# Corrosion in the Petrochemical Industry

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**Essential Research**

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# Preface

*Corrosion in the Petrochemical Industry* collects together authoritative, peer-reviewed data and information on corrosion in the petroleum, petrochemical, and chemical processing industries from a number of ASM International publications. The principal sources are *Corrosion*, Volume 13, and *Failure Analysis and Prevention*, Volume 11, of *ASM Handbook*. Other sources include the *Handbook of Corrosion Data*; *Handbook of Case Histories in Failure Analysis*, Volumes 1 and 2; and Metadex, the Materials Information database of materials abstracts. This information has been carefully selected and edited into one cohesive, comprehensive volume on corrosion phenomena in these industries.

This project was initiated because survey results and other input from ASM members and book buyers indicated a strong interest in collections of ASM data and information repackaged into logical, convenient new configurations. Based on this interest, a team of ASM staff members was assembled to gather additional input and then use it to craft a publication that is highly responsive to the demands of its intended audience. This team effort was led by Grace Davidson, with team members Steve Chang, Karen Germany, Scott Henry, Rich Majoros, Robert Pavlik, Dawn Summerlin, and Reva Zaretsky; Robert Uhl, Director of ASM's Education Department, sponsored the project.

The team chose the subject of corrosion because of the great amount of high-quality ASM published information available on this subject. The team conducted over 100 in-depth phone interviews with ASM book buyers who work or have an interest in the area of corrosion. The results of these phone interviews were then used as input for detailed quality function deployment matrices. (Quality function deployment is a systematic method for organizing and analyzing customer demands in order to develop products that are responsive to those demands.) Out of the quality function deployment process, the team developed three potential outlines, each with a separate area of focus in the field of corrosion. The team then went back to a small group of respondents to the original survey and asked them to review and comment on the outlines, and to rate them according to their apparent usefulness to a clearly defined audience.

The outline selected by this group was the one used to develop this volume. The outline and survey data were turned over to Linda Garverick, who has done a masterful job of compiling and editing the information to turn it into a cohesive, well-rounded publication. ASM International owes a debt of gratitude to the survey respondents who gave so generously of their time, opinions, and expertise to help develop this handbook. Of course, this book would not have been possible without the efforts of the dozens of experts who wrote and reviewed the information it contains.

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# Forms of Corrosion in the Petrochemical Industry

# Forms of Corrosion in the Petrochemical Industry

OVER THE YEARS, corrosion scientists and engineers have recognized that corrosion manifests itself in forms that have certain similarities and therefore can be categorized into specific groups. However, many of these forms are not unique but involve mechanisms that have overlapping characteristics that may influence or control initiation or propagation of a specific type of corrosion.

The most familiar and often used categorization of corrosion is probably the eight forms presented by Fontana and Greene (Ref 1): uniform attack, crevice corrosion, pitting, intergranular corrosion, selective leaching, erosion corrosion, stress corrosion, and hydrogen damage. This classification of corrosion was based on visual characteristics of the morphology of attack. Fontana and Greene's introductory remarks in their chapter on forms of corrosion indicate that this classification is arbitrary and that many of the forms are interrelated, making exact distinction impossible. Other prominent corrosion authors such as Uhlig (Ref 2) and Evans (Ref 3) have avoided a classification format and have simply discussed the classical types of corrosion (for example, pitting and crevice corrosion) as they relate to specific metals and alloys.

Substantial advances in the field of corrosion science have begun to define the mechanisms of many forms of corrosion more clearly. However, rather than placing the mechanisms into distinct categories, the overlap between many of the forms has become greater. For example, there is evidence that hydrogen may dominate the crack initiation or crack propagation portion of fracture in some metal/solution systems where stress-corrosion cracking occurs. Additionally, in some metal systems where dealloying (selective leaching) occurs, this form of corrosion may be a precursor to stress-corrosion cracking.

In a similar vein, the magnitude of contribution of stress or corrosion to stress-corrosion cracking, hydrogen damage, or liquid metal embrittlement is not currently understood and can affect whether just pitting or crevice attack occurs or environmental cracking results. The transition from uniform corrosion to highly localized attack is not clearly understood, and there are conditions where a distinction cannot be drawn.

The forms of corrosion presented in this article were categorized to represent the mechanisms of attack involved rather than to emphasize the visual characteristics. However, as with any classification system, these categories are not distinct or all-inclusive and do not necessarily represent the only mode of attack that may be observed.

## General Corrosion

General corrosion, as described in this article, refers to corrosion dominated by uniform thinning that proceeds without appreciable localized attack. Weathering steels and copper alloys are good examples of materials that typically exhibit general attack, while passive materials, such as stainless steels or nickel-chromium alloys, are generally subject to localized attack. Under specific conditions, however, each material may vary from its normal mode of corrosion. Examples describing the environmental conditions that promote uniform attack will be discussed throughout this article.

In this section, the four specific types of general corrosion most relevant to the petrochemical industry are discussed. Atmospheric corrosion is probably the most common form of corrosion and may well be the most costly. Galvanic corrosion is an electrochemical form of corrosion that protects cathodic areas at the expense of anodic areas. Stray-current corrosion is similar to galvanic corrosion, but does not rely on electrochemically induced driving forces to cause rapid attack. High-temperature (gaseous) corrosion is an area of great concern, particularly for the industrial sector.

As noted in the introduction, some of the categories of general corrosion described in this article also manifest themselves as other forms of corrosive attack, such as stress-corrosion cracking, dealloying, or pitting. However, because uniform thinning plays an important role in all of the categories described, each can and will be discussed under general corrosion.

## Atmospheric Corrosion

Atmospheric corrosion is defined as the corrosion or degradation of material exposed to the air and its pollutants rather than immersed in a liquid. This has been identified as one of the oldest forms of corrosion and has been reported to account for more failures in terms of cost and tonnage than any other single environment.

Many authors classify atmospheric corrosion under categories of dry, damp, and wet, thus emphasizing the different mechanisms of attack under increasing humidity or moisture.

### Types of Atmospheric Corrosion

**Dry Corrosion.** In the absence of moisture, most metals corrode very slowly at ambient temperatures. Accelerated corrosion under dry conditions at elevated temperatures is covered in the section "High-Temperature Corrosion" in this article. Dry corrosion at ambient temperature occurs on metals that have a negative free energy of oxide formation and thus form a rapid thermodynamically stable film in the presence of oxygen. Typically, these films are desirable because they are defect free, nonporous, and self-healing and act as a protective barrier to further corrosive attack of the base metal. Metals such as stainless steels, titanium, and chromium develop this type of protective film. Porous and nonadhering films that form spontaneously on nonpassive metals as unalloyed steel are normally not desirable.

Tarnishing of copper and silver in dry air with traces of hydrogen sulfide ($H_2S$) is an example of a nondesirable film formation at ambient temperatures caused by lattice diffusion. For tarnishing to occur, sulfur impurities must be present. The sulfides increase the likelihood of defects in the oxide-lattice and thus destroy the protective nature of the natural film, which leads to a tarnished surface. Surface moisture is not necessary for tarnishing to occur, and in some cases, such as copper in the presence of trace amounts of $H_2S$, moisture can actually retard the process of tarnishing. In general, dry corrosion plays an insignificant part in atmospheric corrosion as a whole.

**Damp corrosion** requires moisture in the atmosphere and increases in aggressiveness with the moisture content. When the humidity exceeds a critical value, which is around 70% relative humidity, an invisible thin film of moisture will form on the surface of the metal, providing an electrolyte for current transfer. The critical value depends on surface conditions such as cleanliness, corrosion product buildup, or the presence of salts or other contaminants that are hygroscopic and can absorb water at lower relative humidities.

**Wet corrosion** occurs when water pockets or visible water layers are formed on the metal surfaces because of sea spray, rain, or drops of dew. Crevices or condensation traps also promote the

**Fig. 1** Corroded steel formwork on the ceiling of a parking garage. The seams in this corrugated structure act as condensation traps and lead to wet atmospheric corrosion. Courtesy of R.H. Heidersbach, California Polytechnic State University

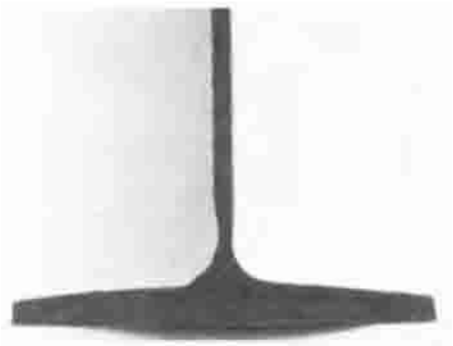


**Fig. 2** Corroded weathering steel I-beam. Note how corrosion has thinned the bottom of the vertical web where corrosion products have fallen and formed a moist corrosive deposit. Courtesy of R.H. Heidersbach, California Polytechnic State University

pooling of water and lead to wet atmospheric corrosion even when the flat surfaces of a metal component appear to be dry (Fig. 1).

During wet corrosion, the solubility of corrosion product can affect the corrosion rate. Typically, when the corrosion product is soluble, the corrosion rate will increase. This occurs because the dissolved ions normally increase the conductivity of the electrolyte and thus decrease the internal resistance to current flow, which will lead to an increased corrosion rate. Under alternating wet and dry conditions, the formation of an insoluble corrosion product on the surface may increase the corrosion rate during the dry cycle by absorbing moisture and continually wetting the surface of the metal.

The rusting of iron and steel and the formation of patina on copper are examples of metals experiencing either damp or wet atmospheric corrosion. Figures 1 to 5 show examples of the damp/wet atmospheric corrosion of weathering steel components.

## Atmospheric Contaminants

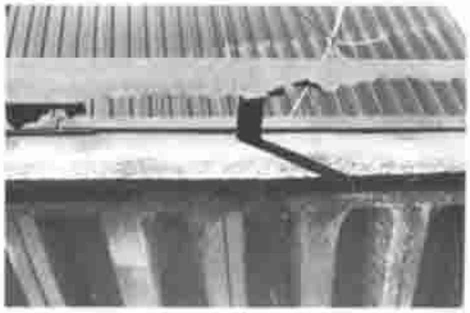


**Fig. 3** Corroded weathering steel gutter. Courtesy of R.H. Heidersbach, California Polytechnic State University

**Fig. 4** Corroded weathering steel highway bridge girder. Courtesy of D. Manning, Ontario Ministry of Highways and Communications

Wet atmospheric corrosion is often controlled by the level of contaminants found in the environment. For example, steel pillars 25 m (80 ft) from the seacoast will corrode 12 times faster than the same steel pillars 250 m (800 ft) further inland. The level of marine salts found at the two locations can explain the difference in the observed corrosion rates. More detailed information on marine atmospheres and their effect on the corrosivity of metals and alloys can be found in the article "Marine Corrosion" in Volume 13 of the *ASM Handbook.*

Industrial atmospheres are more corrosive than rural atmospheres, primarily because of the sulfur compounds produced during the burning of fuels. Sulfur dioxide ($SO_2$) is selectively absorbed on metal surfaces, and under humid conditions the metal oxide surfaces catalyze the $SO_2$ to sulfur trioxide ($SO_3$) and promote the formation of sulfuric acid ($H_2SO_4$) according to the reaction $H_2O + SO_3 \rightarrow H_2SO_4$. An example of $SO_2$-induced corrosion of plain carbon steel is shown in Fig. 6.

**Fig. 5** Corroded regions on a painted highway bridge. Courtesy of R.H. Heidersbach, California Polytechnic State University

**Fig. 6** Delamination of plain carbon steel due to $SO_2$ + ash deposit outside the boiler area of a coal-fired power plant. Courtesy of D.M. Berger, Gilbert/Commonwealth

Small additions of copper (0.1%) will increase the resistance of steel to a sulfur polluted environment by enhancing the formation of a tighter, more protective rust film. Additions of nickel and chromium will accomplish the same end. Nickel and copper alloys form insoluble sulfates that help to protect the base metal and are therefore used extensively in industrial environments. The remarkable longevity of ancient iron is probably due to a $SO_2$-free atmosphere rather than a high degree of resistance to general corrosive attack.

Other major contaminants that promote atmospheric corrosion are nitrogen compounds, $H_2S$, and dust particles. Nitrogen compounds occur naturally during thunderstorms and are added to the environment by the use of ammonia ($NH_3$) base fertilizers. Hydrogen sulfide can be generated naturally by the decomposition of organic sulfur compounds or by sulfate-reducing bacteria (SRB) in polluted rivers. Detailed information on SRB and their effect on alloy corrosion behavior can be found in the section "Localized Corrosion" in this article (see the discussion "Microbiological Corrosion").

Dust particles can be very detrimental to corrosion-resistant metals by adhering to the surface and absorbing water or $H_2SO_4$, and trapping the solution against the surface. Dust particles may also contain contaminants, such as chlorides, that can break down protective surface films and thus initiate corrosion.

Oxygen is not considered a contaminant, but is an essential element of the corrosion process. The normal cathodic reaction is the reduction of oxygen. In polluted areas with high concentrations of $SO_2$, the pH of the surface electrolyte may be low enough so that hydrogen reduction is the principal cathodic reaction. Once a suitable surface electrolyte has been formed by water vapor, oxygen will dissolve in the electrolyte solution and promote the cathodic reaction. Because the water layer on the surface of the metal is extremely thin, the diffusion of oxygen to the surface of the metal occurs very rapidly and does not slow the corrosion rate.

Carbon dioxide ($CO_2$) does not play a significant role in atmospheric corrosion, and in some cases, it will actually decrease corrosion attack.

## Atmospheric Variables

Atmospheric variables such as temperature, climatic conditions, and relative humidity, as well as surface shape and surface conditions that affect the time of wetness, are important factors that influence the rate of corrosive attack. Additional information concerning variables is available in the article "Effects of Environmental Variables on Aqueous Corrosion" in Volume 13 of the *ASM Handbook*.

Surface temperature is a critical variable. As the surface temperature increases, the corrosion rate will rise sharply to the point at which evaporation of the electrolyte takes place. At this temperature, the corrosion rate will decrease quickly.

**Climatic Conditions.** Metal surfaces located in areas where they become wet and retain moisture generally corrode more rapidly than surfaces exposed to rain. The rain has a tendency to wash the surface and remove particles of dust that can lead to differential aeration corrosion. Exceptions would be in areas that are subject to acid rain. Exposure of metals in different months of the year can have a pronounced effect on the corrosion rate. Winter exposure is usually the most severe because of increased combustion products in the air. The presence of $SO_2$ and other sulfur pollutants leads to an aggressive environment and the formation of a less protective corrosion product film on normally passive metals. One should be cautious regarding the month in which outdoor corrosion tests are performed. In locations in which sulfur-containing fuel is not burned during the winter months, the summer months may sometimes lead to higher rates of attack because of the increased surface temperatures.

**Time of Wetness/Relative Humidity.** Time of wetness is a critical variable with respect to the extent of corrosion experienced. The time of wetness determines the duration of the electrochemical process. The thickness and the chemical composition of the water film are both important.

The critical relative humidity is the humidity below which water will not form on a clean metal surface and thus electrochemical or wet corrosion will not occur. The actual relative humidity will change depending on the surface condition of the metal.

For iron, the critical relative humidity appears to be about 60%; at this level, rust slowly begins to form. At 75 to 80% relative humidity, there is a sharp increase in corrosion rate that is speculated to occur because of the capillary condensation of moisture within the rust corrosion product layer. At 90% relative humidity, there is another increase in the corrosion rate corresponding to the vapor pressure of ferrous sulfate. The critical relative humidity for copper, nickel, and zinc also appears to be between 50 and 70%, depending on surface conditions.

The nature of the corrosion product can greatly affect the time of wetness. If the corrosion product film is microporous in nature, capillary condensation can cause the condensation of moisture well below the critical relative humidity value. This occurs because of the differences in vapor pressure as measured over a curved surface as compared to a flat surface. For example, a 1.5-nm capillary will condense moisture at 50% relative humidity; a 36-nm capillary will condense moisture at 98% relative humidity. This phenomenon accounts for the formation of electrolyte in microcracks and in contact angles between dust particles and metal surfaces. The condensation of moisture on a metal surface can also be enhanced by the formation of a saturated solution, which will lower the equilibrium vapor pressure and allow condensation below 100% relative humidity.

Dew formation on metal surfaces can lead to accelerated corrosion because of the tendency of the dew to be acidic as a result of high $SO_2$ values near the ground. The dew can form on open or sheltered surfaces and leads to a corrosive attack of galvanized sheet called white rusting.

The thickness of the electrolyte layer is also an important factor in the corrosion process. Water begins to adhere to a polished metal surface at an estimated 55% relative humidity and will form a thin film, which will increase in thickness as the relative humidity increases. The thin water layers can support an electrochemical reaction, but polarization of the cathodic and anodic sites slows the process as the film thickness decreases and virtually stops at about 60%, the critical relative humidity value. The corrosion rate on a surface reaches a maximum when the water film thickness is above 150 µm. Therefore, not only is the time of wetness an important parameter but the thickness and conductivity of the surface electrolyte must also be known.

**Table 1 Average atmospheric-corrosion rates of various metals for 10- and 20-year exposure times**

Corrosion rates are given in mils/yr (1 mil/yr = 0.025 mm/yr). Values cited are one-half reduction of specimen thickness.

| | Atmosphere | | | | | |
|---|---|---|---|---|---|---|
| | New York, NY (urban-industrial) | | La Jolla, CA (marine) | | State College, PA (rural) | |
| Metal | 10 | 20 | 10 | 20 | 10 | 20 |
| Aluminum | 0.032 | 0.029 | 0.028 | 0.025 | 0.001 | 0.003 |
| Copper | 0.047 | 0.054 | 0.052 | 0.050 | 0.023 | 0.017 |
| Lead | 0.017 | 0.015 | 0.016 | 0.021 | 0.019 | 0.013 |
| Tin | 0.047 | 0.052 | 0.091 | 0.112 | 0.018 | ... |
| Nickel | 0.128 | 0.144 | 0.004 | 0.006 | 0.006 | 0.009 |
| 65% Ni, 32% Cu, 2% Fe, 1% Mn (Monel) | 0.053 | 0.062 | 0.007 | 0.006 | 0.005 | 0.007 |
| Zinc (99.9%) | 0.202 | 0.226 | 0.063 | 0.069 | 0.034 | 0.044 |
| Zinc (99.0%) | 0.193 | 0.218 | 0.069 | 0.068 | 0.042 | 0.043 |
| 0.2% C Steel(a) (0.02% P, 0.05% S, 0.05% Cu, 0.02% Ni, 0.02% Cr) | 0.48 | ... | ... | ... | ... | ... |
| Low-alloy steel(a) (0.1% C, 0.2% P, 0.04% S, 0.03% Ni, 1.1% Cr, 0.4% Cu) | 0.09 | ... | ... | ... | ... | ... |

(a) Kearney, NJ (near New York City). Source: Ref 4

## Atmospheric Corrosion of Specific Metal Systems

Irons and steel, zinc, copper, nickel, and aluminum are the metal systems of major economic importance when dealing with atmospheric corrosion. Table 1 provides an overview of atmospheric corrosion rates of various metals and alloys. Metals that are not particularly resistant to dilute $H_2SO_4$ such as copper, cadmium, nickel, and iron, show more rapid attack in industrial environments. Metals and alloys that are more resistant to $H_2SO_4$, such as lead, aluminum, and stainless steels, are less affected in the industrial environments. Copper forms a protective sulfate patina and is therefore more resistant than nickel. Copper also forms a basic copper chloride in seacoast environments. Nickel is very important in marine atmospheres, but is sensitive to the $H_2SO_4$ found in the industrial environments.

Low-alloy steels that resist atmospheric corrosion are called weathering steels. These alloyed steels form a protective rust film in alternating wet and dry environments. The weathering steels do not perform well under conditions of burial or total immersion. The atmospheric attack of wrought iron can sometimes progress along the internal planes formed during rolling and cause swelling of the material. For this reason, it is best not to cut across the grain boundaries and leave the face exposed to the environment. Stainless steels and aluminum alloys are normally very resistant to atmospheric conditions and will resist tarnishing in industrial, urban, and rural environments.

Lead, aluminum, and copper corrode initially, but form a protective film. In an urban atmosphere, nickel does not form a completely protective film and will experience a parabolic corrosion rate. Zinc attack appears to be linear after an initial period of decreasing corrosion rate. The corrosion rate of steel depends on the alloying elements typically attributed to the compact nature of the rust formed because of the alloying elements.

Copper, lead, and nickel form sulfates on the surface when attacked by dilute $H_2SO_4$. The lead forms a protective film, but the copper and nickel will slough off after a period of time. The protective carbonate film on zinc and cadmium is dissolved, and the metal is readily attacked. The oxide film on iron is formed by the hydrolysis of the ferrous sulfate. More detailed information on each of the metal systems mentioned above can be found in the Section "Specific Alloy Systems" in Volume 13 of the *ASM Handbook.*

### Prevention of Atmospheric Corrosion

Two approaches can be taken to prevent the onset of atmospheric corrosion. The first is a temporary fix that can be used during transport or storage. This consists of lowering the atmospheric humidity by using a desiccant, heating devices, or by treating the surface with a vapor phase or surface inhibitor. Permanent solutions to atmospheric corrosion can be accomplished by either changing the material or by applying a coating. Organic, inorganic, and metallic coatings have been effectively employed.

When using an alloy steel, the addition of small amounts of copper, phosphorus, nickel, and chromium are particularly effective in reducing atmospheric corrosion. It has been reported that copper additives are more effective in temperate climates than in tropical marine regions. The combination of minor elements, such as the addition of chromium and nickel with copper and phosphorus, appears to be very effective for all locations. The effects of alloying additions in ferrous alloys (wrought carbon, alloy, and stainless steels, and cast irons and steels) are detailed in the first five articles of the Section "Specific Alloy Systems" in Volume 13 of the *ASM Handbook.*

## Galvanic Corrosion

Galvanic corrosion occurs when a metal or alloy is electrically coupled to another metal or conducting nonmetal in the same electrolyte. The three essential components are:

- Materials possessing different surface potential
- A common electrolyte
- A common electrical path

A mixed metal system in a common electrolyte that is electrically isolated will not experience galvanic corrosion, regardless of the proximity of the metals or their relative potential or size.

During galvanic coupling, corrosion of the less corrosion-resistant metal increases and the surface becomes anodic, while corrosion of the more corrosion-resistant metal decreases and the surface becomes anodic. The driving force for corrosion or current flow is the potential developed between the dissimilar metals. The extent of accelerated corrosion resulting from galvanic coupling is affected by the following factors:

- The potential difference between the metals or alloys
- The nature of the environment
- The polarization behavior of the metals or alloys
- The geometric relationship of the component metals or alloys

The differences in potential between dissimilar metals or alloys cause electron flow between them when they are electrically coupled in a conductive solution. The direction of flow, and therefore the galvanic behavior, depends on which metal or alloy is more active. Thus, the more active metal or alloy becomes anodic, and the more noble metal or alloy becomes cathodic in the couple. The driving force for galvanic corrosion is the difference in potential between the component metals or alloys.

### Galvanic Series

A galvanic series of metals and alloys is useful for predicting galvanic relationships. Such a series is an arrangement of metals and alloys according to their potentials as measured in a specific electrolyte. The galvanic series allows one to determine which metal or alloy in a galvanic couple is more active. In some cases, the separation between the two metals or alloys in the galvanic series gives an indication of the probable magnitude of corrosive effect.

The potential of a metal or alloy is affected by environmental factors. Corrosion product films and other changes in surface composition can occur in some environments; therefore, no one value can be given for a particular metal or alloy. This requires a galvanic series to be measured in each environment of interest. Most commonly, however, the galvanic series has been constructed from measurements in seawater, as shown in Table 2. With certain exceptions, this series is broadly applicable in other natural waters and in uncontaminated atmospheres.

Because most engineering materials are alloys, the measurement of galvanic corrosion employing actual material is much more useful than predicting current flow from the electromotive force series. Therefore, tabulations such as Table 2 can be very useful.

### Polarization

As stated above, electron flow occurs between metals or alloys in a galvanic couple. This current flow between the more active and more noble members causes shifts in potential due to polarization, because the potentials of the metals or alloys tend to approach each other.

The magnitude of the shift depends on the environment, as does the initial potential. If the more noble metal or alloy is more easily polarized, its potential is shifted more toward the more active metal or alloy potential. The shift in potential of the more active metal or alloy in the direction of the cathode is therefore minimized so that accelerated galvanic corrosion is not as great as would otherwise be expected. On the other hand, when the more noble metal or alloy is not readily polarized, the potential of the more active metal shifts further toward the cathode (that is, in the direction of anodic polarization) such that appreciable accelerated galvanic corrosion occurs.

### Area, Distance, and Geometric Effects

Factors such as area ratios, distance between electrically connected materials, and geometric shapes also affect galvanic-corrosion behavior.

**Area effects** in galvanic corrosion involve the ratio of the surface area of the more noble to the more active member(s). When the surface area of the more noble metal or alloy is large in comparison to the more active member, an unfavorable area ratio exists for the prevailing situation in which a couple is under cathodic control. The anodic current density on the more active metal or alloy is extremely large; therefore, the resulting polarization leads to more pronounced galvanic corrosion. The opposite area ratio—large active member surface, smaller noble member surface—produces only slightly accelerated galvanic effects because of the predominant polarization of the more noble material.

**Effect of Distance.** Dissimilar metals in a galvanic couple that are in close physical proximity usually suffer greater galvanic effects than those that are further apart. The distance effect is dependent on solution conductivity because the path of current flow is the primary consideration. Thus, if dissimilar pipes are butt welded with the electrolyte flowing through them, the most severe corrosion will occur adjacent to the weld on the anodic member.

**Effect of Geometry.** The geometry of the circuit also enters into the effect to the extent that current will not readily flow around corners. This is simply an extension of the principle described above, in which the current takes the path of least resistance.

### Modes of Attack

Galvanic corrosion of the anodic member(s) of a couple may take the form of general or localized corrosion, depending on the configuration

**Table 2 Galvanic series in seawater at 25 °C (77 °F)**

**Corroded end (anodic, or least noble)**
Magnesium
Magnesium alloys
Zinc
Galvanized steel or galvanized wrought iron
Aluminum alloys 5052, 3004, 3003, 1100, 6053, in this order
Cadmium
Aluminum alloys 2117, 2017, 2024, in this order
Low-carbon steel
Wrought iron
Cast iron
Ni-Resist (high-nickel cast iron)
Type 410 stainless steel (active)
50-50 lead-tin solder
Type 304 stainless steel (active)
Type 316 stainless steel (active)
Lead
Tin
Copper alloy C28000 (Muntz metal, 60% Cu)
Copper alloy C67500 (manganese bronze A)
Copper alloys C46400, C46500, C46600, C46700 (naval brass)
Nickel 200 (active)
Inconel alloy 600 (active)
Hastelloy B
Chlorimet 2
Copper alloy C27000 (yellow brass, 65% Cu)
Copper alloys C44300, C44400, C44500 (admiralty brass)
Copper alloys C60800, C61400 (aluminum bronze)
Copper alloy C23000 (red brass, 85% Cu)
Copper C11000 (ETP copper)
Copper alloys C65100, C65500 (silicon bronze)
Copper alloy C71500 (copper nickel, 30% Ni)
Copper alloy C92300, cast (leaded tin bronze G)
Copper alloy C92200, cast (leaded tin bronze M)
Nickel 200 (passive)
Inconel alloy 600 (passive)
Monel alloy 400
Type 410 stainless steel (passive)
Type 304 stainless steel (passive)
Type 316 stainless steel (passive)
Incoloy alloy 825
Inconel alloy 625
Hastelloy C
Chlorimet 3
Silver
Titanium
Graphite
Gold
Platinum
**Protected end (cathodic, or most noble)**

of the couple, the nature of the films induced, and the nature of the metals or alloys involved. Generally, there are five major categories.

**Dissimilar Metals.** The combination of dissimilar metals in engineering design by mechanical or other means is quite common—for example, in heating or cooling coils in vessels, heat exchangers or machinery. Such combinations often lead to galvanic corrosion.

**Nonmetallic Conductors.** Less frequently recognized is the influence of nonmetallic conductors as cathodes in galvanic couples. Carbon brick in vessels is strongly cathodic to the common structural metals and alloys. Impervious graphite, especially in heat-exchanger applications, is cathodic to the less noble metals and alloys. Carbon-filled polymers can act as noble metals in a galvanic couple.

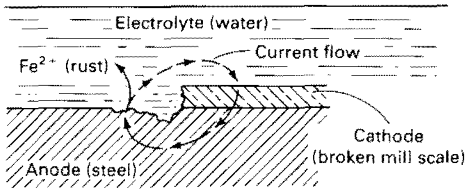


**Fig. 7** Schematic showing how breaks in mill scale ($Fe_3O_4$) can lead to galvanic corrosion of steel

Another example is the behavior of conductive films, such as mill scale (magnetite, $Fe_3O_4$) or iron sulfides on steel, or of lead sulfate on lead. Such films can be cathodic to the base metal exposed at breaks or pores in the scale (Fig. 7) or even to such extraneous items as valves or pumps in a piping system.

**Metallic Coatings.** Two types of metallic coatings are used in engineering design: noble metal coatings and sacrificial metal coatings. Noble metal coatings are used as barrier coatings over a more reactive metal. Galvanic corrosion of the substrate can occur at pores, damage sites, and edges in the noble metal coating. Sacrificial metal coatings provide cathodic protection of the more noble base metal, as in the case of galvanized steel or Alclad aluminum.

**Cathodic Protection.** Magnesium, zinc, and aluminum galvanic (sacrificial) anodes are used in a wide range of cathodic protection applications. The galvanic couple of the more active metal and a more noble structure (usually steel, but sometimes aluminum, as in underground piping) provides galvanic (cathodic) protection, while accelerated corrosion of the sacrificial metal (anode) occurs. The section "Anodic and Cathodic Protection" in the article "Corrosion Protection Methods for the Petrochemical Industry" in this Volume contains information on the principles and applications of this method of corrosion prevention and the selection of anode materials.

**Metal Ion Deposition.** Ions of a more noble metal may be reduced on the surface of a more active metal—for example, copper on aluminum or steel, silver on copper. This process is also known as cementation, especially with regard to aluminum alloys. The resulting metallic deposit provides cathodic sites for further galvanic corrosion of the more active metal.

## Predicting Galvanic Corrosion

The most common method of predicting galvanic corrosion is by immersion testing of the galvanic couple in the environment of interest. Although very time consuming, this is the most desirable method of investigating galvanic corrosion. Initially, screening tests are conducted to eliminate as many candidate materials as possible. These screening tests consist of one or more of the following three electrochemical techniques: potential measurements, current measurements, and polarization measurements. Additional information can be found in the article "Evaluation of Galvanic Corrosion" in Volume 13 of the *ASM Handbook.*

**Potential measurements** are made to construct a galvanic series of metals and alloys, as described above. As a first approximation, the galvanic series is a useful tool. However, it has serious shortcomings. Metals and alloys that form passive films will exhibit varying potentials with time and are therefore difficult to position in the series with certainty. Also, the galvanic series does not provide information on the polarization characteristics of the materials and so is not helpful in predicting the probable magnitude of galvanic effects.

**Measurement of galvanic currents** between coupled metals or alloys is based on the use of a zero-resistance milliammeter. Zero-resistance electrical continuity between the members of the galvanic couple is maintained electronically, while the resulting current is measured with the ammeter. Use of this technique should take into account certain limitations. First, when localized corrosion such as pitting or crevice corrosion is possible in the galvanic couple, long induction periods may be required before these effects are observed. Test periods must be of sufficient duration to take this effect into account. Also the measured galvanic current is not always a true measure of the actual corrosion current, because it is the algebraic sum of the currents due to anodic and cathodic reactions. When cathodic currents are appreciable at the mixed potential of the galvanic couple, the measured galvanic current will be significantly lower than the true current. Therefore, large differences between the true corrosion rate calculated by weight loss and that obtained by galvanic current measurements have been observed.

**Polarization measurements** on the members of a galvanic couple can provide precise information concerning their behavior. The polarization curves and the mixed potential for the galvanically coupled metals in a particular environment can be used to determine the magnitude of the galvanic-corrosion effects as well as the type of corrosion.

An important application in the use of polarization measurements in galvanic corrosion is the prediction of localized corrosion. Polarization techniques and critical potentials are used to measure the susceptibility to pitting and crevice corrosion of metals and alloys coupled in chloride solution. In addition, this technique is valuable in predicting galvanic corrosion among three or more coupled metals or alloys.

## Performance of Alloy Groupings

**Light Metals.** Magnesium occupies an extremely active position in most galvanic series and is therefore highly susceptible to galvanic corrosion. It is widely used as a sacrificial anode in cathodic protection.

Aluminum and its alloys also occupy active positions in the galvanic series and are subject to failure by galvanic attack (Fig. 8 and 9). In chloride-bearing solutions, aluminum alloys are susceptible to galvanically induced localized corrosion, especially in dissimilar-metal crevices. In this type of environment, severe galvanic

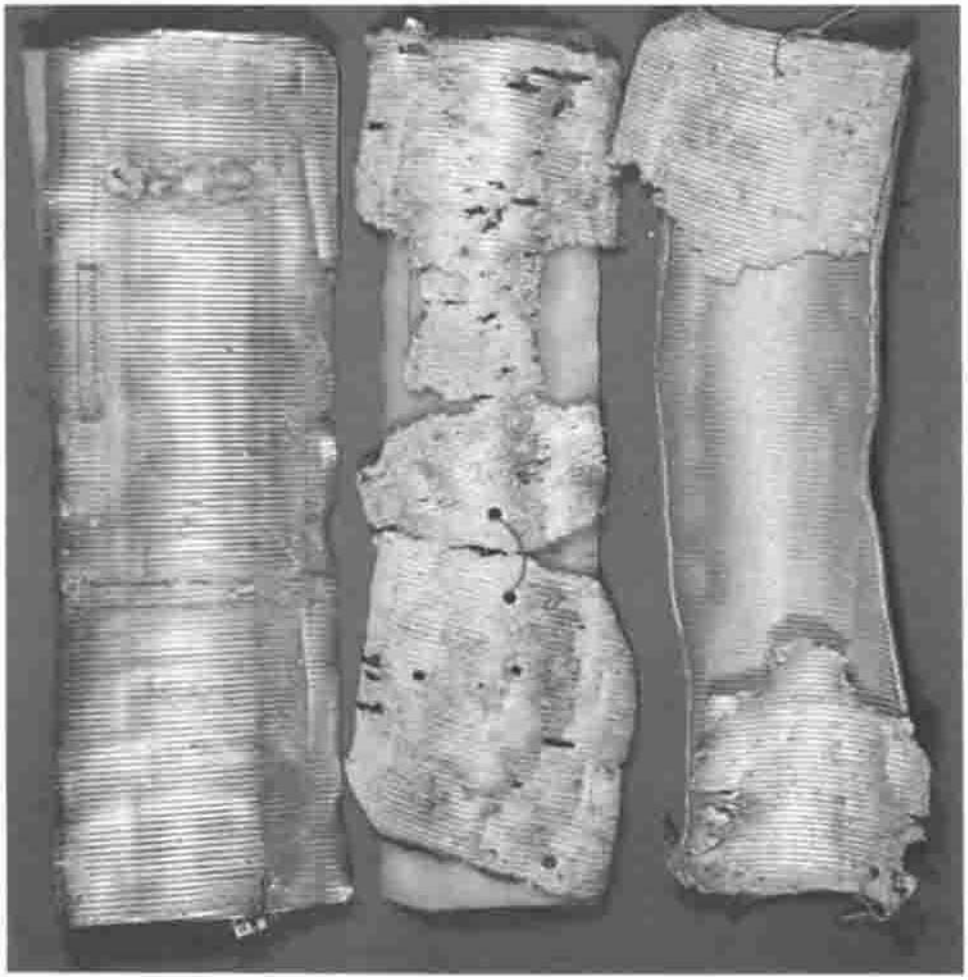


**Fig. 8** Galvanic corrosion of aluminum shielding in buried telephone cable coupled to buried copper plates. Courtesy of R. Baboian, Texas Instruments, Inc.

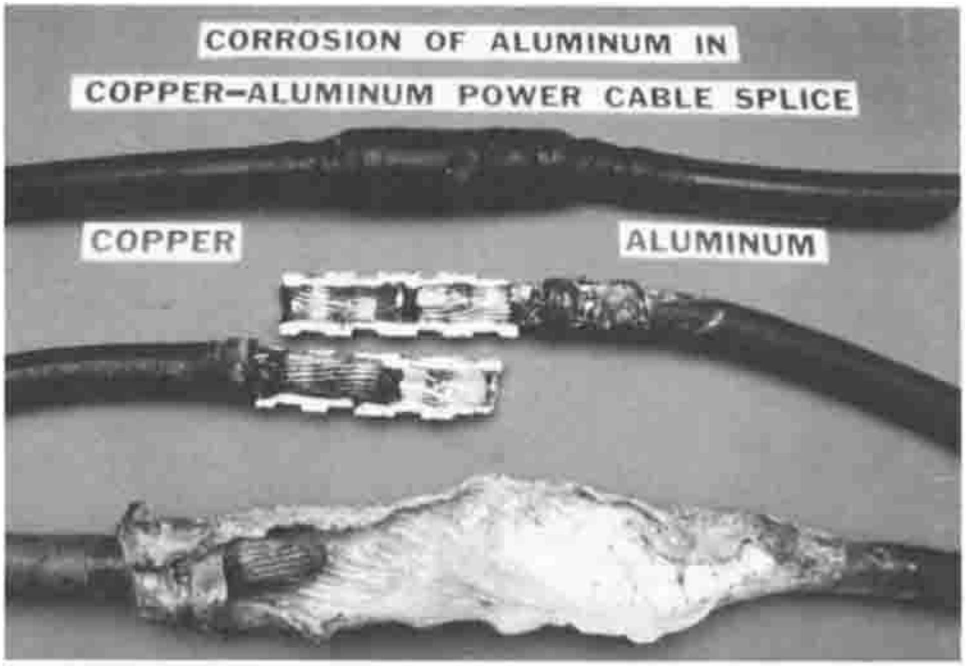


**Fig. 9** Galvanic corrosion of aluminum in buried power cable splice (copper to aluminum). Courtesy of R. Baboian, Texas Instruments, Inc.

effects are observed when aluminum alloys are coupled with more noble metals and alloys. Cementation effects are also observed in the presence of dissolved heavy-metal ions such as copper, mercury, or lead. Some aluminum alloys are used for sacrificial anodes in seawater. An active, anodic alloy is used to clad aluminum, protecting it against pitting in some applications.

In the absence of chlorides or with low concentrations, as in potable water, aluminum and its alloys may be less active because of greater stability of the protective oxide film. Galvanic effects are not as severe under these conditions.

The galvanic-corrosion behavior of magnesium, aluminum, iron and steel, stainless steel, lead, tin, zinc. copper, nickel, cobalt, titanium, zirconium, tantalum, and noble metals are reviewed below. Detailed information on these metals and their alloys can be found in the article "Corrosion of Specific Alloys Systems" in Volume 13 of the *ASM Handbook*. The article "Anodic and Cathodic Protection" in this Volume reviews metals and alloys used as sacrificial (galvanic) and impressed-current anodes.

**Iron and steel** are fairly active materials and require protection against galvanic corrosion by the higher alloys. They are, however, more noble than aluminum and its alloys in chloride solutions. However, in low-chloride waters, a reversal of potential can occur that causes iron or steel to become more active than aluminum. A similar reversal can occur between iron and zinc in hot waters of a specific type of chemistry. Examples of galvanic corrosion of iron and steel are shown in Fig. 10 to 13.

**Stainless Steels.** Galvanic corrosion behavior of stainless steels is difficult to predict because of the influence of passivity. In the common galvanic series, a noble position is assumed by stainless steels in the passive state, while a more active position is assumed in the active state (Table 2). This dual position in galvanic series in chloride-bearing aqueous environments has been the cause of some serious design errors. More precise information on the galvanic behavior of stainless steels can be obtained by using polarization curves, critical potentials, and the mixed potential of the galvanic couple. In chloride-bearing environments, galvanically induced localized corrosion of many stainless steels occurs in couples with copper or nickel and their alloys and with other more noble materials. However, couples of stainless and copper alloys are often used with impunity in freshwater cooling systems. Iron and steel tend to protect stainless steel in aqueous environments when galvanically coupled. The passive behavior of stainless steels makes them easy to polarize; thus, galvanic effects on other metals or alloys tend to be minimized. However, galvanic corrosion of steel can be induced by stainless, particularly in aqueous environments and with adverse area ratios.

**Lead, Tin, and Zinc.** These three materials occupy similar positions in the galvanic series, although zinc is the most active. The oxide films formed on these materials can shift their potentials to more noble values. Thus, in some environments, they may occupy more noble positions than one might otherwise expect. For example, the tin coat-

**Fig. 10** Rust staining of the Statue of Liberty torch due to galvanic corrosion of the iron armature in contact with the copper skin. Courtesy of R. Baboian, Texas Instruments, Inc.

**Fig. 11** Moisture that collected on the inside of the Statue of Liberty caused galvanic corrosion of the iron armature in contact with the copper skin. The copper skin on the nose was ruptured due to mechanical forces of the resulting corrosion products. Courtesy of R. Baboian, Texas Instruments, Inc.

ing in tin cans is anodic to steel under anaerobic conditions in the sealed container, but becomes cathodic when the can is opened and exposed to air. Zinc is an active metal. It is susceptible to galvanic corrosion and is widely used for galvanic anodes, in cathodic protection as a sacrificial coating (for example, galvanizing or electroplating) and as a pigment in certain types of coatings.

