While the concept of removing soluble ions to prevent electrochemical corrosion is logical, no studies provide quantitative assessment to show how stable metals like iron become following attempts to remove their soluble chloride. Equally, there is limited information as to what percentage of chloride present within objects is extracted by a particular treatment and how consistently this occurs.[11,12,29]

4.43.4.2 Washing Methods in Practice

Washing methods are applied to metals to solvate soluble corrosion products and soluble ions adsorbed onto corrosion products. Iron is the most unstable archaeological and historical metal, due to its ability to attract chloride and retain it in a highly soluble form.[10] Washing methods will solvate chloride ions and this allows them to diffuse out of the object.[7,11] This process is hampered by the DPL limiting solution access to the iron surface, where wash solutions must enter pits and micro cracks to exchange with chlorides at anode sites. Chloride removal is diffusion controlled, slow, and is unlikely to be 100% efficient, although efficiency can be improved using chemical additives.[11,12,29] Evidence from a qualitative study of the long-term stability of treated archaeological iron revealed simple washing with hot deionized water to be a poor stabilization system, with 68% of treated objects recorroding.[30] Recent study quantitatively confirms washing in deionized water is an unpredictable treatment that never extracts large amounts of chloride[11] (see Figure 9).

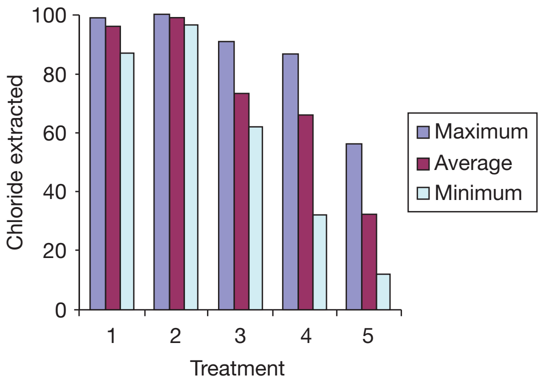

Figure 9 Influence of treatment solution on percentage chloride removal from Roman and Medieval archaeological iron nails. For each treatment method columns show: best extraction; average extracted; worst extraction. Total chloride in nails determined by post treatment digestion. Treatment methods: (1) NaOH/Na_2SO_3 0.5 M aq. (17 nails); (2) NaOH 0.5 M/deoxygenated with nitrogen (10 nails); (3) NaOH 0.5 M aq. (16 nails); (4) Water/deaerated with nitrogen (10 nails); (5) Water (10 nails). Reproduced from Watkinson, D.; Al Zahrani, A. *The Conservator* **2008**, *31*, 75–86.

Their ease of use and low aggression to iron has meant that inhibited wash solutions have been chosen to treat large objects. HMS Holland was the first submarine used by the British Navy. It was fortunate that she lost her tow en route to the breakers yard and sank, as when she was discovered and salvaged many years later she had become an important historical object. Her 19 m length offered challenges to removing the chloride that infused her structure. Health and safety and cost augmented against the use of strongly alkaline wash treatments (see below) and electrolytic desalination (see Section 4.43.4.3). A purpose built treatment tank containing 820 000 dm^3 of Na_2CO_3 was used to provide an inhibited wash relying on diffusion to extract chloride that was continually monitored.[31] Treatment was followed by storage in a building constructed for this purpose maintained at 35% RH to slow down any corrosion from residual chloride. While new study indicates storage at 25% RH would slow iron corrosion significantly more than 35% RH,[11,20,21] any environmental control program must be related to the finance available to sustain it and 35% RH will restrict corrosion better than higher values. This is a typical finance/corrosion control cost benefit assessment that is a factor in the conservation equation. It is often used to influence selection of treatment options and should be considered when developing standards of treatment. Equally object size may dictate which treatments are feasible, as in the case of the Holland.

Alkaline wash systems act as inhibitors and optimize chloride removal.[8,11,12,29] Inhibition provided by alkalis such as NaOH reduces corrosion during treatment. This releases chlorides from their charge balancing role at anodes and allows them to diffuse out into the wash solution, while at the same time the alkali supplies OH^- ions to replace them and associate with Fe^{2+}. Solvation of solid ferrous chloride and surface adsorbed chloride on β-FeOOH occurs, reducing β-FeOOH hygroscopicity and preventing post-treatment corrosion of iron in contact with it.[32] In strong alkali β-FeOOH can transform and this will advantageously release chloride into the wash solution.[28] Since the ionic size of chloride occluded in tunnels within β-FeOOH crystals exceeds the diameter of tunnel entrances it remains trapped and presents no post-treatment corrosion threat, unless conversion of β-FeOOH to α-FeOOH releases this chloride. Post-treatment hydrolysis of residual β-FeOOH to α-FeOOH can occur but is little studied. A 23-year-old dry sample of β-FeOOH was assayed as being 1% α-FeOOH and 99% β-FeOOH.[32] A major study currently underway aims to identify physicochemical transformations of corrosion layers as a function of treatment regimes, using microanalysis techniques to characterize the corrosion products.[33] This will significantly contribute to an understanding of treatment and post-treatment corrosion.

Further improvements in chloride extraction can be produced by deoxygenated NaOH solutions[11] (see **Figure 9**). Passivation of iron in oxygenated NaOH solutions is likely to be incomplete, as NaOH needs to reach all anodes sited at the metal surface to be effective. Consequently, chloride continues to be held as a counter ion and is difficult to wash out. Deoxygenating NaOH solutions with an SO_3^{2-} oxygen scavenger or nitrogen gas stops corrosion and improves chloride extraction.[11] Anecdotal reporting indicates undesirable softening of corrosion products in NaOH solution,[30,34] but no studies offer quantitative evidence of this or address the influence of any chemical treatment residues on iron corrosion products. This merits further attention. Objects should be washed post-treatment in deoxygenated water to flush out chemicals.

A promising variation on alkaline washing currently under investigation is the use of a subcritical high pressure alkali treatment for treating the American Civil War submarine Hunley, which was recovered from a marine environment where she had lain since she sank immediately after becoming the first submarine to sink a warship.[12,29] Treatment transforms corrosion promoting β-FeOOH to the α-FeOOH, Fe_3O_4, and Fe_2O_3 chloride-free phases that are nonaggressive to iron.

Other inhibitors have been tried, notably aqueous washing of archaeological iron with ethylene diamine. Inhibition and a high solution pH (11.5 at 5% (v/v) aq.) aim to prevent corrosion during treatment and aid chloride removal. It is an inferior chloride extractor as compared to 2% NaOH aq.,[34] but has been cited as offering good long-term stability to iron in a qualitative study of treated objects.[30,34]

There is limited information available regarding the amount of chloride removed by treatments as a function of total chloride within the iron, since determining residual chloride requires post-treatment digestion of objects. The small amount of quantified data available indicates that some wash methods are significantly better than others and consistently extract within fixed percentages of chloride.[11,12,29] The limit of detection for measuring chloride extracted into wash baths cannot guarantee iron is chloride free.[11,12] Although it is important to determine whether small residues of chloride are capable of causing significant corrosion of iron, testing the susceptibility of washed iron to corrosion has received little attention. For guaranteed no-corrosion all washed iron should be stored in a controlled environment to a standard equaling that used for unwashed iron, but this makes storage costs the same as for untreated iron.

Studies that qualitatively examine the stability of washed and unwashed iron within museum collections have offered comparative assessment of treatment effectiveness.[30,35,36] While these types of survey offer a genuine insight into treatment outcomes, they are limited by their retrospective nature, wide range of uncontrolled variables and a lack of quantified data. Computer monitoring of RH now offers an opportunity for precise recording of storage environment and new studies of long-term performance of treated objects are overdue. It would also be worth interpreting past studies using new data available on corrosion mechanisms.[2] Until quantitative long-term post-treatment stability testing is carried out and outcomes are linked to chloride residues within objects, washing treatments remain empirical applications best described as having an unpredictable and unknown capacity to remove chloride and enhance object stability. Such studies will prove hard to fund because of their time commitment.

Aluminum alloys are becoming increasingly common in museum exhibits and include aircraft and boats rescued from extreme environments. Once the highly protective nonconducting Al_2O_3 layer on aluminum fails the metal will corrode. This may cause pitting or intergranular corrosion according to alloying and metallography. Chlorides exacerbate corrosion by attacking the Al_2O_3 film and concentrating in pits where they cause low pH, hydrolysis of Al^{3+} and voluminous disfiguring corrosion product at the mouth of the pit.[10] The shape of the object is obscured and ultimately lost with eventual perforation of the metal. Washing to remove soluble chloride can be carried out on objects retaining significant amounts of metal, but those without large quantities of metal will be beyond recovery as corrosion products are nonadherent and friable.

Chemically aided washing was innovatively used to treat a Duralumin (3–5% copper) seaplane float belonging to a Junkers W33 infused with chloride, exhibiting extreme pitting and redeposited copper on its surface that could act as a cathode for continuing corrosion of the aluminum.[37] Washing conditions were carefully manipulated using $(NH_4)_2SO_4/NH_3$ buffer solution to complex Cu^{2+} ions to $Cu(NH_3)_4^{2+}$ and E_0 of the system was lowered to allow corrosion that removed redeposited copper, provided oxygen was present.[37] Thermodynamic data revealed Al_2O_3 was stable in the treatment solution. Its presence on the metal surface protected aluminum at the treatment pH of 9.6 and chloride diffused out of the object following hydrolysis reactions within pits. As with most washing methods employed in conservation, assessment of the success of the treatment was qualitative and reported that the object appeared to be stable 4 months after treatment.

Washing has been employed for copper alloys to deal with the problem of CuCl hydrolyzing to form $Cu_2(OH)_3Cl$ polymorphs that damage and disfigure copper alloy objects.[6,10] Fortunately $Cu_2(OH)_3Cl$ is not hygroscopic and does not cause corrosion of metallic copper in contact with it, although its growth can undermine and lever off overlying patina. Not all copper alloys containing chloride are unstable. MacLeod[38] argues that there is a minimum chloride ion concentration required to support corrosion. The low solubility of CuCl and its positioning within or under Cu_2O means chloride solvation by simple aqueous washing can last years. Washing for up to 2 years in sodium sesquicarbonate ($NaHCO_3 \cdot Na_2CO_3$) at 5% (w/v) pH 10 has been employed to slowly solvate CuCl and supply OH^- to form cuprous oxide (Cu_2O).[6,9] Basic copper carbonate ($CuCO_3Cu(OH)_2$) and chalconatronite $Na_2Cu_2CO_3 \cdot 2H_2O$ may also form and darkening of patina may make the treatment undesirable when aesthetics are an important consideration. It is now more likely to be used as an inhibited wash solution following other treatments like electrolysis (see **Section 4.43.4.4**).

4.43.4.3 Removal of Corrosion Products

Stripping techniques may be employed when ethical arguments allow removal of corrosion, such as preparing lightly corroded industrial and historical steels to receive protective coatings. They may also be used to free archaeological objects from corrosion conglomerates provided substantial amounts of metal remain, as heavily mineralized objects will lose their identity when corrosion is removed.[8,39] While there are several studies looking into the action of stripping agents there is no single definitive comparative assessment that identifies a preferred method for specified alloys. Conservators must evaluate studies or themselves test stripping agents relative to the object they are planning to treat. That stripping is ethically acceptable at all, illustrates how situation ethics dictate conservation procedures.

Traditional acid stripping solutions are aggressive to metal and corrosion products alike and are now largely ignored, except where it is ethical to remove all corrosion products. Copper alloy coins have been separated using complexing agents exhibiting low aggression to metallic copper to remove copper corrosion products. Citric acid is reported as being best in this respect, when compared to alkaline glycerol, alkaline Rochelle salt, sodium hexametaphosphate, and sulfuric acid.[40] Elsewhere alkaline Rochelle salt is reported as being less aggressive than reagents like methanoic acid, alkaline glycerol and alkaline dithionite.[39] Electrochemical assessment of these reagents would help indicate which reagents offer the best removal of corrosion for the least aggression to the parent alloy. Dealloying is a problem. Predictably, metallic lead is lost from copper alloys by alkaline stripping systems and organic acids. Stripping corrosion from copper alloys[38] and iron[41] has been achieved using thiourea ($SC(NH_2)_2$) inhibited citric acid washes. Thiourea controls the aggressive action of citric acid by complexing unstable Cu(I) species, to prevent them forming metallic copper, and by forming stable complexes with Cu(II).[8,38] Phosphoric acid (H_3PO_4) has been used for stripping ferrous metals to leave a ferric phosphate protective film, as has hydrochloric acid with hexamine corrosion inhibitor.[41] All stripping methods require post-treatment washes to remove residual chemicals that would continue to corrode metals. This is often followed by application of a protective coating.

Following citric acid/thiourea treatment of copper alloys, washing in sodium sesquicarbonate is used to neutralize acid and remove CuCl left in crevices and cracks, but this is likely to be incomplete.[38] Washing marine copper alloys revealed the benign nature of this treatment method, as tin, zinc, and lead compounds were not removed from either the corrosion products or copper alloy, whereas washing in deionized water removes metallic lead as the purity of the water prevents formation of protective $PbCO_3$.[38] Washing of iron in inhibited chromate or nitrite solutions following citric acid/thiourea stripping is not environment-friendly, so ecologically superior alkali metal salts of organic carboxylic acids (secacic acid – $NaOOC[CH_2]_8COONa$) have been used to provide washes of similar efficiency.[41] They can also provide long-term inhibitive properties (see **Section 4.43.6.3**) and offer promise for widespread use in conservation following more in-depth testing.