**Copper Alloys.** Copper and its alloys occupy an intermediate position in the galvanic series. They are not readily polarized in chloride-bearing aqueous solutions; therefore, they cause severe accelerated corrosion of more active metals, such as aluminum and its alloys and the ferrous metals. Somewhat similar to the nickel alloys, they lie between the active and passive positions for stainless steels (Table 2) and therefore induce localized corrosion of the active alloys.

**Nickel Alloys.** Nickel and its alloys are not readily polarized and will therefore cause accelerated corrosion of more active materials, such as aluminum and ferrous alloys. In chloride-bearing solutions, nickel is somewhat more noble than copper, and the cupronickels lie somewhere in between. Nickel and its alloys are similar to copper alloys in their effects on stainless steels. In some environments, the cast structure of a nickel weld may be anodic to the wrought parent metals.

The combination of a passive surface with the inherent resistance of nickel-chromium alloys, such as Inconel alloy 600 and Hastelloy alloy C-276, places them in more noble positions in the traditional galvanic series. In chloride-bearing solutions, Inconel alloy 600 is reported to occupy two positions because of existence of active and passive states in a manner similar to the stainless steels (Table 2). These alloys are readily polarized, and galvanic effects on other less noble metals and alloys therefore tend to be minimized.

**Cobalt-base alloys,** most of which are chromium bearing, are resistant to galvanic corro-

**Fig. 12** Galvanic corrosion of painted steel auto body panel in contact with stainless steel wheel opening molding. Courtesy of R. Baboian, Texas Instruments, Inc.

**Fig. 13** Galvanic corrosion of steel pipe at brass fitting in humid marine atmosphere. Courtesy of R. Baboian, Texas Instruments, Inc.

sion because of their noble position in the galvanic series. However, in environments in which their passive film is not stable, they occupy a more active position and can be adversely affected by more noble materials. The fact that they polarize readily tends to reduce their galvanic effects on less noble materials.

**Reactive Metals.** Titanium, zirconium, and tantalum are extremely noble because of their passive films. In general, these alloys are not susceptible to galvanic corrosion, and their ease of polarization tends to minimize adverse galvanic effects on other metals or alloys. Because of the ease with which they pick up hydrogen in the atomic state, they may themselves become embrittled in galvanic couples. Tantalum repair patches in glass-lined vessels have been destroyed by contact with cooling coils or agitators made of less noble alloys. Tantalum is susceptible to attack by alkalies, such as may form in the vicinity of a cathode in neutral solutions.

**Noble Metals.** The term noble metal is applied to silver, gold, and platinum group metals. This designation in itself describes their position in the galvanic series and their corresponding resistance to galvanic corrosion. However, they do not polarize readily and can therefore have a marked effect in galvanic couples with other metals or alloys. This effect is observed with gold and silver coatings on copper, nickel, aluminum, and their alloys.

## Methods of Control

**Materials Selection.** Combinations of metals or alloys widely separated in the relevant galvanic series should be avoided unless the more noble material is easily polarized. Metallic coatings can be used to reduce the separation in the galvanic series, as described below. Additional information is provided in the article "Designing to Minimize Corrosion" in this Volume.

**Environmental Control.** In particular cases, it is possible to reduce or eliminate galvanic-corrosion effects between widely dissimilar metals or alloys in a particular environment. The use of corrosion inhibitors is effective in some cases. Elimination of cathodic depolarizers (deaeration of water by thermomechanical means plus oxygen scavengers such as sodium sulfite or hydrazine) is very effective in some aqueous systems. Such methods are discussed in detail in the sections "Use of Inhibitors" and "Control of Environmental Variables in Water Recirculating Systems" in the article "Corrosion Protection Methods for the Petrochemical Industry" in this Volume.

**Barrier coatings** of a metallic nature have already been discussed. Inert barrier coatings, organic or vitreous, can effectively isolate the metals from the environment. It is extremely dangerous to coat the anodic member of a couple because this may only reduce its area, with severely accelerated attack occurring at holidays in the otherwise protective coating. If inert barrier coatings are employed, both the anode and cathode must be protected—for example, the heads, tubesheets, and first 4 to 6 tube diameters on the tube side of a water-cooled heat exchanger.

**Electrochemical techniques** are comprised of three alternative methodologies: electrical isolation, use of transition materials, and cathodic protection.

*Electrical Isolation.* The joint between dissimilar metals can be isolated to break the electrical continuity. Use of nonmetallic inserts, washers, fittings, and coatings at the joint between the materials will provide sufficient electrical resistance to eliminate galvanic corrosion.

*Transition Materials.* In order to eliminate a dissimilar-metal junction, a transition piece can be introduced. The transition piece consists of the same metals or alloys as in the galvanic couple bonded together in a laminar structure. The transition piece is inserted between the members of the couple such that the similar metals mate with one another. The dissimilar-metal junction then occurs at the bond interface, excluding the electrolyte.

*Cathodic Protection.* Sacrificial metals, such as magnesium or zinc, may be introduced into the galvanic assembly. The most active member will corrode while providing cathodic protection to the other members in the galvanic assembly (for example, zinc anodes in cast iron waterboxes of copper alloy water-cooled heat exchangers). Impressed-current systems can also provide the same effect. Both sacrificial anodes and impressed-current anodes are discussed in the section "Anodic and Cathodic Protection" in the article "Corrosion Protection Methods for the Petrochemical Industry" in this Volume.

**Design.** Unfavorable area ratios should be avoided. Metal combinations should be used in which the more active metal or alloy surface is relatively large. Rivets, bolts, and other fasteners should be of a more noble metal than the material to be fastened. Dissimilar-metal crevices, such as at threaded connections, are to be avoided. Crevices should be sealed, preferably by welding or brazing, although putties are sometimes used effectively. Replaceable sections of the more active member should be used at joints, or the corrosion allowance of this section should be increased, or both. Additional information is available in the article "Designing to Minimize Corrosion" in this Volume.

## Stray-Current Corrosion

Stray-current corrosion, or stray-current electrolysis, is different from natural corrosion because it is caused by an externally induced electrical current and is basically independent of such environmental factors as oxygen concentration or pH. Environmental factors may enhance other corrosion mechanisms involved in the total corrosion process, but the stray-current corrosion portion of the mechanism is unaffected.

Stray currents are defined as those currents that follow paths other than their intended circuit. They leave their intended path because of poor electrical connections within the circuit or poor insulation around the intended conductive material. The escaped current then will pass through the soil, water, or any other suitable electrolyte to find a low-resistant path, such as a buried metal pipe or some other metal structure, and will flow to and from that structure, causing accelerated corrosion.

## Sources of Stray Currents

The electric railways were the major source of stray direct current (dc), but since their demise, the problem has become less common. Other sources, such as cathodic protection systems, electrical welding machines, and grounded dc electric sources, create stray direct currents; therefore, stray-current corrosion does present problems occasionally. For example, stray currents created by an electric welding machine on board ship with a grounded dc line located on shore will cause accelerated attack of the ship's hull as the stray currents generated at the welding electrodes pass out of the ship's hull through the water back to shore.

Stray currents cause accelerated corrosion to occur where they leave the metal structure and enter the surrounding electrolyte. At points where the current enters the structure, the site will become cathodic in nature because of changes in potential, while the area where the current leaves the metal will become anodic. These sites may be hundreds of yards apart. Houses in close proximity can experience dramatically different corrosion characteristics in their water lines. The pipes in one house may be protected, while those next door may be catastrophically failing.

Stray current flowing along a pipeline typically will not cause damage inside the pipe, because of the high conductivity of the metal compared to the fluid in the pipe. The damage occurring at the point where the current reenters the electrolyte will be localized and on the outside surface of the metal. In certain cases in which the pipe has insulated joints and the stray current enters the internal fluid, the corrosion will occur on the inside of the tube.

Damage caused by alternating current (ac) is less than that experienced by dc and decreases in severity as the frequency increases. Damage caused by alternating currents on active-passive metals, such as stainless steel and aluminum, is greater than damage to nonpassive metals, such as iron and zinc. The alternating reduction and oxidation of the surface layers caused by the ac may cause the passive layers to become porous and layered. A major source for ac stray currents is buried power lines.

## Identifying Stray-Current Corrosion

Galvanic corrosion and stray-current corrosion are very similar in that they both show protected cathodic sites and preferentially corroded anodic sites. The major difference is that stray-current corrosion may vary over short periods of time, depending on the varying load of the power source, while galvanic corrosion proceeds at a constant rate because the electrochemical reaction is not dependent on an external current source.

Amphoteric metals such as aluminum and zinc can show signs of corrosion at the cathodic portion of the metal surface because of the build up of alkalies created by the cathodic electrochemical reactions. The extent of this type of corrosion is difficult to determine because it is dependent not only on the amount of current flow but also on the surrounding environment.

It is difficult to distinguish between ordinary corrosion and stray-current corrosion by visual inspection. In some cases, the attack is more localized, causing a concentration of pits that is not normally observed but under specific environmental conditions could occur even without the presence of stray currents. Some researchers have observed that stray-current corrosion tends to cause penetration along the grain boundaries—once again a phenomenon seen under many conditions. In the case of a gray cast iron, selective attack of the ferrite within the metal matrix has been observed. This type of attack can weaken the material and cause premature failure. The magnitude of stray currents is not easy to measure, but potential drops, potential differences, and the measurement of current flow along a buried structure are ways of determining the existence of stray currents.

### Prevention of Stray-Current Corrosion

There are various ways to decrease the chances of stray-current corrosion from occurring. Basically, one should try to stop the leakage of the current from the intended circuit by maintaining good electrical connections and insulation. Therefore, a major factor in controlling stray-current corrosion is the testing for and controlling of the current before it enters the soil or surrounding electrolyte.

If current is escaping and nothing can be done to prevent it, the corrosion of the surrounding metal structures can be mitigated in several ways. One technique is called bonding, which consists of connecting the stray-current conductor with the source ground and thus eliminating the need for the current to leave the metal and enter the soil.

In addition, sacrificial anodes can also be placed in contact with the stray-current conductor to direct the corrosion to a preferred site. Also, dc power source can be placed on line to cause a flow of current in the opposite direction of the stray current and effectively protect the pipe by the impressed current.

Impeding the flow of the stray current along the metallic path by installing insulators is another way to protect an affected structure. Caution is required, however, because the current will flow around the insulators and cause corrosion damage at multiple sites if the source voltages are large. The insulator gaps must be numerous enough to make the current sufficiently small. Current densities passing through the circuit should be kept as low as possible.

Coating a pipe or structure is not an effective way to control the problem unless the coating is flawless. In fact, coatings that are cracked or contain pin holes will accelerate the attack at sites of imperfection.

## High-Temperature Corrosion

When metal is exposed to an oxidizing gas at elevated temperature, corrosion can occur by direct reaction with the gas, without the need for the presence of a liquid electrolyte. This type of corrosion is referred to as tarnishing, high-temperature oxidation, or scaling. The rate of attack increases substantially with temperature. The surface film typically thickens as a result of reaction at the scale/gas or metal/scale interface due to cation or anion transport through the scale, which behaves as a solid electrolyte. For continuous, nonporous scales, ionic transport through the scale is the rate-controlling process. The thermodynamic stability, the ionic defect structure, and certain morphological features of the scale formed are key factors in determining the resistance of an alloy to a specific environment.

Initial film growth is usually very rapid. If the scale is a nonporous solid and completely covers the metal surface, the reaction rate will decrease when the thickness reaches a few thousand angstroms as the transport of reactive species through the film becomes rate controlling. The subsequent corrosion rate depends on the details of this transport mechanism, which may be due to electrical potential or concentration gradients or to migration along preferential paths, and so may correspond to any of several rate laws, as shown in Fig. 14. Where a diffusion process is rate controlling, the kinetics usually follow a parabolic rate law, in which the rate progressively decreases with time. Figure 15(a) illustrates the compact, continuous protective scale of essentially chromium oxide ($Cr_2O_3$) formed on Alloy 800. If the scale is porous (or is formed as a vapor species) or does not completely cover the metal surface, a linear rate is usually experienced.

The latter circumstance can be assessed from the Pilling-Bedworth ratio, which is the ratio of the volumes of oxide produced to the metal consumed by oxidation; values of 1.0 or greater result in complete surface coverage by oxide and, usually, protective behavior. This is not a complete nor foolproof measure for assessing the likelihood of protective scaling behavior. At high temperatures, the growth of nominally protective oxides may be sufficiently rapid that the compressive stresses resulting from a Pilling-Bedworth ratio greater than 1 become sufficiently great that the scale (or alloy) deforms and possibly spalls as a relief mechanism; in some cases, the protection offered by such scales may be low at this point, as shown in Fig. 16.

The desired characteristics for a protective oxide scale include the following:

- High thermodynamic stability (highly negative Gibbs free energy of formation) so that it forms preferentially to other possible reaction products
- Low vapor pressure so that the oxide forms as a solid and does not evaporate into the atmosphere
- Pilling-Bedworth ratio greater than 1.0 so that the oxide completely covers the metal surface
- Low coefficient of diffusion of reactant species (metal cations, and corrodent anions) so that the scale has a slow growth rate
- High melting temperature
- Good adherence to the metal substrate, which usually involves a coefficient of thermal expansion close to that of the metal, and sufficient high-temperature plasticity to resist fracture from differential thermal expansion stresses

High-temperature scales are usually thought of as oxides, but may also be sulfides, possibly carbides, or mixtures of these species. Oxides

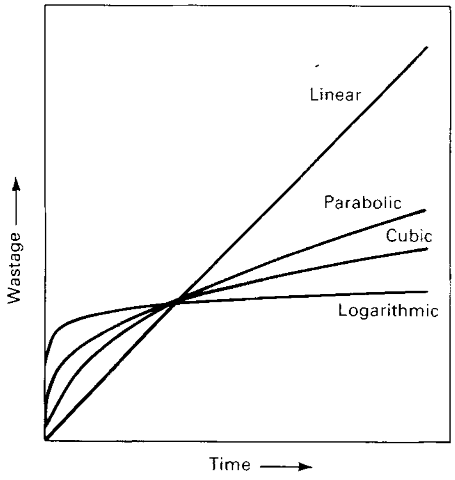


**Fig. 14** Forms of kinetic curves that represent various thermal degradation processes

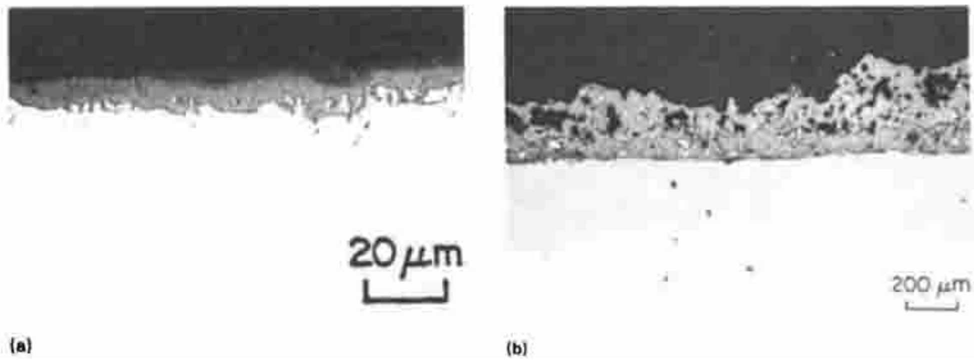


**Fig. 15** Protective and nonprotective scales formed on Alloy 800. (a) $Cr_2O_3$-base protective oxide scale formed in sulfur-free oxidizing gas. (b) Sulfide-oxide scale formed in reducing conditions containing hydrogen sulfide. Courtesy of I.G. Wright, Battelle Columbus Division

and sulfides are nonstoichiometric compounds and semiconductors. There are essentially two types of semiconductors: *p*-type (or positive carrier)—which may have vacancies in its metal lattice, or an excess of anions contained interstitially—and *n*-type (or negative carrier)—which may have an excess of metal ions contained interstitially, or vacant anion lattice sites. For diffusion-controlled scaling, the rate of scale growth can be altered by modification of the concentration of the particular defects involved. For example, *p*-type oxides exhibit increased cationic transport rates (increased oxidation rates) at increased oxygen pressures, while transport in *n*-type oxides is essentially independent of oxygen pressure. Both types of oxide can be doped by the addition of specific ions to the oxide lattice. For *p*-type metal deficit oxides, for example, the addition of cations of higher valence than the native cations results in an increase in the number of cation vacancies and therefore an increase in the oxidation rate, while lower-valence cation additions have the opposite effect.

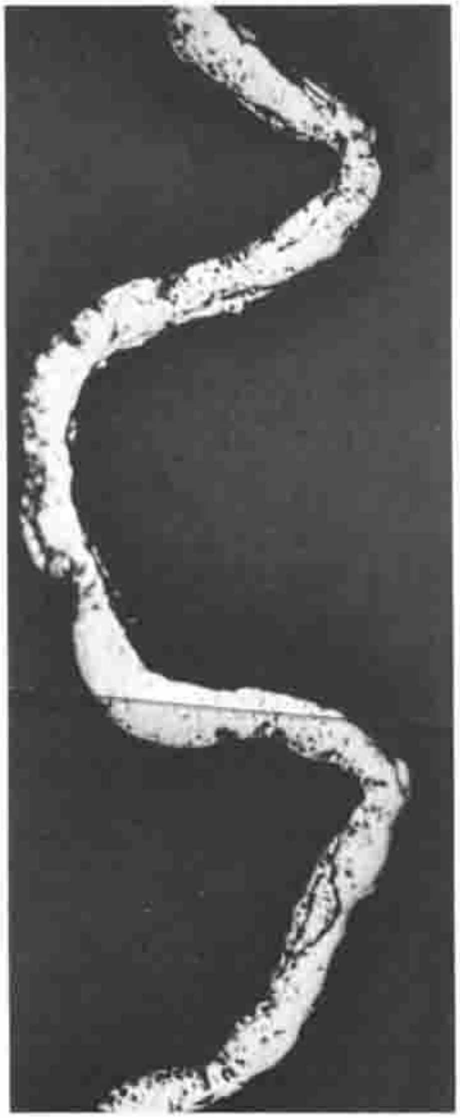


**Fig. 16** $Cr_2O_3$ scale formed on pure chromium at 1100 °C (2012 °F). A Pilling-Bedworth ratio of 2.0 results in high compressive stress in the scale, which is relieved by buckling and spalling. Courtesy of I.G. Wright, Battelle Columbus Division

Sulfides typically exhibit an intrinsically greater rate of transport of anions and cations than the oxides of the same metal and so provide scales that are significantly less protective than oxides. Detailed information on the kinetics of high-temperature corrosion in gases and the thermodynamic stability of oxide/sulfide scales can be found in the article "Fundamentals of Corrosion in Gases" in Volume 13 of the *ASM Handbook.*

## High-Temperature Oxidation

Alloys intended for high-temperature applications are designed to have the capability of forming protective oxide scales. Alternatively, where the alloy has ultrahigh-temperature strength capabilities (which is usually synonymous with reduced levels of protective scale forming elements), it must be protected by a specially designed coating. Oxides that effectively meet the criteria for protective scales listed above and can be formed on practical alloys are limited to $Cr_2O_3$, alumina ($Al_2O_3$), and possibly silicon dioxide ($SiO_2$). In the pure state, $Al_2O_3$ exhibits the slowest transport rates for metal and oxygen ions and so should provide the best oxidation resistance.

Alloying requirements for the production of specific oxide scales have been translated into minimum levels of the scale-forming elements, or combinations of elements, depending on the base alloy composition and the intended service temperature. Figure 17 schematically represents the oxidation rate of iron-chromium alloys (1000 °C, or 1832 °F, in 0.13 atm oxygen) and depicts the types of oxide scale associated with various alloy types. Figure 18 illustrates the morphology of a semiprotective scale formed on a cobalt-chromium alloy. Alloys based on these minimum specifications will form the desired protective oxide upon initial exposure, but because of the accompanying deletion of the scale forming element, they will probably be unable to re-form the protective layer in the event of loss or failure of the initial scale.

A useful concept in assessing the potential high-temperature oxidation behavior of an alloy is that of the reservoir of scale-forming element contained by the alloy in excess of the minimum level (around 20 wt% for iron-chromium alloys at 1000 °C, or 1832 °F, according to Fig. 17). The more likely the service conditions are to cause repeated loss of the protective oxide scale, the greater the reservoir of scale-forming element required in the alloy for continued protection. Extreme cases of this concept result in chromizing or aluminizing to enrich the surface regions of the alloy or in the provision of an external coating rich in the scale-forming elements.

The breakdown of protective scales based on $Cr_2O_3$ or $Al_2O_3$ appears, in the majority of cases, to originate through mechanical means. The most common is spallation as a result of thermal cycling, or loss through impact or abrasion. Typical scale structures on an Fe-18Cr alloy after

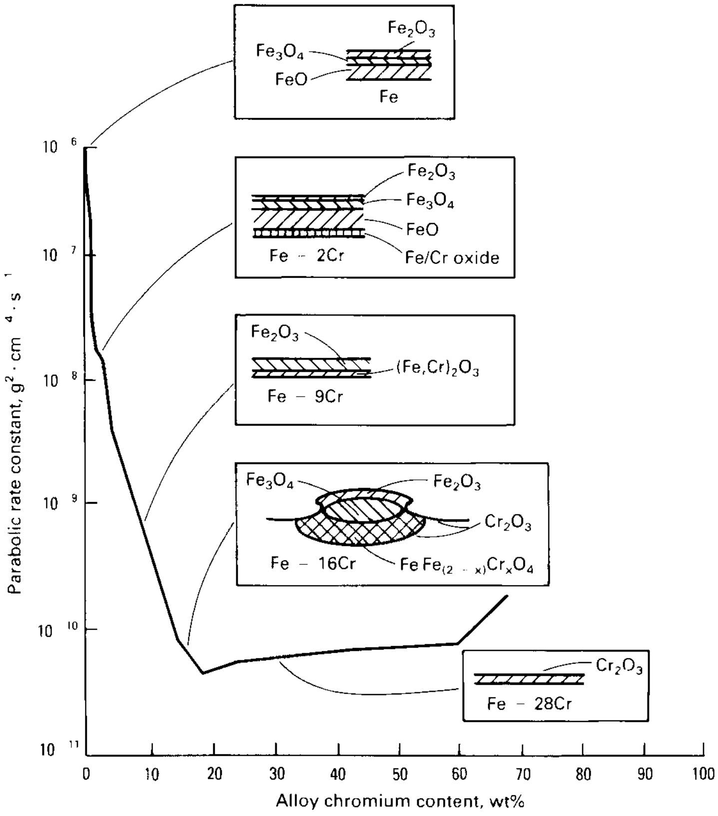


**Fig. 17** Schematic of the variation with alloy chromium content of the oxidation rate and oxide scale structure (based on isothermal studies at 1000 °C, or 1832 °F, in 0.13 atm oxygen)

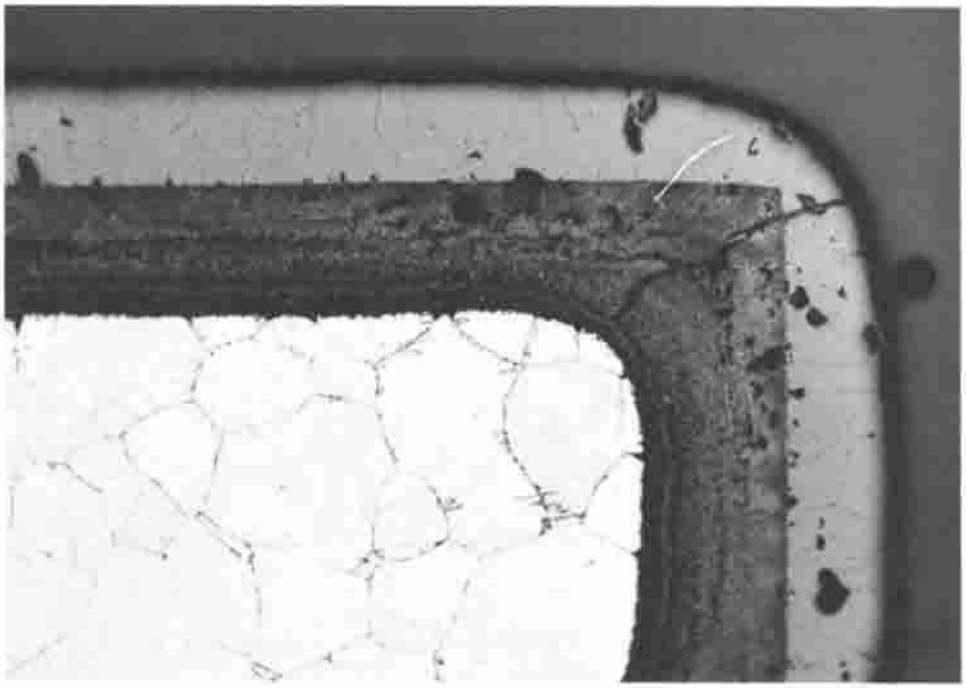
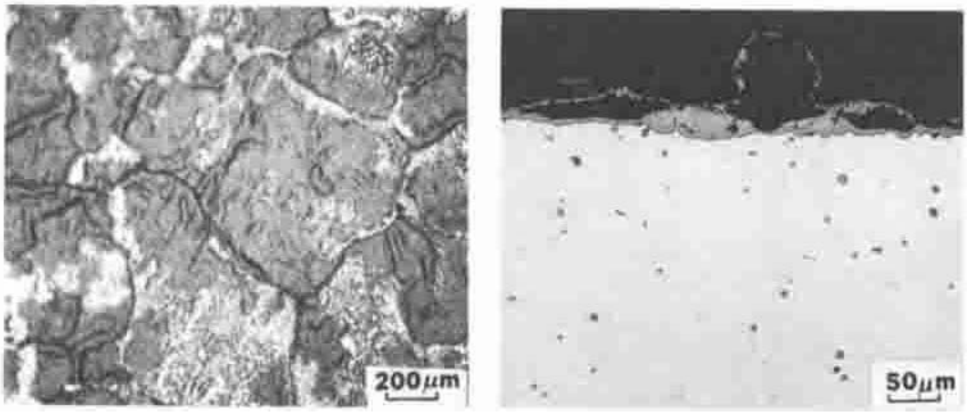


**Fig. 18** Multilayer oxide scale formed on Co-10Cr alloy at 1100 °C (2012 °F). Outer layer is CoO; inner (mottled gray) layer is CoO containing dissolved chromium and particles of Co-Cr spinel. The chromium level in this alloy is insufficient to form a fully protective $Cr_2O_3$ scale. Courtesy of I.G. Wright, Battelle Columbus Division



(a) (b)

**Fig. 19** Topography (a) and cross section (b) of oxide scale formed on Fe-18Cr alloy at 1100 °C (2012 °F). The bright areas on the alloy surface (a) are areas from which scale has spalled. The buckled scale and locally thickened areas (b) are iron-rich oxide. The thin scale layer adjacent to the alloy is $Cr_2O_3$, which controls the oxidation rate. Courtesy of I.G. Wright, Battelle Columbus Division

thermal cycling are shown in Fig. 19. Cases in which the scales have been destroyed chemically are usually related to reactions occurring beneath deposits, especially where these consist of molten species. An additional mode of degradation of protective $Cr_2O_3$ scale is through oxidation to the volatile chromium trioxide ($CrO_3$), which becomes prevalent above about 1010 °C (1850 °F) and is greatly accelerated by high gas flow rates.

Because these protective oxide scales will form wherever the alloy surface is exposed to the ambient environment, they will form at all surface discontinuities; therefore, the possibility exists that notches of oxide will form at occluded angles in the surface, which may eventually serve to initiate or propagate cracks under thermal cycling conditions. The ramifications of stress-assisted oxidation (and of oxidation assisting the applied stress) in the production of failure conditions are not very well understood, but constitute important considerations in practical failure analysis.

## Sulfidation

When the sulfur activity (partial pressure, concentration) of the gaseous environment is sufficiently high, sulfide phases, instead of oxide phases, can be formed. The mechanisms of sulfide formation in gaseous environments and beneath molten-salt deposits have been determined in recent years. In the majority of environments encountered in practice by oxidation-resistant alloys, $Al_2O_3$ or $Cr_2O_3$ should form in preference to any sulfides, and destructive sulfidation attack occurs mainly at sites where the protective oxide has broken down. The role of sulfur, once it has entered the alloy, appears to be to tie up the chromium and aluminum as sulfides, effectively redistributing the protective scale-forming elements near the alloy surface and thus interfering with the process of formation or re-formation of the protective scale. If sufficient sulfur enters the alloy so that all immediately available chromium or aluminum is converted to sulfides, then the less stable sulfides of the base metal may form because of morphological and kinetic reasons. It is these base metal sulfides that are often responsible for the observed accelerated attack, because they grow much faster than the oxides or sulfides of chromium or aluminum; in addition, they have relatively low melting points, so that molten slag phases are often possible. Figure 15 compares a protective (oxide) scale and a nonprotective (sulfide) scale formed on Alloy 800.

Sulfur can transport across continuous protective scales of $Al_2O_3$ and $Cr_2O_3$ under certain conditions, with the result that discrete sulfide precipitates can be observed immediately beneath the scales on alloys that are behaving in a protective manner. For reasons indicated above, as long as the amount of sulfur present as sulfides is small, there is little danger of accelerated attack. However, once sulfides have formed in the alloy, there is a tendency for the sulfide phases to be preferentially oxidized by the encroaching reaction front and for the sulfur to be displaced inward, forming new sulfides deeper in the alloy, often in grain boundaries or at the sites of other chromium- or aluminum-rich phases, such as carbides. In this way, finger-like protrusions of oxide/sulfide can be formed from the alloy surface inward, which may act to localize stress or otherwise reduce the load-bearing section. Such attack of an austenitic stainless steel experienced in a coal gasifier product gas is shown in Fig. 20. The sulfidation behavior of Alloy 800 at temperatures and oxygen and sulfur potentials representative of coal gasification processes is illustrated in Fig. 21 to 23.

## Carburization

As in the case of sulfide penetration, carburization of high-temperature alloys is thermodynamically unlikely except at very low oxygen partial pressures, because the protective oxides of chromium and aluminum are generally more likely to form than the carbides. However, carburization can occur kinetically in many carbon-containing environments. Carbon transport across continuous nonporous scales of $Al_2O_3$ or $Cr_2O_3$ is very slow, and alloy pretreatments likely to promote such scales, such as initially smooth surfaces or preoxidation, have generally been found to be effective in decreasing carburization attack. In practice, the scales formed on high-temperature alloys often consist of multiple layers of oxides resulting from localized bursts of oxide formation in areas where the original

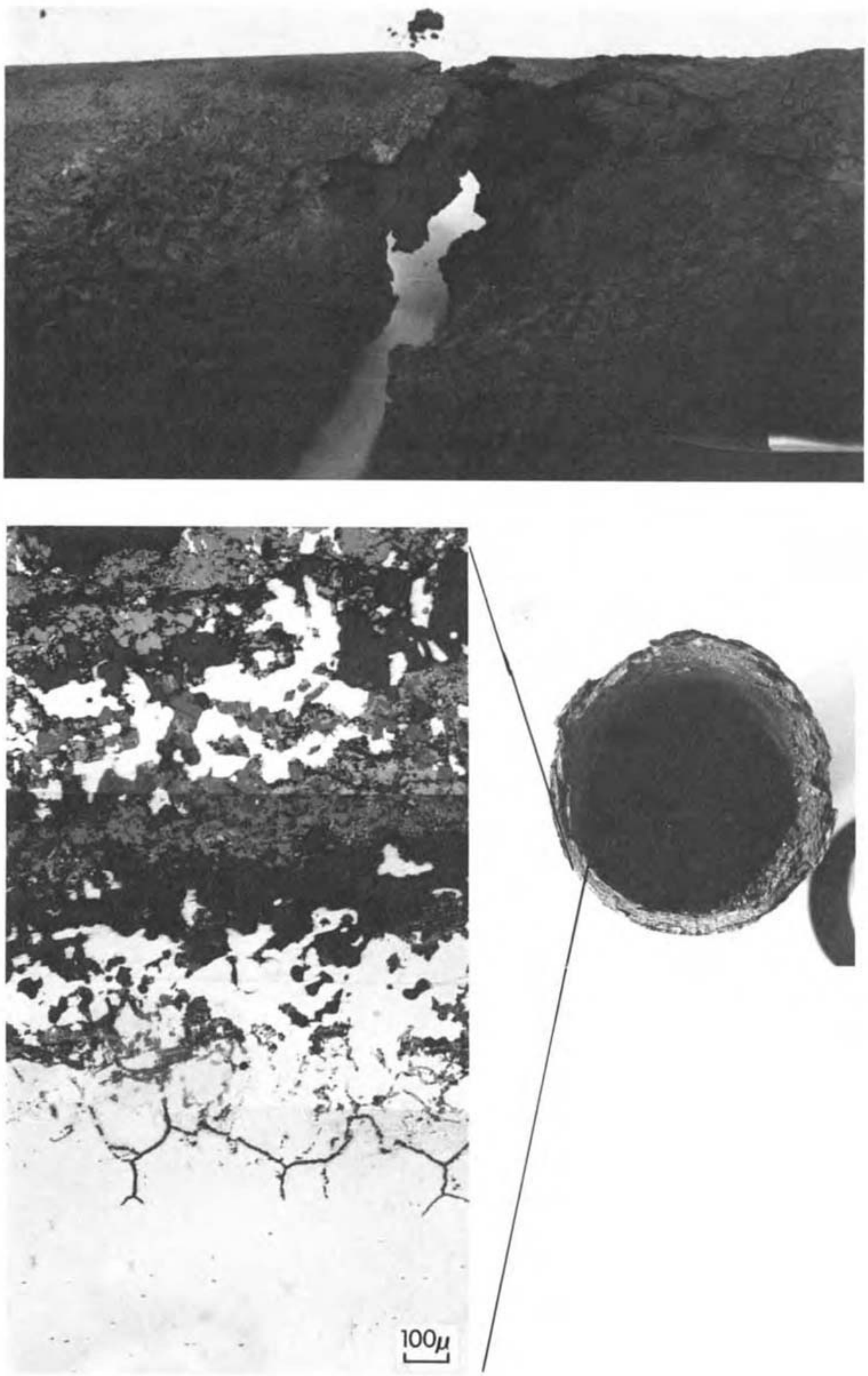


**Fig. 20** Example of high-temperature sulfidation attack in a type 310 heat-exchanger tube after ~100 h at 705 °C (1300 °F) in coal gasifier product gas

scale was broken or lost. The protection is derived from the innermost layer, which is usually richest in chromium or aluminum. Concentration of gaseous species such as carbon monoxide in the outer porous oxide layers appears to be one means by which sufficiently high carbon activities can be generated at the alloy surface for carburization to occur in otherwise oxidizing environments. The creation of localized microenvironments is also possible under deposits that create stagnant conditions not permeable by the ambient gas.

Once inside the alloy, the detrimental effects of the carbon depend on the location, composition, and morphology of the carbides formed. Austenitic steels should carburize more readily than ferritic steels because of the high solubility of carbon in austenite. Iron-chromium alloys containing less than about 13% Cr contain various amounts of austenite, depending on temperature, and should be susceptible to carburization, while alloys with 13 to 20% Cr will form austenite as a result of absorption of small amounts of carbon. Iron-chromium alloys containing more than ~20% Cr can absorb considerable amounts of carbon before austenite forms, becoming principally $(CrFe)_{23}C_6$ and ferrite. An example of rapid high-temperature carburization attack of an austenitic stainless steel is shown in Fig. 24.

Minor alloying elements can exert an influence on the susceptibility to carburization of various alloys. In particular, silicon, niobium, tungsten, titanium, and the rare earths have been noted as promoting resistance to carburization. Experience with aluminum and manganese has been varied, while lead, molybdenum, cobalt, zirconium, and boron are considered detrimental.

### Hydrogen Effects

In hydrogen at elevated temperatures and pressure, there is increasing availability of atomic hydrogen that can easily penetrate metal structures and react internally with reducible species. An example is the attack experienced by carbon steel, in which atomic hydrogen reacts with iron carbide to form methane, which then leads to fissuring of the steel. Alloy steels with stable carbides, such as chromium carbides, are less susceptible to this form of attack. For example, 2.25Cr-1Mo suffers some decarburization in high-temperature high-pressure hydrogen, but is less likely to fissure than carbon steel. The susceptibility of steels to attack by hydrogen can be judged from the Nelson Curves, which indicate the regions of temperature and pressure in which a variety of steels will suffer attack. Nelson curves and examples of high-temperature hydrogen attack of carbon and alloy steels are illustrated and discussed in the article "Corrosion in Petroleum Refining and Petrochemical Operations" in this Volume.

A further example of hydrogen attack is copper containing small amounts of cuprous oxide. This oxide reacts to form steam within the alloy, resulting in significant void formation.

## Localized Corrosion

The forms of corrosion described in this article—pitting, crevice, and biological corrosion—all have the common feature that the corrosion damage produced is localized rather than spread uniformly over the exposed metal surface. This makes these forms of attack more difficult to deal with than those producing a generalized attack

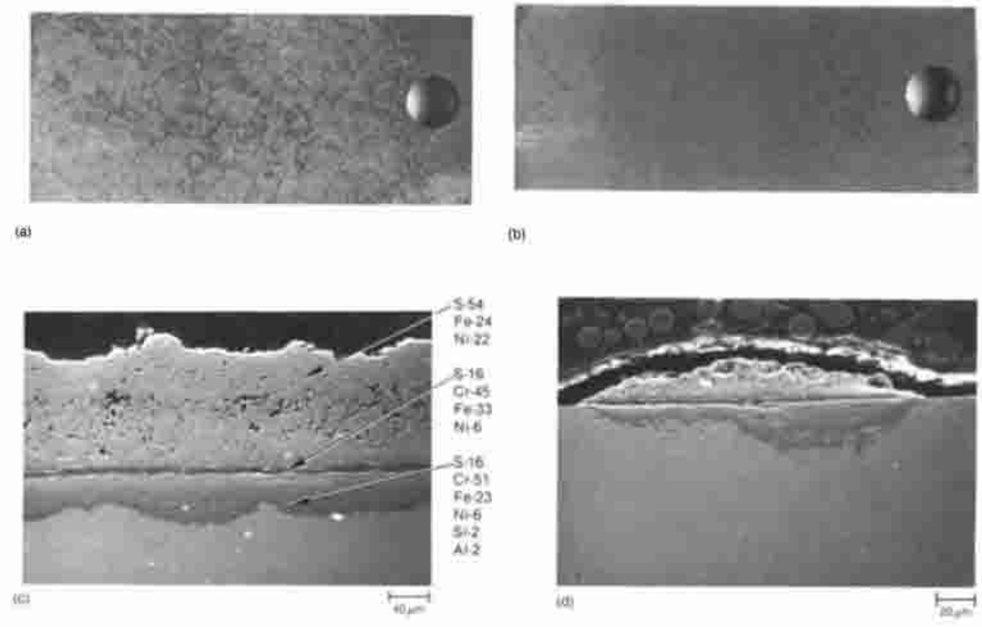


**Fig. 21** Alloy 800 test coupons with a 0.254-mm (0.01-in.) diam grain size exposed to a coal gasifier environment for 100 h. (a) and (c) Tested at 650 °C (1200 °F) and oxygen and sulfur partial pressures of $3 \times 10^{-24}$ atm and $1 \times 10^{-8}$ atm, respectively. (b) and (d) Tested at 650 °C (1200 °F) and $pO_2 = 3 \times 10^{-24}$ atm and $pS_2 = 1 \times 10^{-9}$ atm. SEM micrographs show sulfide scale (c) and an external sulfide formation (d). (a) and (b) ~2×. Courtesy of G.R. Smolik and D.V. Miley, E.G. & G. Idaho, Inc.

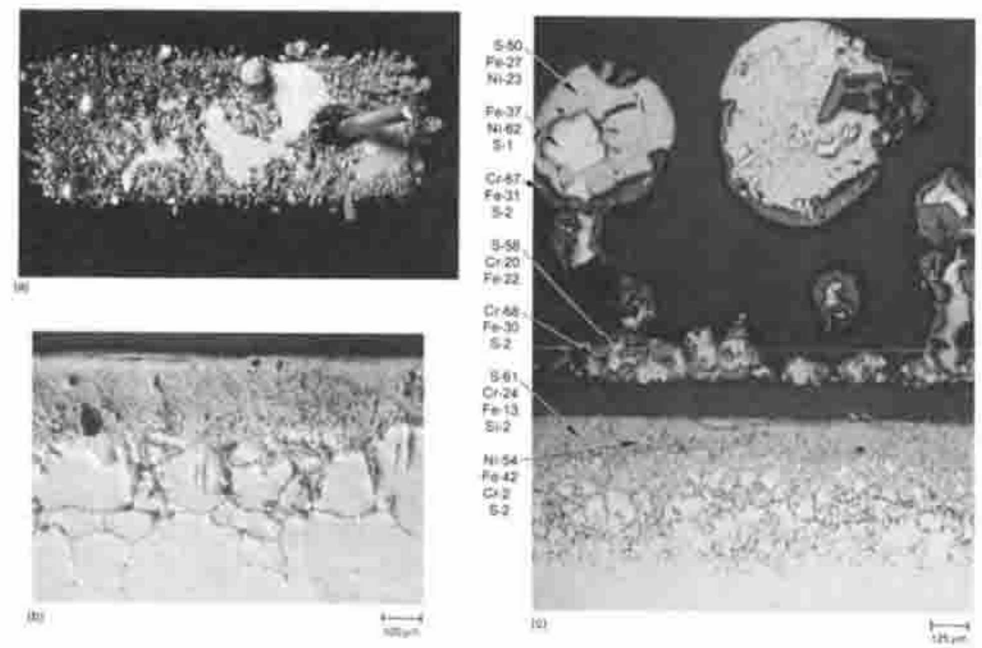


**Fig. 22** Sulfidation attack of Alloy 800 test coupons exposed to a coal gasifier environment ($pO_2 = 3 \times 10^{-20}$ atm and $pS_2 = 1 \times 10^{-7}$ atm) at 870 °C (1600 °F) for 100 h. (a) and (b) Macrograph and micrograph, respectively, of a test coupon with a 0.254-mm (0.01-in.) diam grain size. (c) Micrograph showing external sulfides, sulfide scale, and intergranular sulfidation of a test coupon with a 0.022- to 0.032-mm (0.0008- to 0.0013-in.) diam grain size. (a) ~1.5×. Courtesy of G.R. Smolik and D.V. Miley, E.G. & G. Idaho, Inc.

(see the section "Generalized Corrosion" in this article). Instead of dealing with a slow, relatively uniform loss of metal thickness, the engineer is now faced with high rates of metal penetration at specific sites (or localized deterioration under a coating system in the case of filiform corrosion), while the remainder of the metal (or coating) goes largely unaffected. The attack can also be harder to detect because much of the damage may be subsurface, with only a small opening visible to the eye at the metal surface. Moreover, these forms of attack are economically important and dangerous because they can lead to premature failure of a structure by rapid penetration with little overall weight loss.

The purpose of this article is to provide the engineer with enough information to identify which form of corrosion is taking place on an existing structure or which form of corrosion is likely to occur on a new structure. Therefore, most of this article is devoted to illustrating the appearance of these localized forms of corrosion and to describing the classes of metals and alloys susceptible to them and the environmental conditions under which they occur. Some information is also given on the mechanisms of the attack and measures that can be used to prevent it. More information on prevention can be found in the article "Corrosion Protection Methods for the Petrochemical Industry."

## Pitting Corrosion

Pitting of metals is extremely localized corrosion that generally produces sharply defined holes. The attack on the interior walls of the hole is usually reasonably uniform, but may be irregular where the specific conditions introduce a secondary intergranular attack. Every engineering metal or alloy is susceptible to pitting. Pitting occurs when one area of a metal surface becomes anodic with respect to the rest of the surface or when highly localized changes in the corrodent in contact with the metal, as in crevices, cause accelerated localized attack.

In general, when pitting occurs on a freely accessible clean metal surface, a slight increase in corrosivity of the environment will cause general or uniform corrosion. Pitting on clean surfaces ordinarily represents the start of breakdown of passivity or local breakdown of inhibitor-produced protection. When pits are few and widely separated and the metal surface undergoes little or no general corrosion, there is a high ratio of cathode-to-anode area, and penetration progresses more rapidly than when pits are numerous and close together.

**Difficulty of Detection.** Pitting is one of the most insidious forms of corrosion; it can cause failure by perforation while producing only a small weight loss on the metal. Also, pits are generally small and often remain undetected. A small number of isolated pits on a generally uncorroded surface are easily overlooked. A large number of very small pits on a generally uncorroded surface may not be detected by simple visual examination, or their potential for damage may be underestimated. When pits are accompanied by slight or moderate general corrosion, the corrosion products often mask them.

Pitting is sometimes difficult to detect in laboratory tests and in service, because there may be a period of months or years, depending on the metal and the corrodent, before the pits initiate and develop to a readily visible size. Delayed pitting sometimes occurs after an unpredictable period of time in service, when some change in the environment causes local destruction of a passive film. When this occurs on stainless steels, for example, there is a substantial increase in solution

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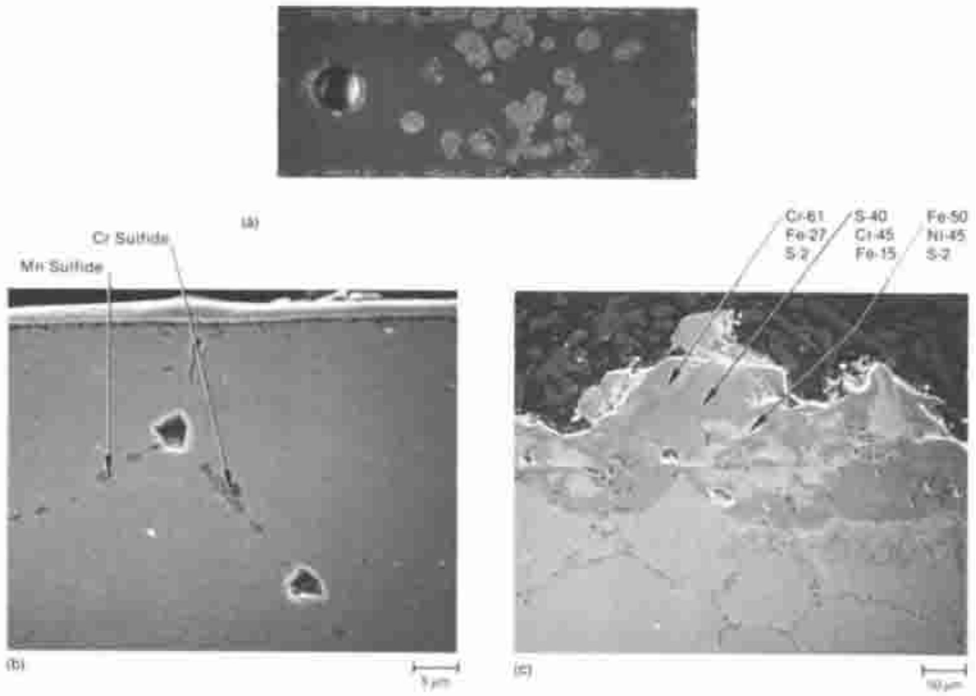

**Fig. 23** Macrograph (a) of an Alloy 800 test coupon with a 0.254-mm (0.01-in.) diam grain size exposed to a coal gasifier environment ($pO_2 = 3 \times 10^{-19}$ atm and $pS_2 = 1 \times 10^{-7}$ atm) at 870 °C (1600 °F) for 100 h. ~1.5×. Micrographs (b) and (c) show cross sections through the $Cr_2O_3$ layer and disrupted oxide region having external sulfides. Courtesy of G.R. Smolik and D.V. Miley, E.G. & G. Idaho, Inc.

potential of the active area, and pitting progresses rapidly.

**Stages of Pitting.** Immediately after a pit has initiated, the local environment and any surface films on the pit-initiation site are unstable, and the pit may become inactive after just a few minutes if convection currents sweep away the locally high concentration of hydrogen ions, chloride ions, or other ions that initiated the local attack. Accordingly, the continued development of pits is favored in a stagnant solution.

When a pit has reached a stable stage, barring drastic changes in the environment, it penetrates the metal at an ever-increasing rate by an autocatalytic process. In the pitting of a metal by an aerated sodium chloride solution, rapid dissolution occurs within the pit, while reduction of oxygen takes place on adjacent surfaces. This process is self-propagating. The rapid dissolution of metal within the pit produces an excess of positive charges in this area, causing migration of chloride ions into the pit.

Thus, in the pit there is a high concentration of $MCl_n$ and, as a result of hydrolysis, a high concentration of hydrogen ions. Both hydrogen and chloride ions stimulate the dissolution of most metals and alloys, and the entire process accelerates with time. Because the solubility of oxygen is virtually zero in concentrated solutions, no reduction of oxygen occurs within a pit. Cathodic reduction of oxygen on the surface areas adjacent to pits tends to suppress corrosion on these surface areas. Thus, isolated pits cathodically protect the surrounding metal surface.

Because the dense, concentrated solution within a pit is necessary for its continuing development, pits are most stable when growing in the direction of gravity. Also, the active anions are more easily retained on the upper surfaces of a piece of metal immersed in or covered by a liquid.

**Some causes of pitting** are local inhomogeneity on the metal surface, local loss of passivity, mechanical or chemical rupture of a protective oxide coating, galvanic corrosion from a relatively distant cathode, and the formation of a metal ion or oxygen concentration cell under a solid deposit (crevice corrosion).

The rate of pitting is related to the aggressiveness of the corrodent at the site of pitting and the electrical conductivity of the solution containing the corrodent. For a given metal, certain specific ions increase the probability of attack from pitting and accelerate that attack once initiated. Pitting is usually associated with metal-environment combinations in which the general corrosion rate is relatively low; for a given combination, the rate of penetration into the metal by pitting can be 10 to 100 times that by general corrosion.

With carbon and low-alloy steels in relatively mild corrodents, pits are often generally distributed over the surface and change locations as they propagate. If they blend together, the individual pits become virtually indistinguishable, and the final effect is a roughened surface but a generally uniform reduction in cross section. If the initial pits on carbon steel do not combine in this

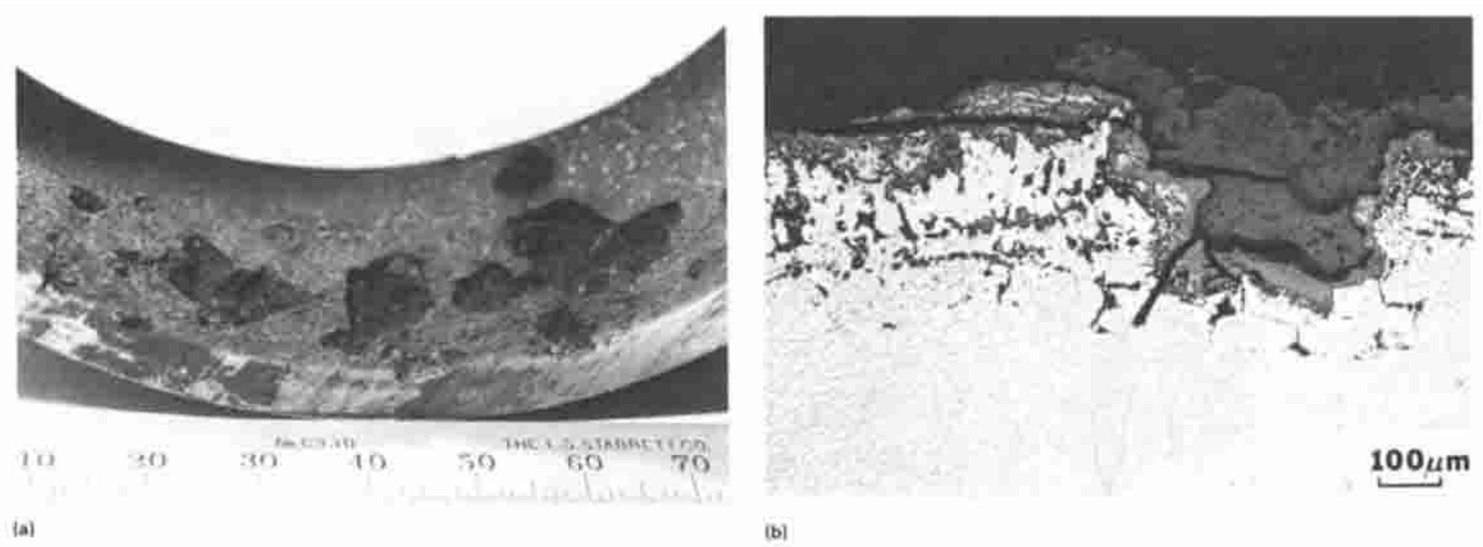

**Fig. 24** Example of high-temperature carburization attack pitting in type 310 reactor wall after ~4000-h exposure to coal gasification product gas. The pits were formed during operation under conditions of high carbon activity in the gas. (a) Overall view of pitting. (b) Section through a pit. Courtesy of I.G. Wright, Battelle Columbus Division

# Corrosion Protection Methods for the Petrochemical Industry

# Corrosion Protection Methods for the Petrochemical Industry

## Fundamentals of Corrosion Protection in Aqueous Solutions

THE IMPORTANT METALS in structures—aluminum, copper, iron, zinc, and so on—are inherently unstable. Their ionic solutions and their carbonates, hydroxides, oxides, sulfides, sulfates, and many other salts are more stable than the free metal under the many conditions to which these metals are exposed. The free energy change for the conversion of these metals to a compound is a large negative value, and the thermodynamic driving force to convert the elemental metal to an oxide or salt is great. Thus, to retain a required physical property of the metal, such as strength, thermal conductivity, magnetic nature, or electrical conductivity, it is essential to protect the metal from the environments to which it is expected to be exposed. This article will describe the various methods that can be used to protect a metallic system against corrosion. These methods can be divided into the following: thermodynamic protection, kinetic protection, barrier protection, structural design, environmental control, and metallurgical design.

The objective of most protective systems is to reduce the rate of corrosion to a value that is tolerable or that will allow the material to attain its normal or desired lifetime. Only in a limited number of cases must corrosion protection be designed to eliminate corrosion completely.

## Protection on a Thermodynamic Basis

This type of protection is based on the requirement that the metal have a high positive value for the free energy change for conversion of the metal to the corrosion products that can form in the environment to which the metal is exposed. For example, the free energy change for the conversion of gold to its oxide is 163,000 J/mol (39,000 cal/mol), and for the conversion of silver to its ion at standard state in an aqueous phase, the free energy change is 77,000 J/mol (18,430 cal/mol). These two metals could *a priori* be expected to resist corrosion when exposed to oxygenated pure water, because the tendency in these systems is for the metal to be more stable than its aquated ion or its oxide. As a general rule, a metal M whose thermodynamic potential in contact with its ions is a high positive value for the reaction $M - ne^- \rightarrow M^{n+}$ is stable in aqueous solutions at room temperature. No blanket statement can be made without full knowledge of the composition of the aqueous phase because some ions and other complexing agents may form complexes that are more thermodynamically stable than the free metal.

Another form of thermodynamic protection is obtained when an external potential is applied such that the metal is stable with respect to the metal ion concentration in the aqueous phase with which it is in contact. For example, if nickel immersed in an aqueous solution of pH 4 is polarized externally to a potential of −0.5 V, elemental nickel is stable with respect to its ions, and nickel will be protected from corrosion. However, this potential is more negative than the potential for the generation of hydrogen, and hydrogen formation may occur.

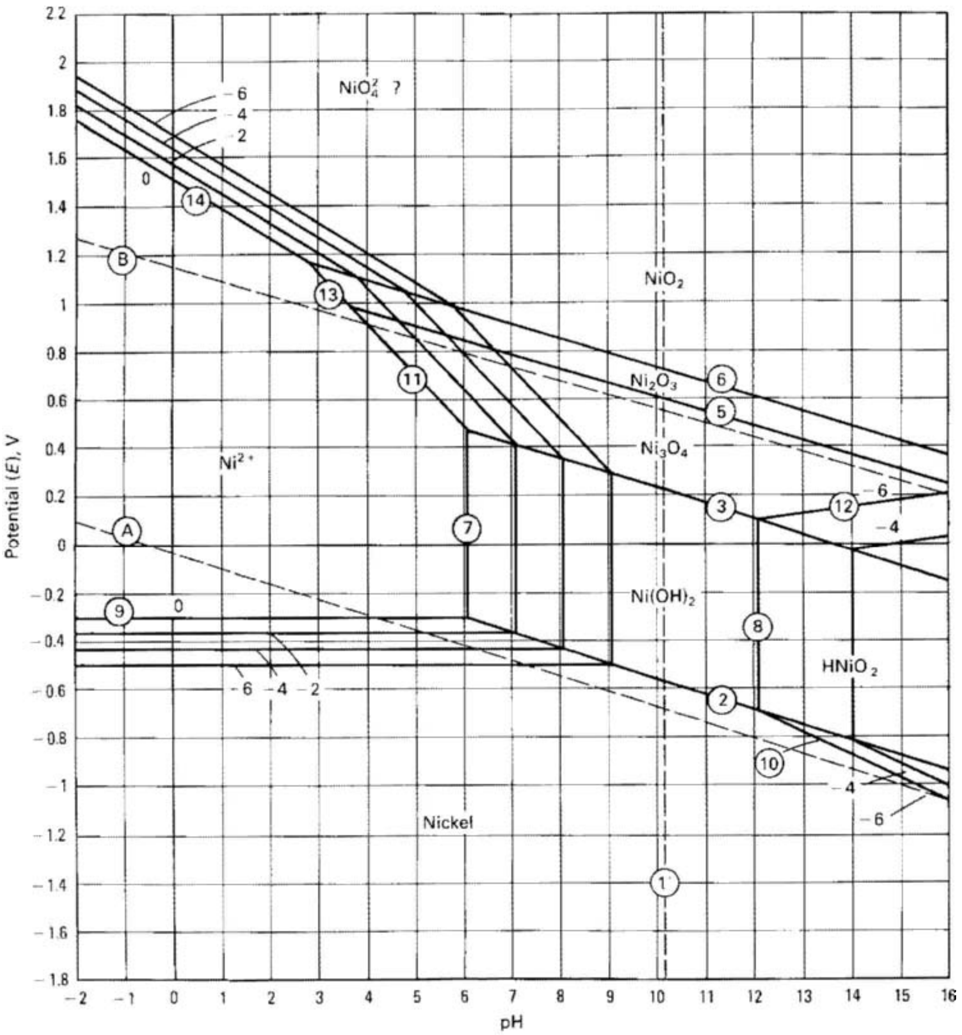

**Fig. 1** The Pourbaix diagram for the nickel-water system at 25 °C (75 °F). See Ref 1 for details. Source: Ref 1

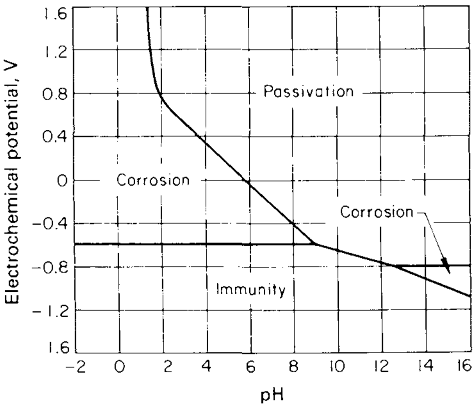

**Fig. 2** Pourbaix diagram showing the theoretical conditions for corrosion, passivation, and immunity of iron in water and dilute aqueous solutions

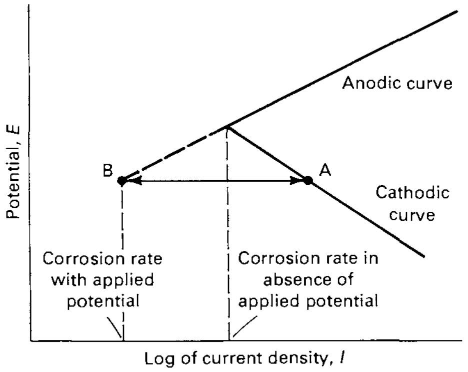

**Fig. 3** Diagram showing how the corrosion rate can be calculated when a cathodic potential is applied. The situation shown is schematic in nature, and other factors must be considered when cathodic protection is applied in practice.

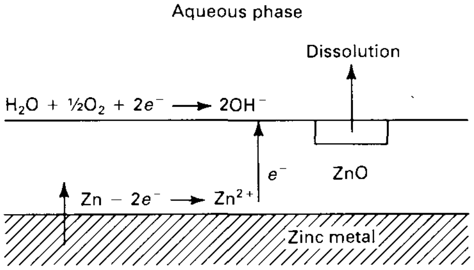

**Fig. 4** The mechanism by which zinc corrodes in a neutral chloride solution. Source: Ref 2

**Pourbaix diagrams** are sometimes used to appraise the relative stabilities of a metal with respect to its ions and its hydrous and anhydrous oxides. These diagrams, which are derived from electrochemical measurements and thermodynamic data, are potential-pH diagrams that relate to the electrochemical and corrosion behavior of metals in water and in aqueous solutions.

Pourbaix diagrams show the conditions of potential and pH under which the metal either does not react (immunity) or can react to form specific oxides or complex ions. They do not provide information on rates of reaction.

Pourbaix diagrams indicate the conditions for which diffusion-boundary films may form on an electrode surface, but they provide no measure of how effective such barrier films may be in the presence of specific anions, such as $SO_4^{2-}$ or $Cl^-$. Similarly, they do not indicate the detailed conditions under which nonstoichiometric metal compound films influence corrosion rates.

However, Pourbaix diagrams outline the nature of the stoichiometric compounds into which any less stable compounds may transform. They relate the possibility of corrosion to the pH of the corrodent and the potential difference between the pure metal and its ions in solution. They show under what pH-potential conditions corrosion might occur and those under which it will not occur, thus providing guidance as to how corrosion can be minimized or avoided. The Pourbaix diagram for nickel is shown in Fig. 1. The dashed line labeled A represents the phase boundary for the equilibrium, $H_2 \rightarrow 2H^+ + 2e^-$. Hydrogen at unit fugacity is stable below this line and the hydrogen ion ($H^+$) at unit activity is stable above.

Figure 2 shows a Pourbaix diagram for iron in water and dilute aqueous solutions. Note that there are zones of corrosion, immunity from corrosion, and passivity.

Some metals besides iron for which Pourbaix diagrams have proved to be especially helpful include tantalum, titanium, aluminum, and magnesium. The diagrams correlate well in a general way with the well-established facts that tantalum is relatively inert, titanium is resistant to a wide range of conditions, aluminum is amphoteric and is attacked by acids and alkalis over a wide range of conditions, and magnesium is very active over a wide range of conditions. Additional information on Pourbaix diagrams can be found in Ref 1.

## Protection on a Kinetic Basis

The corrosion rate of an actively corroding metal is determined by the intersection of the kinetic curves that characterize the anodic and cathodic halves of the corrosion reaction. If the rates of either of these reactions can be changed such that the intersection point is at a lower current density, the corrosion rate is reduced.

A widely used method for taking advantage of the corrosion kinetics is known as cathodic protection. In some cases, the applied potential is not sufficient to polarize the metal into its thermodynamic stability region, such as in the case of nickel described previously. In the kinetics case, a small potential is applied between an inert electrode and the metal to be protected. The potential of the metal is made more negative, and the rate of the anodic reaction is reduced. Figure 3 shows a diagram illustrating the phenomenon of cathodic protection. If a metal exhibiting the anodic and cathodic polarization curves shown in Fig. 3 is polarized to the potential denoted by A—B, the cathodic current density is that shown as A. The extrapolated anodic polarization curve allows calculation of the corrosion rate B. This type of diagram enables calculation of the corrosion rate under any specific applied cathodic potential. More detailed descriptions of the principles and practice of cathodic protection are given in the section "Anodic and Cathodic Protection" in this article.

As stated above, the rate of the overall corrosion reaction is limited by the rate at which the slower of the anodic or cathodic reactions occurs. One of the two reactions is rate controlling. A knowledge of the rate-controlling reaction can often be applied to reducing the corrosion rate. An example is the use of inhibitors that selectively reduce the cathodic hydrogen evolution reaction in the acid pickling of steel. The pickling solution effectively attacks the oxide, with little attack on the base steel, because the anodic corrosion reaction is limited by the low rate of the cathodic hydrogen evolution reaction.

A second example is the corrosion of zinc in neutral chloride solution. As shown in Fig. 4, the anodic reaction occurs at the metal/oxide interface, and the cathodic oxygen reduction reaction occurs at the oxide/solution interface. The electrons formed by the anodic reaction must pass through the oxide to be available for the cathodic reaction on the oxide surface. A reduction in the electron conductivity of the oxide causes a reduction in the rate of electron transfer and a consequent reduction in the corrosion rate. The conductivity of the oxide can be reduced by doping the oxide with cobalt by using a zinc-cobalt alloy or by introducing cobalt into the oxide on the surface by immersion in a solution of cobalt ions (Ref 2).

## Barrier Protection

The concept of barrier protection is very simple: The metal is protected from the environment by coating it with a barrier that resists penetration by aggressive environmental constituents. Five types of barrier coatings will be discussed: anodic oxides, ceramic and inorganic coatings, inhibitors, organic coatings, and phosphate and other conversion coatings.

**Anodic oxides** are widely used to protect aluminum from corrosion. The metal and many of its alloys are anodized in such acids as boric ($B_2O_3 \cdot 3H_2O$), oxalic, phosphoric ($H_3PO_4$), and sulfuric ($H_2SO_4$) under conditions in which an oxide is formed on the surface. The oxides formed in $B_2O_3 \cdot 3H_2O$ are relatively thin and nonporous in nature, but they are not suitable for protecting aluminum against corrosion in aggressive environments. The oxides formed in $H_3PO_4$ or $H_2SO_4$ are many microns thick and are very porous. The porosity is reduced in a second step in which the oxide is sealed in steam, boiling water, or aqueous solutions containing nickel acetate ($Ni(C_2H_3O_2)_2$) or other salts.

The anodizing of aluminum is widely utilized to protect aluminum components on automobiles, buildings, storm doors, and windows. Other metals are protected to a limited extent by anodization before the component is placed in service. Stainless steels and other iron alloys that form passive oxides in aggressive environments are also protected from corrosion by applying an anodic potential while the part is in service. This

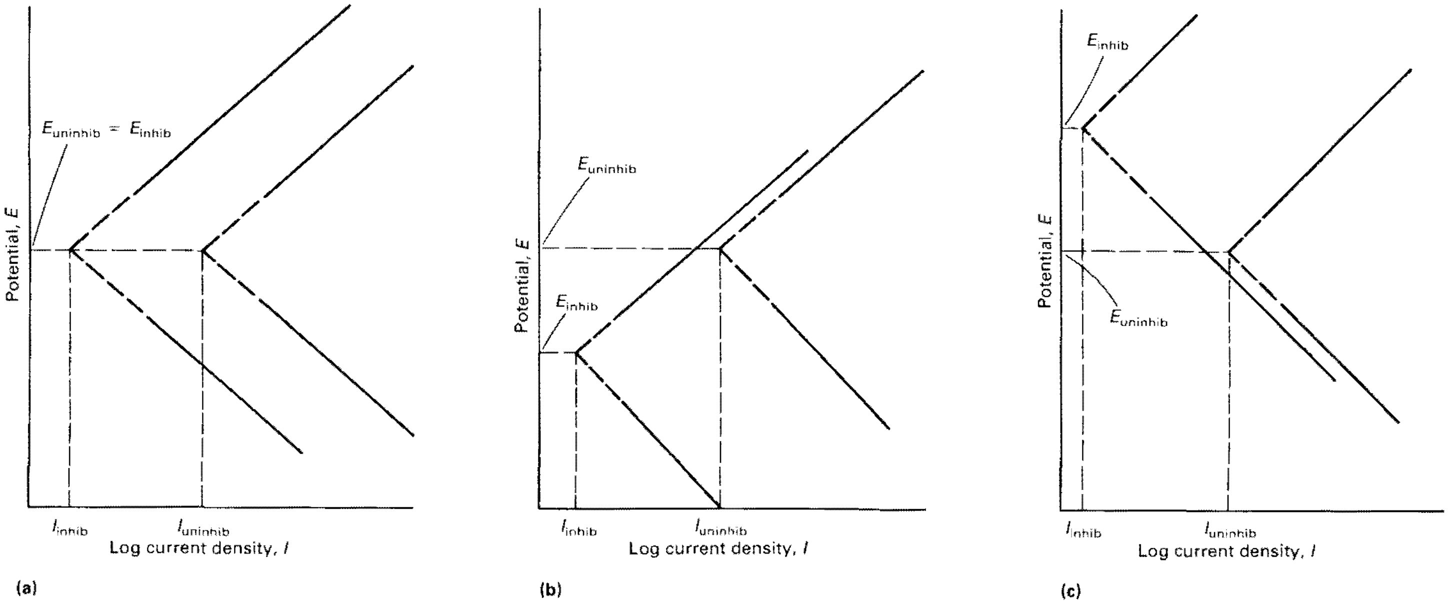

**Fig. 5** Examples of three extreme cases in which corrosion inhibitors affect corrosion kinetics. (a) The inhibitor affects the anodic and cathodic curves to an equal extent. The corrosion rate is reduced, but the corrosion potential remains the same. (b) The corrosion inhibitor affects the cathodic curve extensively, and the potential in the presence of the inhibitor becomes more negative. (c) The corrosion inhibitor affects the anodic curve extensively, and the potential in the presence of the inhibitor becomes more negative.

potential is sufficient to maintain a barrier oxide on the surface. This method, known as anodic protection, is discussed in detail in the section "Anodic and Cathodic Protection" in this article.

**Ceramic coatings** based on special cements are used to protect steel from corrosion. They serve as a barrier and also maintain an alkaline environment at the steel/ceramic interface in which the corrosion rate is low. Inorganic coatings, such as silica, are used to protect stainless steel from tarnishing, and silicon nitride coatings are used to protect some types of components in electronic devices. Many other ceramic and inorganic coatings are used industrially to protect vital components against corrosion.

**Corrosion Inhibitors.** In many cases, the role of inhibitors is to form a surface coating one or several molecular layers thick that serves as a barrier. Many effective organic inhibitors have a reactive group attached to a hydrocarbon. The reactive group interacts with the metal surface, and the hydrocarbon portion of the molecule is in contact with the environment. Cinnamates (salts or esters of cinnamic acid) are used to protect steel surfaces against corrosion in neutral or slightly alkaline media by this mechanism.

The behavior of the corrosion potential can be used to determine which of the half reactions is most affected by the inhibitor. Figure 5 illustrates three cases. In Fig. 5(a), the corrosion inhibitor affects the anodic and cathodic curves equally. The corrosion rate is reduced to the value $I_{\text{inhib}}$, but the corrosion potential is unaffected. In Fig. 5(b), the cathodic reaction is affected to a greater extent, and the corrosion potential moves to a more negative value. In Fig. 5(c), the anodic reaction is affected to a greater extent, and the corrosion potential moves to a more positive value. The change in corrosion potential in the presence of an inhibitor can thus be used to estimate the kinetics of the inhibition. Generally, additional information is needed to draw firm conclusions. More information on the use of inhibitors is available in the section "Use of Inhibitors" in this article.

**Organic coatings** are the most widely used barrier coating for protecting aluminum, steel, and zinc against atmospheric corrosion. The main function of the coating is to serve as a barrier to water, oxygen, and ions and thus prevent the cathodic reaction $H_2O + \frac{1}{2}O_2 + 2e^- \rightarrow 2OH^-$ from occurring beneath the coating. The protective barrier properties may be lost by the collection of water at the interface in the form of a thin layer or as blisters. Once water is present as an aqueous phase at the interface, the electrochemical corrosion reaction is possible by charge transfer laterally between neighboring anodic and cathodic areas or by charge transfer through the coating. Therefore, it is important to have coatings that are good barriers for water. In practice, a second line of defense is used to provide protection if the barrier properties of the organic coating are inadequate. A corrosion inhibitor, such as lead chromate ($PbCrO_4$), is incorporated into the primer. As a water phase develops, some of the chromate is solubilized and is available for inactivating the portions of the surface that are in contact with the aqueous phase.

**Conversion Coatings.** Organic coatings are effective only if they protect the entire metal surface. Because many uses for organic coatings are on automobiles and appliances that may be damaged during service, the damaged area must not lead to total loss of the protective property near the damaged region. Certain conversion coatings provide resistance to lateral loss of corrosion protection. Phosphate coatings, chromate coatings, and mixed oxide coatings are applied before the organic coating. These coatings, intermediate between the metal and the organic coating, are known as conversion coatings because they convert some of the base metal to a coating in which ions of the base metal are a component.

## Protection by Structural Design

Inappropriate design is often the source of severe corrosion. Crevices provide locations where an occluded corrosion cell may develop. Liquid is retained in a crevice long after the atmosphere has a low moisture level; the chemical nature of the ions formed by the corrosion process is acidic, and the corrosion rate is accelerated. The corrosion product occupies a larger volume than the metal from which it is formed, and the expansion forces are often sufficient to break a clamping bolt or cause serious deformation.

Designs that have recesses where rainwater can collect result in longer periods of time during which the metal can support an electrochemical reaction and consequently a higher corrosion rate. Erosive conditions, when combined with a corrosive medium, can lead to rapid corrosion rates. Drain water containing a sediment should not be allowed to drip or run over metal.

Structures should be designed, installed, and used such that the length of time they are wet with water is minimized. The corrosion reaction will only occur when liquid water is present on the metal. Liquid water can occur at relative humidities below 100% when deliquescent salts are present on the surface; therefore, it is useful to remove contaminants at regular intervals. Erosive agents dispersed in flowing liquids should also be avoided. An excellent summary of designing to minimize corrosion is given in Ref 3, and more information on this subject is available in the article "Designing to Minimize Corrosion" in this Volume.

## Protection by Environmental Control

This method of protection is limited to closed systems in which changes in the composition of the corrosion medium can be tolerated. The method depends on removing a constituent of the corrosion reaction from the medium or, in some cases, adding a component to the medium. Constituents that can be removed from the corrosion medium include oxygen; living materials, such as bacteria; erosive components in flowing systems; solid matter that may provide crevicelike situations at the bottom of pipes or tanks; and specific ions, such as chloride ($Cl^-$), that accelerate corrosion processes. Additives that may reduce corrosion in closed systems include agents that control pH, oxidizing agents that destroy organic matter, surface-active agents that maintain sediment in suspension, inhibitors, agents that reduce dissolved oxygen concentration, and materials that remove scale from the surface. Environmental control is a complicated subject, and specialists in cooling water treatment, boiler water treatment, and waste treatment should be consulted.

## Protection by Metallurgical Design

The most obvious aspect of metallurgical design is the use of the proper alloy for the environment against which protection is sought. Economic and lifetime considerations are important factors in the choice of the alloy, and each situation must be considered individually (see the section "Materials Selection" of the article "Designing to Minimize Corrosion" in this Volume). Metallurgical considerations are also necessary once the alloy has been selected. Variables that influence the corrosion rate or sensitivity to fatigue or corrosion cracking include grain size, preferred orientation, presence of inclusions, method of fabrication, surface preparation method, and heat treatment.

# Anodic and Cathodic Protection

Cathodic protection has been used since the middle of the 19th century and has gained widespread acceptance. Anodic protection is sometimes confused with cathodic protection, but the two techniques are fundamentally different. Basically, the difference concerns which electrode is protected; the cathode is protected in cathodic protection, and the anode is protected in anodic protection. However, there are other, more significant theoretical differences. The background and theory of both methods are discussed in Ref 4.

**Cathodic protection** is based on using electrochemistry to slow or stifle the corrosion reaction. Currents generated by galvanic metallic couples or external dc current supplies flow in such a direction as to shift the cathode potential to a value at which the corrosion reaction will not occur. Other descriptions of cathodic protection state that the currents result in the metal to be protected becoming a cathode over the entire metal surface and shifting the anodic reaction to an external electrode. In principle, any corrosion system can be cathodically protected as long as there is a continuous ionic path between the external anode and the metal to be protected. The only limitations are ones of economics and practicality due to current and voltage requirements.

**Anodic protection,** like cathodic protection, is an electrochemical method of controlling corrosion, but is based on a different electrochemical principle. Anodic protection is based on the phenomenon of passivity. A limited number of metals in a limited number of chemicals have the property of passivity. The electrochemical nature of achieving passivity requires that the potential of the metal be controlled. This is not necessary for most of the applications of cathodic protection. Current requirements for anodic protection can be much lower than those required for cathodic protection, but this is not always the case for all systems.

## Anodic Protection

Anodic protection is the most recently developed of all the various corrosion control methods available. This method was first used in the field in the late 1950s. Anodic protection did not become commercially successful until the early 1970s, and it is currently used on a smaller scale than other corrosion control techniques. This article will provide a brief history of the technique, will discuss anodic protection use, and will compare anodic and cathodic protection. A more complete description of all aspects of anodic protection is available in Ref 5.

### History

The scientific principles of passivity on which anodic protection is based can be traced to experiments by Faraday and Schobein in the 19th century (Ref 5). Work by C. Edeleanu published in 1954 (Ref 6) was responsible for further investigations and developments at the Continental Oil Company. This later work resulted in several installations of anodic protection to control the corrosion of chemical plant equipment (Ref 7-10). Simultaneous investigations at the Pulp and Paper Institute of Canada led to installation of anodic protection to protect pulp and paper digesters (Ref 11-13).

Commercialization of anodic protection was begun by Continental Oil Company through licensing agreements, and only a few companies are currently marketing anodic protection. The most active of these companies are Canadian-based corporations that sell, engineer, and install anodic protection systems in the United States.

### Anodic Protection Use

Anodic protection has been most extensively applied to protect equipment used to store and handle sulfuric acid ($H_2SO_4$) (Ref 14). Sales of anodically protected heat exchangers used to cool $H_2SO_4$-manufacturing plants have represented one of the more successful ventures in the past few years. These heat exchangers are sold complete with the anodic protection systems installed and have a commercial advantage in that less costly materials can be used.

Protection of steel $H_2SO_4$ (>78% concentration) storage vessels is perhaps the most common application of anodic protection. Companies in North America and Europe sell systems primarily for these storage vessels and the heat exchangers. There is little activity directed toward developing applications to protect metals from corrosion by other chemicals. However, in Russia, a substantial amount of effort is devoted to installing anodic protection in a wide variety of systems. Several recent applications are discussed in Ref 4.

Anodic protection is used to a lesser degree than the other corrosion control techniques, particularly cathodic protection. This is because of the limitations on metal-chemical systems for which anodic protection will reduce corrosion. In addition, it is possible to accelerate corrosion of the equipment if proper controls are not implemented. The understanding of anodic protection is also not as widespread as for other techniques. Anodic protection does have a place in the corrosion control area, for which it is the most feasible and economical technique, and use of this technique is expected to increase slowly in coming years.

### Background and Theory

Anodic protection can be used to control the corrosion of metals in chemicals that exhibit very interesting behavior when subjected to anodic polarization. This behavior can be studied with

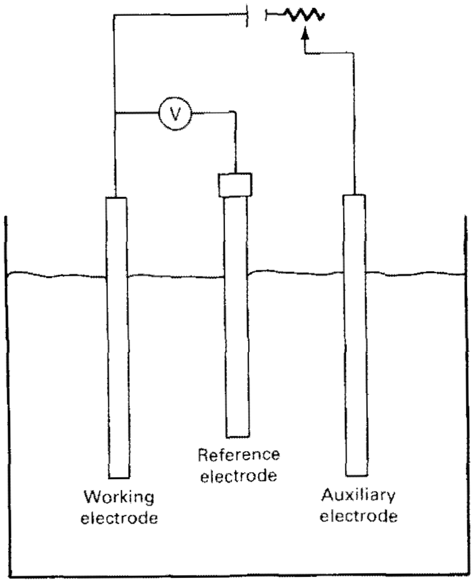

**Fig. 6** Schematic of experimental apparatus used for anodic polarization studies. Current flow between the working electrode and the auxiliary electrode forces a shift in potential between the working electrode and the reference electrode. V, voltmeter. Source: Ref 15

an experimental setup, as illustrated in Fig. 6. When the potential of the working electrode relative to the reference electrode is controlled and shifted in the more anodic (positive) direction, the current required to cause that shift will vary. If the current required for the shift has the general type of behavior with respect to potential shown in Fig. 7, the metal is termed active-passive and can be anodically protected. Few systems exhibit this type of behavior. The metals and solutions that have been found to have active-passive properties and that can be anodically protected include:

| Solutions | Metals |
|---|---|
| Sulfuric acid | Steels |
| Phosphoric acid | Stainless steels |
| Nitric acid | Nickel |
| Nitrate solutions | Nickel alloys |
| Aqueous ammonia | Chromium |
| Organic acids | |
| Caustic solutions | |

The corrosion rate of an active-passive metal can be significantly reduced by shifting the potential of the metal so that it is at a value in the passive range shown in Fig. 7. The current required to shift the potential in the anodic direction from the corrosion potential $E_{corr}$ is several orders of magnitude greater than the current necessary to maintain the potential at a passive value. The current will peak at the potential value shown as $E_p$ (Fig. 7). The current required to achieve passivity (protection) is typically a few hundred milliamps per square foot wetted area. The current necessary to maintain passivity is usually 10.76 $\mu A/m^2$ (1 $\mu A/ft^2$) or less.

This interesting anodic polarization behavior results from the formation of a surface layer on the metal that is relatively insoluble in the chemical environment. This passive film is not yet completely understood.

Passivity is the phenomenon responsible for the high corrosion resistance of stainless steels. It can be variously defined, but a reasonable definition is that passivity is the loss of chemical reactivity experienced by some metals in special environments. These metals and alloys, when passive, behave as noble metals. This noblelike behavior is attributed to the presence of a thin oxide film on the metal surface. The mechanism of formation, the composition, and the structure of the passive film have been extensively studied, but are not well understood.

Passivity can be achieved by alloying and by chemical means in addition to the electrochemical method described in this section. Anodic protection can be used to form the passive film on metals in chemical systems that would normally be corrosive; at other times, anodic protection can be used to maintain the passivity of the metal so that process upsets or changes do not force the metal to become active and corrode.

## Equipment Required for Anodic Protection

Figure 8 shows a schematic of an anodic protection system for a storage vessel. Each of these components has specific requirements that will be discussed below. In addition, the various items used for each component of the system will be briefly described.