Chelating and sequestering agents, such as the sodium salts of ethylenediaminetetraacetic acid (EDTA), have been used extensively in conservation in attempts to dissolve corrosion products without attacking metal. However, they can be slow to act and may be too selective in their action on corrosion products. Careful selection of commercial products is essential to obtain suitable pH values for optimizing complexation. A study examining reaction of disodium edeterate (2NaEDTA) on copper corrosion products and copper metal revealed that chelation rate varied according to corrosion product.[42] This would result in differential removal of corrosion products leaving exposed copper open to the treatment solution. Fortunately, metallic copper was barely attacked by 2NaEDTA over a 30-h period.[42] Dissolved sodium salts of EDTA have also been frequently used to remove corrosion from iron and lead and its alloys.[6,8,31,43] Using compresses allows stripping agents to be used in a controlled manner. Degrigny[44] treated a Citroen caterpillar tracked vehicle used on the trans-Sahara crossing of 1922/23 by this method. It still retained much of its original paint layer. Corroded areas that had sustained paint loss were treated with compresses of tetrasodium edeterate (4NaEDTA) to remove iron corrosion products. This was followed by application of inhibitor (see **Section 4.43.6.2**) and a protective wax coating (see **Section 4.43.5.4.2**) to provide a typical stripping-inhibition-coating treatment regime. All treatment methods were assessed using electrochemical measurements prior to their use. Treatment success was gauged in the usual qualitative manner of visually checking for corrosion as a function of time and no corrosion was visible after 6 months of indoor display. Developing standards for assessing time weighted visual success of treatments set against conservation criteria would produce a useful tool for conservation practice.

Removal of corrosion from copper alloys may also be achieved by alkaline dithionite ($Na_2S_2O_4$) solutions, which provide electrons to reduce corrosion products to finely divided metallic copper.[8,38] Weak heavily corroded objects may be consolidated by this conversion, but there is also a chance they will disintegrate. The skill and knowledge of the conservator are essential as treatment is fast, lasting only a few minutes followed by a wash of several days to remove residual chemicals.[8]

4.43.4.4 Electrolytic Techniques

Electrolysis is employed in conservation either to entirely remove corrosion products from a metal or to aid diffusion of soluble corrosion accelerating ions into an electrolyte, while retaining corrosion layers on the metal. These differing outcomes are achieved by careful control of current density (CD) and in some instances current delivery. The metal is immersed in a suitable electrolyte and made cathodic relative to an inert anode, which protects it from corrosion during electrolysis. Different metals are electrolyzed in differing ways according to the nature of their corrosion products and the treatment goal. It is an extremely useful technique provided its use matches ethical goals and research identifies optimum treatment methodology. Its context within conservation has only been quantitatively established over the past 15 years since the application of potentiometric electrochemical analysis within conservation research.

Procedures vary from metal to metal. Iron is immersed in an electrolyte in which it will remain passive, such as NaOH. Using an imposed current to cathodically protect the iron frees chloride from its counter ion role, allowing it to solvate and diffuse out of the object.[8,12,29] Chloride is drawn to the inert anode and delocalized from the object by diffusion. Maintaining a low CD retains the information rich DPL by avoiding polarization that would produce hydrogen gas which physically dislodged corrosion layers. Reduction of FeOOH corrosion products to Fe_3O_4 can occur and the accompanying increase in density increases porosity which is said to contribute to facilitating diffusion of chloride out of the object.[7,8]

Most quantitative assessment of chloride removal by electrolysis has been carried out on cast iron, whose even corrosion matrix is different to the lamellar structure of corroded wrought iron.[2,8,29] Tests on small cast iron chloride infested samples reveal significant migration of chloride to the anode during electrolysis.[29] Quantitative measurement has shown that electrolysis (CD 10 mA dm^{-3}) in NaOH solution is no better at extracting chloride than aqueous washing in NaOH solution.[12] While washing is easier to carry out than electrolysis, full inhibition of iron corrosion in a 1% NaOH wash solution cannot be guaranteed in the same way as an imposed current protects during electrolysis.

Electrolytic treatments are often favored for large iron objects, as they will remain cathodically protected during the long treatment times required to remove deep-seated chloride. Treatment may take from 1 to 4 years for large cast iron cannon and wrought iron anchors from marine contexts[45] and even very small cast iron samples required over 200 days to desalinate.[12,29] As with most metal treatments, there is no report of any quantitative long-term assessment of post-treatment stability of electrolyzed iron as a function of relative humidity. Intentionally using a high CD to remove all corrosion layers may be ethical for certain industrial and historical objects, provided their corrosion layers contain no information and they retain substantial metal cores. Such treatment would usually be a precursor for the application of protective coatings (see **Section 4.43.5**).

An advantage of electrolytic treatments is their degree of control, as the imposed potential can be matched to specific reduction processes. They are also useful for large objects, as electrolytic treatments can be run for long periods of time with little input from the conservator thereby saving labor. Circumstance must dictate whether electrolysis is possible. *HMS Minerva* was a big gun monitor launched in 1915 and sold as a visitor attraction in 1984. Removal of the high levels of chloride inside her hull was achieved by flooding it with Na_2CO_3 electrolyte and making it cathodic ($35\,mA\,m^{-2}$) relative to stainless steel mesh anodes placed directly above it.[31]

Electrolysis can be used to remove all corrosion from lightly corroded lead to reveal fine details on the metal surface. This is normally carried out in sulfuric acid electrolyte. A brief reversal of the electrode poles upon completing treatment makes the lead anodic and forms an invisible $PbSO_4$ coating that has protective properties in the atmosphere.[43,46] The final 'fresh metal' appearance of lead treated in this way would influence any decision to use this method. Electrolysis of copper alloys to remove potentially reactive CuCl and all other corrosion products is now considered to be aggressive and difficult to control, with a high risk of redepositing reduced copper. Simple electrolysis of copper alloys in water is advocated as deserving of more research, as it can retain the copper corrosion product patina and offer cathodic protection of the metal during treatment.[6]

The inherent insolubility of the silver corrosion products Ag_2S and AgCl prevents the formation of electrolytes on corroded silver exposed to high relative humidity. Consequently their removal is largely an aesthetic act or an information revealing strategy, according to whether the layer is a thin Ag_2S tarnish or a thicker layer of $AgCl/Ag_2S$ that might be found on archaeological silver objects. Once silver is returned to a shiny metal finish the challenge is to apply coatings or control environments to prevent sulfur-based pollutants tarnishing it (see **Section 4.43.5**). Electrolysis removes silver corrosion products within a wide range of operating parameters using electrolytes such as formic acid (5–30%, w/w) or NaOH (5–15%, w/w) with CD of $0.3\text{–}20\,mA\,cm^{-2}$ at 3–12 V.[6,13]

Very low current densities have been used to slowly reduce corrosion on mineralized brittle silver objects to metallic silver, which is retained *in situ* to produce a consolidative effect.[13] Conflicting reports of success make this a high-risk strategy, as weak mineralized silver objects may fall apart during treatment due to reduced coherence of their corrosion layers. Potentiometers have been employed to apply potentiostatic cleaning of silver.[13] This method uses a third reference electrode to control the potential of the cathode and a polarization plot is used to identify reduction potentials of the corrosion products, which are then reduced by setting the object potential to match the reduction potential of the corrosion product. It is a finely controlled system that avoids any unwanted reactions such as hydrogen reduction and is useful for tarnish (Ag_2S) removal.

Once corrosion begins on aluminum and its alloys they corrode rapidly in the atmosphere. Electrolysis can be used to remove chloride corrosion accelerators and unstable corrosion products. Degrigny[47] developed a treatment that cathodically polarized aluminum to constant potential in a buffered deaerated slightly acid citrate solution, with treatment parameters optimized to avoid pitting corrosion from the chlorides extracted into the treatment solution and cathodic corrosion of the metal. Composite aluminum objects associated with other metals like iron are problematic, as significant galvanic couples can be established during treatment. For this type of composite metal object electrolysis is modified. Active polarization of the composite object in an inhibited solution protecting the aluminum alloy from corrosion produces a potential that facilitates formation of a protective magnetite coating on the iron fittings.[48] This is followed by polarization of the object in citric acid solution (pH 7) to remove aluminum corrosion products and chloride. Finally, polarization in deionized water washes out chemicals introduced during treatment. The object is dried and coated with a suitable protective coating (see **Section 4.43.5.4.2**).

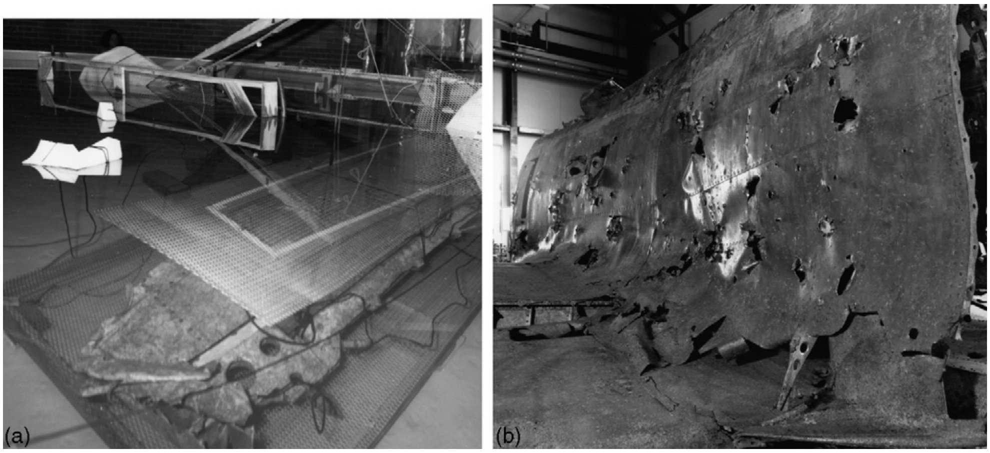

Figure 10 Electrolysis of Japanese 'Oscar' aircraft (a) and completed fuselage (b).[49] Image courtesy of Australian War Museum.

Treatments are often fine tuned to the needs of an object. Adaptation of electrolyzing aluminum omitted the magnetite forming step to treat a WWII Japanese Oscar Ki43II fighter retrieved from a saline swamp.[49] The design utilized a swimming pool, 55 000 l of water and 800 kg of chemicals with expanded stainless steel mesh anodes conformed to the shape of the aircraft and sited 30 cm above its surface (see Figure 10). The inevitable post-treatment flash rusting of ferrous components was dealt with by a tannic acid inhibitor. Original paint and penciled notes on the cockpit fascia were masked prior to treatment. Success was assessed by ongoing observation, as opposed to quantifiable measurements of change or residual chloride in objects.

Imposed currents are used industrially to protect large homogenous steel structures, but heterogeneity and corrosion in historical metal objects produce discontinuities that limit applications of this method for corrosion control. The American Civil War submarine CSS Hunley was recovered in 2000 and stored in a holding tank containing chilled (10 °C) filtered water (see Figure 11).[50] Storage involves the hull being protected by an impressed current monitored by five electrodes, with two large anode segments running the length of the tank. Comparing corrosion rates of an unprotected mild steel test probe with a similar probe with an imposed current indicated that the post-excavation corrosion rate had been reduced by a factor of 8 and now matched pre-disturbance corrosion rates recorded on the seabed.[50] Protection of the hull by sacrificial anodes was rejected as a preservation option, as it would have required 50 cumbersome 20 kg anodes to be attached to the hull.[50] Impressed current was used to reduce corrosion of the USS Monitor's steel structure from $254\ \mu\mathrm{m\ year}^{-1}$ to as little as $25\ \mu\mathrm{m\ year}^{-1}$.[51] Measuring the *in situ* corrosion rates of ship and aircraft wrecks to identify the role of galvanic couplings, concretions, coatings, and environment on their longevity has been extensively studied by MacLeod[52] to develop predictive corrosion control strategies in marine contexts.