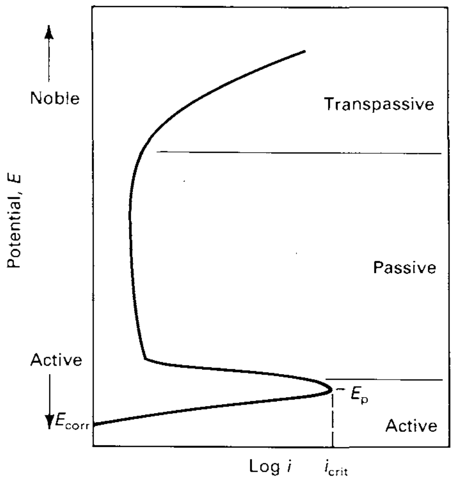

**Fig. 7** Schematic anodic polarization curve. Metal-environment systems that have this type of anodic polarization behavior are termed active-passive and can be anodically protected. Source: Ref 15

**The cathode** should be a permanent-type electrode that is not dissolved by the solution or the currents impressed between the vessel wall and electrode. The cathodes used in most of the first applications of anodic protection were made of platinum-clad brass (Ref 5, 6, 7-10). These electrodes were excellent electrochemically, but they were costly, and the area contacting the solution was limited by this cost. Because the overall circuit resistance between cathode and vessel wall is proportional to the electrode surface area, it is advantageous to use large surface area electrodes. Therefore, many other, less costly metals have been used for cathodes. Metals that have been used for cathodes in anodic protection systems, as well as the chemical environments in which they were used, include:

| Metals | Environment |
|---|---|
| Platinum on brass | Various |
| Steel | Kraft digester liquid |
| Illium G | $H_2SO_4$ (78-105%) |
| Silicon cast iron | $H_2SO_4$ (89-105%) |
| Copper | Hydroxylamine sulfate |
| Stainless steel | Liquid fertilizers (nitrate solutions) |
| Nickel-plated steel | Chemical nickel plating solutions |
| Hastelloy C | Liquid fertilizers (nitrate solutions), $H_2SO_4$, Kraft digester liquid |

The electrode size is chosen to conform to the geometry of the vessel and to provide as large a surface area as possible. The location of the cathode is not a critical factor in simple geometries, such as storage vessels, but in heat exchangers, it is necessary to extend the electrode around the surface to be protected. Multiple cathodes can be used in parallel to distribute the current and to decrease circuit resistance.

**Reference electrodes** must be used in anodic protection systems because the potential of the vessel wall as the anode must be controlled. The reference electrode must have an electrochemical potential that is constant with respect to time and that is minimally affected by changes in temperature and solution composition. Several reference electrodes have been used for anodic protection, including:

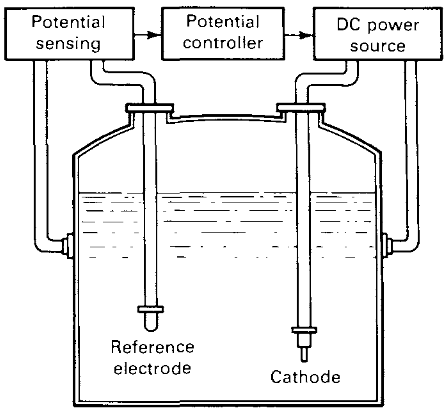

**Fig. 8** Schematic of an anodic protection system. One or more cathodes, a reference electrode, a potential sensing and controlling circuit, and a dc power supply are required for each anodic protection system. The vessel wall is made the anode of the circuit by current forced between the cathode and the tank wall. The currents are controlled so that the potential of the wall with respect to the reference electrode is shifted and maintained in the passive region (see Fig. 7). Source: Ref 5

| Electrode | Solution |
|---|---|
| Calomel | $H_2SO_4$ |
| Ag-AgCl | $H_2SO_4$, Kraft solutions, fertilizer solutions |
| $Mo-MoO_3$ | Sodium carbonate solutions |
| Bismuth | $NH_4OH$ |
| Type 316 stainless steel | Fertilizer solutions, oleum |
| $Hg-HgSO_4$ | $H_2SO_4$, hydroxylamine sulfate |
| Pt-PtO | $H_2SO_4$ |

The reference electrode has been a source of many problems in anodic protection installations because of its more fragile nature with respect to the cathode.

**Potential Control.** As mentioned above, the potential of the vessel wall with respect to the reference electrode must be controlled in anodic protection installations. The potential control circuitry has two functions. First, the potential must be measured and compared to the desired preset value. Second, a control signal must then be sent to the power supply to force the dc current between the cathode and vessel wall. In early systems, this control function was done in an on-off method because of the high costs of electronic circuitry. The more sophisticated and extremely low-cost circuitry currently available has resulted in all systems having a continuous proportional-type control. The amount of current forced through the circuitry is that required to maintain the potential at the preset control point.

**The dc power supplies** have the identical design and requirements as the rectifiers for cathodic protection with one exception. Because of the nature of the active-passive behavior of the vessel, the currents required to maintain the potential of the vessel wall in the passive range can become very small. Some designs of dc power supplies must be specially modified to reduce the minimum amount of current put out of the power supply.

The packaging of these electronic components occasionally involves special requirements because most of the installations are made in chemical plants. Explosion-proof enclosures are sometimes required, and chemically resistant enclosures are necessary in other installations.

## Design Concerns

Design of an anodic protection system requires knowledge of the electrochemical parameters of the metal-solution system, the geometry of the equipment to be protected, any special operational conditions, and the special requirements of the environment around the system. The electrochemical parameters of concern are the potential at which the vessel must be maintained for corrosion protection, the currents required to establish passivity, the currents required to maintain passivity, and the solution resistivity. The electrode potential can be determined directly from the polarization curve. The currents can be estimated from the polarization data, but they are time dependent, and the variation of the currents with respect to time must be estimated. Empirical data available from field installations are the best source of this information (Ref 5).

Solution resistivity is important in the determination of the overall circuit resistance. The power requirements for the dc power supply should be as low as possible to reduce operating costs. The solution resistivity will usually be sufficiently low that the circuit resistance will be controlled by the cathode surface area in contact with the solution.

## Applications

Anodic protection has been used for storage vessels, process reactors, heat exchangers, and transportation vessels containing various corrosive solutions. Sulfuric acid is used in the largest number of systems in operation throughout the world. Anodic protection has been successful in preserving product quality through reduction of metal pickup by the solution, in extending the useful life of the vessels, and in allowing the use of a lower-cost alloy. Examples of these applications will be given below.

**Storage Vessels.** Storage of $H_2SO_4$ in strengths of 93% and above in low-carbon steel vessels has met with some success in terms of vessel life. Anodic protection has been successful in reducing the amount of iron picked up during storage. This enhances the economic worth of the product in that pure acid is more valuable than contaminated acid. Field studies have shown that the iron content of $H_2SO_4$ in concentrations of 93% and above increases at rates of 5 to 20 ppm per day of storage, depending on acid concentration, vessel size, acid residence time, and storage temperature (Ref 5). Several anodic protection systems have been successful in reducing the rates of iron pickup to 1 ppm per day or less. The level of purity of the acid has been sufficient to meet market demands for low iron content acid.

However, tanks constructed since the 1970s have been made with steel containing low amounts of copper. Steel with low copper content will corrode readily in these acids (Ref 16). Anodic protection of the newer vessels has been successful in lowering the corrosion rate by a factor of four to five, and vessel life has been greatly extended.

**Heat Exchangers.** A large market has developed for anodically protected heat exchangers as replacements for cast iron coolers. Shell and tube, spiral, and plate-type exchangers have been sold complete with anodic protection as an integral part of the equipment (Ref 4, 5, 14). Sulfuric acid of 96 to 98% concentration at temperatures up to 110 °C (230 °F) has been handled in AISI type 316 stainless steel exchangers by the use of anodic protection. Corrosion rates have been reduced from unprotected rates of more than 5 mm/yr (200 mils/yr) to less than 0.025 mm/yr (1 mil/yr), and cost savings have been substantial because of extended equipment life and the higher-purity acid that was produced by using these protected heat exchangers. Several other corrosive systems have also been handled in anodically protected heat exchangers (Ref 5).

**Transportation Vessels.** Sulfuric acid will continue to pick up iron during transportation in trucks, railroad cars, and barges. Anodic protection has been applied to these vessels to maintain the purity of the acid and to extend storage time. These applications are described in Ref 4, 5, and 17.

**Galvanic Cathodes.** The potentials of metals have been maintained in the passive region by using the potential differences between metals to achieve anodic protection by galvanic methods. Unlike cathodic protection, nothing is sacrificed, but the protection is achieved. A titanium pipe has been used to protect a steel vessel containing ammonium hydroxide ($NH_4OH$) solution, and platinum has been used to protect a stainless steel tank containing $H_2SO_4$ (Ref 15, 18). A combination of galvanic and impressed current protection that uses graphite cathodes for the anodic protection system is described in Ref 16. The graphite supplies sufficient current to maintain protection, but additional current can be supplied through the graphite electrodes to reestablish protection, if needed.

## Economics

Economic justification of anodic protection is based on the same factors as in any comparison of corrosion control methods. Protection of $H_2SO_4$ storage vessels can be accomplished with baked phenolic linings or anodic protection. Because an anodic protection system has some basic requirements (electrodes, potential controller, and power supply) independent of tank size, anodic protection is more economically feasible for larger tanks. A detailed comparison of the economics of lining and anodically protecting steel storage vessels can be found in Ref 5. This comparison indicates that anodic protection is 42.5% less expensive per ton of acid storage capacity than a baked phenolic lining for a vessel with a capacity of about 18,000 Mg (20,000 tons). Costs of the lining are 74.3% less expensive per ton of acid storage capacity than the anodic protection cost of a 907-Mg (1000-ton) capacity vessel.

Anodic protection for other equipment when a less costly alloy can be used has been compared in terms of economics to the absence of protection. The anodically protected heat exchangers used in $H_2SO_4$-manufacturing plants have been shown to reduce maintenance costs by almost 95% (Ref 20). These reduced maintenance costs, combined with the improved quality of the acid produced in the plant, have provided an attractive return on the investment required for the anodically protected exchangers.

Many other applications of anodic protection have also been found to be economically feasible, by using standard methods of engineering economics comparisons. As experience is gained and confidence in this new method increases, there should be several other applications for which anodic protection will be shown to be the best economic alternative.

# Cathodic Protection

Cathodic protection is an electrochemical means of corrosion control in which the oxidation reaction in a galvanic cell is concentrated at the anode and suppresses corrosion of the cathode in the same cell. Figure 9 shows a simple cathodic protection system. The steel pipeline is cathodically protected by its connection to a sacrificial magnesium anode buried in the same soil electrolyte.

Cathodic protection is different from anodic protection. In cathodic protection, the object to be protected is the cathode, but in anodic protection, the object to be protected is the anode.

Anodic protection can be used on only a limited number of alloys in certain restricted environments, but cathodic protection can, in principle, be applied to any metal. In practice, cathodic protection is primarily used on carbon steel. The effectiveness of cathodic protection allows carbon steel, which has little natural corrosion resistance, to be used in such corrosive environments as seawater, acid soils, salt-laden concrete, and many other corrosive environments. Properly designed and maintained cathodic protection systems can prevent corrosion indefinitely in these environments.

Cathodic protection was first suggested by Sir Humphrey Davy in the 1820s as a means of controlling corrosion on British naval ships (Ref 21). It became common in the 1930s on the Gulf Coast of the United States, where it was used to control the corrosion of pipelines carrying high-pressure hydrocarbons (natural gas and petroleum products). Much of the terminology of cathodic protection still relates to corrosion control of onshore buried steel pipelines.

Virtually all modern pipelines are coated with an organic protective coating that is sup-

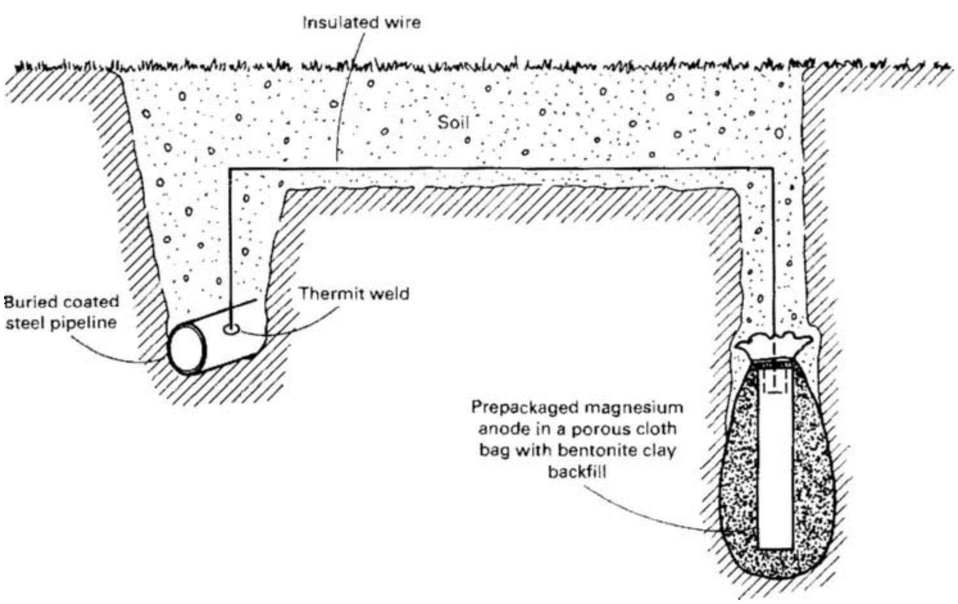

**Fig. 9** Cathodic protection of buried pipeline using a buried magnesium anode

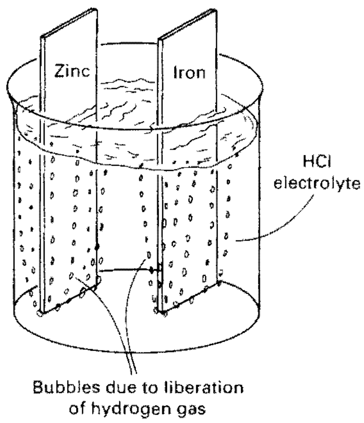

**Fig. 10(a)** Corrosion of zinc and iron in hydrochloric acid

plemented by cathodic protection systems sized to prevent corrosion at holidays in the protective coating (see the article "Corrosion of Petrochemical Pipelines" in this Volume). This combination of protective coating and cathodic protection is used on virtually all immersed or buried carbon steel structures, with the exception of offshore petroleum production platforms and reinforced concrete structures.

Offshore platforms are usually uncoated but cathodically protected. Cathodic protection causes changes in the chemistry of seawater near the protected structure, and this causes the precipitation of a natural coating on the structure that reduces the need for cathodic protection current. Concrete structures normally rely on the protectiveness of the concrete cover to prevent the corrosion of embedded steel. When corrosion of embedded steel occurs because of a loss of this protectiveness, cathodic protection is sometimes used to extend the life of the already deteriorated structure.

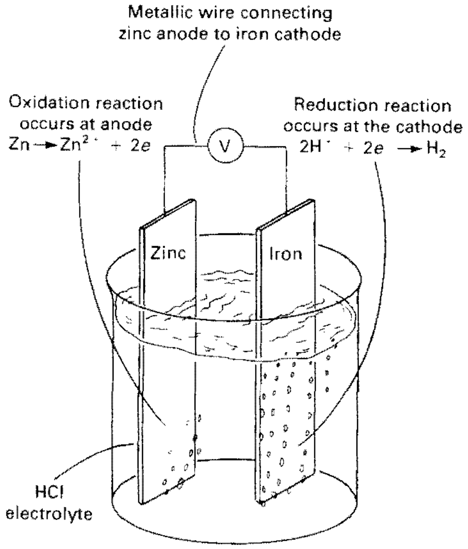

**Fig. 10(b)** Cathodic protection of iron by zinc in hydrochloric acid

## Fundamentals of Cathodic Protection

Table 1 shows the theoretical electrochemical potentials obtained by pure metals in 1 *N* solutions of their own ions. This abbreviated electromotive series is described in most chemistry or corrosion textbooks (Ref 22).

Figure 10(a) shows two of these metals—iron and zinc—separately immersed in a weak mineral acid. The chemical reactions that occur in Fig. 10(a) are:

$$Fe \rightarrow Fe^{2+} + 2e$$
Oxidation reaction (Eq 1a)

**Table 1 Standard electromotive force series for selected metals**

| Metal-metal ion equilibrium (unit activity) | Potential at 25 °C (77 °F), V |
|---|---|
| **Noble or cathodic (protected)** | |
| $Ag/Ag^+$ | +0.80 |
| $Cu/Cu^{2+}$ | +0.34 |
| $H_2/H^+$ | (reference) 0 |
| $Fe/Fe^{2+}$ | −0.44 |
| $Zn/Zn^{2+}$ | −0.76 |
| $Al/Al^{3+}$ | −1.66 |
| $Mg/Mg^{2+}$ | −2.36 |
| **More active or anodic** | |

$$2H^+ + 2e \rightarrow H_2$$
Reduction reaction (Eq 1b)

$$2H^+ + Fe \rightarrow Fe^{2+} + H_2$$
Net reaction (Eq 1c)

$$Zn \rightarrow Zn^{2+} + 2e$$
Oxidation reaction (Eq 2a)

$$2H^+ + 2e \rightarrow H_2$$
Reduction reaction (Eq 2b)

$$2H^+ + Zn \rightarrow Zn^{2+} + H_2$$
Net reaction (Eq 2c)

Both metals corrode, and both corrosion (oxidation) reactions are balanced by an equal reduction reaction, which in both cases involves the liberation of hydrogen gas from the acid environments. The two corrosion reactions are independent of each other and are determined by the corrosivity of hydrochloric acid on the two metals in question.

If the two metals were immersed in the same acid and electrically connected (Fig. 10b), the reactions for zinc would then become:

$$Zn \rightarrow Zn^{2+} + 2e$$
Oxidation (Eq 3a)

$$2H^- + 2e \rightarrow H_2$$
Reduction (Eq 3b)

Almost all of the oxidation reaction (corrosion of zinc) has been concentrated at the zinc electrode (anode) in Fig. 10(b), and almost all of the reduction reaction (hydrogen liberation) has been concentrated at the iron electrode (cathode). The oxidation of the zinc anode in Fig. 10(b) is much faster than that in Fig. 10(a). At the same time, most of the corrosion of iron in Fig. 10(a) has stopped in Fig. 10(b). As shown schematically, the zinc anode in Fig. 10(b) has been used to cathodically protect the iron cathode in Fig. 10(b).

Of course, some corrosion of the iron may still occur; whether or not this happens depends on the relative sizes of the zinc and iron electrodes. Some reduction of hydrogen may still occur on the zinc anode. The anode is the electrode at which a net oxidation reaction occurs, whereas cathodes are electrodes at which net reduction reactions occur. With proper design, the oxidation rate on the cathode will be suppressed to the point at which it becomes negligible. If this takes place, cathodic protection has been achieved.

All cathodic protection systems require an anode, a cathode, an electric circuit between the anode and cathode, and an electrolyte. Thus, cathodic protection will not work on structures exposed to air environments. The air is a poor electrolyte, and it prevents current from flowing from the anode to the cathode.

## Types of Cathodic Protection

There are two types of cathodic protection: sacrificial anode, or passive, systems and impressed-current, or active, systems. Both types are widely used.

Sacrificial anode systems are simpler. They require only a material anodic to the protected steel in the environment of interest. A simple sacrificial anode cathodic protection system used to control corrosion on a buried pipeline is shown in Fig. 9.

Figure 11 shows an impressed-current system used to protect a pipeline. The buried anodes and the pipeline are both connected to an electrical rectifier, which supplies direct current to the buried electrodes (anodes and protected cathode) of the system. Unlike sacrificial anodes, impressed-current anodes need not be naturally anodic to steel. If these electrodes were wired directly to a structure, they would act as cathodes and would cause accelerated corrosion of the structure they are intended to protect. The direct current source reverses the natural polarity and allows the materials to act like anodes. Instead of corrosion of the anodes, some other oxidation reaction, that is, oxygen or chlorine evolution, occurs at the anodes, and the anodes are not consumed.

Impressed-current systems are more complex than sacrificial anode systems. The capital expenses necessary to supply direct current to the system are higher than for a simple connection between an anode and a cathode.

The voltage differences between anode and cathode are limited in sacrificial anode systems to approximately 1 V or even less, depending on the anode material and the specific environment. Impressed-current systems can use larger voltage differences. The larger voltages available with impressed-currents allow remote anode locations, which produce more efficient current distribution patterns along the protected cathode. These larger voltages are also useful in low-conductivity environments, such as freshwater and concrete, in which sacrificial anodes would have insufficient throwing power.

Large voltages can have disadvantages. It is possible to overprotect high-strength steels and cause hydrogen embrittlement. Coating debonding is also possible (Fig. 12). Debonding occurs when moisture penetrates a coating and hydrogen is generated at the metal surface beneath the coating. The gas can accumulate until pressure causes blisters or cracks in the protective coating. Once this coating damage occurs, the demands for protective current increase and may exceed the capabilities of the system.

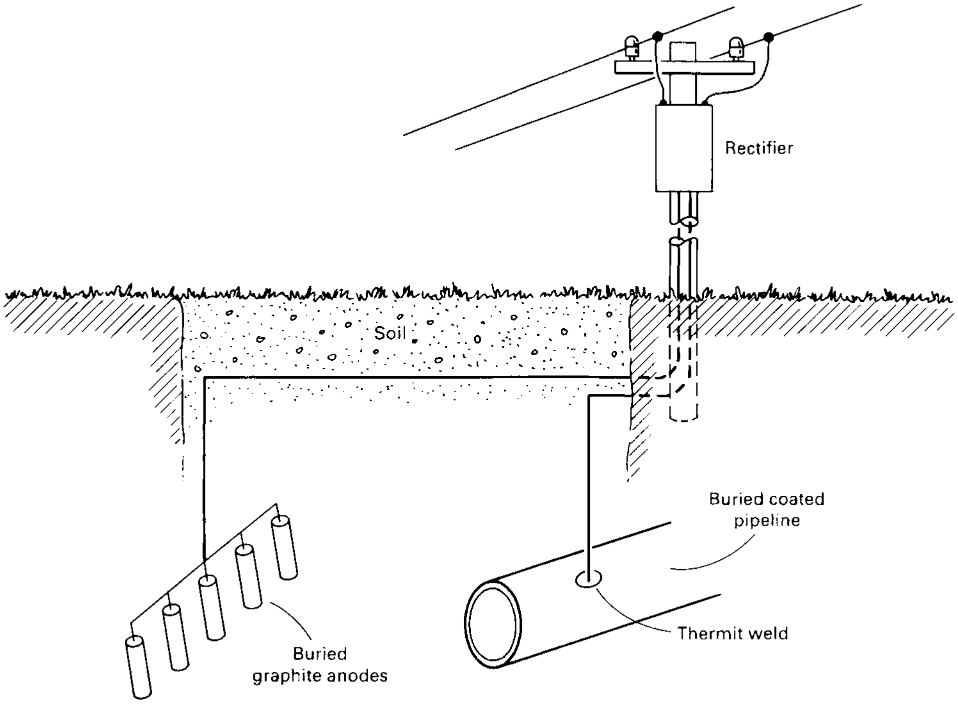

**Fig. 11** Impressed-current cathodic protection of a buried pipeline using graphite anodes

Aluminum is especially vulnerable to overprotection. All cathodic reactions cause the immediate environment to become somewhat more basic (less acidic) than they are in the absence of cathodic protection. Unlike steel, aluminum is an amphoteric metal with increased corrosion susceptibility in acids and bases. If the environment around an aluminum structure becomes too basic, it will corrode at an accelerated rate. Thus, the cathodic protection of aluminum can cause cathodic corrosion if too much current is supplied to the cathode.

Table 2 lists some of the important differences between impressed-current and sacrificial anode cathodic protection systems. Selection of a cathodic protection system usually depends on tradeoffs among the advantages of each type of system. For example, most offshore petroleum production platforms use sacrificial anodes because of their simplicity and reliability, even though the capital costs would be lower with impressed-current systems.

## Criteria for Cathodic Protection

A number of criteria have been used for determining whether or not a structure is cathodically protected from corrosion. This is an area of controversy within the industry, and it is likely that existing standards will change over the next few years. Criteria also differ for buried utilities, offshore structures, and concrete structures.

**Fig. 12** Debonded organic coating near a high-silicon cast iron button anode

The original National Association of Corrosion Engineers specification for buried utility pipelines proposed the following criteria for determining when a steel or cast iron structure is cathodically protected (Ref 23):

- A voltage of −0.85 V relative to a copper/saturated copper sulfate electrode
- A negative (cathodic) voltage shift of at least 300 mV caused by the application of cathodic protection current

**Table 2 Comparison between sacrificial anode and impressed-current cathodic protection systems**

| Sacrificial anode system | Impressed-current system |
|---|---|
| Simple | Complex |
| Low/no maintenance | Requires maintenance |
| Works best in conductive electrolytes | Can work in low-conductivity electrolytes |
| Lower installation costs for smaller installations | Remote anodes possible |
| Higher capital investment for large systems | Low capital investment for large systems |
| | Can cause the following problems:<br>Stray current corrosion<br>Hydrogen embrittlement<br>Coating debonding<br>Cathodic corrosion of aluminum |

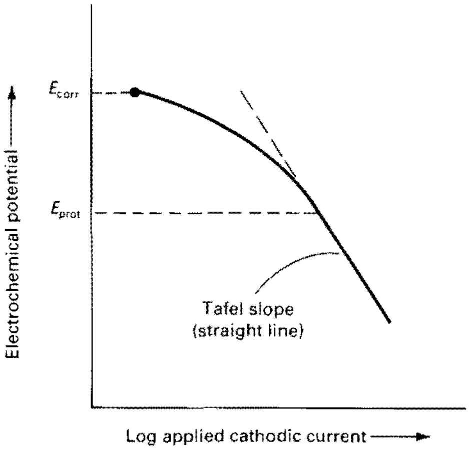

**Fig. 13** Tafel slope criterion for determining cathodic protection

- A minimum negative (cathodic) voltage shift of 100 mV determined by interrupting the current and measuring the voltage decay
- A voltage at least as negative (cathodic) as that originally established at the Tafel segment of the $E$-log $I$ curve (Fig. 13)
- A net protective current from the electrolyte into the surface

**Table 3 Energy characteristics of sacrificial anode alloys**

| Alloy | Energy capability | | Consumption rate | |
|---|---|---|---|---|
| | A·h/kg | A·h/lb | kg/A·yr | lb/A·yr |
| Aluminum-zinc-mercury | 2750-2840 | 1250-1290 | 3.2-3.0 | 7.0-6.8 |
| Aluminum-zinc-indium | 1670-2400 | 760-1090 | 5.2-3.6 | 11.5-8.0 |
| Aluminum-zinc-tin | 920-2600 | 420-1180 | 9.4-3.4 | 20.8-7.4 |
| Zinc | 810 | 370 | 10.7 | 23.7 |
| Magnesium | 1100 | 500 | 7.9 | 17.5 |

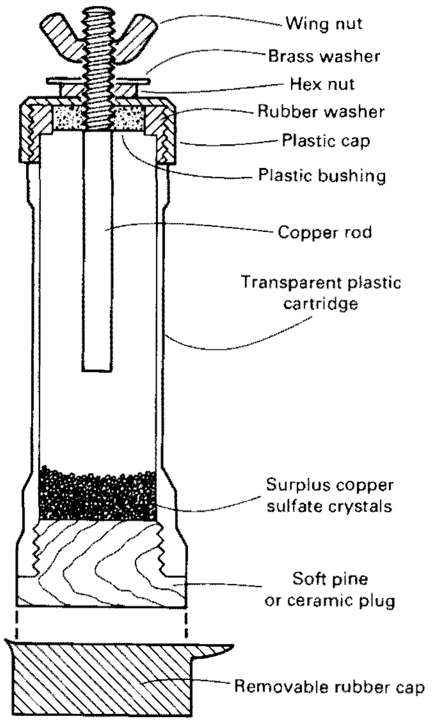

**Fig. 14** Copper-saturated copper sulfate reference electrode

All of the above criteria are currently in use, but the most common and most widely applicable criterion is the −0.85 V versus a copper/copper sulfate reference cell. Most structures can be inspected to determine if they are protected relative to this standard. The only equipment necessary is a reference cell (Fig. 14) and a wire lead that can be connected to the structure in question. The other criteria require recordkeeping, the ability to interrupt current (impossible for most sacrificial anode designs), and more sophisticated survey equipment.

Copper sulfate electrodes can become contaminated by seawater, and it is common to use −0.805 V versus silver/silver chloride as the protection potential for marine structures (Ref 24). Both criteria are the same; only the reference electrode material is different. These criteria are based on early research by the National Bureau of Standards (Ref 23).

The reader is cautioned that the sign convention used in this article agrees with that used by the U.S. cathodic protection industry. Much of the scientific and international literature uses the opposite sign convention for positive and negative electrical terminals. Regardless of the sign convention chosen, the important point is that electrons should flow into the protected structure from the external circuit.

## Anode Materials

Different requirements for sacrificial anodes and impressed-current anodes lead to the use of widely different materials for these applications.

Sacrificial anodes must be anodic to steel in the environment of interest. They must also corrode reliably (avoid passivation). Impressed-current anodes can be cathodic to steel, but they must have low consumption rates when connected to a cathodic protection power source.

**Sacrificial Anodes.** Commercial sacrificial anodes include magnesium, zinc, and aluminum alloys. The energy characteristics of these alloys are given in Table 3.

*Magnesium anodes* are the only sacrificial anodes that are routinely specified for use in buried soil applications. Most magnesium anodes in the United States are supplied with a prepackaged bentonite clay backfill in a permeable cloth sack (Fig. 9). This backfill ensures that the anode will have a conductive environment and will corrode reliably. The additional material is less expensive than the soil resistivity surveys that would be needed to determine if the backfill is necessary.

Some magnesium anodes have been used offshore in recent years in an attempt to polarize the structures to a protected potential faster than would occur if zinc or aluminum alloy anodes were used. Magnesium tends to corrode quite readily in salt water, and most designers avoid the use of magnesium for permanent long-term marine cathodic protection applications.

Figure 15 shows a magnesium anode used to control corrosion on a glass-lined domestic water heater. Similar cathodic protection arrangements are found on most domestic water heaters in the United States.

Zinc is used for cathodic protection in freshwater and marine water. Zinc is especially well suited to cathodic protection on ships that move between salt water and harbors in brackish rivers or estuaries. Figure 16 shows zinc anodes on the underside of a small fishing boat. Aluminum anodes would passivate in the harbors and might not work when they return to sea. Zinc anodes are also used to protect ballast tanks, heat exchangers, and many mechanical components on ships, coastal power plants, and similar structures.

The weight of zinc is an advantage for marine pipelines. Bracelet anodes (Fig. 17) are attached at pipe joints to provide ballast and to prevent corrosion in the water-mud environment, in which aluminum might passivate.

*Aluminum* is used on offshore structures where its light weight provides significant advantages. Welded-on aluminum anodes for an offshore platform are shown in Fig. 18. Aluminum does not passivate in salt water if certain alloying additions, such as tin, antimony, and mercury, are present. Toxicity questions prevent the use of aluminum alloys with mercury additions in U.S. waters.

**Impressed-current anodes** must be corrosion resistant and otherwise durable in the environment in which they are used. Consumption rates for lead alloy, platinum, graphite, and high-silicon cast iron impressed-current anode materials are given in Table 4.

*High-silicon cast iron* (Fe-0.95C-0.75Mn-14.5Si-4.5Cr) is used for onshore cathodic protec-

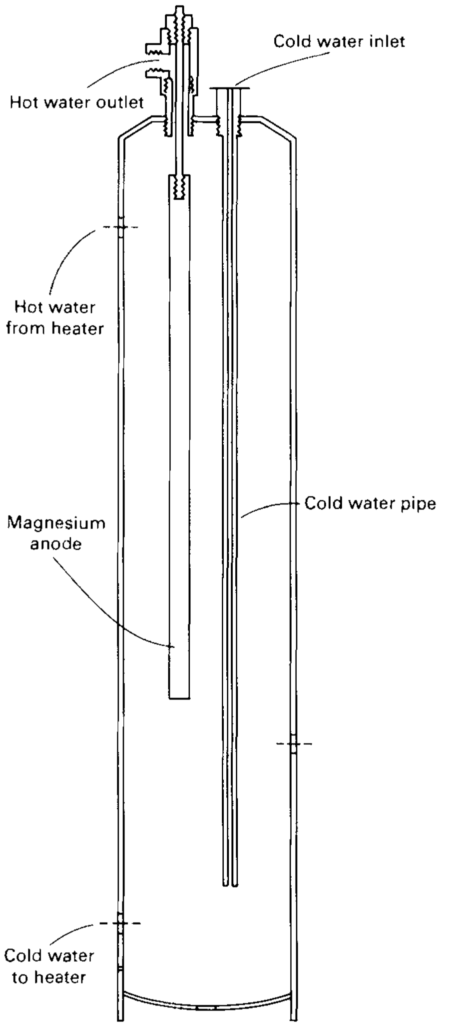

**Fig. 15** Magnesium anode used to cathodically protect glass-lined steel water heater

tion applications and in other locations where abrasion resistance and other mechanical damage considerations are important. High-silicon cast iron anodes are available in solid rods, tubular form, and various cast shapes in a wide variety of sizes to meet the demands of specific applications. For example, solid rods range from 30 mm in diameter × 230 mm in length (1⅛ × 9 in.) at 0.45 kg (1 lb) to 115 mm in diameter × 1525 mm in length (4.5 × 60 in.) at 100 kg (220 lb). The smaller rods are used for protecting underground freshwater storage tanks, and the larger rods are used in more aggressive seawater or ground bed applications. Figure 12 shows a high-silicon cast iron button anode on a navigational lock on the Tennessee River. This anode must withstand collisions with small vessels, trees, rocks, and so on. The coating debonding shown in Fig. 12 is due to improper circuit design and cannot be attributed to the use of high-silicon cast iron anodes. Detailed information on designing impressed-current cathodic protection systems with high-silicon iron anodes is available in Ref 25.

**Fig. 16** Zinc anodes on the underside of a fishing boat

*Graphite anodes* are extensively used for onshore pipeline cathodic protection applications in which they can be buried in multiple-anode ground beds (Fig. 11). Graphite anodes, which have very low electrode-to-environment resistances, are normally available in 75-mm diam × 1525-mm long (3- × 60-in.) and 100-mm diam × 2000-mm (4- × 80-in.) rods. Because of the brittle nature of the materials, graphite must be stored and handled carefully.

*Precious metals* are used for impressed-current anodes because they are highly efficient electrodes and can handle much higher currents than anodes fabricated from other materials. Precious metal anodes are actually platinized titanium or tantalum anodes; the platinum is either clad to or electroplated on the substrate. The small precious metal anode shown in Fig. 19 performs the same function as materials weighing several times more.

*Lead alloy anodes,* containing 2% Ag, or 1% Ag and 6% Sb, are used for cathodic protection systems in seawater. Lead alloy anodes should not be buried in the sea bottom or used in freshwater applications.

*Ceramic anodes* are the newest materials available for cathodic protection anodes. These anodes are supplied either as oxide coatings on transition metal substrates or as bulk ceramics. Their use as cathodic protection anodes for protecting reinforcing steel in concrete is new but the oxide coated transition metal anodes have been used since the late 1960s in the chlor-alkali industry as anodes for chlorine production and seawater electrolysis, and cathodic protection of water tanks and buried steel structures, among other industrial processes.

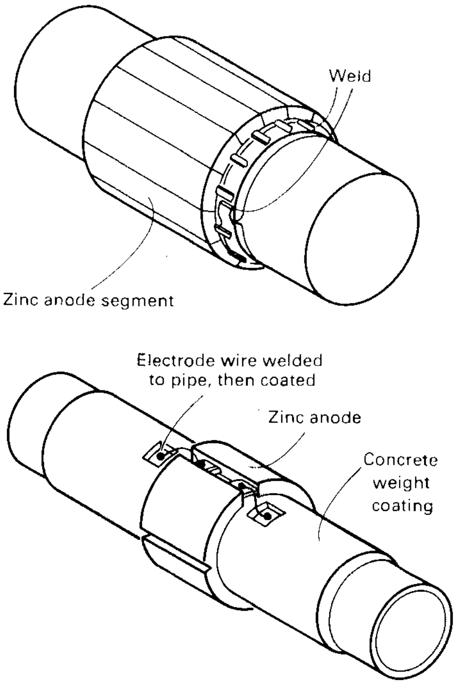

**Fig. 17** Typical pipeline bracelet anodes

The oxide/metal composite anodes for chlorine environments consist of a mixed ruthenium dioxide ($RuO_2$) and titanium oxide ($TiO_2$) coating sintered onto a pure titanium (grade 1) substrate (Ref 26). Such materials, which are produced in sheet, mesh, and wire form, are based on patented dimensionally stable anode (DSA) technology (Ref 26). These anodes are so named because they remain unchanged with regard to their shape, geometry, and dimensions during their entire operating life. Figure 20 shows examples of a mixed oxide/titanium mesh anode, based on DSA technology, that is used to prevent corrosion of reinforcing steel in concrete.

The basic chemical constituents of the bulk ceramic anodes are suboxides of titanium, with $Ti_4O_7$ and $Ti_5O_9$ being the principal components. Such conductive ceramics are resistant to both oxidation and reduction in strong acid and basic environments. Some characteristic properties of conductive ceramics are given in Table 5.

**Table 4 Consumption rates of impressed-current anode materials**

| Material | Typical anode current density | | Consumption rate per A·yr |
|---|---|---|---|
| | A/m² | A/ft² | |
| Pb-6Sb-1Ag | 160-220 | 15-20 | 0.045-0.09 kg (0.1-0.2 lb) |
| Pt (plated on substrate) | 540-1080 | 50-100 | 0.006 g |
| Pt (wire or clad) | 1080-5400 | 100-500 | 0.01 g |
| Graphite | 10.8-40 | 1-4 | 0.225-0.45 kg (0.5-1.0 lb) |
| Fe-14Si-4Cr | 10.8-40 | 1-4 | 0.225-0.45 kg (0.5-1.0 lb) |

## Power Sources

Impressed-current cathodic protection requires external power sources. The most common source of electricity is a local power utility. This will normally involve the dc rectifier arrangement shown in Fig. 11. Remote locations can use solar cells (Fig. 21), thermoelectric cur-

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**Table 5 Properties of bulk ceramic anode materials**

**Electrical resistivity**

$250\text{-}1000 \times 10^{-6}\ \Omega \cdot \text{cm}$. Resistivity decreases as density increases.

**Thermal expansion**

$5 \times 10^{-6}$/°C

**Thermal conductivity**

10 to 20 W/m · K

**Modulus of rupture**

100 MPa (14.5 ksi) and higher. Some grades are 24-34 MPa (3.5-5.0 ksi) for special applications.

**Melting point**

1600 °C (2552 °F)

**Density**

2.5-4.0 g/cm$^3$

**Thermal stability**

Stable to 350 °C (660 °F) in air
Stable to 1350 °C (2460 °F) for nonoxidizing atmosphere

**Overpotentials:**

| Element | Overpotential at 20 °C (68 °F), mV | Current density mA/cm$^2$ | Electrolyte |
|---|---|---|---|
| Oxygen | 1712 | 10 | 1 $M$ $H_2SO_4$ |
| Hydrogen | 784 | 10 | |
| Oxygen | 1674 | 10 | 1 $M$ NaOH |
| Hydrogen | 624 | 10 | |

rent sources, special fuel-driven electric generators, or even windmills.

## Design

Most cathodic protection design is conducted by consulting companies that specialize in corrosion control. Design procedures vary among organizations, but the following general guidelines are frequently followed for onshore buried structures (Ref 27):

- Decide whether impressed-current or sacrificial anodes will be used
- Decide on the design life of the system
- Determine or assume the condition of the coating. From this, the current density for cathodic protection can be estimated
- Calculate the maximum electric current required
- Determine the number and type of anodes required and their respective spacing
- Calculate the ground bed resistance. Figure 22 shows the effect of soil resistivity and pH on the corrosion of zinc sacrificial anodes
- Calculate the lead wire size
- Calculate the required dc voltage
- Determine the rectifier size
- Locate the ground bed

The advent of computers has changed some cathodic protection design, test, and inspection procedures (Ref 28), but most cathodic protection is still designed and tested in the manner described in U.S. government publications from the 1960s and 1970s (Ref 27, 29-31).

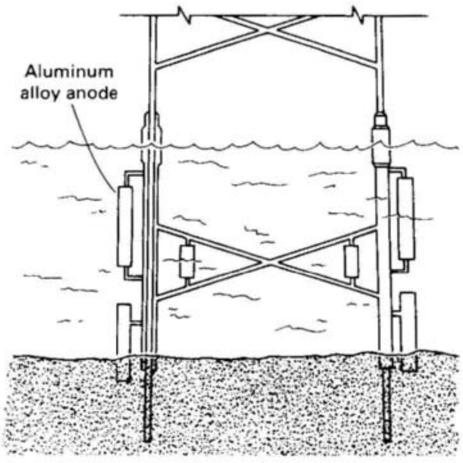

**Fig. 18** Welded-on aluminum sacrificial anodes used to protect an offshore platform

**Fig. 19** Precious metal impressed-current anode on offshore platform prior to launching in the North Sea. Courtesy of W.H. Thomason, Conoco, Inc.

## Cathodic Protection of Marine Pipelines

Corrosion control of marine pipelines is usually achieved through the use of protective coatings and supplemental cathodic protection. A variety of organic protective coatings can be used. They are usually applied in a factory so that the only field-applied coatings are at joints in pipeline sections. Most marine pipelines have an outer "weight coating" of concrete. The cathodic protection system supplements these coatings and is intended to provide corrosion control at holidays (defects) in the protective coating.

**Design Considerations.** The average cathodic protection current density required to protect a marine pipeline will depend on the type of

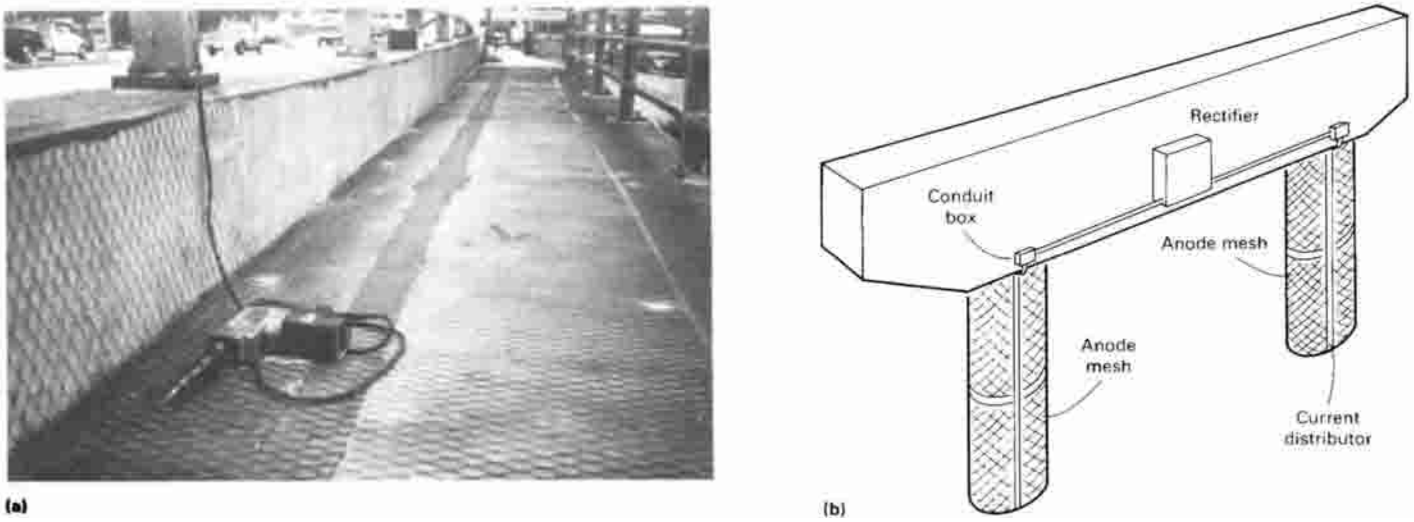

**Fig. 20** Use of mixed oxide/titanium anode mesh for cathodic protection. (a) Sidewalk and barrier wall installation. (b) Installation of anode mesh on a bridge substructure. Courtesy of ELTECH Systems Corporation

# Designing to Minimize Corrosion

# Designing to Minimize Corrosion

FACTORS THAT INFLUENCE the service life of equipment, for example, a chemical process heat exchanger or tank, a bridge, or an automobile chassis, from a corrosion standpoint include the following (Ref 1):

- Design
- Materials of construction
- Specification
- Fabrication and quality control
- Operation
- Maintenance
- Environmental conditions

In weighing the relative importance of these factors, design and materials are of major and equal importance in achieving the desired performance and life. The designer and materials engineer must work closely together to ensure that premature failure will not occur because of design defects or improper material selection. It is also inefficient and costly to use these elements of design and material selection in a compensatory manner.

The first section of this article will discuss the step-by-step process by which materials are selected in order to avoid or minimize corrosion and will include information on materials that are resistant to the various forms of corrosion. Subsequent sections will discuss design details that can be applied to minimize corrosion and the corrosion of weldments.

## Materials Selection

**Review of Operating Conditions.** The first step in the materials selection process is a thorough review of the corrosive environment and equipment operating conditions. This review requires input from knowledgeable process engineers. Precise definition of the chemical environment, including the presence of trace compounds, is vital. For example, the nickel-molybdenum alloy Hastelloy B-2 (UNS N10665) is highly resistant to hydrochloric acid (HCl) up to the atmospheric boiling point. However, the presence of small quantities of oxidizing metal ions, such as ferric ion ($Fe^{3+}$), will result in severe corrosion. Other operating conditions that require definition, especially for equipment used in the chemical-processing industry, include temperatures, pressures, flow rates, liquid versus gaseous phases, aqueous versus anhydrous phases, continuous versus intermittent operation, media used for cooling or heating, external versus internal environment, and product purity.

Abnormal or upset conditions are often overlooked during the selection process. For example, plain carbon steel may be the optimum choice for vessels and piping that must contain noncorrosive hydrocarbon gases, such as ethylene, under pressure at normal temperatures. However, the cooling effect that occurs during venting to the atmosphere, for whatever reason, may lower the temperature of vessels, piping, and relief valves to below the ductile-to-brittle fracture. Thus, the selection of special steels, qualified by impact testing at the lowest expected temperature, would be appropriate.

**Review of Design.** Next, the type and design of the equipment and its various components should be considered, along with size, complexity, and criticality in service. Selecting a material for a simple storage tank generally does not require the same attention and effort as choosing the material of construction for a highly sophisticated chemical process reactor. This is especially true when considering critical, unique pieces of equipment in large, single-train, continuous process plants in which a failure would shut down the entire operation. In this case, great effort is expended to select the optimum material for safe low-maintenance service.

The materials used to join the components into an assembly will require as much attention as the component materials themselves. Many bolted agitator assemblies in reactors, as well as riveted wheels in centrifugal compressors, have failed catastrophically because the bolts or rivets did not have adequate strength or corrosion resistance.

When welding is the joining method, the materials engineer is challenged to ensure that the welds are as corrosion resistant as the base metals. Generally, the weld metal must equal the base metal in chemical composition and must be virtually free of surface defects, such as porosity, slag inclusions, incomplete penetration or lack of fusion, for long maintenance-free service. The challenge is even greater when dissimilar-metal welds are required. Improper selection may allow local attack due to weld metal dilution or may alloy hydrogen-assisted cracking due to hard heat-affected zones (HAZs). More information on preventing corrosion of welds is available in the section "Corrosion of Weldments" in this article.

**Selection of Candidate Materials.** Once the chemical environment, operating conditions, and type and design of the equipment have been defined, consideration of materials of construction is in order. Occasionally, the selection is based on reliable, pertinent past experience and, as such, is well defined. More often, however, selection is anything but straightforward for a number of reasons, such as complex chemical environments and stringent code requirements.

The list of materials to choose from is large and continues to increase. Ferrous and nonferrous metals and alloys, thermoplastics, reinforced thermosetting plastics (RTP), nonmetallic linings, glass, carbon and graphite, and catalyzed resin coatings are among the various materials available. Many materials will be immediately excluded because of service conditions, that is, pressures too high for RTP, temperatures too high for nonmetallic linings and coatings such as rubber or epoxy resins, environment too aggressive for carbon steel, and so on. Remaining choices may still be great in number.

It is always desirable to minimize the list of materials; this allows in-depth evaluation. In other cases, the initial list may be exceptionally small because of limited knowledge about the operating conditions or the complex chemical environment. A search of data sources should follow in either case.

*Literature Survey.* One might begin with a literature survey, using applicable sources such as *Corrosion Abstracts* (Ref 2), along with the *Corrosion Data Surveys* (Ref 3) published by the National Association of Corrosion Engineers (NACE). This technical society, in conjunction with the National Bureau of Standards, has initiated an on-going program to computerize reference data on the performance of materials in corrosive environments.

Other data sources include a wide variety of handbooks, conference proceedings, and literature compilations published by the American Society for Testing and Materials (ASTM), ASM International, and NACE. In addition, expert systems, which are computer programs containing methods and information developed by experts, are the latest tools available for materials selection (Ref 4-7). Such systems are designed to solve problems, make predictions, suggest possible treatments, and offer materials and corrosion advice with a degree of accuracy equaling that of their human counterparts.

Experience and data generated in-house often serve as the most reliable bases for materials selection. Ideally, this is coupled with outside experience, when available, from materials vendors and equipment fabricators to complete this initial screening process. Contacts with clients referred by vendors should not be overlooked for added experience.

At this point, the list of candidate materials should be narrowed to a reasonable number for in-depth evaluation. Final selections should not be based solely on the above data sources, because in most cases the data provided are insufficient for the complete characterization of an environment or a set of conditions.

**Evaluation of Materials.** The in-depth evaluation of each candidate material should begin with a thorough understanding of the product forms available, along with the ease of fabrication by standard methods. For example, it would be wasting time and money to evaluate an Fe-14.5Si alloy for anything but a cast component such as a pump casing or valve body. The alloy is unavailable in any other form. Because of its poor weldability, this alloy should also be ruled out for applications involving welding.

Corrosion testing in representative environments is generally the next step. The extent of the investigation (and determination of test conditions) depends on such factors as (Ref 8):

- Degree of uncertainty after available information has been considered
- The consequences of making a less-than-optimum selection
- The time available for evaluation

Laboratory testing of candidate materials is common and in some cases may be the only means available for final determination. Wherever possible, the actual process fluids should be used. Otherwise, mixtures simulating the actual environment must be selected. There is considerable risk in using the latter, because undefined constituents can have a significant effect on the performance of a particular material.

Depending on the application, weighed and measured coupons of candidate materials are exposed to the corrosive fluids under a variety of conditions ranging from simple static immersion at a controlled temperature to complex testing under combined heat transfer and velocity conditions. Guidance for conducting laboratory corrosion tests is available in Ref 9 and 10. After exposure for a specified length of time (generally a minimum of 1 week), the coupons are, in the case of metals and alloys, cleaned and reweighed, and a corrosion rate is calculated based on weight loss and exposed surface area. The rate is commonly expressed in millimeters of penetration per year or inches or mils (1 mil = 0.001 in.) of penetration per year.

In addition, coupons are examined under a microscope for evidence of local attack, such as pitting, crevice corrosion, and exfoliation. Special coupons, such as galvanic couples, welded, and stressed coupons, are often exposed to determine if other forms of corrosion may occur on certain metals and alloys. These coupons may require metallographic examination for evidence of dealloying (parting), stress-corrosion cracking (SCC), intergranular corrosion, and other corrosion phenomena.

Nonmetallic materials, such as thermoplastics, coatings, reinforced thermosetting resins, elastomers, and ceramics, are also evaluated in laboratory tests, but the criteria are different from those used for metals. First, exposure time must generally be longer (often a minimum of 1 to 3 months) before significant changes occur. Exposure times of 6 months to 1 year are common. Also, corrosion rate calculations based on weight loss and surface area are not applicable in most cases. Of more importance are changes in weight, volume, hardness, strength, and appearance before and after exposure. Corrosion testing and evaluation are covered in detail in the Section "Corrosion Testing and Evaluation" in Volume 13 of the *ASM Handbook*.

If possible, candidate materials should be tested under conditions more like the final application rather than in laboratory glassware, that is, in a semi-works or pilot operation or in full-scale equipment. Generally, the results are more reliable because test coupons are integrated into the process and are exposed to the same conditions as the actual equipment. Because of nonuniform conditions (flows, composition) within process equipment, coupon locations should be carefully selected.

Reliability is further enhanced when it is possible to test full-size components fabricated from candidate materials (Ref 11). Examples include:

- Flanged sections of selected alloys and/or nonmetallics installed in a pipeline
- Experimental alloy impellers in pumps for corrosion and cavitation studies
- Tubing installed in a full-size operating or miniature test heat exchanger to evaluate materials with optimum resistance to corrosion under heat transfer conditions
- Paddles of candidate materials bolted to a reactor agitator for erosion-corrosion studies

The primary disadvantages of this method of testing are the cost of fabrication, installation, removal, and evaluation; the downtime resulting from equipment being taken out of service and dismantled for evaluation; and the fact that a test component could fail prematurely and cause a unit shutdown and/or equipment damage.

**Specifications.** At this point, all candidate materials have been thoroughly evaluated and the materials of construction have been selected for the particular application. Clear and concise specifications must now be prepared to ensure that the material is obtained as ordered and that it meets all the requirements of the application. Perhaps the best known and most widely used specifications are the standards of ASTM. Thousands of specifications for virtually all metal and nonmetal materials of construction are covered in 15 sections encompassing 65 volumes.

Similar standards in countries other than the United States include DIN (Germany), BS (Great Britain), AFNOR (France), UNI (Italy), NBN (Belgium), and JIS (Japan). Other materials specifications that are well known but are more limited in application are those of the Society of Automotive Engineers (SAE) and its Aerospace Materials Specifications (AMS), the American Welding Society (AWS), the American Petroleum Institute (API), and the American National Standards Institute (ANSI).

Fabrication requirements must also be spelled out in detail to avoid mistakes that could shorten the life of the equipment and to satisfy the requirements of state and federal regulatory agencies and insurance companies. The American Society for Mechanical Engineers (ASME) code governs the fabrication of equipment for the chemical, power, and nuclear industries, and the API code governs the fabrication of equipment for the refining industry. Piping for these industries is generally fabricated per applicable ANSI codes. In these codes, allowable stresses for design calculations have been determined for virtually all metals and alloys that might be selected for corrosive (and noncorrosive) service. Where welding is the primary joining method, welding procedures and welders must be qualified before fabrication begins. Testing and quality assurance requirements, such as radiography, hydrostatic testing, and ultrasonic inspection, are also covered in the codes and are specified where applicable to ensure compliance.

The fabricator is generally required to provide detailed drawings that list dimensions, tolerances, all pertinent materials specifications, fabrication and welding details, and testing and quality assurance requirements for review. Prefabrication meetings are held for final review of all drawings and details so that customer and vendor are in agreement. Thus, problems or errors that could lead to costly delays in fabrication or failures in service can be detected early and corrected.

Money spent on inspection and monitoring during equipment fabrication/erection to ensure compliance with specifications is repaid by trouble-free startup and operation of the fabricated assembly. In some cases, every component of an assembly must be tested to avoid excessive corrosion and/or premature failure. For example, an additional quality check of a vessel fabricated from AISI type 316L stainless steel for hot acetic acid service might be to test every plate, flange, nozzle, weld, and so on, for the presence of molybdenum by using a chemical spot test method (Ref 12). The absence of molybdenum, which might indicate the mistaken use of a different stainless steel, such as type 304L, would result in accelerated corrosion in this service. Another example is the testing of every component (including weld metal) of a heat exchanger fabricated from chromium-molybdenum steels for hot high-pressure hydrogen service to avoid the possibility of catastrophic failure by hydrogen attack. The use of portable x-ray fluorescence analyzers for this type of quality assurance testing of critical service components has become quite popular in recent years (Ref 13).

**Follow-Up Monitoring.** Once built, installed, and commissioned in service, the equipment, piping, reactor, heat exchanger, and so on, should be monitored by the materials engineer to confirm the selection of materials of construction and all other requirements for the intended application. Frequent shutdowns for thorough inspections and periodic evaluation of corrosion coupons exposed at key locations in the equipment represent both the ideal and most difficult monitoring techniques to achieve. In actual practice, equipment is generally kept on-stream continuously for long periods of time between shutdowns, so on-stream monitoring techniques must also be used.

In the petroleum industry, the internal corrosion in oil and gas production operations is often monitored with hydrogen probes (Ref 14). These instruments measure hydrogen created by corrosion reactions. A portion of the hydrogen penetrates the vessel or pipeline wall, and the rest of the hydrogen is dissolved in the process fluid or released as gas bubbles. Hydrogen probes measure hydrogen permeation and provide information on the rate of corrosion.

Other on-stream corrosion-monitoring techniques that are used in petroleum and chemical industries include:

- The electrical resistance and linear polarization methods (Ref 15). The former determines corrosion trends with time, and the latter determines an instantaneous corrosion rate.
- Ultrasonic thickness measurement. This is a useful monitoring tool, especially when baseline readings are taken at selected locations before the equipment is placed in service. The inspection locations can be changed if erosion or corrosion areas are localized

With these methods, the materials engineer is able to determine the adequacy of the materials selection and to predict the remaining life so that replacements and/or repairs can be scheduled well in advance of failure. The corrosion test methods discussed above can also be used to evaluate alternate materials that might be more cost effective at the time of replacement of the vessel or a component.

## Selecting Materials to Avoid or Minimize Corrosion

**General Corrosion.** Of the many forms of corrosion, general, or uniform, corrosion is the easiest to evaluate and monitor. Materials selection is usually straightforward. If a material shows only general attack, a low corrosion rate, and negligible contamination of the process fluid and if all other factors, such as cost, availability, and ease of fabrication, are favorable, then that is the material of choice. An acceptable corrosion rate for a relatively low-cost material such as plain carbon steel is about 0.25 mm/yr (10 mils/yr) or less. At this rate and with proper design and adequate corrosion allowance, a car-bon steel vessel will provide many years of low-maintenance service.

For more costly materials, such as the austenitic (300-series) stainless steels and the copper- and nickel-base alloys, a maximum corrosion rate of 0.1 mm/yr (4 mils/yr) is generally acceptable. However, a word of caution is in order. One should never assume, without proper evaluation, that the higher the alloy, the better the corrosion resistance in a given environment. A good example is seawater, which corrodes plain carbon steel fairly uniformly at a rate of 0.1 to 0.2 mm/yr (4 to 8 mils/yr) but severely pits certain austenitic stainless steels.

At times, nonmetallic coatings and linings ranging in thickness from a few tenths to several millimeters are applied to prolong the life of low-cost alloys such as plain carbon steels in environments that cause general corrosion. The thin-film coatings that are widely used include baked phenolics, catalyzed cross-linked epoxy-phenolics, and catalyzed coal tar-epoxy resins (see the article "Organic Coatings and Linings" in Volume 13 of the *ASM Handbook*). It is advisable not to use thin-film coatings in services where the base metal corrosion rate exceeds 0.5 mm/yr (20 mils/yr), because corrosion is often accelerated at holidays (for example, pinholes) in the coating. Thick-film linings include glass, fiber- or flake-reinforced furan, polyester and epoxy resins, hot-applied coal tar enamels, and various elastomers such as natural rubber.

A special case for materials selection under general corrosion conditions is that of contamination of the process fluid by even trace amounts of corrosion products. In this case, product purity, rather than corrosion rate, is the prime consideration. One example is storage of 93% sulfuric acid ($H_2SO_4$) in plain carbon steel at ambient temperature. The general corrosion rate is 0.25 mm/yr (10 mils/yr) or less, but traces of iron impart a color that is objectionable in many applications. Therefore, thin-film baked phenolic coatings are used on carbon steel to minimize or eliminate iron contamination. In the same way, thin-film epoxy coated carbon steel or solid or clad austenitic stainless steels are used to maintain the purity of adipic acid for various food and synthetic fiber applications. More information on this form of corrosion is available in the section "General Corrosion" of the article "Forms of Corrosion in the Petrochemical Industry" in this Volume.

**Localized Corrosion.** Although general corrosion is relatively easy to evaluate and monitor, localized corrosion in such forms as pitting, crevice corrosion, and weld metal attack is at the opposite end of the scale, and materials selection is difficult. Localized corrosion is insidious and often results in failure or even total destruction of equipment without warning.

All metals and alloy systems are susceptible to most forms of localized corrosion by specific environments. For example, carbon or alloy steel pipelines will pit in aggressive soils because of local concentrations of corrosive compounds, differential aeration cells, corrosive bacteria, stray dc currents, or other conditions, and these pipelines generally require a combination of nonmetallic coatings and cathodic protection for long life. Also, holidays in mill scale left on plain carbon steels are sites for pitting because the mill scale is cathodic to the steel surface exposed at the holiday. For this reason, it is advisable to remove all mill scale by sand- or gritblasting before exposing plain carbon steels to corrosive environments.

*Pitting.* Aqueous solutions of chlorides, particularly oxidizing acid salts such as ferric and cupric chlorides, will cause pitting of a number of ferrous and nonferrous metals and alloys under a variety of conditions. The ferritic (400-series) and austenitic stainless steels are very susceptible to chloride pitting (as well as to crevice corrosion and SCC, which are discussed later in this section). Molybdenum as an alloying element is beneficial, so molybdenum-containing stainless steels, such as types 316 and 317, are more resistant than the nonmolybdenum alloys. However, most chloride environments require higher alloys containing greater amounts of chromium and molybdenum, such as Hastelloy alloy G-3 (UNS N06985), Inconel alloy 625 (UNS N06625), and Hastelloy alloy C-22 (UNS N06022), for optimum performance. Exceptions are titanium and its alloys, which show exceptional resistance to aqueous chloride environments (including the oxidizing acid chlorides), and copper, copper-nickel, and nickel-copper alloys, which are widely used in marine applications.

Other noteworthy combinations of metals and corrosive fluids to avoid when selecting materials because of pitting tendencies include:

- Aluminum and aluminum alloys in electrolytes containing ions of such heavy metals as lead, copper, iron, and mercury
- Plain carbon and low-alloy steels in waters containing dissolved oxygen or in waters and soils infected with sulfate-reducing bacteria
- Austenitic stainless steel weldments exposed to stagnant natural waters, particularly U.S. Gulf Coast well waters, which are infected with iron and/or manganese bacteria (Ref 16)

An unusual form of localized corrosion known as end-grain attack has occurred in chemical-processing plants with such specific metal/fluid combinations as austenitic stainless steels in hot nitric acid ($HNO_3$) and organic acids, and plain carbon steels in decanoic acid.

When certain forms of these metals (for example, plates, threaded rods, or pipe nozzle ends) are cut normal to the rolling direction, the ends of nonmetallic inclusions at the cut edges are attacked by the process fluid; this results in small-diameter but deep pits. The solution is to seal the cut edge with a layer of weld metal that is equal to the base metal in composition.

*Crevice corrosion* can occur not only at metal/metal crevices, such as weld backing rings, but also at metal/nonmetallic crevices, such as asbestos-gasketed pipe flanges or under deposits. In some fabricated assemblies, it is possible and cost effective to avoid crevices by careful design. For example, crevice corrosion occurred behind a weld backing strip at the closing seam in a type 304L stainless steel reactor handling hot $HNO_3$. A small amount of corrosion by stagnant acid in the crevice created hexavalent chromium ions ($Cr^{6+}$), which caused accelerated attack; other exposed surfaces in the vessel were unaffected. The closing seam could have been welded from both sides or from one side with a consumable insert ring, which would have avoided the problem. Similar attack has occurred in stainless shell and tube heat exchangers at the rolled tube-to-tube-sheet joints and has been solved by seal welding the joints with appropriate weld filler metal and process.

However, in many cases, crevices are either too costly or impossible to design out of a system, so careful selection of materials is the answer. Titanium is susceptible to crevice corrosion in hot seawater and other hot aqueous chloride environments. Therefore, for a flanged and gasketed piping system in these fluids, commercially pure titanium grade 55 (UNS R50550) may be acceptable for piping, but flanges will require the more crevice attack resistant grade 7 (UNS R52400), which contains 0.15% (nominal) Pd, or grade 12 (UNS R53400), which contains small amounts of molybdenum and nickel. This is more cost effective than selecting the more expensive alloys for the piping as well. Another approach that has been successfully used in these fluids is installation of nickel-impregnated gaskets with grade 55 titanium flanges.

The austenitic stainless steels are susceptible to crevice corrosion in media other than $HNO_3$ solutions. For example, type 304L stainless steel exhibits borderline passivity in hot acetic acid solutions, particularly in crevices. Accordingly, the materials engineer will specify the more crevice corrosion resistant type 316L stainless steel where crevices cannot be avoided, such as piping and vessel flanges, or for the entire fabricated assembly because the cost differential between materials in this case may be negligible.

*Preferential attack* of weld metal is another form of localized corrosion that can be avoided by judicious selection of weld filler metal or weld process. Weld metal corrosion in high nickel-chromium-molybdenum Hastelloy alloy C-276 (UNS N10276) in a hot oxidizing $H_2SO_4$ process stream containing chlorides was eliminated by repair welding with Hastelloy alloy C-22 (UNS N06022). In applications in which type 304L stainless steel is selected for use in hot $HNO_3$ solutions, welds exposed to the process are frequently made by an inert gas process, such as gas tungsten arc or gas metal arc, rather than a flux-utilizing process, such as shielded metal arc. This prevents weld corrosion by eliminating the minute particles of trapped slag that are the sites for initiation of local corrosion. Many other examples of preferential weld metal attack and their solutions are discussed in the section "Corrosion of Weldments" in this article.

Nonmetallic materials of construction are widely used where temperatures, pressures, and stresses are not limiting and in such media as aqueous chloride solutions, which cause localized corrosion of metals and alloys. Examples in which lower-cost nonmetallic constructions are selected over expensive high alloys include the following:

- Rubber-lined steel for water treatment ion exchange resin beds, which must be periodically regenerated with salt brine or dilute mineral acids or caustic solutions
- Glass-lined steel for reaction vessels in chlorinated hydrocarbon service
- Acid-proof brick and membrane lined steel for higher temperature, and solid RTP polyester and vinyl-ester construction for lower temperature, flue gas and chlorine neutralization scrubbers

It should be apparent that an in-depth evaluation of candidate materials for environments that can cause localized corrosion is imperative in order to select the optimum material of construction. In particular, corrosion test coupons should reflect the final fabricated component—that is, include crevices and weldments where applicable—and should be examined critically under the microscope for evidence of local attack. In cases in which the more common 300- and 400-series stainless steels fall short, the newer ferritics, such as 26Cr-1Mo (UNS S44627) and 27Cr-3Mo-2Ni (UNS S44660), and the duplex ferritic-austenitic alloys, such as 26Cr-1.5Ni-4.5Mo (UNS S32900) and 26Cr-5Ni-2Cu-3.3Mo (UNS S32550), should be evaluated as potentially lower-cost alternatives to higher alloys. Finally, proven nonmetallic materials (for example, the RTPs), used either as linings for lower-cost metals (such as plain carbon steel) or for solid construction, should not be overlooked. More information on the mechanisms of pitting, crevice corrosion, and other forms of localized attack is available in the section "Localized Corrosion" of the article "Forms of Corrosion in the Petrochemical Industry."

**Galvanic corrosion** is quite possibly the only form of corrosion that can be beneficial as well as harmful. The materials engineer will frequently select galvanic corrosion—that is, cathodic protection using sacrificial metal anodes or coatings of magnesium, zinc, or aluminum—to stifle existing, or prevent new, corrosion of structures fabricated primarily from plain carbon or low-alloy steels—for example, bridges, underground and underwater pipelines, auto frames, off-shore drilling rigs, and well casings. All too often, however, galvanic corrosion caused by contact between dissimilar metals in the same environment is harmful. Examples are:

- Unprotected underground plain carbon steel pipelines connected to above-ground tanks and other structures that are electrically grounded with buried copper rods or cables
- Stainless steel shafts in "canned" pumps rotating in carbon or graphite bushings in a strong electrolyte
- Copper-nickel or stainless steel heat exchanger tubes rolled in plain carbon steel tubesheets exposed to river water for cooling
- Aluminum thermostat housings on cast iron auto engine blocks in contact with glycol-water mixtures

Newer designs that require several different metals for various reasons such as cost and physical, mechanical, and/or electrical properties present a challenge to the materials engineer with regard to selection for the avoidance of galvanic corrosion. Knowledge of the galvanic series of metals based on the electrochemical potential between a metal and a reference electrode in a given environment is essential. A practical galvanic series for metals and alloys in seawater is given in Table 1.

A word of caution: Metals behave differently in different environments; that is, the relative positions of metals and alloys in the galvanic series can vary significantly from one environment to another. In fact, variations within the same environment can occur with changes in such factors as temperature, solution concentration, degree of agitation or aeration, and metal surface condition. Thus, galvanic series that are based on seawater or other standard electrolytes are worthwhile for initial materials selection for multiple metal/alloy systems in a given environment. However, additional tests should be carried out in the stated environment by using the anodic polarization measurements described in ASTM G 5 (Ref 10). Suitable metal combinations can be determined by examining and superimposing polarization curves of candidate metals and by estimating the mixed potential values (Ref 18).

In conclusion, the selection of dissimilar metals that are far apart on any galvanic series should be avoided unless provisions are made for sacrificial corrosion of one for another, as in cathodic protection. Otherwise, dissimilar-metal applications in corrosive environments should be approached with extreme caution and should be thoroughly investigated before making the final selections. The section "Galvanic Corrosion" of the article "General Corrosion" of the article "Forms of Corrosion in the Petrochemical Industry" in this Volume contains more information on galvanic attack.

**Intergranular corrosion** is a selective form of corrosion that proceeds along individual grain boundaries, with the majority of the grain being unaffected. Intergranular corrosion can affect certain alloys that are highly resistant to general and localized attack; noteworthy are several of the 300- and 400-series stainless steels and austenitic higher-nickel alloys. These alloys are made susceptible to intergranular corrosion by sensitization—that is, the precipitation of chromium carbides and/or nitrides at grain boundaries during exposure to temperatures from 450 °C (840 °F) to 870 °C (1600 °F), with the maximum effect occurring near 675 °C (1250 °F). Exposure to such temperatures can occur during processing at the mill, welding and other fabrication operations, or by plant service conditions. The resulting depletion in chromium adjacent to the chromium-rich carbides/nitrides provides a selective path for intergranular corrosion by specific media, such as hot oxidizing (nitric, chromic) and hot organic (acetic, formic) acids.

Susceptible stainless steels are those that have normal carbon contents (generally >0.04%) and do not contain carbide-stabilizing elements (titanium and niobium). Examples are AISI types 302, 304, 309, 310, 316, 317, 430, and 446. Susceptible higher-nickel alloys include Inconel alloys 600 (UNS N06600) and 601 (UNS N06601), Incoloy alloy 800 (UNS N08800) despite the presence of titanium, Incoloy 800H (UNS N08810), Nickel 200 (UNS N02200), and Hastelloy alloys B (UNS N10001) and C (UNS N10002). Intergranular corrosion in these alloys is avoided by one or a combination of the following:

- Keep the alloy in the solution heat-treated condition at all times
- Limit interstitial elements, primarily carbon and nitrogen, to the lowest practical levels

**Table 1 Practical galvanic series of metals and alloys in seawater**

**Least noble; most anodic; most susceptible to corrosion**
Magnesium and its alloys
Zinc
Aluminum and its alloys
Cadmium
Plain carbon and low-alloy steels
Gray and ductile cast irons
Nickel cast irons
Type 410 stainless steel (active)
50Pb-50Sn solder
Type 304 and 316 stainless steels (active)
Lead
Tin
Muntz metal, manganese bronze, naval brass
Nickel (active)
Inconel 600 (active)
Yellow and red brasses, aluminum and silicon bronzes
Copper and copper-nickel alloys
Nickel (passive)
Inconel 600 (passive)
Monel 400
Titanium
Type 304 and 316 stainless steels (passive)
Silver, gold, platinum
**Most noble; most cathodic; least susceptible to corrosion**

Source: Ref 17 (condensed and modified from the original to include the precious metals)

**Table 2 Partial listing of environments known to cause intergranular corrosion in sensitized austenitic stainless steels**

| Environment | Concentration, % | Temperature, °C (°F) |
|---|---|---|
| Nitric acid | 1 | Boiling |
| | 10 | Boiling |
| | 30 | Boiling |
| | 65 | 60 (140) to boiling |
| | 90 | Room to boiling |
| | 98 | Room to boiling |
| Lactic acid | 50-85 | Boiling |
| Sulfuric acid | 30 | Room |
| | 95 | Room |
| Acetic acid | 99.5 | Boiling |
| Formic acid | 90 | Boiling |
| | 10 (plus $Fe^{3+}$) | Boiling |
| Chromic acid | 10 | Boiling |
| Oxalic acid | 10 (plus $Fe^{3+}$) | Boiling |
| Phosphoric acid | 60-85 | Boiling |
| Hydrofluoric acid | 2 (plus $Fe^{3+}$) | 77 (170) |
| Ferric chloride | 5 | Boiling |
| | 25 | Room |
| Acetic acid/anhydride mixture | Unknown | 100-110 (212-230) |
| Maleic anhydride | Unknown | 60 (140) |
| Cornstarch slurry, pH 1.5 | Unknown | 49 (120) |
| Seawater | ... | Room |
| Sugar liquor, pH 7 | 66-67 | 75 (167) |
| Phthalic anhydride (crude) | Unknown | 232 (450) |

- Add carbide-stabilizing elements, such as titanium, niobium, and tantalum, along with a stabilizing heat treatment where necessary

In general, these alloys are purchased from the mill in the solution heat-treated condition, a requirement of most specifications. With regard to the austenitic stainless steels, solution heat treating consists of heating to a minimum temperature of 1040 °C (1905 °F) to dissolve all the carbides, followed by rapid cooling in water or air to prevent sensitization.

Preserving the solution-treated condition is difficult, except for certain applications in which reheating is not a requirement of fabrication. One example is a pump shaft machined from forged or rolled and solution heat-treated bar stock. However, most applications for these alloys, such as piping components and pressure vessels, require hot rolling (for example, of plate) or hot bending (for example, of pipe) and welding; these practices, as discussed earlier, can cause sensitization. Solution heat treating after fabrication is generally impractical, because of the possibility of irreparable damage due to distortion or excessive scaling or because of the inability to cool rapidly enough through the critical sensitization temperature range.

Therefore, in most applications involving exposure to environments that cause intergranular corrosion, the low-carbon/nitrogen or stabilized alloy grades are specified. The new ferritic stainless steel UNS S44800 with 0.025% C (maximum) plus nitrogen is replacing the higher-carbon 446 grade in applications in which resistance to intergranular corrosion is a requirement. Types 304L, 316L, and 317L, with carbon and nitrogen contents limited to 0.03% (maximum) and 0.10% (maximum), respectively, are used instead of their higher-carbon counterparts. The newer nickel-chromium alloy 904L (UNS N08904), with 0.02% maximum carbon, and the high-nickel Hastelloy alloys C-22 (UNS N06022) and B-2 (UNS N10665), which have maximum carbon contents of 0.015% and 0.01%, respectively, are now being used almost exclusively in the as-welded condition without intergranular corrosion problems.

These low carbon levels are readily and economically achieved with the advent of the argon oxygen decarburization (AOD) refining process used by most alloy producers. By limiting the interstitial element content, sensitization is limited or avoided entirely during subsequent welding and other reheating operations. However, designers should be aware of the fact that lowering the carbon/nitrogen content also lowers the maximum allowable design stresses, as noted in appropriate sections of applicable fabrication codes, such as ASME Section 8, Division 1 for unfired pressure vessels and ANSI B31.3 for process piping.

Commercially pure Nickel 200 is a special case. With a maximum carbon content of 0.15%, Nickel 200 will precipitate elemental carbon or graphite in the grain boundaries when heated in the range of 315 to 760 °C (600 to 1400 °F). This results in embrittlement and susceptibility to intergranular corrosion in certain environments, such as high-temperature caustic. Where embrittlement and intergranular corrosion must be avoided, Nickel 201 (UNS N02201) with a maximum carbon content of 0.02% is specified.

Titanium as a carbide-stabilizing element is used in several ferritic and austenitic stainless steels, including types 409, 439, 316Ti, and 321, as well as the higher-nickel Incoloy alloy 825 (UNS N08825), at a minimum concentration of about five times the carbon plus nitrogen content. In the same way, niobium, generally with tantalum, is used in types 309Cb, 310Cb, and 347 austenitic stainless steels at a minimum combined concentration of about ten times the carbon content.

The higher-nickel alloys 20Cb-3, Inconel 625, and Hastelloy G contain even higher concentrations of niobium—up to a maximum of about 4% in the case of alloy 625. In general, when stabilized alloys are heated in the sensitizing temperature range, chromium depletion at the grain boundaries does not occur, because the stabilizing elements have a greater affinity for carbon than does chromium.

Under certain conditions, however, stabilized alloys will sensitize, especially during multipass welding or cross welding. They are also susceptible to a highly localized form of intergranular corrosion known as knife-line attack, which occurs in base metal at the weld fusion line. In some cases, these alloys are given stabilizing heat treatments after solution heat treatment for maximum resistance to intergranular corrosion in the as-welded condition. For example, type 321 stainless steel is stabilize annealed at 900 °C (1650 °F) for 2 h, and alloys 825 and 20Cb-3 at 940 °C (1725 °F) for 1 h, before fabrication to avoid sensitization and knife-line attack. So treated, type 321 may still be susceptible because titanium has a tendency to form an oxide during welding; therefore, its role as a carbide stabilizer may be diminished. For this reason, type 321 is always welded with a niobium-stabilized weld filler metal, such as type 347 stainless.

Some specialty alloys have low interstitial element content plus the addition of stabilizing elements for resistance to intergranular corrosion. These alloys include the higher-nickel Hastelloy alloy G-3 (UNS N06985), which contains 0.015% C (maximum) and niobium plus tantalum up to 0.5%, and the newer ferritic stainless steels (Ref 19) listed below:

- UNS S44627: 26% Cr, 1% Mo, 0.01% C (max), 0.015% N (max), 0.2% Nb (max)
- UNS S44635: 25% Cr, 4% Ni, 4% Mo, 0.025% C (max), 0.035% N (max), 0.80% Ti + Nb (max)
- UNS S44660: 26% Cr, 2% Ni, 3% Mo, 0.03% C (max), 0.04% N (max), 1.0% Ti + Nb (max)
- UNS S44735: 29% Cr, 0.5% Ni, 4% Mo, 0.03% C (max), 0.045% N (max), 1.0% Ti + Nb (max)

The new ferritic stainless steels were developed primarily for heat-exchanger tubing applications for use in place of the higher-carbon unstabilized type 446 stainless steel. These ferritic stainless steels have many useful properties.

As discussed previously, specific corrosion environments cause intergranular corrosion in specific metal and alloy systems. A wealth of information, both published (Ref 20) and unpublished, has been developed on corrodents that cause intergranular corrosion in sensitized austenitic stainless steels; a partial listing appears in Table 2. The low-carbon/nitrogen or stabilized grades are specified for applications in which the austenitics have satisfactory general and localized corrosion resistance in these environments and in which sensitization by such operations as welding and hot forming will undoubtedly occur.

Evaluation tests for intergranular corrosion are conducted to determine if purchased materials have the correct chemical composition and are in the properly heat-treated condition to resist intergranular corrosion in service (Ref 21). Evaluation testing is imperative for a number of reasons:

- The stainless steels and nickel-base alloys to which these tests are applied are relatively expensive
- These materials are frequently specified for critical applications in the petrochemical, process, and power industries
- The principal cost associated with a corrosion failure is generally that of production loss, not replacement
- For maximum cost effectiveness, these materials should be used in their best possible metallurgical and corrosion-resistant conditions

Most of the evaluation tests are described in detail in ASTM standards.

Intergranular corrosion is rare in nonsensitized ferritic and austenitic stainless steels and nickel-base alloys, but one environment known to be an exception is boiling $HNO_3$ containing an oxidizing ion such as dichromate (Ref 22), vanadate, and/or cupric. Intergranular corrosion has also occurred in low-carbon, stabilized and/or properly solution heat-treated alloys cast in resin sand molds (Ref 23). Car-bon pickup on the surface of the castings from metal-resin reactions has resulted in severe intergranular corrosion in certain environments. Susceptibility goes undetected in the evaluation tests mentioned above because test samples obtained from castings generally have the carbon-rich layers removed. This problem is avoided by casting these alloys in ceramic noncarbonaceous molds.

Other metals, such as magnesium, aluminum, lead, zinc, copper, and certain alloys, are susceptible to intergranular corrosion under very specific conditions. Very few case histories are reported in the literature. Intergranular SCC is discussed in the following section. More information on intergranular corrosion is available in the section "Metallurgically Influenced Corrosion" of the article "Forms of Corrosion in the Petrochemical Industry" in this Volume.

**Stress-corrosion cracking** is a type of environmental cracking caused by the simultaneous action of a corrodent and sustained tensile stress. The following discussion deals primarily with anodic SCC. Anodic SCC is believed to be a delayed cracking phenomenon that occurs in normally ductile materials under the stress resulting from accelerated electrochemical corrosion at anodic sites of the material as well as at the crack tip. Another type of environmental cracking, hydrogen stress cracking, is discussed later in this article (see also the section "Environmentally Induced Cracking" of the article "Forms of Corrosion in the Petrochemical Industry" in this Volume).

The National Association of Corrosion Engineers, the Materials Technology Institute of the Chemical Process Industries, and others have published tables of corrodents known to cause SCC of various metal alloy systems (Ref 24-26). Table 3 lists these data in condensed form and covers the SCC environments of major importance to the materials engineer. This table, as well as those published in the literature, should be used only as a guide for screening candidate materials for further in-depth investigation, testing, and evaluation.

Stress-corrosion cracking is not a certainty in the listed environments under all conditions. Metals and alloys that are indicated as being susceptible can give good service under specific conditions. For example, referring to Table 3:

- Anhydrous ammonia will cause SCC in carbon steels, but rarely at temperatures below 0 °C (32 °F) and only when such impurities as air or oxygen are present; addition of a minimum of 0.2% $H_2O$ will inhibit SCC
- Aqueous fluorides and hydrofluoric acid (HF) primarily affect Monel alloy 400 (UNS N04400) in the nickel alloys system; others are resistant
- Steam is known to cause SCC only in aluminum bronzes and silicon bronzes in the copper alloys system
- Polythionic acid only cracks sensitized austenitic stainless steels and nickel alloys; SCC is avoided by solution annealing heat treatments or selection of stabilized or low-carbon alloys

Stress-corrosion cracking is often sudden and unpredictable, occurring after as little as a few hours exposure or after months or even years of satisfactory service. Cracking occurs frequently in the absence of other forms of corrosion, such as general attack or crevice attack. Virtually all alloy systems are susceptible to SCC by a specific corrodent under a specific set of conditions, that is, concentration, temperature, stress level, and so on. Only the ferritic stainless steels as a class are resistant to many of the environments that cause SCC in other alloy systems, but they are susceptible to other forms of corrosion by some of these environments.