4.43.4.5 Hydrogen Reduction

Removal of chloride from iron using hydrogen reduction at temperatures of over 800 °C was once seen as a way forward for large chloride contaminated marine objects but is now rarely used. The treatment uses a hydrogen/nitrogen gas mix to reduce chloride bearing compounds at around 350 °C, iron oxides above 570 °C and fully volatilizes iron chlorides and any NaCl present on marine iron at 800 °C.[8,30] High capital outlay, stringent safety measures designed to prevent oxyhydrogen explosions and ethical concerns that changes to metallographic structure compromise technological data and object history limit its use. It may be argued that it is still a viable treatment for cast iron cannon from marine contexts, where technology is well reported and where objects may be considered to be effectively untreatable in any other way due to the amount of deep-seated chloride within them. The technique is reported to provide good post-treatment stability, but suggestion that the method can offer stabilization by reducing corrosion product to metallic iron is challenged by the instability of the reactive pyrophoric iron it produces.[53] Another heat assisted expensive reduction process used in conservation is gas plasma. It has been used

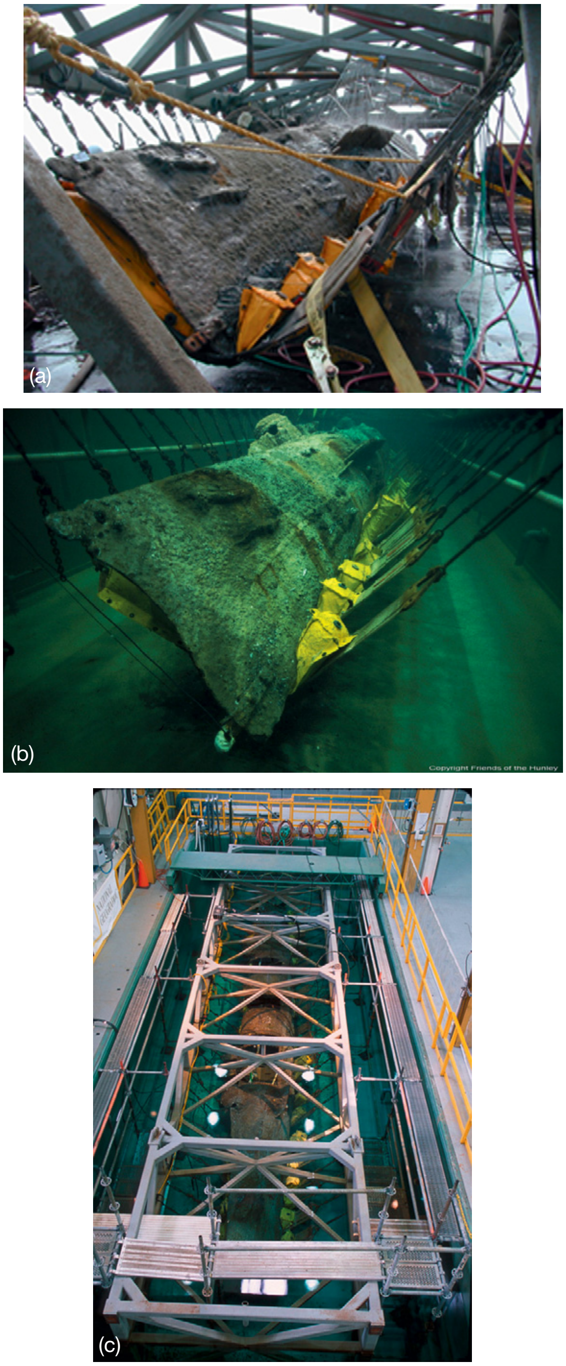

Figure 11 The H.L. Hunley submarine was lifted from the seabed in a metal frame (a) that was then stored in a large holding tank (b) protected by an impressed current (c).[50] Images courtesy Friends of the Hunley.

to aid chloride removal from iron by reducing FeOOH to denser Fe_3O_4 to produce a more porous corrosion product layer that aids removal of chloride in subsequent aqueous alkaline treatments.[54]

4.43.5 Coatings

4.43.5.1 Coating Rationale and Research

Conservation coatings are normally applied as barriers to combat ingress of gaseous, aqueous, or particulate agencies of decay. They may be treatments in their own right or form part of a treatment regime, such as when they are applied as moisture barriers following attempts to remove chloride from iron using washing treatments. Coatings applied to silver must have good gas barrier properties to reduce ingress of H_2S and thereby prevent tarnish.[13] Resistance to vapors such as volatile carbonyl pollutants is important for lead, copper alloys, zinc, and aluminum.[15,18,43]

The role of a coating, environment in which it must be effective and the nature of the metal surface dictate coating choice. An absence of standardized procedures for testing coating effectiveness on cultural metals hinders the use of published material for comparatively identifying the most suitable coating for use in a specific context. While some popular coatings still mostly have qualitative data to support their use, there exists a considerable amount of useful information within conservation literature and there is a move toward providing quantitative data and standardized testing.[3] Both qualitative and quantitative assessment of coating performance within conservation now employs electrochemistry and modern methods of instrumentation in conjunction with increased collaboration with corrosion scientists.[2–4,55]

The concept of manufacturing conservation specific coatings is largely a redundant approach, since conservation viability is cultural rather than commercial as there is no significant financial gain for potential manufacturers in such a small market. Increasing collaboration with industrial partners would benefit conservation and reveal its links to industrial applications. Both industry and conservation seek low toxicity, easy application, predictive performance, and low cost for their coatings. Additionally conservation has stringent ethical guidelines that require coatings to have enhanced life span, long-term reversibility and minimal visible impact to the object upon application or ageing. Object context may modify these goals to some extent. Coatings that offer good protection from corrosion, but are aesthetically displeasing, may be acceptable for objects in long-term storage provided they are easy to remove for display purposes. Since the conservation ideal is for indefinite preservation coatings should be long lasting and low maintenance during their lifespan. Demand for long-term durability and guaranteed reversibility remain at odds with coating design. While cross-linking polyurethanes have renowned barrier properties their irreversibility, without significant mechanical action coupled with aggressive solvents, rules them out for most conservation applications. Since minimal intervention with an object is contravened by applying a coating and by its future removal, its application is only ethical provided there is evidence that it significantly improves corrosion protection.

Conservation coatings must often perform well on porous, uneven oxidized metal surfaces that may be fragile and chemically unstable. No coating is perfect and this type of surface will result in a large number of coating imperfections. This complicates the testing of coatings for conservation applications, as producing test samples with suitably corroded surfaces to match corrosion patinas developed over years or centuries in the ground or air may be impossible. The alternative of using original materials suffers from reproducibility problems and may be subject to ethical constraints. In some instances actual objects are used to test products. The baton from the bronze equestrian statue of the famous fifteenth century mercenary Bartolomeo Colleoni (see Figure 12), which is sited opposite the Ospedale San Marco in Venice, was used to compare the performance of organo-silane coatings (see Section 4.43.5.4.4), synthetic waxes (see Section 4.43.5.4.2) and acrylic (see Section 4.43.5.4.1) coatings in tandem with tests on naturally aged metal samples.[56] This approach links the intrinsic properties of coatings to real-life applications and contexts. Samples are not reproducible but performance can be linked to tests on prepared and reproducible samples. Two-phase test systems, where materials are laboratory tested on reproducible samples by accelerated and natural ageing, then tested on objects in real life environments were employed in the PROMET project.[3] This system should be applied to generate evidence-based advice for practical conservators regarding contextual use of materials.

Coatings on metals are used extensively within conservation, but the absence of industry standards makes it difficult to identify the best coating for defined contexts. Much published work produces useful stand-alone data. This usually compares groups of coatings using highly specific goals and personalized test regimes to deal with the multiple numbers of variables within the test procedures. The demands and complexity of coating use in metals conservation means that many studies naturally attempt to review many aspects of a chosen group of coatings. A stepped study that examines and compares the performance of coatings in relation to a single variable then moves onto the next would gradually build into a detailed review of materials. Unfortunately, this approach demands significant time and resource commitment and would necessarily be a team project requiring long-term major coordination. Conservation research is not lavishly funded. Collaborative research projects are currently underway or recently completed.[2,3] Their work could offer platforms for movement towards industry recognized standards for testing. Significant coordination and standardization were evident in the recent EU 6th Framework PROMET project.[3] It sought to identify suitable coatings for use on metals within museums surrounding the Mediterranean basin and aimed to identify a methodology for developing and testing inhibitors and coatings for use on iron and copper alloys in museum environments. Additionally it was looking towards environment friendly inhibitor systems.

Figure 12 The baton from the right hand of the fifteenth century statue of the codotteri Bartolomeo Colleoni in Venice was used for trialing protective coatings. Reproduced from Joseph, E.; Letardi, P.; Mazzeo, R.; Prati, S.; Vandini, M. In *Metal 07, Book 5, Protection of Metal Artefacts*, Interim Meeting of the ICOM-CC Metal WG Amsterdam, 17–21 September 2007; Degrigny, C., Van Langh, R., Joosten, I., Ankersmit, B., Eds.; Rijksmuseum: Amsterdam, 2007.

Many researchers modify international standards or use them unchanged for testing materials and designing experiments. Overall, there remains a need for developing test procedures that support conservation goals and facilitate comparative performance testing of coating materials for use in conservation. A conservation-specific accelerated corrosion test standard could be used to model the demands of conservation practice. Coating performance in its operational environment is of crucial importance, as it determines its maintenance requirements and life-span. Although laboratory studies, instrumental analysis and electrochemistry can establish intrinsic performance characteristics of coatings according to a set of fixed variables, they cannot offer quantitative assessment of real-time *in situ* performance within museum stores, display cases and outdoor environments. Laboratory testing is useful for establishing which coatings are unsuitable for use and for comparative performance testing in specified conditions. Coatings identified as good performers within the laboratory may fail in the field because certain parameters could not be effectively replicated in the laboratory. However, appropriately designed accelerated ageing normally offers an indication of the relative performance of materials.

Within testing processes examining coating performance a recurring theme is that application methods often dictate whether a coating performs well or badly. The procedure here may be critical. Inappropriate coating methods may negate differences between coatings. A coating with intrinsically better barrier properties may fail at the same rate as one that offers poorer barrier properties because of application methods. Standardizing application methods to ensure variable control is an appropriate experimental procedure, but it may not reflect how the coating will perform in practice where the condition of the object, surface morphology and positioning can dictate whether application is by spray, brush, or cloth. How coatings perform as a function of their application method is as important as their intrinsic properties and should form a major part of testing. A coating with only mediocre barrier properties may perform well if its physical properties suit a particular application procedure. Spraying is often a favored coating method, but coatings of the cellulose nitrate lacquer Frigiline™ on silver were found to fail unevenly due to thickness variations and discontinuities that resulted from spraying.[57] Brushing is known to offer preferential failure in troughs created by the brush stroke and solid wax coatings may have to be applied as polishes. The nature of the surface of the object may also favor different methods of application and mobile self-healing films may be essential in certain environments. The coating itself may dictate which application methods are possible to use. This overall complex equation must be effectively worked into research studies if results are to be of maximum practical use.

4.43.5.2 Metal Surfaces and Patinas

A major hurdle to the successful application of coatings within conservation is surface preparation. Only in specific circumstances is it ethical to remove patinas and corrosion from surfaces. Within museums equipped with dedicated micro- or macroenvironmental control and monitoring, bare metal surfaces on historical metals may be left uncoated. However, without environmental controls silver tarnishes rapidly in the presence of very low concentrations of sulfur pollutants like H_2S and forms Ag_2S[8,10,13,57] and lead and copper alloys are attacked by low concentrations of organic acids.[2,6,8,10,15,18,19,47] Preventive conservation is the preferred option to control pollutant availability and attack, but coatings offer an alternative strategy where sources of pollution cannot be eliminated. Potential for disaster exists in mixed displays or with composite objects, such as when an unstable cellulose acetate object emits acetic acid into an enclosed showcase it shares with a lead object.

Patinas on many metals offer an information resource and provide aesthetic attraction. They may be deliberately applied or naturally formed corrosion layers. Deliberately patinated or polished copper alloy statuary is often modified by corrosion from pollution, rain, and particulates that form corrosion products that may undermine, obscure, or destroy the original patina and outermost metal surfaces[6,19] see **Figure 12**). The extent of corrosion will relate to metal composition, climate, location, preexisting patina and the solubility, morphology, uniformity, and adherence of new corrosion products.[6,10,19] Run marks, differential corrosion from pitting, differing colors and textures produced by climate, pollution, composition, and object morphology can entirely ruin object aesthetics and offer a porous uneven surface that will not accept a continuous coating. Wear marks on patinas can be important to retain as part of the history or present life of an object (see **Figure 13**). Whether total or partial removal of patina is appropriate, in return for improved object stability and surface preparation for coating, presents ethical and aesthetic dilemmas for the conservator.

Apart from ethical considerations, establishing the role of a patina in the corrosion process can help decide whether to remove it as part of a corrosion control strategy. Equally an understanding of patina stability

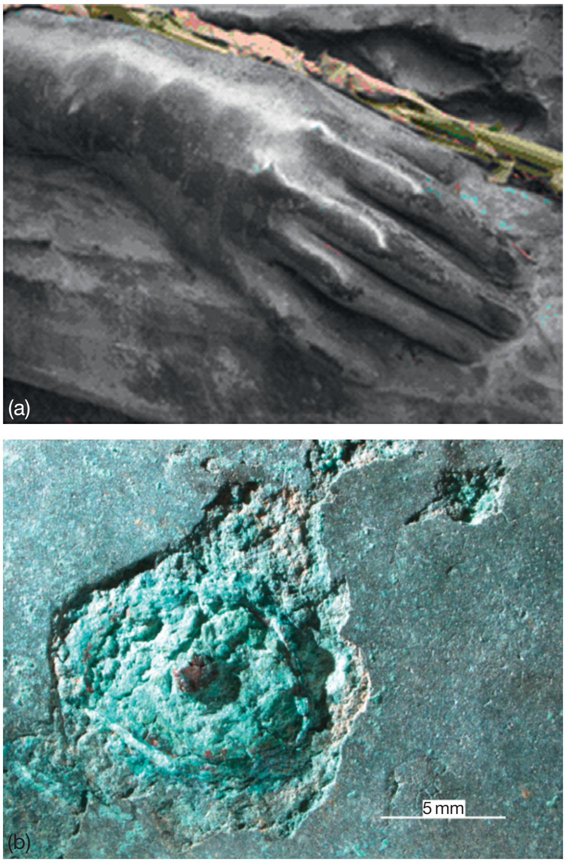

Figure 13 Constant touching of this copper alloy hand has created a wear mark patina that now forms part of the object history and presents a dilemma for conservation planning (a). Achieving a continuous coating on archaeological copper alloys is problematic due local corrosion and differential patina (b).

and protectiveness contributes to developing corrosion control strategy by offering a measuring point for monitoring, assessing, and predicting patina deterioration with time.[58] Nondestructive *in situ* analysis has been used to identify variance of electrochemical stability within patinas to locate areas that offered high stable electrode potential relative to the base metal, as they provide good corrosion protection.[59] Results revealed that unsightly black crusts offered more protection than visually acceptable blue/green corrosion product layers. This creates an aesthetic dilemma for conservation strategies based on patina retention. Understanding the contribution of corrosion layers to the corrosion process makes it easier to determine if interventive treatments are a better corrosion control option than noninterventive monitoring strategies.