The combination of aqueous chlorides and austenitic stainless steels is probably the most important from the standpoints of occurrence, economics, and investigation. Although the mechanism and boundary conditions for chloride SCC are still not fully defined, it is reasonably safe to state that chloride SCC of austenitic stainless steels:

- Seldom occurs at metal temperatures below 60 °C (140 °F) and above 200 °C (390 °F)
- Requires an aqueous environment containing dissolved air or oxygen or other oxidizing agent
- Occurs at very low tensile stress levels such that stress-relieving heat treatments are seldom effective as a preventive measure
- Affects all the austenitic stainless steels about equally with regard to susceptibility, time to failure, and so on
- Is characterized by transgranular branchlike cracking as seen under a metallurgical microscope

So many materials and environments are sources of chlorides that they are hard to avoid (Ref 27). Significant costs for repairs and replacements, as well as lost utility, have occurred through the years in the petrochemical industry as a result of chloride SCC:

- In water-cooled heat exchangers from chlorides in the cooling water
- Under thermal insulation allowed to deteriorate and become soaked with water that leached chlorides from the insulation
- Under chloride-bearing plastics, elastomers, and adhesives on tapes

In the case of shell and tube heat exchangers, in which chloride-bearing waters are used for cooling, a number of preventive measures are available. In vertical units with water on the shell side, cracking occurs most often at the external surfaces of the tubes under the top tubesheet (Ref 28). This is a dead space (air pocket) at which chlorides are allowed to concentrate by alternate wetting and drying of tubing surfaces. Adding vents to the top tube-sheet sometimes alleviates this problem by eliminating the dead space and allowing complete water flooding of all tubing surfaces (Ref 29).

However, in many cases, this approach results in only a nominal increase in time to failure or no benefit whatsoever, because of other inherent deficiencies, such as low water flows or throttling water flow to control process temperatures. Thus, a material more resistant to chloride SCC is required, such as the austenitic higher-nickel Incoloy alloys 800 (UNS N08800) and 825 (UNS N08825); Inconel 600 (UNS N06600); ferritic stainless steels such as type 430 (UNS S43000), 26Cr-1Mo (UNS S44627), and SC-1 (UNS S44660); duplex stainless steels such as Ferralium 255 (UNS S32550) and AISI type 329 (UNS S32900); or titanium. In this case, selection depends primarily on economics, that is, the least expensive material that will resist process-side corrosion as well as water-side SCC.

Alloys are said to be either resistant or immune to chloride SCC, depending on how they perform in accelerated laboratory tests. In general, an alloy is immune if it passes the boiling 42% magnesium chloride test conducted according to ASTM G 36. Examples are Inconel alloy 600, 26Cr-1Mo, and grade 3 commercially pure titanium (UNS R50550). Industry has recognized the severity of this test and has devised other accelerated laboratory tests, such as boiling 25% sodium chloride and the Wick Test (ASTM C 692), that are more representative of actual conditions in the field (Ref 30). Thus, alloys that fail the G 36 test but pass the C 692 test, such as Incoloy 800, alloy 2205 (UNS S31803), and 20 Mo6 (UNS N08026), typically provide many

**Table 3 Some environment-alloy combinations known to result in SCC**

| Environment | Alloy system | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Aluminum alloys | Carbon steels | Copper alloys | Nickel alloys | Stainless steels | | | Titanium alloys | Zirconium alloys |
| | | | | | austenitic | duplex | martensitic | | |
| Amines, aqueous | ... | ● | ● | ... | ... | ... | ... | ... | ... |
| Ammonia, anhydrous | ... | ● | ... | ... | ... | ... | ... | ... | ... |
| Ammonia, aqueous | ... | ... | ● | ... | ... | ... | ... | ... | ... |
| Bromine | ... | ... | ... | ... | ... | ... | ... | ... | ● |
| Carbonates, aqueous | ... | ● | ... | ... | ... | ... | ... | ... | ... |
| Carbon monoxide, carbon dioxide, water mixture | ... | ● | ... | ... | ... | ... | ... | ... | ... |
| Chlorides, aqueous | ● | ... | ... | ● | ● | ● | ... | ... | ● |
| Chlorides, concentrated, boiling | ... | ... | ... | ● | ● | ● | ... | ... | ... |
| Chlorides, dry, hot | ... | ... | ... | ● | ... | ... | ... | ● | ... |
| Chlorinated solvents | ... | ... | ... | ... | ... | ... | ... | ● | ● |
| Cyanides, aqueous, acidified | ... | ● | ... | ... | ... | ... | ... | ... | ... |
| Fluorides, aqueous | ... | ... | ... | ● | ... | ... | ... | ... | ... |
| Hydrochloric acid | ... | ... | ... | ... | ... | ... | ... | ● | ... |
| Hydrofluoric acid | ... | ... | ... | ● | ... | ... | ... | ... | ... |
| Hydroxides, aqueous | ... | ● | ... | ... | ● | ● | ● | ... | ... |
| Hydroxides, concentrated, hot | ... | ... | ... | ● | ● | ● | ● | ... | ... |
| Methanol plus halides | ... | ... | ... | ... | ... | ... | ... | ● | ● |
| Nitrates, aqueous | ... | ● | ● | ... | ... | ... | ● | ... | ... |
| Nitric acid, concentrated | ... | ... | ... | ... | ... | ... | ... | ... | ● |
| Nitric acid, fuming | ... | ... | ... | ... | ... | ... | ... | ● | ... |
| Nitrides, aqueous | ... | ... | ● | ... | ... | ... | ... | ... | ... |
| Nitrogen tetroxide | ... | ... | ... | ... | ... | ... | ... | ● | ... |
| Polythionic acids | ... | ... | ... | ● | ● | ... | ... | ... | ... |
| Steam | ... | ... | ● | ... | ... | ... | ... | ... | ... |
| Sulfides plus chlorides, aqueous | ... | ... | ... | ... | ● | ● | ● | ... | ... |
| Sulfurous acid | ... | ... | ... | ... | ● | ... | ... | ... | ... |
| Water, high-purity, hot | ● | ... | ... | ● | ... | ... | ... | ... | ... |

years of service as tubes in water-cooled heat exchangers. (The austenitic 300-series stainless steels, as a class, fail all of the accelerated laboratory chloride SCC tests mentioned above.)

Unfortunately, all of the immune and resistant alloys are more expensive than most of the austenitic stainless steels. A more cost-effective application of some of these alloys involves a procedure known as safe ending, in which short lengths (for example, 0.3 to 0.6 m, or 12 to 24 in.) are butt welded to the austenitic stainless steel tubes. The SCC-resistant ends are positioned in the exchanger at the point of greatest exposure to SCC conditions, that is, under the top tubesheet. Safe-ended tubes have extended the life of austenitic stainless steel tubing severalfold, with only a nominal increase in cost. Of course, the dissimilar metals must be weld compatible; this eliminates the use of titanium for safe ending.

Another cost-effective answer to chloride SCC in heat exchangers is bimetallic tubing, in which the austenitic stainless steel required for process-side corrosion resistance is clad with a water-side SCC- and corrosion-resistant material such as 90Cu-10Ni (UNS C70600) (Ref 31). Still another answer is cathodic protection with a sacrificial metal coating such as lead containing 2% Sn and 2% Sb applied by hot dipping or flame spraying (Ref 32).

Chloride SCC under insulation can be prevented by keeping it dry, but this is easier said than done in many cases. It is particularly difficult in humid, high annual rainfall climates, such as the Gulf Coast area of the United States, and where insulated equipment must be washed down periodically or is exposed to fire control deluge systems that are periodically activated (Ref 33). Under these conditions, three preventive measures are applied, as follows.

The first preventive measure is the addition of sodium metasilicate as an SCC inhibitor to the insulation at a minimum concentration of ten times the chloride content. The inhibitor is activated when the insulation becomes wet and is effective only when it wets the stainless steel surface. For maximum protection, metasilicate is painted on the vessel or piping before the installation of inhibited insulation. However, SCC has occurred after many years of service under inhibited insulation that was allowed to become so wet that the water-soluble inhibitor was leached out to a point below the minimum concentration required for prevention of SCC.

Second is protective coating of the vessel or piping before insulation. Catalyzed high build epoxy paints are effective to about 100 °C (212 °F), catalyzed coal tar-epoxy enamels to about 150 °C (300 °F), and silicone-base coatings to about 200 °C (390 °F). These coatings are even more effective if the stainless steel surfaces are heavily sandblasted before coating. Sandblasting peens the surface to a depth of 0.01 to 0.1 mm (0.4 to 4 mils), and this results in a layer under compressive stresses that counteract the tensile stresses required for SCC (peening will be discussed later in this article).

The third preventive measure is cathodic protection of the vessel or piping with aluminum foil under insulation (Ref 34). This method is claimed to provide both a physical barrier to chloride migration to stainless steel surfaces as well as cathodic protection when the insulation becomes wet, and it is effective at vessel temperatures between 60 and 500 °C (140 to 930 °F). However, the foil is attacked by the alkaline (generally) leachates from the insulation and must be renewed periodically.

Other important environments that cause SCC of stainless steels are hydroxide (caustic) solutions, sulfurous acid, and polythionic acids. Caustic SCC of austenitic stainless steels can be both transgranular and intergranular and is a function of solution concentration and temperature. It seldom occurs at temperatures below 120 °C (250 °F). At higher temperatures, the newer ferritic stainless steels, nickel, and high-nickel alloys provide outstanding service; 26Cr-1Mo stainless steel has found widespread application in heat-exchanger tube bundles serving caustic evaporators at 170 to 200 °C (340 to 390 °F). Nickel 200 and 201 as well as Inconel alloy 600 are resistant to 300 °C (570 °F) in caustic concentrations to 70%.

Polythionic acid and sulfurous acid will cause SCC in sensitized nonstabilized austenitic stainless steels and nickel-base alloys. Cracking is always intergranular and requires relatively low tensile stresses for initiation and propagation. As-welded, normal carbon grades, such as types 304 and 316 and Incoloy alloy 800, are particularly susceptible to SCC in weld HAZs. Low-carbon (<0.03% C) and stabilized grades, such as types 321 and 347, are resistant, especially after receiving a stabilizing heat treatment. The normal carbon grades in the solution heat-treated condition are also resistant. Susceptibility to polythionic acid SCC can be determined by laboratory corrosion testing according to ASTM G 35.

Polythionic acid and sulfurous acid SCC are major considerations in the petroleum-refining industry, especially in desulfurizer, hydrocracker, and reformer processes (Ref 35, 36). These acids form in process units during shutdowns when equipment and piping containing sulfide deposits and scales are opened and exposed to air and moisture. Preventive measures include flushing with alkaline solutions to neutralize sulfides before shutdown and purging with dry nitrogen during shutdown according to recommended practices established by NACE (Ref 37).

Cast austenitic stainless steels such as Alloy Casting Institute (ACI) types CF-8 (UNS J92600) and CF-8M (UNS J92900) are inherently more resistant (but not immune) to chloride SCC than their wrought counterparts (types 304 and 316, respectively) for several reasons. Castings generally have lower residual stresses than wrought alloys after solution-annealing heat treatments, and service-applied stresses are often lower because of heavy section thicknesses. However, the principal reason for improved SCC resistance is the presence of varying amounts of free ferrite, resulting in a duplex austenitic-ferritic microstructure. Free ferrite is primarily attributed to additions of 1 to 2% Si to improve fluidity during pouring and to resist hot cracking during cooling of the casting.

During work conducted some years ago on the development of the duplex cast ACI alloy CD-4MCu (UNS J93370), researchers noted improved resistance to chloride SCC in cast alloys containing high ferrite; this confirmed observations in the field by materials engineers (Ref 38). A significant improvement in SCC resistance occurred with ferrite contents in the range 13 to 20 vol% and greater. This led to the development of alloys with controlled ferrite content by balancing chemical composition. Ferrite formation is promoted by chromium and by elements that act like chromium, such as silicon, niobium, and molybdenum. Nickel and elements that act like nickel (carbon, manganese, nitrogen) retard ferrite formation. When specified, ferrite is typically controlled at the foundry by adjusting chromium toward the upper end of the specification range, and nickel toward the lower end, along with the silicon addition.

Resistance to SCC in these alloys is believed to be a result of the keying action of ferrite particles (Ref 39). This action blocks direct propagation of SCC through the austenitic matrix. Along with this benefit, however, are improvements in strength, weldability, and resistance to general corrosion, particularly in hot concentrated nitric, acetic, phosphoric, and sulfuric acids and mixed nitric-hydrofluoric acid (Ref 40). The American Society for Testing and Materials has recognized alloys produced with controlled ferrite content in specification A 351. However, users are cautioned to limit applications to a maximum temperature of 425 °C (800 °F) because of the thermal instability of these grades.

A number of measures for preventing SCC of austenitic stainless steels have already been discussed. Two additional measures worthy of consideration are stress-relieving heat treatments and shop peening. The typical stress-relieving temperature for plain carbon steels—595 °C (1100 °F)—is only slightly effective for the austenitics, which require slow cooling from about 900 °C (1650 °F) for effective relief of residual stresses from such operations as welding. However, such treatments may not prevent, but only prolong, the time to failure; chloride SCC of austenitic stainless steels can occur at very low stress levels. Also, these elevated temperatures may cause unwanted distortion of complex and/or highly stressed structures and will sensitize susceptible alloys. This sensitization will result in intergranular corrosion or intergranular SCC.

Shot peening is the controlled bombardment of a metal surface with round, hard steel shot for the purpose of introducing compressive stresses in surface layers. These compressive stresses counteract the tensile stresses required for SCC. The depth of the resultant cold-worked layers is generally in the range 0.1 to 0.5 mm (4 to 20 mils); 100% coverage is required. In laboratory tests in boiling 42% magnesium chloride, shot-peened type 304 stainless steel U-bend samples showed no SCC after more than 1000 h of exposure, but nonpeened control samples all cracked in approximately 1 h (Ref 41). Successful applications in the chemical-processing industries include a type 316 stainless steel centrifuge exposed to an organic chloride process stream (Ref 42) and numerous storage tanks exposed to a variety of SCC conditions (Ref 43).

The exposure of shot-peened surfaces to excessive temperatures or to environments that cause excessive general or pitting corrosion should be avoided. Temperatures above 565 °C (1050 °F) will relieve the beneficial compressive stresses and reduce the overall benefits of shot peening. Once the relatively thin layers of residual compressive stress are penetrated by general corrosion or pitting, SCC can occur.

Plain carbon steels are susceptible to SCC by several corrodents of economic importance, including aqueous solutions of amines, carbonates, acidified cyanides, hydroxides, nitrates, and anhydrous ammonia. Susceptible steels in common use throughout the petrochemical-processing industry include ASTM A106 grade B for piping, A285 grade C for tanks, and A 515 grade 70 for pressure vessels. Cracking is both intergranular and transgranular; the former occurs in hot hydroxides and nitrates, and the latter in warm acidified cyanide solutions.

The temperature and concentration limits for the SCC susceptibility of carbon steels in caustic soda (sodium hydroxide) are fairly well defined; they have been derived from field experience and reproduced in chart form (Fig. 1). These limits for the other aqueous SCC environments mentioned above are not nearly as well defined. For example, SCC was not considered to be a problem at temperatures below 88 °C (190 °F) in aqueous monoethanolamine and diethanolamine solutions used for scrubbing carbon dioxide and hydrogen sulfide out of natural gas and hydrogen-rich synthesis gas streams. However, recent experience in petroleum refineries has resulted in general agreement that SCC preventive measures, such as thermal stress relief, must be applied to plain carbon steels in aqueous amines at all temperatures and concentrations.

With regard to anhydrous ammonia, the SCC of plain carbon and low-alloy steels occurs at ambient temperatures when air or oxygen is present as a contaminant at concentrations of only a few parts per million (Ref 45). Most of the adverse experience has been with the nonstress-relieved higher-strength quenched-and-tempered steels, such as the grades covered in ASTM A 517. Cracking seldom occurs at temperatures below 0 °C (32 °F) and is virtually nonexistent at or below −33 °C (−28 °F), a common temperature for storage at atmospheric pressure. Water is an effective SCC inhibitor at a minimum concentration of 0.2% by weight.

Thermal stress relief is perhaps the single most effective measure for preventing, or at least greatly prolonging, the time to SCC of plain carbon and low-alloy steels in all of the environments mentioned above. However, temperature is a more important factor than time at temperature. There is general agreement that stress-relieving temperatures below 595 °C (1100 °F), regardless of the hold time, are not effective for preventing SCC. In fact, the recommended minimum temperature for some environments, such as aqueous acidified cyanides, is 650 °C (1200 °F). As with any thermal treatment, special precautions must be observed, such as adequate support to avoid distortion and the removal of dirt, grease, and other foreign material that might react with the structure at elevated temperatures.

The above comments on thermal stress relief apply to new carbon steel piping and vessels. Stress-corrosion cracking has been found in such vessels as horizontal pressure storage tanks ("bullets") that were stress relieved after SCC was found in the original as-welded vessels and were repaired by grinding and welding (Ref 45). Undoubtedly, the stress-relieving temperatures propagated tiny cracks that were not detected during repairs.

Just as aqueous chloride is a potent SCC environment for austenitic stainless steels, aqueous ammonia causes extensive cracking in copper-

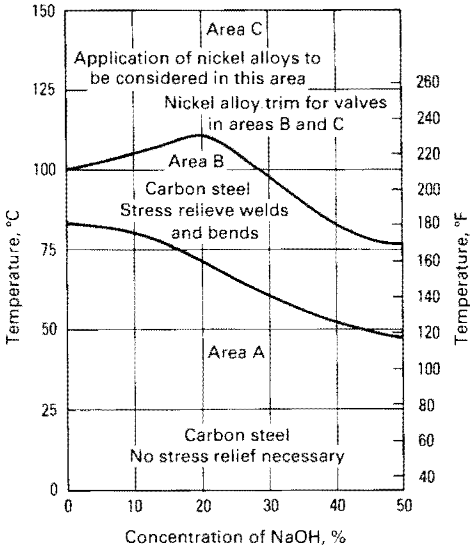

**Fig. 1** Temperature and concentration limits for SCC susceptibility of carbon steels in caustic soda. Source: Ref 44

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base alloys. Virtually all copper alloys, as well as pure copper itself, can be made to crack in this environment. The most susceptible alloys are the brasses containing more than 15% Zn, such as admiralty brass (UNS C44300, 28% Zn), yellow brass (UNS C27000, 34% Zn), and Muntz metal (UNS C28000, 40% Zn), followed by red brass (UNS C23000, 15% Zn) and several bronzes. The least susceptible alloys are 90Cu-10Ni (UNS C70600), 70Cu-30Ni (UNS C71500), and unalloyed copper.

The conditions that are conducive to SCC by aqueous ammonia are water, ammonia, air or oxygen, and tensile stress in the metal. Cracking is always intergranular, requires only trace quantities of ammonia in many cases, and occurs at ambient temperature. For example, U-bends in admiralty brass condenser tubes cracked in warm water from a cooling tower that contained 15 to 25 ppm ammonia because of close proximity to an ammonia plant. Other sources of ammonia include the decomposition of amines and the microbiological breakdown of organic matter.

Thermal stress relief is generally not one of the better preventive measures, because ammoniacal SCC occurs at relatively low stress levels. In fairly mild ammoniacal environments, such as the cooling tower water system mentioned above, the copper-nickel alloys, particularly 90Cu-10Ni, give good service. Small quantities of hydrogen sulfide have been found to inhibit SCC of brasses in petroleum refinery process streams, probably by reducing the dissolved oxygen content (Ref 46).

Another potent SCC agent for copper alloys is steam, but susceptibility is limited primarily to the higher-strength bronzes alloyed with aluminum (for example, UNS C61400) or silicon (for example, UNS C65500). In this regard, one noteworthy design to avoid is dimpled jacket construction. Severe SCC occurred at plug welds in a silicon bronze steam jacket on a similar alloy vessel used for heating a waste $H_2SO_4$ stream.

Stress-corrosion cracking of aluminum and its alloys in the chemical-processing industries is rare, because the lower-strength alloys in predominant use are resistant. These include the commercially pure alloy 1100, manganese alloy 3003, and magnesium alloys 5052 and 5083. Susceptible alloys are the high-strength grades of economic importance in the aircraft and aerospace industries, such as the copper alloys 2014 (UNS A92014) and 2024 (UNS A92024) and the copper-zinc-magnesium alloys 7075 (UNS A97075) and 7178 (UNS A97178). These alloys, heat treated to maximum strength levels, are susceptible to SCC in humid air containing traces of chlorides (Ref 47).

Titanium (UNS R50550 and other unalloyed grades) has found increasing application in the chemical-processing industries, primarily as a replacement for austenitic stainless steels, because of outstanding resistance to corrosion by hot, concentrated oxidizing acids, such as $HNO_3$, and virtual immunity to pitting and SCC by hot aqueous chloride solutions. However, titanium and, to a greater extent, its higher-strength alloys (for example, UNS R56400) are susceptible to SCC in a variety of environments, including anhydrous alcohols (methanol, ethanol) containing traces of halides, anhydrous red fuming $HNO_3$, anhydrous hot chlorides, some important industrial organic solvents (carbon tetrachloride, trichloroethane, and so on), anhydrous nitrogen tetroxide, and HCl.

In general, SCC preventive measures, such as thermal stress relief, cathodic protection, or inhibition, have not been used to any great extent with titanium and its alloys, although water additions are reported to inhibit cracking in anhydrous red fuming $HNO_3$ and anhydrous nitrogen tetroxide (Ref 48). Rather, SCC is prevented by avoiding contact with specific cracking agents.

Zirconium (UNS R60702) and, to a greater extent, its alloys (for example, UNS R60705) exhibit SCC behavior similar to that of titanium and its alloys in anhydrous alcohols containing traces of halides and in chlorinated organic solvents. Stress-corrosion cracking also occurs in aqueous ferric and cupric chloride solutions and hot concentrated $HNO_3$, especially when sustained tensile stresses are high. Because threshold stresses for SCC are high in comparison to yield strengths, thermal stress relief is a practical preventive measure. Holding temperatures between 650 and 850 °C (1200 and 1560 °F) are reported to be effective (Ref 49).

As a class, nickel-base alloys are susceptible to SCC by a wide variety of corrodents. However, in most cases, the corrodents are specific to a few, but not all, of the alloys in this class. For example, sensitized alloys 800 and 600 crack in thiosulfate solutions and polythionic acids, but the stabilized alloys Incoloy 825 and Inconel 625 are resistant. The latter alloys are particularly applicable in petrochemical process streams containing chlorides along with polythionic acids. In the nuclear power industry, Inconel 600 and weld metal alloys 82 (UNS N06082) and 182 (UNS W86182) crack intergranularly in crevices in high-purity water containing oxygen at elevated temperatures and pressures (Ref 50). In the absence of crevices, these alloys are resistant. Inconel alloy 690 (UNS N06690) is resistant under all conditions. Nickel 200 and 201, Monel 400, Inconel 600 and 690, and Incoloy 800 are susceptible to SCC in caustic solutions over a wide range of concentrations and at temperatures above 290 °C (550 °F). Cracking is predominantly intergranular. The presence of oxygen and chlorides, which are common contaminants, tends to accelerate cracking, especially in Inconel alloy 600. Fairly high stress levels are generally required. Failures have occurred in steam generator tubes serving nuclear power plants from caustic concentrated on tube surfaces in crevices or as a result of a hot wall effect and/or poor water circulation. This experience prompted considerable research (Ref 51-57). In general, Nickel 200 and 201 and the nickel-chromium-iron-Inconel alloys 690 and 600 appear to be the most resistant under the various conditions tested, although they are not immune to caustic SCC.

Other SCC environments of importance with regard to nickel-base alloys, specifically Monel 400, are acidic fluoride solutions and HF. Monel 400 is susceptible to SCC in cold-worked or as-welded conditions, but is resistant in annealed or thermally stress-relieved conditions (Ref 58). Free air or oxygen accelerates corrosion rates and SCC tendency. However, Monel 400 has excellent general corrosion resistance over a broad range of temperatures and concentrations, so its use in HF alkylation units and other process streams containing HF or fluorides is widespread (Ref 59). Thermal stress relief at a minimum temperature of 540 °C (1000 °F), followed by slow cooling, will prevent SCC or will greatly prolong time to failure.

Corrosion-resistant polymers, such as thermoplastic and thermosetting resins, that are of interest to the materials engineer are susceptible to two forms of cracking in specific environments (Ref 60):

- Environmental stress cracking, which occurs when the polymer is stressed (residual or applied) and exposed to an organic solvent or aqueous solution of a wetting agent
- Craze cracking, which consists of a multitude of fine cracks that develop in contact with organic liquids or vapors, with or without the presence of mechanical stresses

For example, high-density polyethylene may crack in the presence of benzene or ethylene dichloride, and polystyrene may crack in the presence of aliphatic hydrocarbons (Ref 61). The mechanisms for these phenomena are not completely understood. Cracking may initiate at minute particles of low molecular weight polymers in the higher molecular weight polymer matrix. Thus, when evaluating polymers for corrosive service, test specimens should be stressed before exposure and should be

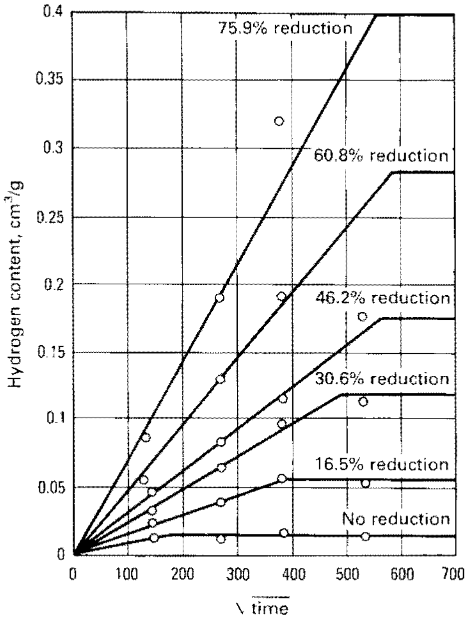

**Fig. 2** Effect of cold reduction on rate of hydrogen adsorption in carbon steel. Test performed on wire stock in 1 *N* $H_2SO_4$ at 35 °C (95 °F); original rod diameter was 13 mm (½ in.). Source: Ref 75

# Corrosion in the Chemical Processing Industry

# Corrosion in the Chemical Processing Industry

THIS ARTICLE covers two groups of subjects: one concerns significant problems in the control of corrosion and protection of chemical-processing equipment, and the other concerns the handling and corrosive effects of the most commercially important acids and bases produced and used by the chemical-processing industries.

Environmental protection is of primary importance to the processing industries. Unexpected corrosion failures, which could cause the release of chemicals, cannot be tolerated. Methods of preventing and detecting corrosion hidden under thermal insulation are described in the section "Corrosion Under Thermal Insulation" in this article. The causes of unexpected corrosion failures from process and environmental variables are covered in the section "Effects of Process and Environmental Variables" in this article. Fouling of equipment and piping can lead to premature failures, release of chemicals, and reduced efficiency. Three methods of cleaning are described in the section "Chemical Cleaning of Process Equipment" in this article.

The Sections on corrosion by commercially important acids and bases briefly discuss the various grades, methods of manufacture, the most common materials of construction, and their effect on a broad range of metals and nonmetals. The latest developments in corrosion-resistant alloys, plastics, and electrochemical techniques, such as anodic polarization, applicable to each chemical are also covered in this article.

Many of the materials and techniques used to combat corrosion in the chemical-processing industries were developed by processing companies in response to corrosion problems in their plants. One large chemical company, for example, recognized more than 50 years ago the basic importance of both unit operations and materials in the design and construction of the large-scale plants emerging from their research and established a technical division with two groups at its experimental station. The materials group developed silicon bronze (Copper Development Association, CDA, C65500), Alloy Casting Institute (ACI) CN-7M stainless steel casting alloy (Alloy 20), 20Cb-3 stainless steel (Ref 1), dispersion-strengthened nickel-base corrosion- and wear-resistant alloys, and other significant advancements in new metals. Several of the larger chemical companies were also instrumental in the commercialization of titanium (Ref 1). Corrosion engineers employed by a large German chemical company were responsible for the development of Hastelloy C-276.

Corrosion monitoring using instantaneous corrosion measurement is based on an electrochemical theory formulated by the employees of a major chemical industry firm (Ref 2). Their work on polarization also led to the design of the titanium-palladium alloy, with its broader range of passivity in reducing environments. The many chemically resistant plastics and elastomers used in chemical-processing industry plants today were also developed by the industry.

The chemical-processing industry has undergone profound changes in the past decade. Energy costs, environmental considerations, and employee and public health concerns have brought about changes in plant construction. Plants are now more energy efficient and less polluting. Also, fewer large plants are being built. High-value, low-volume specialty chemicals and biotechnical products are favored over the commodity products. The resulting products are often of high purity. Electronic grades of acids are not uncommon. High-quality products often require more corrosion-resistant materials for equipment and containers for shipping and storage. Titanium alloys are routinely considered for chemical applications, and zirconium, niobium, and tantalum are also being used more often (Ref 3). More expensive materials are more affordable in small equipment, for which design and fabrication costs represent a higher percentage of the installed cost than the cost of the materials used in fabrication. Purity levels can also be

**Table 1** Effects of process variables on corrosion of metals in aggressive environments

| Process variable | Carbon steels | Austenitic stainless steels | Nickel, nickel-copper alloys | Nickel-copper, nickel-chromium-molybdenum alloys | Titanium | Zirconium | Copper, copper alloys |
|---|---|---|---|---|---|---|---|
| Velocity | | | | | | | |
| Increasing | >(a) | 0 to > | 0 to > | 0 to > | 0(b) | 0 | > |
| Decreasing | <L(c)(d) | <L | 0 to < | 0 to < | 0 | 0 | < |
| Aeration | > | 0 to < | > | V(e) | 0 to < | 0 | > |
| Galvanic couple | > | 0 | 0 | 0 | HE(f) | HE | 0 |
| Impurities | | | | | | | |
| Nonchloride oxidants | V | < | > | V | 0 | 0 | > |
| $FeCl_3$, $CuCl_2$ | > | >L, SCC(g) | > | 0 to > | 0 | >E(h) | > |
| Neutral chlorides | > | >L, SCC | 0 | 0 to > | 0, unless H(j) | 0 | > |
| Ammonia | 0 | 0 | > | 0 | 0 | 0 | >SCC |
| Sodium, potassium | 0, SCC if H | 0, SCC if H | 0 | 0 | 0, unless H | 0 | 0, unless H |
| Fluorides | 0 | 0 | 0 | 0 | > | > | 0 |
| Nitrites | V | V | > | V | 0(k) | 0 | >SCC |
| Nitrates | <, SCC | 0 to < | 0 | 0 | 0 | 0 | 0 |
| HCl in chlorine | > | > | > | > | >(m) | > | > |
| Mercury | 0 | 0 | 0, SCC if H | 0 | 0, unless H | 0 | >SCC |
| Sulfur compounds | V | 0, SCC if S(n) | > | 0, SCC if S | 0 | 0 | > |

(a) >, generally increases attack. (b) 0, generally has no effect on metal in question. (c) <, generally decreases attack. (d) L, local attack or crevice corrosion is possible. (e) V, may increase or decrease attack, depending on specific alloy and environment. (f) HE, hydrogen embrittlement is possible. (g) SCC, stress-corrosion cracking is possible. (h) E, embrittlement. (j) H, hot (from 80 to 150 °C, or 175 to 300 °F, depeding on variable and alloy). (k) Except in fuming $HNO_3$. (m) Except for dilute solutions. (n) S, sensitized by heat treatment improved by electrochemical means, such as the anodic or cathodic protection of steel storage tanks and stainless steel coolers and liners.

## Corrosive Effects of Process and Environmental Variables

Two chemical-processing plants making the same product and using the same or a similar process will sometimes have different experiences with corrosion. At one plant, a steel pipeline may last for many years in a given service, yet an identical pipeline may fail within weeks or months in the same service at another plant. A major piece of equipment may suddenly fail after 15 or 20 years of service as a result of less than 1 ppm of metal ion contamination in a new source of raw material.

In designing a chemical-processing plant, considerable attention is paid to fluid flows, sizings of lines, pumps and processing equipment, and temperatures and pressures. Materials are selected on the basis of past experience, corrosion tests, the literature, and the recommendations of material suppliers. The nominal compositions of process streams and raw materials are known with some accuracy. Occasionally, however, variables come into play that cause corrosion failures. Table 1 lists variables that can affect the performance of metals in corrosive environments.

### Plant Environment

One factor that is occasionally overlooked is the surrounding environment. For example, the instrument tubing at a new facility, built at an existing chemical plant in West Virginia, consisted of a combination of copper (C12200) tubing and yellow brass (C27000) fittings. However, within a few weeks, the fittings had failed by stress-corrosion cracking (SCC). The new building was located near, and downwind of, another facility that occasionally vented small amounts of nitric oxide (NO) to the atmosphere (Ref 4).

Tests later showed that brass samples would fail by SCC if exposed to the source of NO emissions. An expensive shutdown was necessary to replace all of the instrument tubing and fittings with stainless steel.

Similar failures of brass heat exchangers have occurred as a result of their proximity to sources of ammonia ($NH_3$). In one case, cooling tower water became contaminated with a few parts per million of $NH_3$ when an ammonia-manufacturing plant was built nearby. In another case, the admiralty brass (C44400) heat-exchanger tubing in a large air compressor stress cracked in cold-worked areas after it was installed about 30 m (100 ft) from a building in which laboratory reagents, including ammonium hydroxide ($NH_4OH$) and nitric acid ($HNO_3$), were bottled.

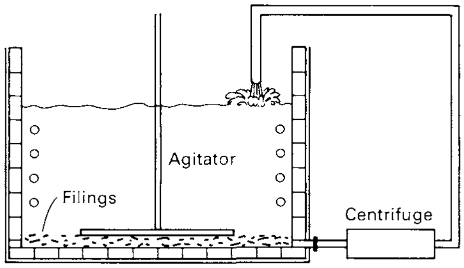

**Fig. 1** Equipment used for iron reduction and removal of spent filings

### Cooling Water

The quality of water used to cool shell and tube heat exchangers can vary from season to season and year to year, particularly if the water is taken from a river that discharges into a bay or sea. In one case, for example, a plant had 64 identical AISI type 304 stainless steel condensers cooled on the shell side, with river water that varied in chloride content from less than 50 ppm to as high as 2000 ppm. The stainless steel tubes failed by external pitting at baffles. It was discovered that an almost perfect correlation could be obtained by plotting the average monthly chloride content against the number of leaking condensers retubed that month.

In a similar case, a series of stainless steel heat exchangers cooled with recirculating treated water had been in service for more than 10 years (Ref 5). During an emergency, untreated river water was used to cool the units for about 48 h. Several weeks later, five of the coolers failed by massive chloride SCC. There was a large buildup of dried mud in the units, which caused reduced heat transfer and higher wall temperatures.

### Steam

The corrosive properties of the steam that will be used in a plant are seldom considered, particularly if the steam will be supplied by a public utility or power plant that has good boiler water treatment that will prevent condensate corrosion. However, the impurities in steam can cause corrosion problems.

At one site, for example, high-pressure steam was purchased from a central power station; pressure was reduced to 2.76 MPa (400 psi) as it entered the plant. Some years later, plant operators decided to cool the superheated steam by spraying with deionized water at a point just beyond the depressurizing valve. There were no problems until 15 years later, when it became necessary to replace and reroute part of the steam line inside the plant. Within a few months, cracks and resulting leaks appeared adjacent to and across the welded joints in the new piping. The plant operators blamed the welding contractor for poor welding.

However, metallographic examination showed that the cracking was the result of caustic embrittlement. The deionized water contained 10 ppm of sodium, which formed concentrated sodium hydroxide (NaOH) as the water evaporated. The older piping did not crack, because it had been stress relieved by the superheated steam over a period of years before cooling of the steam was initiated.

A similar case was reported in which a stainless steel bellows in a 2.76-MPa (400-psi) steam line failed by caustic cracking (Ref 4). The failure was attributed to carryover of boiler compounds.

### Aeration

The design of the plant and, in particular, equipment selection can influence the amount of air introduced into a process stream, which in turn may profoundly affect corrosion. This can account for different corrosion experiences in plants having identical chemistries and products.

Solid-liquid separation can be accomplished in several ways. Some methods, such as centrifuging, can cause more aeration than others—pressure filtration, for example—with occasional disastrous results.

In iron reductions, iron filings and dilute hydrochloric acid (HCl) are agitated with an organic nitro compound, which is reduced to an amine by the hydrogen evolved. In the design of one such unit, for example, a Monel 400 centrifuge (Fig. 1), coils, and agitator were selected based on laboratory corrosion tests and general experience with units using filter presses having no return stream. Aeration caused by the centrifuge, together with a return pipe that terminated in the vapor space of the vessel, caused conversion of ferrous chloride ($FeCl_2$) to ferric chloride ($FeCl_3$), with resulting rapid corrosion of all Monel 400 parts. The temporary solution involved blanketing the equipment with nitrogen, extending the return pipe below the liquid level, and adding a corrosion inhibitor.

In a caustic chlorine plant, steel piping that transferred saturated alkaline brine at ambient temperature failed by crevice corrosion and pitting shortly after start-up, although steel piping had been successfully used at other plants. Failure was attributed to aeration caused by centrifuges removing precipitated salt from caustic liquors and returning the salt to the dissolver.

### Start-Up and Shutdown Conditions

Start-ups and shutdowns are variables that can easily be overlooked in the design stage or conducted improperly by operations. Such a case was reported in a high-sulfur coal gasification plant operating at 430 to 595 °C (800 to 1100 °F) (Ref 6). A designer selected type 310 stainless steel rather than type 304 because he felt that the higher chromium content of the type 310 would result in improved high-temperature resistance. The unit failed, however, by massive intergranular polythionic acid SCC that occurred during the first shutdown.

This type of corrosion occurs in sensitized stainless steels in an acidic sulfide environment in the presence of air. It can be mitigated by following the guidelines in National Association of Corrosion Engineers (NACE) stan-dard RP-01-70 (Ref 7). Perhaps a better approach is to use a carbide-stabilized grade of stainless steel, such as type 347 or type 321.

In another example, silicate cement was selected for use with unalloyed tantalum repair plugs in a new glass-lined vessel and its accessories for a bromination process, because bromine would attack the organic cement that is normally used with the plugs. The vessel was obtained plug-free, but the agitator and baffle both required tantalum plugs. As part of the start-up procedure, plant operators boiled out the equipment with water. This dissolved the silicate cement. When the vessel was placed in operation, the bromine attacked the steel under the plugs. The agitator dissolved, leaving only the stub revolving above the liquid level.

In a third case, type 304 stainless steel was correctly selected for a 99% sulfuric acid ($H_2SO_4$) pipeline. During the first shutdown, the plant operators decided to blow the acid out of the line. They used compressed air, which was unwise, because compressed air is commonly saturated with water. Within a few days, leaks were discovered adjacent to some welds where dilute acid had accumulated. Dry nitrogen is now used to blow out the line, which has been in service for 20 years and as many shutdowns.

## Seasonal Temperature Changes

Ambient temperature is an important variable that can vary widely. Metal parts exposed to the sun may reach 60 °C (140 °F) in the summer. In one case, for example, a steel pipeline carrying 98% $H_2SO_4$ was supplied with properly designed steam tracing that maintained a maximum temperature of 50 °C (125 °F) during the winter (Ref 6). During the summer, the line failed by corrosion. The steam had not been disconnected, and the temperature of the line exceeded 70 °C (150 °F).

Heat exchangers (Fig. 2) are usually designed conservatively for summer water temperatures. During the winter, the colder cooling water can cause a lower exit process temperature than desired. To correct this problem, plant operators will frequently decrease the water flow. All too often, the water flow is throttled at the water inlet. This can result in a fluctuating liquid level, with buildup of solids, pitting, and/or SCC of tubes. The correct arrangement, with the water control valve on the discharge line, is shown in Fig. 2.

## Variable Process Flow Rates

Plants are frequently operated at flow rates other than design capacity. They may be turned down to considerably less than capacity or pushed above it by eliminating bottlenecks. Either condition can cause corrosion problems.

In an $H_2SO_4$ plant, for example, the last 150 mm (6 in.) of the steel waste heat boiler tubes were safe-ended with alloy 20Cb-3 stainless steel to protect against dew-point corrosion. (Safe ending is the welding of a length of corrosion-resistant tubing to the end of a less resistant material.) Unfortunately, the steel tubes corroded upstream of the alloy. The process was not operated within reasonable design limits. Corrosion resistance in this case would have required 1.8 m (6 ft) rather than 150 mm (6 in.) of safe-ending because the tubes were operating at 66 °C (119 °F) below the design temperature and well below the dew point.

In another case, a five-pass Monel 400 heat exchanger was used to vaporize anhydrous hydrofluoric acid (HF). Severe corrosion occurred throughout the fifth and part of the fourth pass, with no corrosion in the first three passes. Insufficient flow caused nonvolatile acid impurities, present in the HF at part per million levels, to be concentrated in the last one-plus passes.

In a third example, plant operators decided to install a higher-capacity pump to reduce the time required to transfer a charge of 98% $H_2SO_4$ through a steel line from 1 h to 15 min. This also increased the velocity from less than 0.6 m/s (2 ft/s) to more than 1.5 m/s (5 ft/s). The line failed within a week.

In another instance, a Monel 400 shell and tube heat exchanger had given satisfactory service in an organic acid oil for more than 5 years. The exchanger was a two-pass unit with a divider plate in the bottom head. The bottom head also contained the inlet and outlet nozzles. The divider plate was gasketed to a groove in the tubesheet. The velocity through the unit was increased by increasing the pump pressure. Because it was not designed for the higher pressure, the divider plate deflected, allowing the gasket to blow out. The product bypassed the divider at high velocity, which caused the unit to fail by erosion-corrosion.

## Impurities

A principal cause of unexpected corrosion failures is the presence of small amounts of impurities in the chemical environment. Producers of $H_2SO_4$ sometimes provide facilities to recover spent acid as a service to their customers, who would otherwise have difficulty in disposing of the acid in an environmentally acceptable manner. The acid, contaminated with organic matter, is burned, and the hot gases travel through a waste heat boiler.

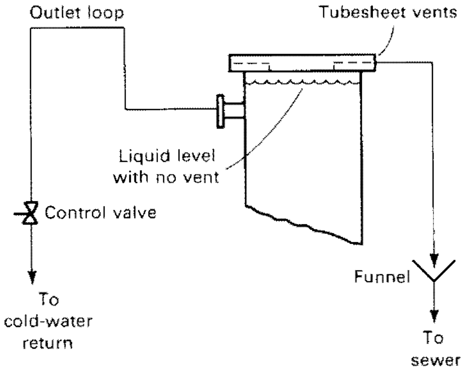

**Fig. 2** Correct piping arrangement for venting fixed tubesheet heat exchangers. Source: Ref 8

The operators of one such plant, for example, discovered that the steel tubes of their waste heat boiler had short service lives. Examination of the tubes showed that they were being attacked by a molten slag from the spent acid. Analysis showed that the slag had a high phosphate and lead content, a low melting point, and was very corrosive to steel when molten.

In another plant, zinc chloride ($ZnCl_2$) is made by dissolving zinc recovered from galvanizing operations and from other sources in HCl, treating the various chemicals, and concentrating the salt solution by evaporation. The nickel coils in a concentrating tank pitted and had short service lives. After a 30-day test, a zirconium coil appeared to be unaffected; therefore, a zirconium coil was installed in the tank. It failed after only 6 months of service. Failure was traced to a galvanizing company that had used fluorides in its flux. Zirconium is not resistant to fluorides.

At a New Jersey plant, a titanium-clad autoclave was used for the air-$HNO_3$ procedure in the manufacture of an organic acid. After several years of successful operation, the liquid-phase surfaces were found to be pitted and cratered, although they were unattacked when inspected a few weeks earlier. The presence of $H_2SO_4$ was suspected. Investigation revealed that a trailer of mixed $H_2SO_4$ and $HNO_3$ had been mistakenly unloaded into an $HNO_3$ tank.

In another example, a Monel 400 petrochemical plant extraction unit handling 40 to 65% $H_2SO_4$ and alcohol at 30 to 40 °C (85 to 100 °F) had given satisfactory service for 17 years, with a 5-year life expectancy for heat-exchanger tubes (Ref 9). Unexpectedly, tubes began to fail within 5 weeks. Replacement piping failed in as little as 3 weeks, predominately at welds. Laboratory analyses revealed that the plant solutions contained copper in quantities greater than could be explained by the simple dissolution of Monel 400. Tests showed that copper was being leached from the surfaces in a manner similar to zinc in a dezincification process.

Investigation uncovered that there had been a change in the feedstock supply. The new supply was contaminated with a few parts per million of copper ions. This contamination initiated the corrosion process, which fed upon itself by leaching more copper ions from the surface of the Monel 400.

In a similar case, a Monel 400 isomerization reactor was built based on laboratory corrosion tests and plant tests, with corrosion coupons in different locations in a glass-lined isomerizer (Ref 6). The process involved heating terpenes in the presence of $H_2SO_4$, followed by decantation, with the acid layer returned to the reactor. Precautions were taken to provide a nonaerated system by using a nitrogen blanket.

Shortly after the Monel 400 reactor was installed, the $H_2SO_4$ was found to be discolored, and excessive corrosion was discovered. Successive isomerizations using the recycled $H_2SO_4$ had caused a buildup of cupric ion ($Cu^{2+}$). Sulfuric acid with 0.5 ppm or more $Cu^{2+}$ ion will cause autocatalytic destruction of Monel 400, as was found in the earlier case. The copper can come from an outside source, excessive corrosion, or buildup of corrosion products from recycling. Once started, this reaction is almost impossible to stop, because the Monel 400 surfaces become a ready source of more copper.

At another plant, 20Cb-3 stainless steel piping had been used for many years to handle denitrated 80% $H_2SO_4$ at 50 °C (120 °F). Unexpectedly, a number of failures occurred. Potentiostatic studies, using diluted reagent grade acid, showed that 20Cb-3 stainless steel should be passive under these conditions. The plant operators, some distance from the laboratory, continued to complain about the shortened service life of the piping, and plant acid was eventually shipped to the laboratory. The potentiostatic plot showed borderline active-passive behavior. Further studies showed that an extremely small amount of $HNO_3$ present in the denitrated acid caused the unstability and that the absence of all $HNO_3$ or the presence of more than a critical amount promoted passivity. The efficient, but not perfect, operation of the denitrating system caused the corrosion.

## Water

One of the most important process variables, from the corrosion viewpoint, is the amount of water in a process stream. The water may be present as water vapor in a gas stream or may be soluble. Water is most likely to contribute to corrosion when it is present as a separate liquid phase, particularly in the presence of hydrogen chloride ($HCl \cdot H_2O$), which has a great affinity for water (Fig. 3).

When the water is present as vapor, it is likely to condense at cold spots, such as pipe supports welded directly to process piping or in nozzles in the top or vapor phase of reactors, even though the lines and nozzles are insulated. Hydrogen chloride raises the dew point. Chlorinations are a particular problem for several reasons. Commercial chlorine contains variable amounts of water, up to 50 ppm or more, because the solubility limit of water in HCl is about 200 ppm at room temperature. The $HCl \cdot H_2O$ is about 200 ppm at room temperature. The $HCl \cdot H_2O$ formed during chlorinations reduces the solubility of water in chlorine to well below 50 ppm at room temperature (Fig. 3). The condensate of water-chlorine-$HCl \cdot H_2O$ is corrosive to all metals except tantalum.

For example, stainless steel reactors are used in the manufacture of fluorinated hydrocarbon refrigerants from chlorinated hydrocarbons by reacting them with HF in the presence of chlorine and a catalyst. After many years of service, the cover of a reactor exhibited chloride SCC just below two nozzles. Higher-than-normal water content in one or more of the reactants had caused condensation in the blind nozzles. The condensate evaporated when it ran onto the cover, causing concentration of chloride salts and subsequent chloride SCC. Steam tracing of the nozzles (Fig. 4) prevented condensation and corrected the problem.

In the same plant, a column was installed to recover excess chlorine from a supposedly dry process stream containing fluorocarbon, $HCl \cdot H_2O$, traces of HF, and chlorine. The brine-cooled condenser had 20Cb-3 stainless steel tubes. A few weeks after start-up, the tubes failed from process-side corrosion. Attack occurred preferentially on the coldest side of the tubes facing the brine flow. The unit was temporarily retubed with heavy-wall steel tubes. After a few weeks, these tubes leaked. The brine was drained from the shell, and almost immediately, the steel tubes caught on fire. The hydrogen generated by corrosion of the outside of the tubes reacted exothermically with the chlorine present, raising the temperature of the tubes to the ignition temperature of steel in chlorine (about 250 °C, or 480 °F). The process of removing chlorine by distillation was abandoned. No metallic heat-exchanger tube is available that will resist aqueous HCl saturated with chlorine in the presence of acid fluorides.

The trace amounts of water in the stream fed to the column were not detectable by the analytical methods used at the plant; the water was present in small but variable amounts. The presence of large amounts of $HCl \cdot H_2O$ raised the dew point enough to cause the water to condense on the coldest parts of the tube walls.

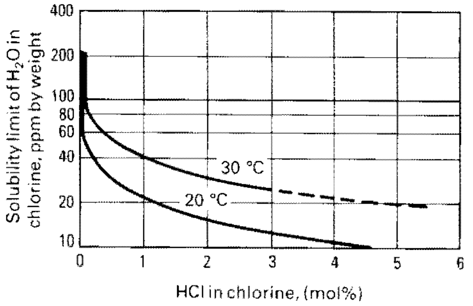

**Fig. 3** Effect of HCl on solubility of water in chlorine. Source: Ref 10

# Cleaning Process Equipment

Process equipment and piping must be cleaned to prevent contamination of a process or product, to improve the operation of a process, to reduce the opportunity for premature failure, and to prepare equipment for inspection. However, equipment should be cleaned only for good reason. In addition to the cost of unnecessary cleaning, problems may be introduced. For example, most chemical cleaning processes cause some metal loss. In other cases, washing before cleaning may cause accelerated corrosion, such as during the preparation of a concentrated $H_2SO_4$ storage tank for inspection. Other potential problems are:

- Difficulties associated with pumping hot corrosives through temporary connections
- Difficulties associated with a crowded work space, for example, during a turnaround
- The need to dispose of wastes
- The possibility of generating toxic or flammable by-products during cleaning

There are four types of equipment cleaning: preoperational, chemical, mechanical, and online. These must be evaluated for each job in order to select the most cost-effective. To make a sound evaluation, the deposit to be removed must be thoroughly characterized.

## Fouling of Equipment

Deposits that cause fouling accumulate in equipment and piping and impede heat transfer or fluid flow or cause product contamination. Deposits may be organic, inorganic, or a mixture of the two. Scales are crystalline deposits that precipitate in a system (Table 2). There are four principal sources of deposits: water-side, fire-side, process-side, and preoperational.

**Water-side deposits** are of many types. Hardness (calcium and magnesium) based deposits and iron oxide are the most common water-side deposits and often affect boilers and cooling systems. Process and oil leaks can foul boilers and cooling systems. Biofouling, mud, and debris are often found in cooling systems. Treatment chemicals, if not properly controlled, can add to deposits and scale. Silica can form hard, adherent deposits in boilers, steam turbines, and cooling systems. Corrosion products can add to deposits.

**Fire-side deposits** can be extremely corrosive. Slags from burning oil and wastes can corrode boiler equipment if they become moist. Fly ash deposits can accumulate in coal-fired boilers. Gas-fired boilers are generally clean. Some compounds that are burned in incinerators or waste heat boilers can seriously corrode or erode boiler tubes.

**Process-Side Deposits.** There are many types of process-side deposits. Organic residues, tars, and coke are common in the petroleum and petrochemical industries. Iron oxide and sulfides are often present in these organic deposits. Sulfate deposits are common in $H_2SO_4$ plants. Iron-, copper-, and nickel-containing deposits often occur in HF plants.

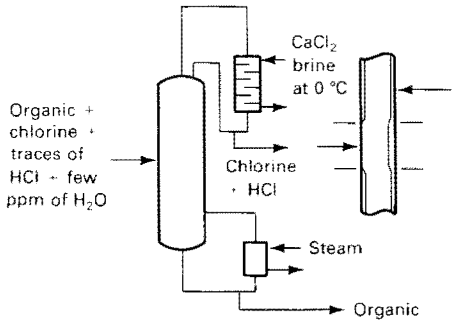

**Fig. 4** Arrangement of chlorine recovery column and corrosion pattern on condenser tubes. Source: Ref 11

### Table 2 Summary of common types of scale-forming minerals

| Scale | Chemical formula |
|---|---|
| **General** | |
| Sodium iron silicate | $NaFe(SiO_3)_2$ |
| Barium sulfate | $BaSO_4$ |
| Sodium aluminum silicate | $NaAl\ Si_2O_6 \cdot H_2O$ |
| Aragonite (rhombic crystals) | $CaCO_3$ |
| Calcium carbonate—(hexagonal crystal) | $CaCO_3$ |
| Calcium sulfate | $CaSO_4$ |
| Magnesium carbonate and hydroxide | $3MgCO_3 \cdot Mg(OH)_2 \cdot 3H_2O$ |
| Calcium phosphate | $Ca_{10}(OH)_2(PO_4)_6$ |
| Iron oxide | Alpha FeO (OH) |
| Iron oxide—magnetite | $Fe_3O_4$ |
| Iron oxide—red | $Fe_2O_3$ |
| Iron chrome spinels | $CrFe_2O_4$ |
| Iron sulfide | FeS |
| Magnesium hydroxide | $Mg(OH)_2$ |
| Magnesium oxide | MgO |
| Manganese dioxide | $MnO_2$ |
| Aluminum silicate | $Al_2O_3 \cdot 4SiO_2 \cdot 4H_2O$ |
| Sodium aluminum silicate | $Na_8Al_6Si_6O_{24} \cdot SO_4$ |
| Calcium sodium silicate | $4CaO \cdot Na_2O \cdot 6SiO_2 \cdot H_2O$ |
| Magnesium silicate | $Mg_3Si_2O_7 \cdot 2H_2O$ |
| Silica | $SiO_2$ |
| Sodium aluminum silicate | $Na_8Al_6Si_6O_{24} \cdot Cl_2$ |
| Magnesium iron aluminum silicate | $(Mg,Fe)_3(Si,Al)_4O_{10}(OH)_2 \cdot 4H_2O$ |
| Calcium silicate | $5CaO \cdot 5SiO_2 \cdot H_2O$ |
| **Copper or copper alloy equipment** | |
| Copper iron sulfide | CuFeS |
| Copper sulfide | CuS and $Cu_2S$ |
| Basic copper chloride | $CuCl_2 \cdot 3Cu(OH)_2$ |
| Copper oxide | $Cu_2O$ |
| Chalcopyrite | $CuFeS_2$ |
| Beta zinc sulfide | ZnS |
| Green basic carbonate | $CuCO_3Cu(OH)_2$ |

Organic deposits may develop through the polymerization of leaking gases or from the decomposition of process constituents. In some cases, organics help to bond inorganic deposits, such as iron oxides or sulfides.

Some process-side deposits are pyrophoric when exposed to air or oxygen. The most common is iron sulfide, which is likely to be found in natural-gas- and petroleum-refining processes or when aqueous solutions of hydrogen sulfide ($H_2S$) are dried in the absence of air.

**Preoperational deposits** are formed during the fabrication and erection of process equipment and piping. In addition to mill scale residues, metal surfaces become coated with dirt, oil, grease, weld spatter, pipe-threading compound, protective shop coatings, and corrosion products.

Highly alloyed materials, such as stainless steels, nickel-base alloys, reactive metals, or high-temperature alloys, may become contaminated with iron from tooling; zinc, cadmium, and aluminum from scaffolding; and zinc, sulfur, and chlorine in certain marking materials. These elements can cause corrosion or embrittlement.

## Critical Equipment Areas

Requirements for cleaning will vary with the type of equipment. The operating characteristics and design must be assessed before selecting a cleaning method.

### Table 3 Components of boiler deposits

| Mineral | Formula | Nature of deposit | Usual location and form |
|---|---|---|---|
| Acmite | $Na_2O \cdot Fe_2O_3 \cdot 4SiO_2$ | Hard, adherent | Tube scale under hydroxyapatite or serpentine |
| Alpha quartz | $SiO_2$ | Hard, adherent | Turbine blades, mud drum, tube scale |
| Amphibole | $MgO \cdot SiO_2$ | Adherent binder | Tube scale and sludge |
| Analcite | $Na_2O \cdot Al_2O_3 \cdot 4SiO_2 \cdot 2H_2O$ | Hard, adherent | Tube scale under hydroxyapatite or serpentine |
| Anhydrite | $CaSO_4$ | Hard, adherent | Tube scale, generating tubes |
| Aragonite | $CaCO_3$ | Hard, adherent | Tube scale, feed lines, sludge |
| Brucite | $Mg(OH)_2$ | Flocculent | Sludge in mud drum and water wall headers |
| Copper | Cu | Electroplated layer | Boiler tubes and turbine blades |
| Cuprite | $Cu_2O$ | Adherent layer | Turbine blades, boiler deposits |
| Gypsum | $CaSO_4 \cdot 2H_2O$ | Hard, adherent | Tube scale, generating tubes |
| Hematite | $Fe_2O_3$ | Binder | Throughout boiler |
| Hydroxyapatite | $Ca_{10}(PO_4)_6(OH)_2$ | Flocculent | Mud drum, water walls, sludge |
| Magnesium phosphate | $Mg_3(PO_4)_2$ | Adherent binder | Tubes, mud drum, water walls |
| Magnetite | $Fe_3O_4$ | Protective film | All internal surfaces |
| Noselite | $4Na_2O \cdot 3Al_2O_3 \cdot 6SiO_2 \cdot SO_4$ | Hard, adherent | Tube scale |
| Pectolite | $Na_2O \cdot 4CaO \cdot 6SiO_2 \cdot H_2O$ | Hard, adherent | Tube scale |
| Serpentine | $3MgO \cdot 2SiO_2 \cdot H_2O$ | Flocculent | Sludge |
| Sodalite | $3Na_2O \cdot 3Al_2O_3 \cdot 6SiO_2 \cdot 2NaCl$ | Hard, adherent | Tube scale |
| Xonotlite | $5CaO \cdot 5SiO_2 \cdot H_2O$ | Hard, adherent | Tube scale |

**Columns.** The two critical areas for deposit formation in a column are at the trays, where vapor passes through a valve, sieve, flapper, or riser, and in the flash zone, where vapor condenses. Operating history sometimes indicates which areas require cleaning; for example, the vapor line is suspect if the column vapor rate becomes limiting. Inspection is necessary to determine the extent and location of fouling.

**Glass-lined vessels** require special attention when their water jackets are chemically cleaned. The recommendations of the manufacturer must be followed. The most commonly recommended cleaning solution is dilute alkaline sodium hypochlorite (NaClO) (Ref 12). If strong acids are used, atomic (nascent) hydrogen formed by corrosion diffuses into the shell and recombines as hydrogen molecules at the glass/metal interface, which causes spalling of the glass.

**Oxygen, chlorine, and fluorine piping systems** must be free of organic contaminants. Organic materials, particularly hydrocarbon greases and oils, react violently with these chemicals. Preoperational cleaning is mandatory in such cases (Ref 13). After cleaning, the lines should be blown dry, using oil-free nitrogen or air.

## Identification of Deposits

To select an effective cleaning procedure, the deposit must be characterized, or identified. The sample should represent the deposit in the most critical fouling area. For exchangers and boilers, this is the highest heat transfer section. Expediency should not dictate the location of the sample. A cleaning procedure should not be based on a sample of loose deposit from a noncritical area, because the sample at this location may not be representative. Table 3 lists some common components of boiler deposits.

When removed by scraping, the samples should be as intact as possible. They should be removed to the base metal, taking care not to introduce any metallic chips from the blade or substrate. Thickness, density, porosity, type (homogeneous or layered), and color should be noted.

When only a limited amount of deposit is available, replication tape is a useful method of removing it. Polyvinyl chloride (PVC) or other chloride-containing tapes should not be used on stainless steels, which are susceptible to chloride pitting and stress cracking.

Many analytical techniques are used to characterize deposit samples. Typical methods include x-ray diffraction, optical emission spectroscopy, and x-ray spectrometry. Most chemical cleaning contractors, water treatment supplies, and analytical laboratories have the facilities to characterize deposits.

## Preoperational Cleaning

Unlike process- or water-side deposits, the types of deposits in original equipment are easily categorized (Ref 14). Preoperational cleaning should include consideration of the degree of cleanliness required and the material of construction. Areas where preoperational cleaning is used include:

- Process equipment start-up, boilers, and steam-generating and compression systems
- Lubricating oil systems before oil flushing
- Critical services, such as oxygen, chlorine, or fluorine piping
- Water treatment and inhibition programs

**Boilers** are cleaned to remove oils, grease, and mill scale. When boilers are coated with heavy protective greases, two-stage cleaning (for organic and inorganic deposit removal) should be used. A degreasing step using alkaline boilout solutions or emulsions is first used. Common second-step solvents include chelants, organic acids, or HF.

**Columns** contain similar contaminants. They are cleaned by fill and soak, cascade, or foam methods, using solvents similar to those used for boilers. The design of the column may eliminate certain methods, such as cascade cleaning for a packed column.

**Shell and Tube Heat Exchangers.** The most serious fouling is found on the interior (tube side) or exterior (shell side) of the tubes. Other locations are on the shell side at baffles or drain nozzles. Figure 5 shows a fouled heat-exchanger tube bundle.

The head should be removed for inspection if tube-side fouling of the tubes is suspected. The shell is more difficult to inspect, unless the tube bundle is removable, but limited information may be gained through nozzles.

Heat-exchanger tubes may be cleaned mechanically or chemically. Mechanical cleaning may damage tubes. Individual tubes should not be steam blown, because this may damage rolled tube joints. Tubes should not be hammered with any metallic tool, and scraping or rodding should be done with care because any scoring or gouging can lead to premature failure. High-pressure and ultrahigh-pressure water cleaning are preferred.

Chemical cleaning methods use circulation, fill and soak, or foam. However, severely blocked tubes may resist the entry of the cleaning agent or may retain it beyond the neutralization step of the cleaning process, leading to corrosion during shutdown or in service.

Heat-exchanger shells are normally chemically cleaned using the circulation or the fill and soak method. If the tube bundle is removable, mechanical cleaning with high-pressure or ultrahigh-pressure water is a good technique.

**Boilers.** Typical water-side deposits found in boilers are listed in Table 3. Deposits vary depending on raw water composition, feedwater treatment, and operating pressure.

The heaviest deposition occurs in tubes with the highest heat input, an area that may be physically impossible to inspect. A tube section can be taken from the area where deposition is known to be heaviest in order to characterize the deposit. Although various yardsticks (in grams of scale per square foot) have been proposed for determining the need to clean, each case should be individually evaluated. Factors to be considered are the degree of fouling, the type of service, the reliability required, the operating history, and future operation.

Chemical cleaning of the water side is generally more effective than mechanical cleaning, particularly in designs with heavily swaged tubes and tight bends. Preoperational cleaning of boilers must be conducted to allow the steel surface to develop a protective film of magnetite ($Fe_3O_4$) when the boiler is put into service and to remove mill scale.

**Furnaces.** The external fouling of furnace tubes depends on the nature of the fuel. Oil-burning furnaces usually have significantly more deposit formation and corrosion problems than coal-burning types, while natural-gas-burning furnaces have very few problems.

Slag accumulates when metallic salts and oxides are vaporized and condense in various parts of the furnace. Because its melting point is relatively low, the slag forms a sticky corrosive deposit of various salts, primarily sodium and vanadium. These slags should be mechanically removed by chipping or dry sandblasting. Wet cleaning methods may cause acid formation. For internally coked tubes, steam-air decoking or mechanical cleaning is preferred.

**Pumps and Compressors.** Cooling water jackets are often chemically cleaned to remove iron oxide, water-formed scale, and possible oil infiltration. All loose material is first removed by opening the clean-out plates and flushing. A two-stage chemical cleaning process is then used, first to dissolve any organic deposits and then to remove inorganic scales. The acidic cleaner selected for inorganic scales should be compatible with the materials of construction.

**Piping** may contain various contaminants, including dirt, loose paint, sand and grit, varnish, grease and oils, weld spatter, mill scale, and rust. Piping should first be inspected and all construction debris removed. Dirt, loose paint, sand, and grit are removed by flushing with clean water or blowing with dry compressed air or steam. Varnish, grease, and oils are removed by steam blasting with detergent or hot water containing an alkaline degreasing agent. Mechanical cleaning may be required, depending on the amount of weld spatter, mill scale, and rust. The piping may then be chemically cleaned if necessary, using organic acids and chelants, followed by neutralizing and passivating.

Moisture removal may be required for such specific applications as compressor or refrigeration piping. When all traces of moisture must be removed, the system can be filled with alcohol, evacuated to evaporate the alcohol, then flushed with an inert gas.

Piping carrying oxygen, chlorine, and fluorine requires stringent cleaning to remove organic contamination. No organic-containing residues can be permitted (Ref 13).

## Chemical Cleaning

Chemical cleaning is the use of chemicals to dissolve or loosen deposits from process equipment and piping. It offers several advantages over mechanical cleaning, including more uniform removal, no need to dismantle equipment, lower overall cost (generally), and longer intervals between cleanings. In some cases, chemical cleaning is the only practical method.

The primary disadvantages of chemical cleaning are the possibility of excessive equipment corrosion and solvent disposal. Chemical cleaning solvents must be assessed in a corrosion test program before their field acceptance.

Chemical cleaning is performed by a contractor who specializes in this work. Some cleaning procedures are protected by patents.

### Chemical Cleaning Methods

There are six major chemical cleaning methods: circulation, fill and soak, cascade, foam, vapor phase organic, and steam-injected cleaning. A seventh variation is discussed in the section "On-Line Cleaning" in this article.

**Fig. 5** Fouled heat-exchanger tube bundle

**Circulation,** the most common method, is applied to columns, heat exchangers, cooling water jackets, and so on, where the total volume required to fill the equipment is not excessive. The equipment is arranged such that it can be filled with the cleaning solution and circulated by a pump to maintain flow through the system. Movement of solution through the equipment greatly assists the cleaning action. As cleaning progresses, temperature and concentration are measured in order to monitor the progress. The cleaner may be replenished (sweetened) occasionally to maintain efficiency. Corrosion coupons or on-line monitoring determines the effect of the cleaning chemicals on the equipment materials.

With circulation cleaning, the rate of flow through the equipment is critical. Large-diameter connections are preferred, and a high-capacity pump may be necessary to produce the required circulation. After cleaning, the equipment is drained, neutralized, flushed, and passivated.

**Fill and soak cleaning** involves filling the equipment with the cleaner and draining it after a set period of time. This may be repeated several times. The equipment is then water flushed to remove loose insolubles and residual chemicals.

Fill and soak cleaning offers limited circulation. The poor access of fresh cleaning solution to the metal, together with the inability to maintain solution temperature, may cause the cleaning action to cease.

The method is limited to relatively small equipment containing light amounts of highly soluble fouling and to equipment in which circulation cannot be properly controlled. Because good agitation is achieved only during the flushing stage, flushing should be as thorough as possible. Circulation and fill and soak cleaning are sometimes used alternately.

**Cascade cleaning,** a modification of the circulation method, is usually applied to columns with trays. The column is partially filled, and the liquid is continuously drawn from the reservoir and pumped to the highest point. The liquid then cascades down through the column, cleaning surfaces as it passes over them. The liquid draw-off point must be suitably located to avoid recirculation of loosed foulants. High-capacity pumps and large-diameter piping are required to achieve the necessary transfer of liquid to produce a flow pattern that will contact all fouled surfaces within the column.

The cascade method is primarily used in large columns and is suitable for most types, except for packed columns. Cleaning is not effective in inaccessible areas, such as the underside of trays, due to poor contact with the cleaning solution. Contact may be improved by injecting air or nitrogen at the base of the column. If steam is used to heat the chemicals, the location of the steam injection point should not lead to localized overheating. High temperature can also increase corrosion in the vapor space.

**Foam cleaning** uses a static foam generator that employs air or nitrogen to produce a foamed solvent. Foam stabilizers are required to prolong foam life and increase the effectiveness of the cleaning chemicals. Foam cleaning is used on equipment that cannot support full or partial filling with liquid. Foam cleaning results in significantly less liquid volume for disposal compared with other methods.

**Vapor phase organic cleaning** is used in equipment that is difficult to clean with liquids. For example, vaporized organic solvents are used to remove organic deposits from columns. The organic solvent is vaporized, injected into the top of the column, condensed, collected in a circulation tank, and revaporized.

The principal concerns are the handling and disposal of the solvent and its flammability (when applicable). The recirculating tank should be purged and blanketed with nitrogen, fitted with an adequate venting and condensing system, and grounded to prevent accumulation of an electrical charge.

**Steam-injected cleaning** involves the injection of a concentrated mixture of cleaning chemicals into a stream of fast-moving steam. The steam is injected at one end of the system and condensed at the other. The steam atomizes the chemicals, increasing their effectiveness, and ensures good contact with the metal surface.

Steam-injected cleaning is very effective for critical piping systems. As with foam cleaning, the method produces a relatively low amount of liquid for disposal.

## Chemical Cleaning Solutions

A wide variety of standard chemical cleaning solutions are available (Table 4). Many proprietary solutions are based on these chemicals. Some are patented or involve patented equipment. Chemical cleaning contractors are the best source of information on standard or patented techniques.

Most chemical cleaning contractors calculate the concentration of chemicals in weight percent, but some use volume percent. The user must be aware of this. For example, a 10 wt% solution of HCl is equivalent to 25 vol% of the normal 30% concentrated HCl.

Chemical cleaning solutions include mineral acids, organic acids, bases, complexing agents, oxidizing agents, reducing agents, and organic solvents. Inhibitors and surfactants are added to reduce corrosion and to improve cleaning efficiency. Following the cleaning cycle, a passivating agent can be introduced to prevent further corrosion or to remove trace ion contamination.

Mineral acids are strong scale dissolvers. They include HCl, hydrochloric/ammonium bifluoride ($HCl/NH_4HF_2$), sulfamic acid ($NH_2SO_3H$), $HNO_3$, phosphoric acid ($H_3PO_4$), and $H_2SO_4$.

Organic acids are much weaker. They are often used in combination with other chemicals to complex scales. An advantage of organic acids is that they can be disposed of by incineration. They include formic (HCOOH), hydroxyacetic-formic, acetic ($CH_3COOH$), and citric acid.

Bases are principally used to remove grease or organic deposits. They include alkaline boilout solutions and emulsions.

Complexing agents are chemicals that combine with metallic ions to form complex ions, which are ions having two or more radicals capable of independent existence. Ferricyanide $[Fe(CN_6)]^{4-}$ is an example of a complex ion. Complexing agents are of two types: chelants and sequestrants. Chelants complex the metallic ion into a ring structure that is difficult to ionize, and sequestrants complex the metallic ion into a structure that is water soluble.

Oxidizing agents are used to oxidize compounds present in deposits to make them suitable for dissolution. They include chromic acid ($H_2CrO_4$), potassium permanganate ($KMnO_4$), and sodium nitrite ($NaNO_2$).

Reducing agents are used to reduce compounds in deposits to a form that makes them suitable for dissolution and to prevent the formation of hazardous by-products. They include sodium hydrosulfite ($NaHSO_2$) and oxalic acid.

Inhibitors are specific compounds that are added to cleaning chemicals to diminish their corrosive effect on metals. Most inhibitors are proprietary, and recommendations for their use are available from the supplier.

Surfactants are added to chemical cleaning solutions to improve their wetting characteristics. They are also used to improve the performance of inhibitors, emulsify oils, improve the characteristics of foaming solvents, and act as detergents in acid and alkali solutions. As with inhibitors, most surfactants are proprietary products.

**Hydrochloric acid** is the least expensive and most widely used solvent for water-side deposits on steels. The concentration and temperature vary from 5 to 15% and 50 to 80 °C (120 to 175 °F). The acid must be replenished if the concentration falls below 4%.

Hydrochloric acid must always be used with a filming inhibitor to minimize corrosion. Inhib-

**Table 4 Scales and solvents**

| Scale component | Solvent(a) | Testing conditions |
|---|---|---|
| Iron oxide | 5 to 15% HCl | 65-80 °C (150-175 °F) |
| $Fe_3O_4$ (magnetite or mill scale) | 2% hydroxyacetic/1 formic | 65-80 °C (150-175 °F) circulating |
| $Fe_2O_3$ (red iron oxide or red rust) | Monoammoniated citric acid | 85-105 °C (185-220 °F) circulating |
| | Ammonium EDTA | 75-150 °C (170-300 °F) circulating |
| | EDTA organic acid mixures | 40-65 °C (100-150 °F) circulating |
| Copper, oxides | Copper complexor in HCl | 65 °C (150 °F) |
| | Ammoniacal bromate | 50-85 °C (120-185 °F) |
| | Monoammoniated citric acid | 60-85 °C (140-185 °F), pH 9 to 11 |
| | Ammonium persulfate | Below 40 °C (100 °F) |
| | Ammonium EDTA | 65-85 °C (150-185 °F), pH 9 to 11 |
| Calcium carbonate | 5 to 15% HCl | Preferably not above 65 °C (150 °F) |
| | 7 to 10% sulfamic acid | Do not exceed 60 °C (140 °F) |
| | Sodium EDTA | Circulate at 60-150 °C (150-300 °F) |
| Calcium sulfate | Sodium EDTA | Circulate at 60-150 °C (150-300 °F) |
| | 1% NaOH-5% HCl | Circulate at 50-65 °C (120-150 °F) |
| | EDTA organic acid mixtures | 40-65 °C (100-150 °F) circulating |
| Hydroxyapatite of phosphate compounds ($Ca_{10}(OH)_2 \cdot (PO_4)_6$) | 5 to 10% HCl | Preferably above 65 °C (150 °F) |
| | Sodium EDTA | Undesirable to add fluoric<br>Circulate at 65-150 °C (150-300 °F) |
| | Sulfamic acid 7 to 10% | Do not exceed 60 °C (140 °F) |
| Silicate compounds, for example, acmite ($NaFe(SiO_3)_2$) and analcite ($NaAlSi_2O_6 \cdot H_2O$) | Prolonged treatment with 0.5 to 1% soda ash at 345 kPa (50 psi), follow with HCl containing fluoride | Alkaline preboil at 345-690 kPa (50-100 psi) for 12 to 16 h |
| Pedtolite ($4Ca \cdot Na_2O \cdot 6SiO_2 \cdot H_2O$)<br>Serpentine ($Mg_3Si_2O_7 \cdot 2H_2O$) | HCl containing ammonium bifluoride | 65-80 °C (150-175 °F) |
| Sulfides ferrous: troilite (FeS) and pyrrhotite (FeS) | HCl, inhibited | Heat slowly to avoid sudden release of $H_2S$ toxic gas |
| Disulfides: $FeS_2$, marcasite and $FeS_2$, pyrite | Chromic acid, followed by HCl | Boiling 7 to 10% chromic acid, followed by inhibited HCl |
| Organic residues<br>Organo lignins<br>Algae<br>Some polymeric residues | Potassium permanganate, followed by HCl containing oxalic acid | Circulate at 100 °C (210 °F), add 1 to 2% $KMnO_4$ solution. Oxalic acid added to HCl controls release of chlorine toxic gas |

(a) The chemicals listed are to be considered possible solvents only. There are many alternative solvents for each deposit listed.

ited HCl is usually suitable for cleaning carbon or alloy steel, cast iron, brasses, bronzes, copper-nickel alloys, and Monel 400.

Hydrochloric acid, even inhibited, is not recommended for cleaning stainless steels, Incoloy 800, Inconel 600, aluminum, or galvanized steel. Its applicability for cleaning titanium or zirconium depends on the oxidizing contaminants present in the acid.

**Hydrochloric Acid/Ammonium Bifluoride.** The addition of about 1% $NH_4HF_2$ releases HF, which not only improves the potency of the HCl but, more important, also aids in dissolving silicate scales. A filming inhibitor should be added. Materials compatibility is similar to that of HCl except that titanium, zirconium, or tantalum should never be exposed to an acid containing $NH_4HF_2$.

**Hydrofluoric acid** can be used as a preoperational cleaner to remove mill scale, at 1 to 2% and 80 °C (175 °F). It is not widely used in North America, because of unfamiliarity and perceived handling difficulties.

**Sulfuric acid** is used on a limited scale, from 5 to 10% at temperatures up to 80 °C (180 °F). Although inexpensive, it has several disadvantages, including the extreme care required during handling and the precipitation of calcium sulfate ($CaSO_4$) with deposits containing calcium salts.

When inhibited, $H_2SO_4$ may be used on carbon steel, austenitic stainless steels, copper-nickel alloys, admiralty brass, aluminum bronze, and Monel 400. Sulfuric acid should not be used on aluminum or galvanized steel.

**Nitric acid** is primarily used for cleaning stainless steel, titanium, or zirconium. It is an extremely strong oxidizer and is rarely used, because of handling difficulties. Conventional inhibitors, detergents, and other additives are not stable in $HNO_3$. It should not be used on carbon steel, copper alloys, or Monel 400. Piping for handling $HNO_3$ should be lined with stainless steel or polytetrafluoroethylene (PTFE).

**Phosphoric acid** is sometimes used at 2% and 50 °C (120 °F) for 4 to 6 h to pickle and passivate steel piping. It is not as effective as HCl in removing iron oxide scale, but is preferred for cleaning stainless steels.

Phosphoric acid was originally used for removing mill scale from new boilers because it also helped passivate the surface. It is also used to brighten aluminum.

**Sulfamic acid** is used from 7 to 10% up to 60 °C (140 °F) to remove calcium and other carbonate scales and also iron oxides. It is not as effective as HCl on iron oxides. If $NH_2SO_3H$ is heated above 75 to 80 °C (170 to 180 °F), it begins to hydrolyze to $H_2SO_4$, greatly reducing its effectiveness. If mixed with sodium chloride (NaCl), HCl is slowly released, and the mixture is more effective in removing iron oxide deposits.

Although relatively expensive, $NH_2SO_3H$ is reasonably safe to handle and may be transported solid and diluted on-site. This greatly facilitates handling and makes it preferred for in-house cleaning.

Inhibited $NH_2SO_3H$ can be used to clean carbon steel, copper, admiralty brass, cast iron, and Monel 400. Without the chloride addition, it is effective on most stainless steels. The addition of ferric ion ($Fe^{3+}$) is used to protect 400-series stainless steels.

**Formic acid** is generally used as a mixture with citric acid or HCl because alone it is unable to remove iron oxide deposits. Formic acid can be used on stainless steels, is relatively inexpensive, and can be disposed of by incineration.

**Hydroxyacetic-formic acid** is used as a 2:1% hydroxyacetic-formic mixture at 80 to 105 °C (180 to 220 °F) to remove iron oxide and calcium deposits. When added, $NH_4HF_2$ will also remove silica-containing deposits. The acid must be inhibited for use on carbon steel.

Hydroxyacetic-formic acid is especially advantageous in nondrainable sections of reactors or boilers, because it may be decomposed to harmless by-products by heating to 150 to 175 °C (300 to 350 °F). The primary use of this cleaner is to remove $Fe_3O_4$ in critical boilers and in superheater sections of other boilers. It can be used on stainless steels and is applicable in mixed-metal systems.

**Acetic acid** is used to clean calcium carbonate scales, but it is ineffective in removing iron oxide deposits. Weaker than formic acid, it may be preferred where extremely long contact times are necessary.

**Citric acid** at 3% and 65 °C (150 °F) is used to clean iron oxide deposits from aluminum or titanium. Monoammoniated citric acid is effective in removing iron oxide deposits at pH 3.5. By adjusting the pH to 9 and adding an oxidant, such as $NaNO_2$, copper can be removed with the same solution. This technique is patented. Citric acid is also used to scavenge residual iron oxide from boilers after HCl cleaning in order to facilitate passivation treatment.

**Alkaline boilout solutions** are used to emulsify and disperse various oils, greases, and organic contaminants from new steel or stainless steel equipment, such as drum boilers and retubed heat exchangers. Examples are combinations of NaOH, trisodium phosphate ($Na_3PO_4$, or TSP), sodium carbonate ($Na_2CO_3$, or soda ash), and sodium silicate ($Na_2SiO_3$). These are added in concentrations of 0.5 to 1% and boiled or circulated for many hours, often under pressure. A low-sudsing dishwasher-type detergent is usually added. Proprietary compositions are available from suppliers.

Some operators avoid using NaOH because of the possibility of SCC (caustic embrittlement) of steel. A controlled amount of sodium nitrate ($NaNO_3$) may be added to the NaOH to inhibit cracking.

**Alkaline emulsions** are used to remove coatings of oily material from inorganic deposits that prevent their dissolution by cleaning chemicals. For light-bodied oil, a $Na_3PO_4$-surfactant combination may be circulated for a few hours at 95 °C (200 °F) to remove it. The equipment is then flushed with water.

**Chelants** will complex such deposits as iron oxide or copper. They include ethylenediaminetetraacetic acid (EDTA), citric acid, gluconic acid, and nitroacetic acid.

Chelating agents must by pH adjusted by using acids or alkalis, depending on the type of chelating agent and the scale constituents to be complexed. For example, under alkaline conditions, the sodium salt of EDTA will complex calcium-containing deposits, but it will not remove iron oxide.

The most common chelating agent is the ammonium salt of EDTA, which is used to remove $Fe_3O_4$ scale from boilers at 75 to 150 °C (170 to 300 °F). Following this, the solution is oxidized using air to remove copper. This solution must be inhibited to prevent corrosion of the steel.

Some chelating processes are patented, such as the Alkaline Copper Removal Process (Ref 15), which uses triammonium EDTA at a pH of 9.2 for removing copper and iron oxides from a boiler while it is intermittently fired. Another patented chelating agent is the Citrosolv Process (Ref 16), which uses inhibited ammoniated citric acid to dissolve iron oxides and copper in utility steam generators. Chelating agents can often be incinerated, minimizing disposal problems.

Copper complexers, such as thiourea and hexhydropyrimidine-2-thione, are added to HCl when both iron and copper oxide deposits are present. The complexers help dissolve the copper and prevent it from plating out on steel in the system.