Disfiguring, unstable and aesthetically displeasing patinas formed by corrosion may be removed, either to reveal metal or a selected corrosion product layer in preparation for repatination and/or adding a protective coating.[6] Repatination may even form part of a corrosion control strategy, as some patinas may offer a degree of protection by acting as partial barriers to moisture, electrical conduction, and gases.[6] Instrumental analysis and historical research to determine the original appearance of a metal object is a prerequisite to selecting a repatination process. Working objects and industrial equipment that never developed a patina or were frequently repainted may in some instances be stripped to the metal surface, provided their history is not compromised by loss of data such as paint layer sequences. Analysis of paint layers would determine if this was likely to occur. Stripping processes like electrolysis, chemical dissolution and complexation, which remove corrosion prior to applying coatings should provide for lower maintenance of coatings, all other factors being equal. Yet there remain ethical dilemmas concerning the stripping of historical metals.[60] During its working life a cog may have uncorroded teeth that developed a surface finish from work, with a corrosion patina on its 'noncontact' body that can also be associated with its working life; should conservation retain both these layers?

4.43.5.3 Preparing Surfaces on Cultural Objects to Receive Coatings

Surface preparation of objects may take the form of mechanically removing disfiguring corrosion to reveal the 'original' surface of the object or the marker layer for this. In archaeology it is normal to use mechanical systems to remove corrosion to reveal the object shape and surface detail.[7] For historical metals preparation may involve mechanical cleaning systems, chemicals, or electrolysis. Precious metals may be polished to a high shine as the goal of coating is to ensure that future repolishing occurs as infrequently as possible. In all cases it is best to remove soluble corrosion accelerators before applying coatings.

Outdoor statuary is cleaned according to the goals of the conservation process, taking account of ethics and aesthetics. Preparing surfaces by stripping patinas is normally unacceptable due to ethical constraints and aesthetic outcomes (see Figure 14). All processes must involve minimum loss of material. Choosing a cleaning method normally relates to how it physically modifies surfaces and alters appearance, rather than its impact on metal stability by removing corrosion accelerators or making a surface more coating friendly, unless it is being prepared for paint. Cleaning methods

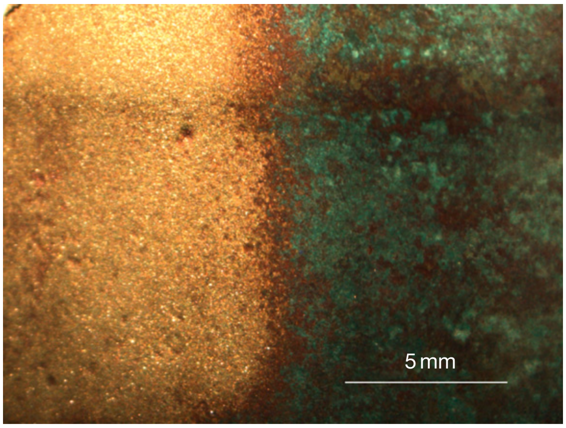

Figure 14 This contrast between a surface retaining its uncleaned patina and a section cleaned by airbrasion with aluminum oxide starkly reveals the tension between best practice for preparing surfaces to receive coatings and the aesthetic and ethical constructs of conservation.

will influence the effectiveness of coatings, as leaving corrosion products and patinas *in situ* influences their adhesion and distribution.

Most studies qualitatively compare the effects of cleaning methods on specific metal surfaces. Dry particulate abrasion, pressurized water and chemicals have variously been compared for cleaning patinated copper.[61] One study serves to illustrate some of the decision making associated with cleaning surfaces. It compared cleaning of a patinated copper alloy token by abrasion techniques employing glass beads, walnut shell, corn cobs, and sodium bicarbonate delivered at pressures between 1.38×10^5 and 5.52×10^5 Pa with simple abrasion using Al_2O_3, pressurized water and chemical cleaning by complexation (solution comprising KNaTartarate, 2NaEDTA, NaOH, and fumed silica applied in a cellulose ether gel pack).[61] Postcleaning samples were exposed to synthetic rain and their corrosion was monitored.

Results of these tests reveal the general dilemma produced when trying to balance effectiveness with aesthetics and ethics. Although chemical cleaning offered the most stable substrate, as observed after 1 year, it produced the most visually altered surface by removing all overlying green corrosion products to leave only orange/brown Cu_2O *in situ*. Predictably the softest corrosion products disappeared from the mechanically abraded objects, which were less stable than the chemically treated sections. Pressurized water produced the least visual change, but removed the most soluble corrosion products leaving the metal actively corroding after a year. None of the methods entirely stabilized the metal and various corrosion products were left *in situ*, neither did they remove all corrosion accelerators. Other workers have expressed concern at indiscriminate surface preparations that fail to recognize the importance of original coatings on metals like aluminum.[16] Glass beads have been cited as being too damaging on finishes on aluminum alloys, but airbrasion can be retained by use of plastic beads at 1.0×10^5 Pa.[16]

Preparing historical metals and objects d'art that traditionally carry a shine for the application of coatings involves either chemical or physical removal of tarnish. Removing H_2S tarnish from silver can be achieved by chemicals or abrasion.[13] Chemicals are aggressive and may lead to differential corrosion and surface enrichment of alloys such that loss of copper alloyed with silver leaves a soft and porous silver enriched surface. They may also leave residues that are too aggressive and these have been tested to determine their impact on the object and develop a protocol for treatment. Polishes remove metal and produce surface scratching. Studies of polishing methods concentrate on the loss of metal incurred and scratching of the surface, with $CaCO_3$ being a favored inert polish for silver.[62] Chemicals are normally only preferred for heavy tarnish due to the risks of preferential leaching of alloying components and the need for acidified complexing agents to remove Ag_2S.[12] Potentiometric methods mentioned earlier can also be used to remove silver tarnish (see Section 4.43.4.4). Focus should be on identifying the least interventive method that offers the best surface for receiving a coating.

4.43.5.4 Coatings in Conservation Practice

There are a small range of generic coatings in general use within conservation and there is no definitive comparative study which clearly identifies the most successful coating for any given context. Preferences and trends exist for various chemical groupings and products.[3] Coatings are reviewed below by chemical affiliation, rather than their application to specific metals. Trade names are used in general discussion, having initially defined the chemistry of the product.

4.43.5.4.1 Acrylic coatings

The Paraloid™ range of acrylics, known as Acryloid™ in USA, is commonly used within conservation practice. Other acrylics are used according to availability, which means geography can dictate choice of materials. Survey reveals that only a few coatings are routinely used, with Paraloid B72™ (70 methyl methlacrylate/30 ethyl acrylate copolymer) being one of the most popular general purpose surface coatings for cultural metals. Its long-term reversibility and application as a coating, consolidant, and adhesive make it a workhorse within conservation and a comparative performance standard in many test procedures.[3] Performance of Paraloid B72™ and an ethylene based commercial coating Poligen ES 91009™ were compared, both alone and with added inhibitor as coatings on fresh and precorroded coupons of steel exposed to cycling γ (90% at 35 °C to 55% at 25 °C) to simulate extreme museum environmental fluctuations.[3] Performance was assessed qualitatively by visual interpretation and quantitatively using EIS and polarization techniques.[3,63] Poligen ES 91009™ was more effective than Paraloid™, and added inhibitors failed to significantly improve the performance of either coating. Long-term exposure of similar test coupons in museum environments confirmed that although Paraloid B72™ gave 'quite satisfactory results,' it failed at edges producing filiform corrosion.[3] This was recognized as being problematic where much cultural material like edged weapons and armor had multiple thin edge sections. The importance of environment was revealed in these tests as matched sample sets performed differently over similar exposure times within museums in differing Mediterranean countries. Application method was again revealed as being an important variable. In one test, a 250 μm layer of polyurethane (Rylard™ boat varnish) performed much better than either Paraloid B72™ (40 μm) or an innovative physical vapor deposition system (<1 μm).[3] Standardizing test methodology by employing aged coupons and using laboratory and onsite real-time testing in monitored environments offers a solid test platform for cultural metals and for the evolution of assessment standards. Yet outcomes discounted certain products due to outright failure, it proved difficult to quantify the performance of some of the more successful coatings. Overall, the study revealed weaknesses in the performance of traditional conservation materials and identified the newly tested Poligen ES 91009™ as offering promise for the future.

The inability to separate lead organ pipes from oak supporting frames emitting organic acids in European Baroque organs led to a research program that tested the ability of coatings and inhibitors to prevent the corrosion of lead by organic acids.[64,65] Using an aqueous washing strategy to remove soluble lead methanoates and ethanoates acting as electrolytes failed to reduce the corrosion rate upon reexposure of the lead to the methanoic (170 ppb $Pb(CHOO)_2$) and ethanoic acid (195 ppb $Pb(CH_3COO)_2$).[65] Coatings alone produced limited protection, with Paraloid B72™ offering no protection, microcrystalline wax providing uneven protection and various inhibitors had little effect.[64,65] This is of concern as Paraloid B72™ has long been used as a coating on lead. Treatment must be effective for the long term, due to the cost and logistics of coating the organ pipes. Nanotechnology is now being tested in a preventive treatment using $Ca(OH)_2$ nanoparticles to control acid emission from the wood.[64]

Incralac™ lacquer comprises Paraloid B44™ (ethyl methacrylate/butyl acrylate copolymer) with added epoxidised soya bean oil as a leveling agent and benzoriazole as a UV absorber[6] and is industry designed for protecting copper alloys. It has been extensively used both on archaeological and outdoor copper alloys since the 1960s. Its application aesthetically changes bronzes by darkening their surface.[56] However, outdoor exposure is likely to result in optical changes to most coatings as they weather and collect dirt. Good electrochemical impedance measurements recorded for fresh Incralac™ coatings on polished and unpolished bronze, implied good coverage and low porosity, but after natural ageing on a rooftop in Canberra for 4 years impedance was the same as for uncoated metal.[57] Although two coats improved performance the time-related failure remained the same. Poor long-term performance was also found in 10-year-old Incralac™ coating on a gilt bronze statue in New York.[6] It was entirely cracked and its insolubility was likely due to cross linking exacerbated by the loss of the BTA UV stabilizer which was absent in the aged lacquer, which required strong solvents and physical intervention to reverse it. Inhibitors such as benzotriazole (see **Section 4.43.6.1**) have been used to prime bronze surfaces prior to applying Incralac™.[6] The manufacturer reports a 5-year lifespan with removal instructions recognizing its reduced solubility with age, but a 2-year lifespan on outdoor copper alloy monuments is more common. The outdoor performance of Incralac™ is limited when measured against conservation goals of low maintenance, good protection, and reversibility but it continues to be used in the absence of any quantitative proof of significantly better performing alternatives.[6] Survey suggests Incralac™ is now less commonly used on historical and archaeological metals inside museums, apparently in favor of Paraloid B72™.[3]

Solvent-based acrylic resins and their aqueous dispersions have been tested as H_2S barriers in a program comparing them to vinyl acetates, cellulose nitrate and microcrystalline wax.[66] Acrylic dispersion systems performed better than the acrylic resin solutions and were equal performers with vinyl acetate and cellulose nitrate, but the defining factor in protectiveness of all the coatings tested was their evenness and thickness. Uneven coatings produced differential tarnishing. Microcrystalline wax (Renaissance Wax™) produced the worst result because its solid state made it difficult to apply. The conflict between good experimental procedure and practical use of coatings is reflected by drying coatings for 8 months prior to testing them with H_2S, as this is unlikely to reflect the procedure within museum contexts.

Fragile metal objects are held together by impregnating them with polymers using immersion systems. Acrylic polymers like Paraloid B72™, microcrystalline waxes and occasionally, epoxy resins are used for fragile iron.[7,36] Unsurprisingly, long-term survey reveals that iron objects washed to remove chloride and then consolidated with epoxy resins survive better than washed iron that remained unconsolidated.[36] Epoxy resin coating offers a degree of protection against moisture ingress and its strength as an adhesive retains the physical integrity of the iron even if it corrodes.[36] While the insolubility of epoxy resins appears to contravene the central conservation concept of reversibility, its use is measured against increased longevity of the iron as a cultural resource. The influence of ethics on treatment choice takes account of both the prevailing situation and the ultimate goal of prolonging the functional life of an object.

In reality even the use of a reversible consolidant is effectively an irreversible process. Since its use implicitly acknowledges it is essential for retaining the physical integrity of an object, overcoming consolidant/metal interactions to remove it would likely result in object fragmentation. While there have been no conservation studies on the influence of epoxy resins on the corrosion of metals, less viscous short chain aliphatic epoxy resins suited to consolidation processes produce more OH groups upon cross-linking than aromatic epoxy oligomers, which means they attract more water from the atmosphere and this may facilitate greater corrosion. Trapping moisture within iron objects by using consolidants and coatings runs the risk of creating microclimates that may accelerate and localize corrosion.

4.43.5.4.2 Waxes

Microcrystalline waxes are commonly used as coatings in conservation, especially on smooth even steel surfaces such as armor[3] and patinated outdoor monuments.[6] Recent E_{corr} studies revealed one such wax offered little or no protection when compared to the acrylic Paraloid B72™ and polyethylene wax Poligen ES™ on smooth steel in contact with electrolytes.[3] Interpreting this failure illustrates the importance of taking account of environment and metal substrate, as when microcrystalline waxes were tested on lead exposed to atmospheres containing organic acid vapor they performed significantly better than Paraloid B72™.[65]

Renaissance™ and Cosmoloid 80H™ waxes are the most commonly cited microcrystalline waxes in conservation literature. Typically in conservation, particular commercial products tend to be preferred for use over long time periods.[3] In what is often a nonevidence-based manner the perception grows that they are ‘proven’ products. Replacing popular coatings that are no longer being manufactured presents a problem. An extensive study was set up to find the best commercially available alternative for a microcrystalline wax being phased out of production. A range of microcrystalline waxes and a low melting point (80–100 °C) polyethylene wax were compared using electrochemical impedance spectroscopy and immersion in 0.1 M NaCl, supported by real-time atmospheric exposure.[55,67] BeSq 2095™ microcrystalline wax performed similarly to TWA 2095™ which was being phased out. Real-time testing was an essential part of this study and identified complete failure of the waxes over a 4-year exposure period. As reported for many other test procedures it was the application method that once again provided a significant influence on performance. BeSq 2095™ microcrystalline wax performed better when applied in a molten state, which produced crystalline lamellae, whereas polyethylene wax offered best protection when buffed onto bronze surfaces.

Protection of bronze ethnographic and artistic objects with waxes provides a transparent coating with a degree of color saturation that meets aesthetic goals. Sticky aesthetically displeasing mobile wax coatings that alter color saturation of surfaces are not used in conservation, unless the object is to be stored. A number of commercial products comprising wax and volatile corrosion inhibitor additive were ranked as better performing coatings for outdoor bronze sculpture, as compared to the conventional microcrystalline wax Besq 195™ using electrochemical impedance spectroscopy.[67] Dinitrol 4010™ performed best. It is used by the aerospace industry to protect engines in storage.[68] and it is a preferred choice for electrolyzed aluminum alloys,[16,47,68] although a note of caution was expressed on the use of inhibited commercial waxes for aluminum alloys without first examining their relationship with the corrosion processes taking place.[16] A Focke-Wulf 190 aero engine treated by electrolysis was coated with a 40 µm layer of Dinitrol

4010™ post treatment,[68] which has good protective properties and is favored by the aircraft industry because it has no adverse affect on rubber and plastics.

Wax coatings are considered to be high maintenance options for outdoor bronzes, as compared to acrylics. However, they are used as sacrificial topcoats on outdoor bronze statuary where they protect the underlying acrylic layer from degradation. A three-phase system of Benzotriazole inhibitor primer, Incralac™ main coat and microcrystalline wax topcoat has been employed by a number of workers and offers a more robust protective system.[6]

4.43.5.4.3 Cellulose nitrate

Before the introduction of the Paraloid™ range of acrylics, cellulose nitrate was commonly used in conservation as an adhesive and a coating. It has proven long-term reversibility and its properties and decay have been extensively reported. Long-term performance studies discounted its effectiveness as a coating on archaeological iron.[3,34] Although it has been in long-term use as an antitarnish coating on silver the cellulose nitrate lacquer Agateen™ only equaled the performance of acrylic and vinyl acetate emulsions in laboratory tests.[66] As with many other coating studies on silver, tarnishing from sulfur was strongly influenced by coating methods and the quality of their application.[57,66] Anecdotal reporting suggests recoating silver to protect against tarnishing is necessary every 10 years. This is an expensive and time consuming exercise for a large silver collection, so coating lifetime has been explored using accelerated ageing tests.[69] These revealed that light and relative humidity had a pronounced effect on the lifetime of the commonly used cellulose nitrate lacquer Frigilene™. Extrapolating the results of the accelerated tarnishing tests indicated that Frigiline™ should still protect from tarnishing after 10 years in mid-range relative humidity values. Calculations did not account for thermal effects inherent in accelerated ageing tests, so lacquer lifetime was expected to be greater than 10 years' exposure at room temperature.

Appropriately these laboratory tests are being evaluated by English Heritage using real-time monitoring of the Waterloo silver centerpiece in Apsley House, London. In several years' time the final outcome will offer insight into the effectiveness and value of the test procedures, as much as the performance of Frigiline™ lacquer as a gas barrier. Focused pragmatic studies such as this offer tangible evidence for choosing materials fit for task and for devising long-term conservation planning and budgeting. The reported testing supplied sufficient information for the production of a predictive conservation strategy. Benign impact on metal, proven reversibility, and long operational lifespan are the main essentials for conservation planning, which, in this instance, revealed that cellulose nitrate was a good choice for antitarnish coatings on silver. Although investigations into the surface chemistry relationships between cellulose nitrate and silver would offer insight into mechanisms of protection and failure, it is not necessary in order to devise a preservation strategy.

4.43.5.4.4 Silanes

While organosilicon compounds are extensively used in industry,[70] they have received limited attention in conservation practice. It appears that there is much scope for employing them on cultural metals as hydrophobic barriers, as they are largely invisible on surfaces, are good water repellents and are capable of bonding to corrosion products.[70] Barrier properties of silanes can be improved with the inclusion of inorganic additives like silica plates, which can reduce water permeability and aid reversibility. Eventually silanes will be broken down by water reaching the metal–silane interface, where it reverses the Si–O–Me bond that was formed by hydrolysis to protect the metal. Applying thicker films cannot be used to counter this as they tend to be too brittle and application difficulties are experienced.[70]

Organic–inorganic polymer systems produced by hydrolysis and condensation reactions of alkoxy silanes and organo-functional alkoxy silanes have been tested on bronze, fresh, and precorroded steel in the form of the Ormocer™ (ORganically MOdified CERamic) family of lacquers produced by the Frauhofer Institute in Munich.[71] Good adhesion to metal surfaces and their hydrated corrosion products should occur due to the presence of Si–OH and Si–O–R groups in the polymer and an organic polymeric network results from the cross linkable functional groups of alkoxy compounds ($R{-}Si(OR)_3$). Ormocer™ lacquers can be modified to produce differing elasticity, by reacting their main cross linkable component glycidoxypropyl trimethoxy silane with alkoxy and hydroxy silanes.[71]

These lacquers significantly outperformed waxes in laboratory-based accelerated (SO_2) corrosion tests and outdoor exposure using various international standards.[72] Application method and concentration proved important to performance. Monolayers (4–8 μm) and bilayers (10–12 μm), applied by spray, darkened metals and the monolayer performed better than the bilayer on patinated metal. This data indicates that it may be a promising coating for corroded metals, but technical and ethical boundaries must be crossed when using it. Ormocer™ requires methylene chloride paint stripper to reverse it. Testing this lacquer in SO_2 contaminated environments reflects its initial conception for use within industrial contexts, where polluted environments offer significant threat. Despite the siting of many cultural metal objects in urban contexts surprisingly few studies within conservation examine coating performance in SO_2 contaminated conditions.

As in other areas of conservation comparative studies dominate conservation research into silanes. An EU research project (ARCHITECH) seeking to identify better coatings for outdoor art works is examining silane coatings, copper oxalate patinas and increasing the thickness of Cu_2O layers to improve the natural protectiveness of patina on copper alloys.[56] Comparing selected silanes to the commonly used Incralac™ acrylic coating revealed them to perform only equally well, which is not encouraging given the overall weak outdoor performance of Incralac™ (see **Section 4.43.5.4.1**). The fact that Incralac™ altered the chroma of the metal surface more than the silanes[56] does not seem to offer strong support for using silanes. The fact that Ormocer™ showed better adhesion than Incralac™ in high humidity[72] may be of use, but such conditions are likely to more readily induce its hydrolysis. The PROMET project included Silane A (5% γ-mercatopropyltrimethoxysilane; 2%bis-(trimethoxysilylpropyl)amine; 1% hydrated tetraethoxysilane; 92% ethanol) in its comparative testing regime.[3] This offered best protection for bronze in long-term real-time testing, as compared to Paraloid B72™ and selected corrosion inhibitors. However, all systems failed over the test period. There are many difficulties to overcome if silanes are to be successfully used on cultural metals.

4.43.6 Inhibitors in Conservation

Inhibitors are used selectively and, in many cases, empirically in conservation practice, either alone or in combination with coatings. While their use is governed by the usual ethical constraints of appearance and reversibility, fashion also has an input. For instance the blackening of iron by tannate inhibitors may be deemed to be ethically acceptable on archaeological iron, as it could be argued that visual changes do not stray too far from the appearance of the gray/black DPL layer retained on objects.[2] This encapsulates the flexible nature of ethics and aesthetics within conservation, as the slight darkening of patinas on copper alloys caused by the use of benzotriazole is cited as being of concern by some authors. Whether inhibitor use in conservation can be reconciled with the goal of stabilizing metals is debatable, as inhibitors slow rather than prevent corrosion.

No inhibitors have been specifically developed for use in conservation practice. They are borrowed from industrial contexts, where they have been assessed for use in specific operational environments on particular alloys. As with protective coatings inhibitors are required to be effective in the presence of corrosion products. This presents difficulties, as soluble corrosion accelerators like chloride ions normally interfere with their action. Low inhibitor toxicity is also a requirement, as objects remain in the public domain where they must be accessible and easy to handle. This tends to rule out many vapor phase inhibitors, as these are often based on volatile and toxic amine base compounds. Attempts have been made to find less toxic alternatives and cheap natural inhibitors. Recently extract of seed oil from the cactus *Oputunia ficus indica* was used to formulate an inhibitor that contained long chain fatty acids, triethanolamine, and potassium hydroxide[3] but it failed to offer protection when compared to a range of coatings. This is likely due to poor film formation, as a continuous film reportedly constitutes its inhibitive properties. In the same tests, adding corrosion inhibitors to films failed to improve their protective properties significantly.[3]

4.43.6.1 Benzotriazole (BTA)

1,2,3-Benzotriazole is the most successful commercial inhibitor used in conservation practice. It is applied to prevent corrosion of chloride contaminated copper alloys.[6] There is some discussion whether it is the inhibitive properties of BTA or the barrier properties of Cu–BTA films that infer protection to patinated chloride containing copper alloys. The Cu(I)–BTA inhibitor complex films formed on copper, copper alloys, and Cu_2O surfaces have excellent adhesion from primary and secondary bonding and likely play the dominant role in the protection of patinated copper alloys by limiting water, ion, and oxygen ingress to reactive metal and mineral surfaces.[2,73,74] The film tolerates chloride ions and low-pH environments and reacts with CuCl to produce a BTA–chloride compound that is stable at high humidity[72] (see

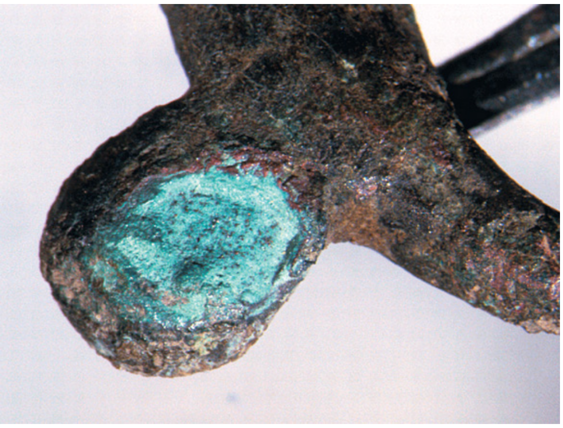

Figure 15 Benzotriazole was specifically applied in conservation practice to combat 'bronze disease'; the growth of voluminous Cu_2OH_3Cl polymorphs at the Cu_2O–CuCl interface beneath shape-retaining overlying corrosion layers. Their loss is visible on this Roman pin.

Figure 15). Compared to a range of other nitrogen or sulfur-containing organic compounds it is more effective (99%) at inhibiting hydrolysis of CuCl to $Cu_2(OH)_3Cl$ and although both 2-mercapto-benzimidazole (98% effective) and 2-mercapto-benzothiazole (97% effective) approach its inhibitive properties, they form aesthetically unacceptable white and yellow complexes with CuCl.[75] The black-green coating BTA produces when it reacts with CuCl is probably why BTA is noted for darkening patinas on copper alloys. This is a small trade-off for its proven effectiveness at preventing corrosion.

There is no definitive agreed and tested protocol for its use. It is normally used as a 3% solution in alcohol or 1% in water, with no quantitative evidence to support suggested treatment times that range from paintbrush application through a few hours in vacuum to several days soaking. Archaeological and deeply pitted copper alloys often prove difficult to stabilize using BTA solutions, as hydrolysis within pits creates a low pH that interferes with the formation of an effective Cu–BTA coating. This is overcome by pretreatment of pits with Na_2CO_3 but at an aesthetic cost of producing brown-colored spots.[6]

Factors influencing copper–BTA reactions and the nature of the resulting film include the condition and oxidation state of the reacting surface, potential, temperature, pH, and chloride and oxygen concentrations. Thus Cu(I) complexes formed in acid corrosive environments tend to be thicker, less polymerized, and more permeable to oxygen than equivalent films formed in neutral and deaerated conditions.[73] This diversity in film formation indicates that there would be considerable benefit in tests designed to examine the nature of the films formed to determine optimum application conditions. For instance, it appears that deoxygenated solutions may offer an advantage over current oxygenated treatment environments and short treatment times could explain why BTA sometimes fails to inhibit corrosion. Tests on artificial patinas have shown that it takes several days for reaction with brochantite ($Cu_4SO_4(OH)_6$), which is a common corrosion product on outdoor statuary in urban areas, to go to completion.[38,74] Although the acid by product of this reaction lowers pH as concentrations of BTA increase, a dilemma exists as treatment must ensure there is excess BTA present to repair any damage to the protective BTA polymeric film formed.[74]

Use of BTA on outdoor statuary requires a regular maintenance program, as BTA is likely to be lost from effects of rain-wash due to its solubility and volatilization because of its low vapor pressure. The use of BTA as a primer coated with protective lacquer(s) should prolong its effectiveness. Additionally, BTA also forms Pb–BTA and PbO–BTA compounds as crystalline polymeric films which have been shown to protect lead within leaded bronzes from corrosion by organic acids[76] and Zn(II)–inhibitor complexes have been detected on copper alloy.[2] In contrast electrochemical measurements showed silicon bronzes had lower organic inhibitor efficiency as silica is poorly reactive towards BTA.[2] It is clearly important to know what copper alloy is being treated to assess likely inhibitor effectiveness.

Whether copper alloys routinely require treatment with BTA is questionable. What percentage of objects would have remained stable, even if they had not been treated with BTA, is unknown. Many patinated copper alloys treated by BTA appear stable in museum environments, although this observation remains unsupported by quantitative data. A study of surface chemistry reactions with the typical corrosion profiles found on copper alloy objects and quantitative long-term studies of copper alloy object stability following treatment with BTA would determine its inhibitive powers relative to the conservation goals of longevity and predictive success.

Despite its proven inhibitive success, workers still seek alternatives to BTA mainly due to toxicity worries and its high cost. While no better inhibitor for cultural corroded copper alloys has been recorded, synergistic inhibitive effects have been identified when using BTA with other inhibitors that included 5-amino-2-mercapto-1,3,4-thiadazole.[77] Caution is required when mixing inhibitors as the formation of differing BTA complexes can lower performance of BTA.[75] Recently BTA with a hydrophobic alkyl side chain (C6-BTA) has been tested on the basis that the side chain will better repel aqueous electrolyte.[2] A more novel use for BTA is as an inhibitive washing procedure for marine iron, where it forms Cu(I) complexes and Cu(II) species and prevents corrosion while the water wash extracts chloride from CuCl.[38] A big advantage of using a BTA preservation strategy on copper alloys is that it can be applied without any surface preparation, which is ideal where patina is part of the intrinsic value of the object. Ensuring access to the Cu_2O layer that is normally situated next to the metal or integrated with CuCl sited there will provide the best opportunity for treatment success, due to the ability of BTA to react with this oxide. Unfortunately, removing the overlying green brochantite/antlertite/malachite patinas to reveal orange/red Cu_2O would be visually unacceptable in many instances.

4.43.6.2 Tannins

As conservation seeks to balance its goals with global concerns regarding toxicity and carbon footprints, testing low toxicity inhibitors derived from natural sources like plant extracts is of interest. Tannin plant extracts have been used intermittently in conservation since the 1960s and are reported to act as rust converters, leaving a black inhibitive film on the metal. Treatment involves either immersion in tannin solutions or, more likely, painting onto objects. Currently there is no quantitative in-depth study of their action within conservation contexts or any data that offers quantified guidance for optimum treatment concentrations or application procedures.

It is well known that condensed tannins applied either in water or solvent to rust-covered iron offer inhibitive properties by forming ferric–tannate complexes that act as insoluble barriers and phosphoric acid is said to improve inhibitive properties. Tannate-coated iron performed well in long-term storage according to a qualitative survey of archaeological iron.[30] While this provides useful information, post-treatment stability studies for determining treatment success should be controlled and semiquantitative with clear links to environmental variables, rather than retrospective examinations of treated objects.

Iron stripped by 4NaEDTA was coated with a mixture of phosphoric and tannic acids to inhibit further corrosion, following electrochemical testing to determine optimum concentrations and combinations of inhibitor.[44] A recent study identifying optimum concentrations of tannin and phosphoric acid for inhibiting corrosion of rusted iron in a 3.5% NaCl solution indicates the importance of research and testing to optimize tannin applications to meet the prevailing circumstances. In this study, E_{corr} values showed that phosphoric acid reduced the inhibitive properties of mangrove tannins at low pH (0.5 and 2.0), yet when used alone at higher pH (5.5) it offered improved inhibition as compared to tannin/phosphate mixtures.[78] Corroding archaeological iron has varying pH across its surface due to hydrolysis of anodically produced Fe^{2+} and its thick corrosion layers. Any testing of tannins for use in conservation practice should be tailored to the corrosion model extant.

As with other protective surface coatings testing the stability of treated objects at typical storage humidities is necessary and, until this is achieved, application of tannins in conservation will retain a degree of empiricism. To date, no inhibitor has been shown to have effective long-term inhibitive action on chloride-contaminated archaeological iron retaining its corrosion layers and exposed to mid to high relative humidities. Commercial tannate-based inhibitors have been tested and shown to be effective for inhibiting internal corrosion of boilers in the working nineteenth-century paddle steamer PS Enterprise between its weekly use on lake Burley Griffin, Australia[79] (see **Figure 16**). In these closed systems the boiler retains its water and inhibition results from a combination of reducing the availability of oxygen, formation of iron tannate film and precipitation of dissolved salts as sludge.

4.43.6.3 Carboxylates

Sodium carboxylates ($CH_3(CH_2)_{n-2}COONa$ – usually $n = C_{10}$ or C_{12}) derived from vegetable oils have been used on copper alloys and iron to form inhibitive copper and iron carboxylates.[2,3,41,80–82] Like tannates, they are environmentally friendly. They have been linked to conservation in tests on corroded iron and copper coupons and blank standards.[41,80] Potentiodynamic curves revealed they offered slightly better inhibition than mimosa tannin solutions and considerably better protection than phosphates tested on bare clean steel coupons.[80] A further advantage is that the nanomeric hydrophobic iron carboxylate soap layer formed by reaction with iron cations[79] is not aesthetically disfiguring, as is a black iron tannate layer. Carboxylates readily reverse in ethanol, which may mean they are best suited to indoor applications. Long-term

Figure 16 Tannates are used to protect the boilers in this 19th-century paddle steamer belonging to the National Museum of Australia. Image courtesy of David Hallam.

real-time testing using precorroded metal coupons indicated that sodium decanoate offers temporary protection on partially oxidized historic steels and may be considered as an alternative to Paraloid B72™.[3] It also offered good protection for copper alloys.

Carboxylates were originally tested in conservation as inhibitors for preventing corrosion of lead by volatile organic acids.[81] Polarization plots produced by modeling corrosion of inhibited lead by these acids indicated that sodium decanoate and undecanoate protected best against corrosion, whereas phosphate inhibitors actually increased corrosion rates.[65] Real-time X-ray diffraction studied the resistance of lead carboxylate ($CH_3(CH_2)_8COO)_2Pb$) films to acetic acid vapor and revealed considerable protective properties, but ultimate failure.[82] Carboxylates appear to delay corrosion by organic acids, but ultimately they cannot prevent it. As in other areas of conservation, contextual needs dictate preservation strategies, while these tests showed carboxylates as being unsuitable for preserving church organs, they may be considered suitable where lead is more accessible and easy to monitor to determine if retreatment is necessary.

4.43.7 Painted Metals

4.43.7.1 Removing Paint

Conservation ethics normally dictate that original or later paintwork that offers either a record of the history of the object or milestones in its life should be preserved. The preservation of fragmentary original paint surfaces is challenging, as pitting and corrosion undermining paint are a threat to paint integrity and are difficult to stabilize. In such instances environmental control may be the only option guaranteed to prevent ongoing corrosion beneath the paint layer. There are instances where ethical arguments support refinishing the surfaces of cultural objects either to their original specification or to an improved standard in order to offer the best opportunity for longevity. This should not compromise the future interpretation of the object.

Refinishing may be acceptable when there is no original paint layer remaining and replicating an original finish offers significantly increased object longevity. A combination of refinishing and preservation of original surfaces may be adopted in some instances.[83] If the condition of the metal allows, refinishing offers opportunity for highly specified surface preparation. It may also be possible to apply modern paint systems if visual appearance rather than replication of the original recipe is deemed to be the most important interpretive factor. Stripping to the bare metal for repainting should involve minimal loss of the original metal.

4.43.7.2 Refinishing Painted Surfaces

Preparation of historic metal surfaces to receive paint must always minimize loss of metal. Commercial conservation programs often adhere to international standards for preparing surfaces, such as SSPC, NACE, and Swedish Standards. This offers the client a defined measuring point within the contract of work. Repainting the upper hull of the SS Great Britain was justified on the basis of continual repaints during the working life of the ship and the presence of a failing modern paint layer. The hull above the waterline was to be exposed to the British climate and merited the best possible protection from the elements.[25] It was stripped to near white metal (SA2.5) using high pressure water lances (2500 bar) and for weaker areas crushed Australian Garnet (8 bar) in preparation for painting (see Figure 17). Although this removed several microns of original wrought iron, it was reasoned to be ethical as this thickness of metal would inevitably be lost through future corrosion if preparation was not so stringent. The paint system chosen was typical for creating a durable, long-lived outdoor protective coating on a well prepared surface. A three-phase treatment comprising a 2-pack zinc-rich epoxy primer followed by 2-pack high-build main coat paint system with a urethane UV-resistant topcoat, produced a total paint thickness of 225–250 µm[25] (see Figure 17). The preferred method of application involved an airless spray at 207×10^5 Pa with brushing when the spray could not be used. Life expectancy of this layer with appropriate maintenance is predicted at 15 years.

Often it is not possible to prepare corroded metal surfaces to a high standard. In this instance original lead-based paints are preferred, both to replicate original paint layers and because of their perceived longevity. Since health and safety considerations make their manufacture costly and their use has environmental implications, aluminum-based primers are normally used instead. Ferro zinc (HMG Paints) is a rust conversion paint that was used to paint the monitor HMS Minerva after electrolysis.[31] The range of historic alloys and the inability to effectively prepare many surfaces beyond SA 1 or 2 means that each surface offers a unique coating problem. Consequently conservation designs often test paint adherence using a pull-off test (ASTM D 4541-02 or ISO 4624) before applying it to an entire surface. Reports on the longevity of painted surfaces relative to the prepainting condition of the surface and the paint system applied are not reported and this offers another area for research that could act as a platform for designing industry standards. Silanes are used for preparing metals for paint within industry,[70] but this has not been reported in conservation practice.

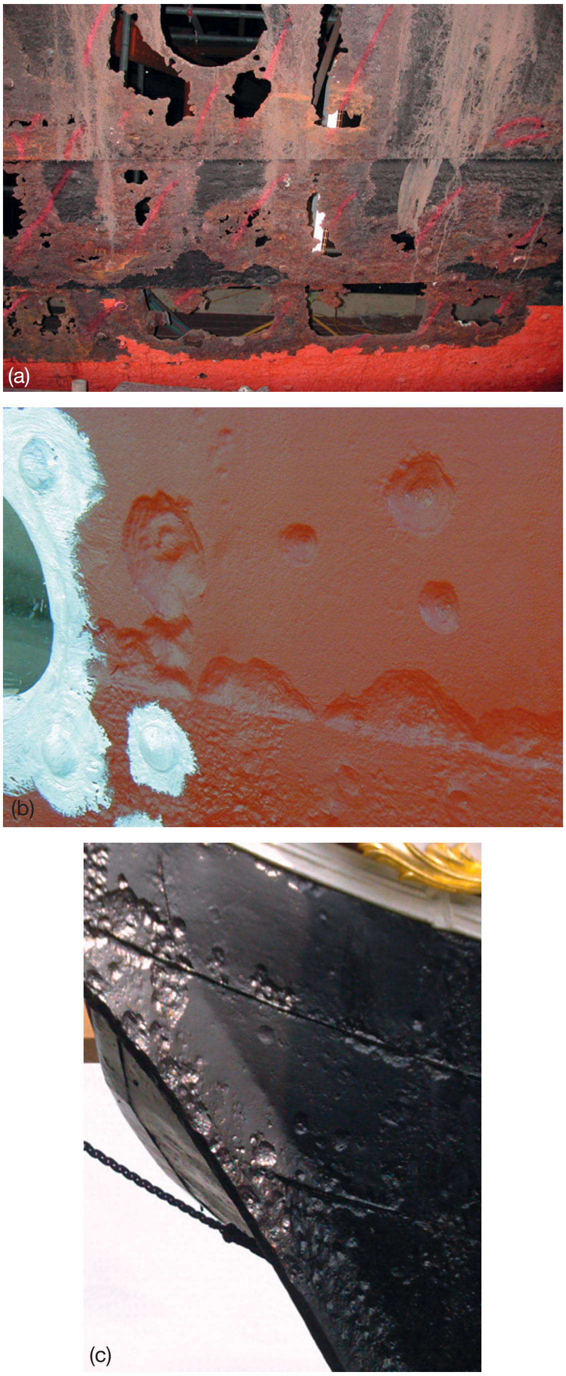

Figure 17 Surface preparation to SA2.5 standard on the SS Great Britain and the completed paint schedule.[25] Images courtesy of Eura Conservation Ltd.

Where sections of metal have entirely corroded away, decisions regarding a course of action have to account for ethical, technical, and corrosion considerations. Structural problems require structural solutions but care must be taken not to create galvanic cells by repairing with alloys of differing potential from the original metal. Equally, where structural

Figure 18 Challenges in metal conservation extend beyond museum interiors to whole sites such as housing at Valparaiso (UNESCO World Heritage site) and abandoned factory settlements like Stromness (South Georgia) whaling station. Images courtesy of Eura Conservation Ltd.

integrity is not a concern it is possible to use glass reinforced plastics and epoxy systems.[25]

4.43.8 Overview

The overall equation for preserving cultural metals is a complex mixture of material science, context, and ethics. During the past 40 years, conservation has developed links with corrosion science that have led to greater understanding of corrosion processes, which, in turn, supports investigation into treatment mechanisms and methods. This has been extensively boosted over the past 15 years by increased application of modern instrumental analysis in conservation research. Much greater opportunity exists for collaboration between conservators and corrosion scientists to develop a synergistic relationship for solving the problems of preserving 'metallic heritage.'

Within conservation there are normally multiple preservation options, either due to insufficient evidence to identify one treatment as being significantly better than another or because of differing, but equally valid ethical arguments allow for a range of conservation routes and outcomes. Thus, within this review, large iron chloride-infested naval vessels were treated in four different ways in attempts to stabilize them. HMS Holland was washed in an inhibitive solution to extract chloride[31]; CSS Hunley will be treated by a newly researched washing method employing alkali and pressure[12,28,29]; HMS Minerva was electrolyzed to remove chloride[31]; SS Great Britain used environmental control to prevent corrosion.[11,25,32] All methods are either supported by new research or utilize universally applied treatment techniques. They also have a strong treatment rationale with practical arguments to support the course of action taken. While there will always be diverging views and arguments on appropriate ethical strategies, there remains the opportunity to ensure treatments are researched and optimized. Conservation is a staged process with systematic treatments. There is initially a rationalizing process to decide a course of action, which is then split into treatment stages. As an example, chloride removal from iron might be followed by an inhibitive treatment, over which a coating is applied and the result is subjected to long-term monitoring that assesses outcomes and provides data for future action. Large-scale complex contextual combinations will challenge this approach. At Valparaiso *ad hoc* steel houses form a world heritage site (see **Figure 18**). They are lived in and offer the challenge of corroding sheet steel, galvanized structures and various paint regimes. Besides finding safe, proven treatment procedures, complex decisions exist on retention of paint, set against a backdrop of what the occupants want and expect, relative to their standard of living. Should the structures eventually become a museum or continue to be lived in? Deserted, but equally daunting, are the remains of a whaling station at Stromness, South Georgia. Remoteness, climate influences, and cost offer significant challenges here. An overarching consideration is climate change and how it will influence corrosion.

Conservation should define standards of preservation, starting with costly indefinite survival of metals down to the guarantee of only a few months preservation. Developing such a scale goes beyond the science of preservation to its ethics. It may be argued that national icons providing cornerstones in societies merit the cost of indefinite preservation, but commonplace archaeological iron that is to be analyzed, recorded, and published is preserved only for the duration of the analysis and publication process. Counter arguments would focus on the importance of future research into material such as archaeological iron. Suggesting a scale of importance will necessitate extensive ethical debate about how to define importance. In the modern world of diminishing resources, carbon footprints and concern over environmental impact, there are difficult decisions to make and responsibilities to accept for the action taken. Focused coordinated research in collaboration with corrosion scientists can contribute towards informing these decisions for metals preservation.

References

1. Caple, C. *Conservation Skills;* Routledge: London, 2000.
2. Dillmann, P.; Beranger, G.; Piccardo, P.; Mathiesen, H., Eds. *Corrosion of Metallic Heritage Artefacts: Investigation, Conservation and Prediction of Long-term Behaviour*; Woodhead: Cambridge, UK, 2007.
3. Argyropoulous, V. Ed. *Metals and Museums in the Mediterranean; Protecting, Preserving and Interpreting*; TEI of Athens: Greece, 2008.
4. Costa, V. In *Conservation Science 2002*; Papers from the Conference held in Edingburgh, Scotland 22–24 May 2002. Townsend, J. H., Eremin, K., Adriaens, A., Eds.; Archetype Publications: London, 2002.
5. icom-cc.icom.museum/Documents/WorkingGroup/Metals/Bromec.
6. Scott, D. A. *Copper and Bronze in Art; Corrosion, Colourants and Conservation;* Getty Trust Publications, Getty Conservation Institute: USA, 2002.
7. Cronyn, J. *The Elements of Archaeological Conservation;* Routledge: London, 1990.
8. Pearson, C. *Conservation of Marine Archaeological Objects;* Butterworths: London, 1987.
9. Ashley-Smith, J. *Risk Assessment for Object Conservation;* Butterworth-Heinmann: Oxford, 1999.
10. Selwyn, L. *Metals and Corrosion: A Handbook for the Conservation Profesional;* Canadian Conservation Institute: Ottowa, 2004.
11. Watkinson, D.; Al Zahrani, A. *The Conservator* **2008**, *31*, 75–86.
12. Drews, M. J.; de Viviés, P.; González, N. G.; Mardikian, P. In *Metal 04*; Proceedings of the International Conference on Metals Conservation, Canberra, 4–8 October 2004; Ashton, J., Hallam, D., Eds.; National Museum of Australia: Canberra, Australia, 2004.
13. Costa, V. *Rev. Conservat.* **2001**, *2*, 18–34.
14. Cassar, M. *Environmental Management; Guidelines for Museums and Galleries;* Routledge: London, 1994.
15. Green, L. R.; Thickett, D. In *Saving the Twentieth Century*; The Conservation of Modern Materials, Proceedings of a Conference Symposium 91 – Saving the Twentieth

Century, 15–20 September 1991; Grattan, D. W., Ed.; Canadian Conservation Institute: Ottowa, Canada, 1993.
16. Adams, C.; Hallam, D. In *Saving the Twentieth Century*; The Conservation of Modern Materials, Proceedings of a Conference Symposium 91 – Saving the Twentieth Century, 15–20 September 1991; Grattan, D. W., Ed.; Canadian Conservation Institute: Ottowa, Canada, 1993.
17. Green, L. R.; Thickett, D. *Stud. Conservat.* **1995**, *40*, 145.
18. Thickett, D.; Bradley, S.; Lee, L. In *Metal 98*; Proceedings of the international conference on metals conservation. Draguignan-Figanieres, France, 27–29 May 1998; Mourney, W., Robbiola, L., Eds.; James and James: London, 1998.
19. Leygraf, C.; Graedel, T. *Atmospheric Corrosion;* Wiley Interscience, 2000.
20. Watkinson, D.; Lewis, M. R. T *Stud. Conservat.* **2005**, *50*, 241–252.
21. Thickett, D.; Odlyha, M. In *Conservation of Archaeological Materials*: Current Trends and Future Directions. Williamsburg, Virginia, 13–17 November 2005. American Institute for Conservation Postprints 9. Washington, DC, in press.
22. Thickett, D.; Luxford, N. In *Metal 07, Book 5, Protection of Metal Artefacts*, Interim Meeting of the ICOM-CC Metal WG Amsterdam, 17–21 September 2007; Degrigny, C., Van Langh, R., Joosten, I., Ankersmit, B., Eds.; Rijksmuseum: Amsterdam, 2007.
23. Weintraub, S. In *Object Speciality Group Postprints 9, 2002*; American Institute for Conservation: Washington DC, 2002.
24. Thickett, D.; Luxford, N. *The Conservator* **2006**, *29*, 19–34.
25. Watkinson, D.; Tanner, M.; Turner, R.; Lewis, M. *The Conservator* **2005**, *29*, 73–86.
26. Green, L.; Blackshaw, S. In *Metal 95*; Proceedings of the International Conference on Metals Conservation Semur en Auxois, 25–28 September 1995; Macleod, I., Pennec, S. L., Robbiola, L., Eds.; James and James: London, 1997.
27. Mathias, C.; Ramsdale, K.; Nixon, D. In *Metal 04*; Proceedings of the International Conference on Metals Conservation, Canberra, 4–8 October 2004; Ashton, J., Hallam, D., Eds.; National Museum of Australia: Canberra, Australia, 2004.
28. de Viviés, P.; Cook, D.; Drews, M. J.; González, N.; Mardikian, P.; Memet, J. B. In *Metal 07, Book 5, Protection of Metal Artefacts*, Interim Meeting of the ICOM-CC Metal WG Amsterdam, 17–21 September 2007; Degrigny, C., Van Langh, R., Joosten, I., Ankersmit, B., Eds.; Rijksmuseum: Amsterdam, 2007.
29. González, N.; Cook, D.; de Viviés, P.; Drews, M. J.; Mardikian, P. In *Metal 07, Book 3, Use of Elecrtochemical Techniques in Metal Conservation*; Interim Meeting of the ICOM-CC Metal WG Amsterdam, 17–21 September 2007; Degrigny, C., Van Langh, R., Joosten, I., Ankersmit, B., Eds.; Rijksmuseum: Amsterdam, 2007.
30. Selwyn, L. S.; Logan, J. A. In *International Council for Museums Committee for Conservation 10th Triennial Meeting,* 22–27 August 1993; Washington, D. C., Bridgland, J., Eds.; International Council for Museums, James and Jame: Washington, DC, 1993.
31. Barker, D. In *Conservation Science Heritage Materials*; May, E., Jones, M., Eds.; RSC Publishing: Cambridge, 2006.
32. Watkinson, D.; Lewis, M. R. T. In *Materials Issues in Art and Archaeology VII*, Symposium Proceedings of the Materials Research Society of America; *Vol.* 852; Vandiver, P. B., Mass, J. L., Murray, A., Eds.; Materials Research Society: Warrendale, PA, 2005.
33. Réguer, S.; Neff, D.; Remazeilles, C.; Guilmeinot, E.; Nicot, F.; Pele, C.; Meguelati, M.; Mirambert, F.; Dillmann, P.; , Refait, P.; *et al.* In *Metal 07, Book 2, Innovative investigation of metal Artefacts*; Interim Meeting of the ICOM-CC Metal WG Amsterdam, 17–21 September 2007; Degrigny, C., Van Langh, R., Joosten, I., Ankersmit, B., Eds.; Rijksmuseum: Amsterdam, 2007.
34. Selwyn, L. S.; Argyropoulos, V. *Stud. Conservat.* **2005**, *50*, 81–99.
35. Keene, S. V In *Ancient and Historic Metals: Conservation and Scientific Research*; Scott, D. A., Podanay, J., Consadine, B., Eds.; Getty Conservation Institute: Los Angles, 1991; pp 249–264.
36. Keene, S. V.; Orton, C. *Stud. Conservat.* **1985**, *30*, 1–7.
37. MacLeod, I. D. *Stud. Conservat.* **1983**, *28*, 1–7.
38. MacLeod, I. D. *Stud. Conservat.* **1987**, *32*, 1–13.
39. Thickett, D.; Enderly, C. In *The Interface Between Science and the Conservator*; British Museum Occasional Paper No. 116, Bradley, S., Ed.; The British Museum: London, 1997.
40. Merk, L. E. *Stud. Conservat.* **1978**, *33*, 1522.
41. Otiento-Alego, V.; Thurrowgood, D.; Creagh, D. C.; Bailey, G. In *Conservation Science 2002*; Papers from the Conference held in Edingburgh, Scotland, 22–24 May 2002; Townsend, J. H., Eremin, K., Adriaens, A., Eds.; Archetype Publications: London, 2002.
42. Huda, K. *Stud. Conservat.* **2002**, *47*, 211–214.
43. Costa, V.; Urban, F. *Rev. Conservat.* **2005**, *6*, 48–62.
44. Degrigny, C. *Stud. Conservat.* **1995**, *40*, 227–236.
45. Guilminot, E.; Baron, G.; Memet, J. B.; Huet, N.; le Noc, E.; Roze, J. P. In *Metal 07, Book 3, Use of Elecrtochemical Techniques in Metal Conservation*; Interim Meeting of the ICOM-CC Metal WG Amsterdam, 17–21 September 2007; Degrigny, C., Van Langh, R., Joosten, I., Ankersmit, B., Eds.; Rijksmuseum: Amsterdam, 2007.
46. Degrigny, C.; Le Gall, R. *Stud. Conservat.* **1999**, *3*, 157–169.
47. Degrigny, C. In *Saving the Twentieth Century*; The Conservation of Modern Materials, Proceedings of a Conference Symposium 91 – Saving the Twentieth Century, 15–20 September 1991; Grattan, D. W., Ed.; Canadian Conservation Institute: Ottowa, Canada, 1993.
48. Hallam, D. L.; Adams, C. D.; Bailey, G.; Heath, G. A In *Metal 95*, Proceedings of the International Conference on Metals Conservation Semur en Auxois, 25–28 September 1995; Macleod, I., Pennec, S. L., Robbiola, L., Eds.; James and James: London, 1997.
49. Bailey, G. T. In *Metal 04*, Proceedings of the International Conference on Metals Conservation, Canberra, October 4–8, 2004; Ashton, J., Hallam, D., Eds.; National Museum of Australia: Canberra, Australia, 2004.
50. Mardikian, P. *Int. J. Nautical Archaeol.* **2004**, *33*, 137–148.
51. Nordgren, E.; Goncalves, P.; Shindelholtz, E.; Brossia, C. S.; Yunovich, M. In *Metal 07, Book 3, Use of Elecrtochemical Techniques in Metal Conservation*; Interim Meeting of the ICOM-CC Metal WG Amsterdam, 17–21 September 2007; Degrigny, C., Van Langh, R., Joosten, I., Ankersmit, B., Eds.; Rijksmuseum: Amsterdam, 2007.
52. MacLeod I. D. *Conservat. Mgmt Archaeol. Sites* **2006**, *7*, 203–223
53. Birchenall, E. C.; Meussner, R. A. In ; Brown, F. B., Ed.; *Corrosion and Metal Artifacts: A Dialogue Between Conservators, Archaeologists and Corrosion Scientists*; National Bureau of Standards Special Publication, Vol. 479, 1977.
54. Schmidt-Ott, K.; Boissonnas, V. *Stud. Conservat.* **2002**, *47*, 81–87.
55. Price, C.; Hallam, D.; Aston, J.; Heath, G.; Creagh, D. In *Metal 95*, Proceedings of the International Conference on Metals Conservation Semur en Auxois, 25–28 September 1995; Macleod, I., Pennec, S. L., Robbiola, L., Eds.; James and James: London, 1997.

56. Joseph, E.; Letardi, P.; Mazzeo, R.; Prati, S.; Vandini, M. In *Metal 07, Book 5, Protection of Metal Artefacts*, Interim Meeting of the ICOM-CC Metal WG Amsterdam, 17–21 September 2007; Degrigny, C., Van Langh, R., Joosten, I., Ankersmit, B., Eds.; Rijksmuseum: Amsterdam, 2007.
57. Thickett, D.; Hockey, M. In *Conservation Science 2002*; Papers from the Conference held in Edingburgh, Scotland, 22–24 May 2002; Townsend, J. H., Eremin, K., Adriaens, A., Eds.; Archetype Publications: London, 2002.
58. Rosales, B.; Vera, R.; Moriena, G. *Corros. Sci.* **1999**, *41*, 625–651.
59. Cicileo, G. P.; Crespo, M. A.; Rosales, B. M. *Corros. Sci.* **2004**, *46*, 929–953.
60. Prytulak, G. In *Industrial Collections: Care and Conservation*; Proceedings of a Conference hosted by The Council of Museums in Wales and The United Kingdom institute for Conservation, Cardiff, 9–11 April 1997; Dollery, D., Henderson, J., Eds.; CMW and UKIC: Cardiff, 1999.
61. Lins, A. In *Dialogue 89 – The Conservation of Bronze Sculpture in the Outdoor Environment: A Dialogue Among Conservators, Curators, Environmental Scientists, and Corrosion Engineers*; Drayman-Weisser, T., Ed.; National Association of Corrosion Engineers: Houston, 1992.
62. Wharton, G.; Maish, S. L.; Ginell, W. S *J. Am. Inst. Conservat.* **1990**, *29*, 13–31.
63. Cano, E.; Bastidas, D. M.; Argyropoulos, V.; Siatou, A. In *Strategies for Saving our Cultural Heritage*; International Conference on Conservation Strategies for Saving Indoor Metallic Collections, Cairo, 25 February–1 March 2007; Argyropoulous, V., Hein, A., Abdel Harith, M., Eds.; Technological Educational Institute of Athens: Athens, Greece, 2007.
64. Aslund, A.; Bergsten, C. J.; Chiavari, C.; Martini, C.; Niklasson, A.; Prandstraller, D.; Svensson, J. E. In *Metal 07, Book 5, Protection of Metal Artefacts*, Interim Meeting of the ICOM-CC Metal WG Amsterdam, 17–21 September 2007; Degrigny, C., Van Langh, R., Joosten, I., Ankersmit, B., Eds.; Rijksmuseum: Amsterdam, 2007.
65. Chiavari, C.; Martini, G.; Poli, D.; Prandstraller, D. In *Metal 04*, Proceedings of the International Conference on Metals Conservation, Canberra, 4–8 October 2004; Ashton, J., Hallam, D., Eds.; National Museum of Australia: Canberra, Australia, 2004.
66. Grabow, N.; Smith, C.; Grissom, C.; Brostoff, L. In *Metal 07, Book 5, Protection of Metal Artefacts*, Interim Meeting of the ICOM-CC Metal WG Amsterdam, 17–21 September 2007; Degrigny, C., Van Langh, R., Joosten, I., Ankersmit, B., Eds.; Rijksmuseum: Amsterdam, 2007.
67. Otieno–Alego, V.; Heath, G.; Hallam, D.; Creagh, D. In *Metal 98*, Proceedings of the International Conference on Metals Conservation, Draguignan-Figanieres, France, 27–29 May 1998; Mourney, W., Robbiola, L., Eds.; James and James: London, 1998.
68. Degrigny, C. *Stud. Conservat.* **1995**, *40*, 10–18.
69. Luxford, N.; Thickett, D. In *Metal 07, Book 5, Protection of Metal Artefacts*, Interim Meeting of the ICOM-CC Metal WG Amsterdam, 17–21 September 2007; Degrigny, C., Van Langh, R., Joosten, I., Ankersmit, B., Eds.; Rijksmuseum: Amsterdam, 2007.
70. van Ooij, W. J.; Zhu, D.; Stacy, M.; Seth, T.; Mugada, J.; Gandhi, J.; Puomi, P. *Tsinghua Sci. Technol.* **2005,** *10*(6), 639–664.
71. Piltz, M.; Romich, H. In *Metal 95*, Proceedings of the International Conference on Metals Conservation Semur en Auxois, 25–28 September 1995; Macleod, I., Pennec, S. L., Robbiola, L., Eds.; James and James: London, 1997.
72. Seipert, B.; Pilz, M.; Kiesenberg, J. In *Metal 98*, Proceedings of the International Conference on Metals Conservation, Draguignan-Figanieres, France, 27–29 May 1998; Mourney, W., Robbiola, L., Eds.; James and James: London, 1998.
73. Brostoff, R. In *Metal 95*, Proceedings of the International Conference on Metals Conservation Semur en Auxois, 25–28 September 1995; Macleod, I., Pennec, S. L., Robbiola, L., Eds.; James and James: London, 1997.
74. Turgoose, S.; Duncan, S. In *Dialogue 89 – The Conservation of Bronze Sculpture in the Outdoor Environment: A Dialogue Among Conservators, Curators, Environmental Scientists, and Corrosion Engineers*; Drayman-Weisser, T., Ed.; National Association of Corrosion Engineers: Houston, 1992.
75. Faltermeir, R. T. *Stud. Conservat.* **1999**, *44*, 121–128.
76. Sharma, V. C.; Shankar, U.; Singh, T. *Stud. Conservat.* **2003**, *48*, 203–209.
77. Golfimistou, S.; Merkel, J. F In *Metal 07, Book 5, Protection of Metal Artefacts*, Interim Meeting of the ICOM-CC Metal WG Amsterdam, 17–21 September 2007; Degrigny, C., Van Langh, R., Joosten, I., Ankersmit, B., Eds.; Rijksmuseu: Amsterdam, 2007.
78. Rahin, A. A.; Rocca, E.; Steinmetz, J.; Kassim, M. J. *Corros. Sci.* **2008**, *50*, 1546–1550.
79. Greiner, A.; Hallam, D.; Thurrowgood, D.; Creagh, D. In *Metal 07, Book 5, Protection of Metal Artefacts*, Interim Meeting of the ICOM-CC Metal WG Amsterdam, 17–21 September 2007; Degrigny, C., Van Langh, R., Joosten, I., Ankersmit, B., Eds.; Rijksmuseum: Amsterdam, 2007.
80. Hollner, S.; Mirambet, F.; Rocca, E.; Steinmetz, J. In *Metal 07, Book 5, Protection of Metal Artefacts*, Interim Meeting of the ICOM-CC Metal WG Amsterdam, 17–21 September 2007; Degrigny, C., Van Langh, R., Joosten, I., Ankersmit, B., Eds.; Rijksmuseum: Amsterdam, 2007.
81. Rocca, E.; Steinmetz, J. *Corros. Sci.* **2001**, *43*, 891–902.
82. Dowsett, M.; Adiaens, A.; Scotte, B.; Jones, G.; Bouchenoire, L. In *Metal 07, Book 5, Protection of Metal Artefacts*, Interim Meeting of the ICOM-CC Metal WG Amsterdam, 17–21 September 2007; Degrigny, C., Van Langh, R., Joosten, I., Ankersmit, B., Eds.; Rijksmuseum: Amsterdam, 2007.
83. Thurowgood, D.; Sattler, U.; Wehner, K. In *Metal 07, Book 1, When Archaeometry and Conservation Meet*; Interim Meeting of the ICOM-CC Metal WG Amsterdam, 17–21 September 2007; Degrigny, C., Van Langh, R., Joosten, I., Ankersmit, B., Eds.; Rijksmuseum: Amsterdam, 2007.

Symbols and Abbreviations

SI Units

SI Base Units	*Name*	*Symbol*
Length (l)	metre	m
Mass (m)	kilogram	kg
Time (t)	second	s
Current (I)	ampere	A
Temperature (T)	kelvin	K
Amount of substance	mole	mol
Luminous intensity	candela	cd

Named Derived SI Units [note 1]	*Name*	*Symbol*	*Relation to SI Base Units*
Frequency (Hz)	hertz	Hz	s^{-1}
Celcius temperature	degree celcius	°C	K
Force (F)	newton	N	$m\ kg\ s^{-2}$
Pressure, stress (P)	pascal	Pa ($N\ m^{-2}$)	$m^{-1}\ kg\ s^{-2}$
Energy, work, amount of heat	joule	J	$m^2\ kg\ s^{-2}$
Power	watt	W	$m^2\ kg\ s^{-3}$
Electric charge	coulomb	C	A s
Electric potential difference	volt	V	$m^2\ kg\ s^{-3}\ A^{-1}$
Current density	ampere per square metre	i	$A\ m^{-2}$
Electric resistance (R)	ohm	Ω	$m^2\ kg\ s^{-3}\ A^{-2}$
Electric conductance	siemens	S	$m^{-2}\ kg^{-1}\ s^3\ A^2$
Capacitance (C)	farad	F	$m^{-2}\ kg^{-1}\ s^4\ A^2$
Area	square metre	A	m^2
Volume	cubic metre	V	m^3
Density	kilogram per cubic metre	ρ	$kg\ m^{-3}$
Amount concentration	mole per cubic metre	-	$mol\ m^{-3}$

Non-SI Units	*Name*	*Symbol*	*Relation to SI Units*
Volume	litre [note 2]	L,l	dm^3
Concentration	molarity [note 3]	M	$mol\ d_m^{-3}$
Concentration	molality	m	$mol\ kg^{-1}$
Potential	electrochemical potential	E	V
Diffusion	diffusion coefficient	D	$m^2\ s^{-1}$
Pressure	bar [note 4]	bar	$100\ kN\ m^{-2}$
Pressure	atmosphere	atm	$101.325\ kN\ m^{-2}$

Notes

1. This is not a complete listing (the Bureau International des Poids et Mesures is the official source for information on SI units, and readers are referred to their web site at www.bipm.org for further information).
2. The standard SI unit of volume is m^3 however the litre (Both upper (L) and lowercase symbols are in use although the former is preferred to avoid confusion with the number 1), equivalent to 1 dm^3, is in widespread use (and is permitted).
3. The standard SI unit of concentration is $mol\ m^{-3}$ however, molarity (M) is in widespread use although it is deprecated.
4. The standard unit of pressure is $N\ m^{-2}$ (Pa), however ‘bar’ and ‘atmosphere’ are in widespread use (although deprecated) especially for reporting of atmospheric air and gas pressures.

SI Prefixes

Factor	*Name*	*Symbol*	*Factor*	*Name*	*Symbol*
10^{15}	peta	P	0.1	deci	d
10^{12}	tera	T	0.01	centi	c
10^{9}	giga	G	10^{-3}	milli	m
10^{6}	mega	M	10^{-6}	micro	µ
10^{3}	kilo	k	10^{-9}	nano	n
100	hecto	h	10^{-12}	pico	p
10	deca	da	10^{-15}	femto	f

Fundamental Physical Constants

Symbol	*Name*	*Value*
c	speed of light in vacuum	$2.99792 \times 10^{5}\ \mathrm{m\,s^{-1}}$
k	Boltzmann constant	$1.38065 \times 10^{-23}\ \mathrm{J\,K^{-1}}$
e	elementary charge	$1.60218 \times 10^{-19}\ \mathrm{C}$
eV	electron volt	$1.60218 \times 10^{-19}\ \mathrm{J}$
ε_o	electric constant (permittivity)	$8.85419 \times 10^{-12}\ \mathrm{F\,m^{-1}}$
F	Faraday constant/ The Faraday	$96\,485\ \mathrm{C\,mol^{-1}}$
m_u	atomic mass constant	$1.6605 \times 10^{-27}\ \mathrm{kg}$
N_A	Avogadro constant	$6.02214 \times 10^{23}\ \mathrm{mol^{-1}}$
R	molar gas constant	$8.31447\ \mathrm{J\,K^{-1}\,mol^{-1}}$
V_m	molar volume of ideal gas (at STP, see below)	$22.414 \times 10^{-3}\ \mathrm{m^{3}\,mol^{-1}}$

Source: National Institute of Standards and Technology, USA (NIST): www.nist.gov

Standard Temperature and Pressure

Standard Temperature and Pressure (STP) for gases, which should not be confused with the standard state (or standard conditions), see below, is defined in a number of different ways:

Temperature	*Pressure*	*Standards authority*
0°C / 273.15K	100 kPa	IUPAC[†] – current definition
0°C / 273.15K	101.325 kPa	IUPAC – former definition, NIST – current definition
25°C / 298.15K	100 kPa	NIST – definition for standard atmospheric temperature and pressure (SATP)
20°C / 293.15K	101.325 kPa	Normal Temperature and Pressure (NTP – used in oil and gas industry)

[†] International Union of Pure and Applied Chemistry.

Standard State

Definition from: Compendium of chemical terminology, IUPAC, 2nd edition (1997):

"The state of a system chosen as standard for reference by convention; three standard states are recognized:

- For a gas phase it is the (hypothetical) state of the pure substance in the gaseous phase at the *standard pressure* $p = p^\circ$, assuming ideal behaviour.

- For a pure phase, or a mixture, or a solvent in the liquid or solid state it is the state of the pure substance in the liquid or solid phase at the standard pressure $p = p^\circ$.
- For a solute in solution it is the (hypothetical) state of solute at the standard molality (i.e. mol kg^{-1}) m°, standard pressure p° or standard concentration c° and exhibiting infinitely dilute solution behaviour.

For a pure substance the concept of standard state applies to the substance in a well defined state of aggregation at a well defined but arbitrarily chosen standard pressure."

The standard state is thus defined as the condition where all chemical species are at a thermo-dynamic activity equal to one and that the total gas pressure is 100 kPa (1 bar). Note that the temperature is not defined and should therefore be specified explicitly.

Common Suffixes

Suffix	*Meaning*
$_o$ (as in i_o)	equilibrium
$_a$ (as in E_a)	anode/anodic
$_c$ (as in E_c)	cathode/cathodic
$_l$ (as in i_l)	limiting
$_{corr}$ (as in i_{corr})	corrosion
$_{pass}$ (as in i_{pass})	passive
$^\circ$ (as in E°)	at the standard state