**Chromic acid** is used at 7 to 10%, primarily to remove iron pyrite and certain carbonaceous deposits that are insoluble in HCl. The iron pyrite is oxidized to the sulfate without the evolution of $H_2S$. With carbonaceous deposits, $H_2CrO_4$ degrades the tar that holds the deposits together.

Chromic acid is a strong oxidizing agent and should not be used on copper, brass, bronze, aluminum, zinc, or cast iron. It is acceptable on carbon steel and stainless steel. Steel piping should be used for handling it because nonmetallic hose materials, other than PTFE, are rapidly degraded.

**Caustic permanganate** is widely employed as a pretreatment in refinery-cleaning operations to remove carbonaceous deposits coupled with pyrophoric sulfides. A solution of 1% NaOH and 0.7% $KMnO_4$ is used at 65 to 80 °C (150 to 175 °F). This converts iron sulfide to iron oxide and sulfur, both of which can be removed with acid cleaning. Little or no $H_2S$ is generated. If HCl is used for the acid-cleaning step, oxalic acid should be added to reduce any chlorine gas that might be evolved upon reaction with the insoluble manganese formed during the first stage of cleaning.

**Table 5 Classification of selected corrosion inhibitors**

| Cathodic | Anodic | General adsorption |
|---|---|---|
| Alkylamines | Benzotriazole (H) | Acetylenic alcohols |
| Benzotriazole (L) | Mannich bases | Benzotriazole |
| Diphenylamine | Pyridines | Dibenzylsulfoxide |
| Thioureas (L) | Quinolines | Diphenylamine |
|  | Thiols | Furfuraldehyde |
|  | Thioureas (H) |  |

L, at low concentration; H, at high concentration

**Organic solvents** used to dissolve organic deposits include kerosene, xylene, toluene, xylene bottoms, heavy aromatic naphtha, 1,1,1-trichloroethane, N-methyl-2-pyrrolidone, alcohols, glycols, and ortho-dichlorobenzene (Ref 17).

Some solvents are strictly regulated by Environmental Protection Agency (EPA), Occupational Safety and Health Administration (OSHA), and state and local regulations. The use of any solvents should be carefully reviewed. With few exceptions, rubber hoses or rubber-lined equipment should not be used to handle organic solvents.

**Organic emulsions** are solvent-based cleaners for heavy organic deposits, such as tar, asphalts, and polymers. These solutions typically consist of an aromatic solvent, a chlorinated hydrocarbon, and emulsifying agents. The mixture should be capable of being heated to 65 to 70 °C (150 to 160 °F). A thorough rinsing step is necessary to remove the sludge left behind when the cleaning agent is drained. The possibility of hydrolysis of the chlorinated hydrocarbons prevents use of these mixtures on stainless steels.

**Passivating solutions** are used to prevent carbon steel from rusting after acid cleaning, before it is returned to service. The term passivation is also applied to procedures that are used to remove surface iron contamination from stainless steel and titanium equipment.

Most passivating solutions for carbon steel are alkaline and contain an oxidizing agent, even if it is only air. They are applied after rinsing and neutralization.

For the passivation of stainless steel and titanium, mild iron contamination may be removed by using a mixture of 1% each of citric acid and $HNO_3$. For more persistent contamination, strong $HNO_3$ solutions must be used (Ref 18).

**Corrosion inhibitors** are added to chemical cleaning agents to permit effective cleaning without excessive corrosion of the equipment. Most inhibitor formulations are organic compounds and function in three ways (Table 5):

- Cathodic inhibitors impede the cathodic half of the corrosion reaction, for example, $2H^+ + 2e^- \rightarrow H_2$
- Anodic inhibitors limit the anodic half of the corrosion reaction, for example, $Fe \rightarrow Fe^{2+} + 2e^-$
- Adsorption inhibitors form a physical barrier on the metal surface and prevent corrosion

Inhibitors must be capable of dispersing or dissolving in the chemical cleaning solution, both fresh and contaminated. They must also be compatible with the equipment materials of construction, for example, low-chloride inhibitors should be used on stainless steels.

The concentration of the inhibitor used is related to the type of solvent, its temperature, the equipment materials of construction, the surface-to-volume ratio in the equipment, and the degree of turbulence. Typical film-forming inhibitor concentrations for mineral acids on steel are of the order of less than 0.2%.

Most common inhibitors are proprietary formulations, and technical data may be obtained from suppliers. Inhibitors often contain dyes, which confirm whether or not the inhibitor has been added.

## Chemical Cleaning Procedures

In addition to selecting the optimum solvent, other factors essential to successful chemical cleaning are the development of a safe and effective procedure and the prevention of excessive equipment corrosion. Selection of the chemical cleaning contractor is important because the quality of individual crews can vary. Also, the contractor must have the ability and experience to use specific procedures, some of which may require unique steps or patented procedures. The proposed procedure should be written and included in a scope of work that is mutually agreeable to the owner and the contractor. When the job is complete, the key elements must be documented.

**Planning Stage.** The proposed cleaning procedure should be reviewed with the contractor or personnel who will conduct the cleaning. The procedure should outline the specific duties of the contractor and the owner and should include the following:

- Listing of all chemicals used, including primary solvent and corrosion inhibitor, surfactants, emulsifiers, neutralizers, passivators, and antifoams
- Solution contact times, temperatures, and pressures
- Method of corrosion control and monitoring
- Special contractor equipment required, such as filter elements, high-volume pumps, and heat exchangers
- Contractor safety procedures and owner safety requirements, for example, methods of treating hazardous by-products, such as $H_2S$ and hydrogen cyanide (HCN), which may be generated during cleaning
- Disposal requirements for waste material, including adherence to federal, state, and local regulations
- Lay-up requirements after cleaning, if equipment is not to be used immediately

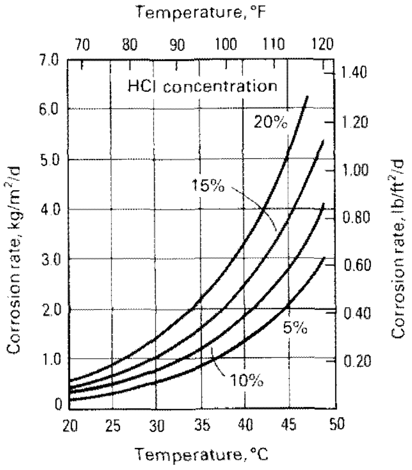

**Fig. 6** Effect of temperature on corrosion of low-car-bon steel in uninhibited HCl

When mutually agreed upon, the procedure is developed into a scope of work.

**Cleaning Stage.** The equipment is readied for cleaning. After isolation, all restrictions, such as orifice plates, should be removed. Tubes of a shell and tube heat exchanger should be cleaned of obstructions before chemical cleaning. Failure to free the tubes could result in solvent remaining in tubes and possible damage at start-up. In general, the chemical cleaning operation consists of the following steps:

- Leak testing of contractor fittings
- Hooking up of cleaning system
- Establishment of circulation rate and temperature
- Blending in of chemicals
- Circulation and monitoring, which include recording of solvent strength and deposit removal. If the solvent strength remains constant for two or more consecutive readings, cleaning is usually considered complete
- Draining system of solvent
- Flushing with water
- Neutralizing, if an acidic solvent was used
- Passivation, if required
- Inspection and evaluation of cleaning

**Documentation of Cleaning.** A simple format will include relevant information on the equipment temperature, materials of construction, chemicals, method of circulation, time of circulation, and evaluation of equipment. The format may be modified for different pieces of equipment.

**Corrosion Monitoring in Chemical Cleaning.** Chemical cleaning introduces the real possibility of equipment damage from corrosion. Various precautions may be taken to eliminate damage or to reduce the corrosion rate to acceptable levels, such as reducing the cleaning temperature or contact time. Corrosion monitoring during chemical cleaning may consist of on-line electrochemical monitoring, corrosion coupons, or a bypass spool piece containing a sample of the deposit.

On-line electrochemical monitoring provides an instant record of the corrosion rate during cleaning. However, localized corrosion effects are not indicated.

Corrosion coupons should be representative of the materials of construction of the equipment being cleaned. They should be insulated from one another to avoid galvanic effect. If necessary, special coupons, such as U-bends, should be included to check for SCC. The corrosion rates of coupons are generally higher than the actual corrosion rate of the equipment during the cleaning cycle. However, excessively high coupon rates suggest that cleaning has been performed outside of the desired range of temperature, chemical concentration, or circulation rate. Experience dictates acceptable corrosion rates obtained from corrosion coupons. Localized corrosion observed on coupons is unacceptable. A bypass spool piece containing a sample of the deposit is the ideal coupon because it will indicate the effectiveness of the cleaning as well as the condition of the metal after cleaning.

Corrosion should be monitored during every chemical operation. Post-inspection is extremely important to check for damage and to gage the effectiveness of cleaning. Certain scales may increase the corrosiveness of the chemical cleaning solution as they dissolve.

**Corrosion Rate.** Chemical cleaning contractors measure the general corrosion rate in pounds per square foot per day ($lb/ft^2/d$). This unit is converted to mils per year (mils/yr) by using a factor that varies with the density of the metal under consideration. To obtain mils per year, multiply pounds per square foot per day by $70.3 \times 10^3$/density (grams per cubic centimeter). For steel, $0.01\ lb/ft^2/d = 91$ mils/yr.

A significantly higher corrosion rate is tolerable during chemical cleaning than would be allowed in service. For example, 400 mils/yr obtained from coupons may be acceptable for carbon steel. With relatively thick components, such as pump casings, even higher rates may be tolerable. Less than 200 mils/yr should be the goal. Localized corrosion—for example, pitting or SCC—is not tolerable.

**Localized Corrosion.** The principal forms of localized corrosion that occur during chemical cleaning are pitting, SCC, and under-deposit corrosion (crevice corrosion).

*Pitting* occurs when filming inhibitors break down or there is insufficient inhibitor addition. Pitting will also occur with HCl and incompatible metals, such as aluminum or stainless steels. Oxidizing conditions, such as free $Fe^{3+}$ ion, and the presence of the chloride ion ($Cl^-$) will also encourage pitting in metals resistant to general corrosion, especially the active-passive metals mentioned. Pitting is especially harmful on thin-wall equipment, for example, heat-exchanger tubes.

*Stress-corrosion cracking* is likely to occur in specific chemical alloy combinations when the threshold temperature and concentration requirements for cracking are exceeded. This usually occurs in vapor spaces, splash zones, or crevices where the cleaning agent can concentrate. If the chemical cannot be washed out, SCC may occur later, for example, during service. The two most common situations to guard against are the hydroxyl ion ($OH^-$), for example, from caustic, with carbon steel and the $Cl^-$ ion, for example, from HCl, with austenitic stainless steels. In some cases, an inhibitor can be added to minimize cracking. Hydrogen-assisted cracking may also occur in hardenable low-alloy and stainless steels in specific heat-treated conditions during acid cleaning.

*Under-deposit corrosion* occurs when cleaning is incomplete and the deposits left behind harbor or concentrate corrosives. The corrosion is difficult to see because it is hidden by the deposits.

**Temperature, Pressure, and Flow Rate.** Of these factors that affect corrosion rate, temperature is the most significant. The higher the temperature of the solvent, the more effective the cleaning generally is. However, corrosion rate increases significantly with temperature and limits the temperature that can be used (Fig. 6). Increasing temperature also increases the amount of inhibitor required.

Each cleaning operation should include a review of the pressure (hydrostatic and gas) that may be experienced. Acceptable limits should not be exceeded. For example, in one operation, impervious graphite heat-exchanger tube failures were significantly reduced when the recirculating solvent pressure was decreased from 690 to 207 kPa (100 to 30 psig).

It is extremely difficult to relate flow rate or solution velocity directly to the corrosion rate. This is because the key to increased corrosion rate is turbulence. Experience is the best indicator of velocity or flow limitations during chemical cleaning.

**Ferric ion corrosion** is a form of general or localized corrosion that occurs on carbon steel, nickel, Monel 400, copper, brass, and zirconium during chemical cleaning. The effect is worst with HCl (because of the presence of the $Cl^-$ ion), but can also occur in other mineral acids, citric acid, EDTA chelant formulations, and HCOOH.

Ferric iron corrosion occurs when there are heavy deposits of iron oxide coupled with aeration during cleaning. Dissolution during cleaning, together with aeration, generates the $Fe^{3+}$ ion, which corrodes steel as follows:

$$2Fe^{3+} + Fe \rightarrow 3Fe^{2+} \qquad \text{(Eq 1)}$$

Other metals can also be corroded because of the oxidizing nature of the $Fe^{3+}$ ion, especially if the $Cl^-$ ion is present.

Ferric ion corrosion may be prevented with specific inhibitors, for example, stannous chloride ($SnCl_2$). It prevents the formation of $Fe^{3+}$ ion, as follows:

$$\begin{aligned} &Sn^{2+} \rightarrow Sn^{4+} + 2e^- \\ &Sn^{2+} + 2Fe^{3+} \rightarrow Sn^{4+} + 2Fe^{2+} \qquad \text{(Eq 2)} \end{aligned}$$

Proprietary $Fe^{3+}$ ion corrosion inhibitors are also available.

Even if an $Fe^{3+}$ ion inhibitor is added, the total iron content (ferrous and ferric) must be monitored regularly (at least every 30 min) during cleaning. Measurement of the $Fe^{3+}$ ion content may be misleading. When the iron content reaches 2 to 3%, the solution should be removed.

**Sulfide Corrosion.** Sulfides are present in many refinery deposits, and $H_2S$ may be released when sulfides are contacted by acid cleaning solutions. Sulfides and $H_2S$ are extremely corrosive and reduce the effectiveness of corrosion inhibitors. Hydrogen sulfide will also crack hardenable low-alloy steels and blister low-strength carbon steels.

Corrosion problems with sulfides and $H_2S$ may be reduced by lowering the acid concentration and temperature. Inhibitors are effective in preventing cracking or blistering.

Sulfide stringers present in free-machining steels have increased susceptibility toward corrosion during acid cleaning. Selenium-containing free-machining steels or low-sulfur regular grades are less susceptible to attack.

**Effectiveness of Corrosion Inhibitor.** A useful qualitative test to check whether a filming inhibitor has been added to the system before circulation is the steel wool test. In this test, a small wad of steel wool is completely immersed in a beaker containing the inhibited acid at the strength and temperature to be used during cleaning. If the inhibitor addition is effective, there should be no hydrogen evolution from the beaker for at least 5 min and the wad of steel wool should remain at the bottom of the beaker.

As noted above, by-products formed during cleaning can reduce the effectiveness of the corrosion inhibitor. Also, increasing temperature and concentration of cleaning chemicals usually necessitates a greater dose of inhibitor.

## Mechanical Cleaning

Mechanical cleaning is extensively used to clean many types of equipment. There are three broad categories: hydraulic, abrasive, and thermal.

The hydraulic category includes water cleaning, high-pressure water blasting, ultrahigh-pressure water blasting, and ultrasonic cleaning. The abrasive category includes rodding, drilling, sandblasting, pigging and scraping, turbining, and explosive removal. The thermal category includes steam cleaning.

**Hydraulic cleaning** is carried out at pressures from 2070 kPa to 221 MPa (300 to 32 000 psig).

*Water cleaning* is often used to flush mud and debris from pipelines at pressures to 2070 kPa (300 psig). Slug flow flushing with air injection will obtain better scouring and will conserve water. Water, coupled with a pipeline pig, is often effective in removing scale and corrosion products from lines.

**High-pressure water cleaning,** the most common form of mechanical cleaning, is carried out at pressures of 6.9 to 69 MPa (1000 to 10 000 psig). It is used to remove such deposits as light rusting, minerals, and polymers. There are three types of high-pressure water cleaning: tube lancing, line moling, and shotgun jetting.

In tube lancing, a rigid or flexible lance is used to clean the inside of tube bundles, and the operation is repeated for each tube. In line moling, a short self-propelled jet nozzle (mole) and a high-pressure hose are used to clean the inside of piping. In shotgun jetting, a relatively short handheld gun (shotgun) is used to clean surfaces that cannot be cleaned practically by the other means. Shotgun jetting is not effective in cleaning tubes.

High-pressure water cleaning reduces the risk of corrosion damage to equipment, and disposal of the water is less of a problem than with chemical cleaning. Also, the risk of generating hazardous or toxic by-products is eliminated.

The jet stream is provided by an operator holding a water lance. The lowest pressure with appropriate volume of water is selected, consistent with achieving the required degree of cleaning. This is dictated by experience and risk to personnel.

High-pressure water cleaning must be done by trained personnel using appropriate safety devices and regularly inspected equipment. The area around the job should be suitably barricaded and sign posted.

Line friction leads to a significant loss of pump pressure. To counteract friction loss when pumping through a long hose, organic polymers have been developed that, when added to water in concentrations as low as 0.05 to 0.1%, reduce friction loss as much as 90%.

*Ultrahigh-pressure water blasting* is conducted at 221 MPa (32 000 psig), using a flow rate of 1 to 4 gal/min. The low flow rate means there is a very low back thrust, allowing the equipment to be operated in congested work spaces with a higher degree of safety. The ultrahigh pressure and low volume of delivery are achieved by using intensifiers rather than the standard plunger pumps. Nozzle configurations are tailored to the application. The nozzle is usually held 19 to 100 mm (3/4 to 4 in.) away from the workpiece. The tooling is specially designed for specific applications, primarily scale, rust, and polymer removal; tube bundle cleaning; and such specialized items as cleaning turbines, diaphragms, and rotors. Cleaning is not effective around more than one 90° turn. The low volume of water minimizes disposal problems.

The technique is particularly advantageous where high-pressure water blasting is ineffective and sandblasting is not desirable, for example, adjacent to pumps, valves, and compressors. Ultrahigh-pressure water blasting has been cost-effective in preparing surfaces for inspection, such as the wet fluorescent magnetic-particle inspection of deaerator welds. In these cases, an inhibitor is added to the water to prevent flash rusting.

Ultrahigh-pressure water blasting is a proprietary process and is limited to a few vendors who tailor their tools to specific jobs. It is more expensive than high-pressure water blasting, but has the advantages of quality and speed.

**Abrasive cleaning** is implemented where hydraulic cleaning may not be practical.

*Rodding* is used for lightly plugged heat-exchanger tubes where scale has not built up. Care should be taken to prevent scoring of the tubes.

*Drilling* may be used on tightly plugged heat-exchanger tubes. The drill is hollow, and a fluid connection is used to flush out freed material, eliminating the need to pull the drill out to clear the point and remove loose material.

*Sandblasting* involves cleaning the internal surface of process lines and equipment by using an abrasive blasting tool. These are available for different pipe sizes. A standard sandblast nozzle is used that impinges the sand against the conical carbide tip of the nozzle, spraying the sand out radially against the walls of the tube. A circular end plate removes most of the sand as the tool is pulled back out of the pipe.

*Piping and Scraping.* Pipeline pigs and scrapers are sometimes used, alone or with special chemicals, to clean pipelines. This is a combination of mechanical and chemical cleaning.

The pig is a flexible bullet-shaped foam cylinder that is propelled through the pipeline with water. A typical system consists of several pigs, launching and trapping facilities, and a water source. Pigging has been used to clean lines from 25 to 914 mm (1 to 36 in.) in diameter.

*Turbining* is a tube- or pipe-cleaning method that uses air, steam, or water to drive a motor that turns cutters, brushes, or knockers in order to remove deposits. Many different heads are available for different deposits and equipment, including models for curved tubes.

Overzealous turbining may damage pipes because the cutter types will cut into the base metal. Also, turbining is relatively slow and costly compared to other mechanical and chemical methods.

*Explosive removal* of pipe deposits requires experience and has been used on hard and brittle deposits in piping. Primacord is manufactured in various degrees of explosive power; selection of the proper strength depends on pipe size and type of deposit.

**Thermal cleaning** is the third major mechanical cleaning method.

*Steam cleaning* can be used to remove mill scale and debris from lines and equipment. When mixed with oxygen, steam cleaning can remove coke and polymers from equipment.

### On-Line Cleaning

The cleaning methods discussed so far require that the equipment be removed from service and opened to some degree for the cleaning. In some cases, on-line cleaning is effective and more convenient. On-line cleaning can be chemical or mechanical, infrequent or regularly scheduled. Effective on-line cleaning can save time and labor and can prevent a shutdown. Examples of on-line cleaning include:

- Side-stream filtration
- Air bumping of heat exchangers
- Washing soft deposits from steam turbines
- Reversing flow in heat exchangers
- Passing brushes or sponge balls through exchanger tubes
- Depressing pH or adding sequestrants and dispersants in a cooling water system
- Increasing chelant or dispersant feed to a boiler

Not all cleaning jobs are conducive to on-line cleaning. Hard or insoluble deposits may not be removed effectively. In boilers, if the deposit is heavy, on-line cleaning may cause the deposit to slough and plug tubes—possibly leading to tube failures. Also, some on-line cleaning costs can be high, for example, the initial cost of installing brushes or sponge balls to clean heat exchangers. Each case must be evaluated individually to determine if on-line cleaning will be cost-effective.

## Corrosion Under Thermal Insulation

The proliferation in recent years of corrosion failures of both steel and stainless steel under insulation has caused this problem to be of great concern to the operators of petroleum-, gas-, and chemical-processing plants. Piping and vessels are insulated to conserve energy by keeping cold processes cold and hot processes hot. Once a vessel is covered with insulation and operating satisfactorily, concern for the condition of the metal under insulation usually diminishes. Thus, corrosion of steel and SCC of stainless steel begins and develops insidiously, often with serious and costly consequences many years later. To deal with corrosion under insulation effectively and economically, a systems approach must be developed that considers the metal surface, temperatures, water, insulation, and design.

Corrosion of steel under insulation did not receive a great deal of attention by the corrosion engineering community until the late 1970s and early 1980s. Although considerable attention was being given to the SCC of stainless steel under insulation (see below), steel vessels and piping were rarely mentioned. This situation existed because of the slow corrosion rate of the steel equipment, together with the fact that many large hydrocarbon-processing plants were built 10 to 20 years earlier.

The most significant turn of events, which fortunately revealed the corrosion problem to many, was the energy shortage and the resultant emphasis on energy conservation. The effort to conserve energy soon led to replacement of much of the 10- to 20-year-old insulation with more efficient systems. As the old insulations were removed, localized, often severe corrosion damage was found.

**Fig. 7** Heavy corrosion of a steel support bracket where it passed through cellular glass insulation on a cold-temperature column. Moisture condensed on the column shell where the support was warmed by the extended attachment.

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In 1978, the Materials Technology Institute (MTI) of the Chemical Process Industry initiated a project at Battelle Columbus Laboratories to define the problem of corrosion of steel equipment under thermal insulation and identify nondestructive techniques potentially capable of detecting such corrosion (Ref 19). This work on nondestructive testing for corrosion under insulation has been continued by MTI through a second and third phase, leading to a new electromagnetic technique. Another example of the recent interest in this corrosion problem was the Joint Conference on Corrosion Under Insulation held in San Antonio, TX, in October of 1983 (Ref 20).

Stress-corrosion cracking of stainless steel under thermal insulation has been observed and recognized for many years (Ref 21, 22). The collection of and concentration of chlorides on austenitic stainless steels can lead to rapid failure of expensive equipment. The study of this phenomenon has attracted much attention, and many approaches have been attempted in order to alleviate the problem. The roles of the insulation materials, atmospheres, moisture entry, and operating temperature have been investigated (Ref 20). Many of these concepts can also be applied to the general corrosion of steel under insulation. This section is divided into two parts: one discusses steel, and the other discusses stainless steel, because the nature of the problem, aside from the presence of insulation, is different.

## Corrosion of Steel Under Insulation

**The Problem.** Steel does not corrode simply because it is covered with insulation. Steel corrodes when it contacts water and a free supply of oxygen. The primary role of insulation in this type of corrosion is to produce an annular space in which water can collect on the metal surface and remain, with full access to oxygen (air).

The most active sites are those where the steel passes through the insulation and on horizontal metal shapes—for example, insulation support rings where water can collect. Figures 7 to 9 show some of the types of damage that occur near insulation entry points.

The other major corrosion problem develops in situations where there are cycling temperatures that vary from below the dew point to above ambient. In this case, the classic wet/dry cycle occurs when the cold metal develops water condensation that is then baked off during the hot/dry cycle. The transition from cold/wet to hot/dry includes an interim period of damp/warm conditions with attendant high corrosion rates. Figures 10 and 11 show examples. In both cases, if the lines had operated constantly either cold or hot, no significant corrosion would have developed.

**The Mechanism.** The corrosion rate of steel in water is largely controlled by two factors: temperature and availability of oxygen. In the absence of oxygen, steel corrosion is negligible.

In an open system, the oxygen content decreases with increasing temperature to the point where corrosion decreases even though the temperature continues to increase (Fig. 12). A number of recent case histories of corrosion under insulation have been reviewed, and the estimated corrosion rates have also been plotted in Fig. 12. These field data confirm that corrosion of steel under insulation increases steadily with increasing temperature, matching the curve for a closed system.

The problem of steel corrosion under insulation can be classified as equivalent to corrosion in a closed hot-water system. The thermal insulation does not corrode the steel, but, more correctly, forms an annular space where moisture collects. The insulation also forms a barrier to the escape of water or water vapors, which hastens the normal corrosion rate of wet steel.

In an attempt to determine which insulation contributes most and which contributes least to corrosion of steel, tests were conducted that compared 12 common insulation materials (Ref 23). After a 1-year exposure to the elements, dousing with water, and daily heating with steam, it was concluded that, although the insulation materials that absorbed water developed higher corrosion rates than those that did not, the difference between the two was not great. Therefore, efforts to select a type of insulation to prevent corrosion would not be practical. Field observation and reports from the literature confirm that corrosion of steel occurs under any and all types of insulation.

**Prevention.** One attempt to prevent corrosion damage involves adding a corrosion inhibitor to the insulation. Inhibitors such as $Na_2SiO_3$ are added for this purpose. The practical effects of such an approach are questionable. In one set of laboratory tests, inhibited insulation material was submerged in water, then set out to dry. After several cycles of wetting and drying, the insulation was found to have no benefit over uninhibited insulation of the same brand.

A corrosion inhibitor for insulation must be water soluble so that it can be dissolved and carried to the steel surface. If the insulation is waterproofed on the outside, water will enter through cracks and openings in the insulation system. This water is in the annulus and contacts only the inner surface of the insulation. The water-soluble inhibitor will soon be extracted and displaced by the water running down the vessel walls. Therefore, relying upon a consumable inhibitor for long-term protection may not be dependable.

If water entry to the insulation/steel annulus is the problem, perhaps the solution lies in more effective waterproofing. Advancements in various metal jacketings, sealants, and mastics have improved the protection of insulation materials from water, weather, and man. However, these waterproofing systems probably do not prevent water entry, because, in order to seal and prevent the annulus from breathing with temperature changes, the seal would have to be equivalent to a pressure vessel.

Waterproofing systems are designed to keep the insulation dry. They are not capable of preventing water vapor and air from contacting the annular space. In fact, a waterproofing system keeps the water vapor in the annulus and effectively produces the hot-water closed system, with attendant high corrosion rates.

Therefore, selection of insulation, inhibiting the insulation, and waterproofing of the insulation are not effective deterrents to corrosion. Instead, a high-quality protective coating, correctly applied to the steel before insulation, can offer long-term protection. Although a specific coating system cannot be recommended, the requirements that must be met by the coating can be specified.

**Fig. 8** Corrosion around the ladder clip of a gas-processing column. The column was painted with an inadequate protective coating (0.05 mm, or 2 mils, of epoxy) that could not prevent corrosion near the moisture entry points.

**Fig. 9** Steel pipe corroded on the bottom side where a poorly sealed insulation joint allowed water to enter the insulation/pipe annulus. The moisture ran around the pipe and collected on the bottom.

# Corrosion in Petroleum Production Operations

# Corrosion in Petroleum Production Operations

THE PRODUCTION of oil and gas, its transportation and refining, and its subsequent use as fuel and raw materials for chemicals constitute a complex and demanding process. Various problems are encountered in this process, and corrosion is a major one. The costs of lost time, the replacement of materials of construction, and the constant personnel involvement in corrosion control are substantial and, if not controlled, can be catastrophic. The control of corrosion through the use of coatings, metallurgy, nonmetallic materials of construction, cathodic protection, inhibitors, and other methods has evolved into a science in its own right and has created industries devoted solely to corrosion control in specific areas.

This article will discuss the particular corrosion problems encountered, the methods of control used in petroleum production, and the storage and transportation of oil and gas to the refinery. Refinery corrosion is discussed in the article "Corrosion in Petroleum Refining and Petrochemical Operations" in this Volume.

## Causes of Corrosion

The forms of corrosion commonly encountered in the petrochemical industry are discussed in the chapter "Forms of Corrosion in the Petrochemical Industry" in this Volume. This article concentrates on aspects of corrosion unique to oil and gas production.

There are several environmental factors that are more or less unique to oil and gas production. Most unique, of course, are the environments encountered in actual production formations, which, in the absence of contamination, are devoid of oxygen. *In situ* corrosives are limited to carbon dioxide, hydrogen sulfide, polysulfides, organic acids, and elemental sulfur. Additional unique aspects are the extremes of temperature and, particularly, pressure encountered. In deep gas wells (6000 m, or 20,000 ft), temperatures approaching 230 °C (450 °F) have been measured, and partial pressures of $CO_2$ and $H_2S$ of the order of 20.7 MPa (3000 psi) and 48 MPa (7000 psi), respectively, have been encountered.

Convenient access to the most important literature on $H_2S$ corrosion (particularly with regard to sulfide stress cracking) and $CO_2$ corrosion is available in Ref 1 and 2. Supplemental information is provided in Ref 3 and 4.

To the initially oxygen-free geologic environment, a variety of oxygen-contaminated fluids may be introduced. Examples are drilling muds, which are used during drilling and maintenance of wells; dense brines; water and carbon dioxide injected for secondary oil recovery; and hydrochloric acid injected to aid formation permeability. Some of these fluids are inherently corrosive; others are potentially corrosive only when contaminated with oxygen.

Oxygen is also responsible for the external corrosion of offshore platforms and drilling rigs. In oil and gas production, highly stressed structural members are directly exposed to a corrosive seawater environment. This makes corrosion fatigue a particular concern.

Another unique aspect of oil and gas production operations, particularly in older fields, is the almost exclusive use of carbon and low-alloy steels. Only recently has any extensive use of corrosion-resistant alloys been justified.

## Oxygen

Although it is not normally present at depths more than approximately 100 m (330 ft) below the surface, oxygen is nevertheless responsible for a great deal of the corrosion encountered in oil and gas production. However, oxygen-induced internal corrosion problems tend to be greater in oil production, where much of the processing and handling occurs at near-ambient pressure. This makes oxygen contamination through leaking pump seals, casing and process vents, open hatches, and open handling (as in mud pits during drilling, trucking, and so on) highly likely. Also, failure of oxygen removal processes (gas stripping and chemical scavenging) is a relatively common occurrence in waterflood systems (see the discussion "Secondary Recovery Operations" in this article).

A number of the properties of oxygen contribute to its uniqueness as a corrosive. Oxygen is a strong oxidant. This means that even trace concentrations can be harmful, and the corrosion potential of steel (almost 1.3 V) is high enough to overcome very substantial potential drops between anodic and cathodic sites. Also, the kinetics of oxygen reduction on a metal or conductive oxide surface are relatively fast. This, coupled with the low solubility of oxygen in water and brines, tends to produce conditions in which the mass transport of oxygen is the rate-limiting step in the corrosion of carbon and low-alloy steels in nonacidic environments.

Mass transport is important in a number of aspects of oxygen corrosion and corrosion control. On newly installed bare steel offshore structures, mass transport of oxygen governs current requirements for cathodic protection. Poor mass transport under deposits and in crevices promotes localization of attack. In the final analysis, limiting the mass transport of oxygen plays a critical role in much of the corrosion control in oxygenated systems.

The crucial role of mass transport can be illustrated as follows. At ambient conditions, water equilibrated with air will contain on the order of 7 to 8 ppm of oxygen. Under such conditions, mass-transport-limited rates of general corrosion of steel range from about 0.25 mm/yr (10 mils/yr) in a stagnant system to 15 mm/yr (600 mils/yr) in a highly turbulent one. However, by chemically scavenging the oxygen concentration down to the order of 7 to 8 ppb, the corresponding rates are reduced to less than about 0.01 mm/yr (0.4 mils/yr). Such rates are acceptable. However, under these conditions, magnetite forms as a stable protective corrosion product film and further lowers the corrosion rate by introducing a slower, anodically controlling step.

An even more fundamental role of magnetite should be acknowledged. This is the protection of the steel surface from reaction with water or the hydrogen ions contained in the water. Therefore, if an excess of a chelating agent such as ethylenediamine tetraacetic acid (EDTA) dissolves a protective magnetite film ($Fe_3O_4$), as would normally occur in regions of high turbulence, rapid corrosion ensues, despite the absence of oxygen.

## Hydrogen Sulfide, Polysulfides, and Sulfur

Hydrogen sulfide, when dissolved in water, is a weak acid and is therefore corrosive because it is a source of hydrogen ions. In the absence of buffering ions, water equilibrated with 1 atm of $H_2S$ has a pH of about 4. However, under high-pressure formation conditions, pH values as low as 3 have been calculated.

Hydrogen sulfide can also play other roles in corrosion in oil and gas production. It acts as a catalyst to promote absorption by steel of atomic hydrogen formed by the cathodic reduction of hydrogen ions. This accounts for its role in promoting sulfide stress cracking of high-strength steels (yield strength greater than approximately 690 MPa, or 100 ksi) (Ref 5).

Hydrogen sulfide also reacts with elemental sulfur. In a gas phase with a high $H_2S$ partial pressure, sulfanes (free acid forms of a polysulfide) are formed so that elemental sulfur is rendered mobile and is produced along with the remaining gaseous constituents. However, as the pressure decreases traveling up the production tubing, the sulfanes dissociate and elemental sulfur precipitates. Various solvent treatments are used to avoid plugging by such sulfur.

In the aqueous phase, under acidic conditions, sulfanes are also largely dissociated in $H_2S$ and elemental sulfur. However, enough strongly oxidizing species can remain either as polysulfide ions or as traces of sulfanes to play a significant role in corrosion reactions. Oxygen contamination of sour ($H_2S$-containing) systems can also result in polysulfide formation.

Iron sulfide corrosion products can be important in corrosion control. Because of the low solubility, rapid precipitation, and mechanical properties of such corrosion products, velocity effects are generally not encountered in sour systems. Satisfactory inhibition at velocities up to 30 m/s (100 ft/s) has been proved.

The great range of possible iron sulfide corrosion products and their possible effects on corrosion have been extensively studied (Ref 6-9), but little of immediate practical value has resulted. At lower temperatures and $H_2S$ partial pressures, an adequately protective film often forms. The absence of chloride salts strongly promotes this condition, and the absence of oxygen is absolutely essential.

At the high temperatures (150 to 230 °C, or 300 to 450 °F) and $H_2S$ partial pressures (thousands of pounds per square inch) encountered in deep sour gas wells, a so-called barnacle type of localized corrosion (Ref 10) can occur, resulting in corrosion rates of several hundred mils per year (Ref 11). This type of attack is strongly promoted by polysulfide-type species and requires the presence of some minimum chloride concentration. Although initially recognized in deep sour well environments, this same mechanism may operate at lower rates under much milder conditions.

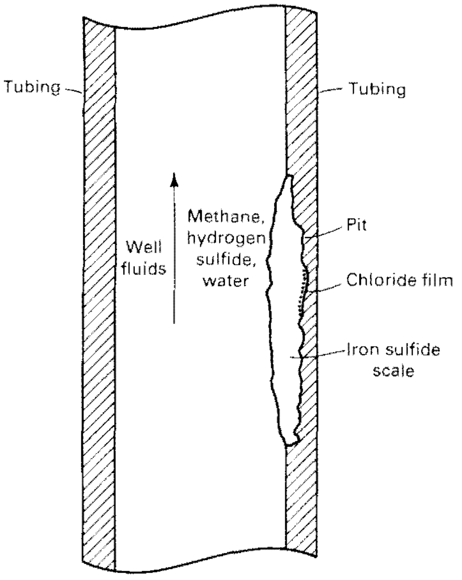

**Fig. 1** Schematic showing the barnacle mechanism of sour pitting corrosion. Source: Ref 11

In the barnacle mechanism (Fig. 1), corrosion can be sustained beneath thick but porous iron sulfide deposits (primarily pyrrhotite, $FeS_{1.15}$) because the FeS surface is an effective cathode. The anodic reaction beneath the FeS deposit is dependent on the presence of a thin layer of concentrated $FeCl_2$ at the Fe/FeS interface. This intervening $FeCl_2$ layer is acidic due to ferrous ion hydrolysis, thus preventing precipitation of FeS directly on the corroding steel surface and enabling the anodic reaction to be sustained by the cathodic reaction on the external FeS surface.

## Carbon Dioxide

Carbon dioxide, like $H_2S$, is a weakly acidic gas and becomes corrosive when dissolved in water. However, $CO_2$ must first hydrate to carbonic acid ($H_2CO_3$) (a relatively slow reaction) before it is acidic. There are other marked differences between the two systems. Velocity effects are very important in the $CO_2$ system; corrosion rates can reach very high levels (thousands of mils per year), and the presence of salts is often unimportant.

Whether or not corrosion in a $CO_2$ system is inherently controlled or uncontrolled depends critically on the factors governing the deposition and retention of a protective iron carbonate (siderite, $FeCO_3$) scale. On the other hand, there are the factors that determine the rate of corrosion on bare steel. These latter factors govern the importance of maintaining corrosion control.

Bare steel corrosion rates can be calculated from Eq 1, which was developed on the basis of electrochemical studies of the aqueous $CO_2$/carbon steel system (Ref 12):

$$\log R = A - \frac{2320}{t + 273} - \frac{5.55t}{1000} + 0.67 \log \bar{p} \qquad \text{(Eq 1)}$$

where $R$ is the corrosion rate, $t$ is temperature (°C), A is a constant, and $\bar{p}$ is $CO_2$ partial pressure. When $R$ is calculated in millimeters per year and $\bar{p}$ is in atmospheres, A = 7.96. When $R$ is calculated in mils per year and $\bar{p}$ is in pounds per square inch, A = 8.78.

Corrosion rates calculated with Eq 1 reach 25 mm/yr (1000 mils/yr) at 65 °C (150 °F) and 1 MPa (150 psi) $CO_2$ pressure, and 250 mm/yr (10 000 mils/yr) at 82 °C (180 °F) and 16 MPa (2300 psi) $CO_2$ pressure. Obviously, such rates are unacceptable. An alternative, idealized condition occurs when a protective carbonate scale is present and when the corrosion rate is limited by the need to replenish the film lost due to solubility in the aqueous phase. Under such conditions, the rates calculated for a hypothetical sweet ($CO_2$-containing) gas well reached a maximum of about 0.15 mm/yr (6 mils/yr) as compared to calculated bare metal rates of 500 to 2000 mm/yr (20 000 to 80 000 mils/yr) (Ref 13).

Conditions favoring the formation of a protective iron carbonate scale are:

- Elevated-temperature (decreased scale solubility, decreased $CO_2$ solubility, and accelerated precipitation kinetics)
- Increased pH, as occurs in bicarbonate-containing waters (decreased solubility)
- Lack of turbulence

Turbulence is often the critical factor in pushing a sweet system into a corrosive regime. Excessive degrees of turbulence prevent either the formation or retention of a protective iron carbonate film.

The critical velocity equation has been used to estimate when excessive turbulence can be expected in a $CO_2$ system (Ref 14). There is no doubt that the velocity effect is real, but there is some question as to whether this exact form of the equation is the appropriate one:

$$\text{Critical velocity} = \frac{K}{\sqrt{\rho}} \qquad \text{(Eq 2)}$$

where velocity is calculated in feet per second, K is a constant, and ρ is the density of the produced fluid (liquid + gas combined). When ρ is in kilograms per cubic meter, K = 7.6; for ρ in pounds per cubic foot, K = 100.

When both $H_2S$ and $CO_2$ are present, simplified calculations indicate that iron sulfide may be the corrosion product scale when the $H_2S/CO_2$ ratio exceeds about 1/500 (Ref 13); sour system considerations would then be expected to apply. Even in a strictly $CO_2$ system, iron carbonate may not always be the corrosion product. Magnetite may form instead. Figure 2 shows the stability fields expected for siderite and magnetite as a function of the redox potential (expressed here in terms of hydrogen fugacity) of the system (Ref 13). In actual experience, corrosion product scales are often found to consist of mixtures or layers of siderite and magnetite.

Iron carbonate lacks conductivity and therefore does not provide an efficient cathode surface. Thus, the types of pitting mechanisms found in oxygenated and in $H_2S$-containing systems do not occur. Rather, generalized corrosion occurs at any regions not covered by the protective scale. The result is that on any bare metal the anodic and cathodic regions are so microscopically dispersed that salt—to provide conductivity— is not needed to achieve the corrosion rates predicted by Eq 1.

## Strong Acids

Strong acids are often pumped into wells to stimulate production by increasing formation permeability. For limestone formations, 15 and 28% hydrochloric acids are commonly used. For sandstones, additions of 3% HF are necessary. In deep sour gas wells where HCl inhibitors lose effectiveness, 12% formic acid has been used.

Corrosion control is normally achieved by a combination of inhibition and limiting exposure time between 2 and 12 h. If corrosion-resistant alloys are present (austenitic and duplex stainless steels, and so on), concern for stress-corrosion cracking (SCC) and inhibitor ineffectiveness (respectively) may rule out the use of HCl.

## Concentrated Brines

Dense halide brines of the cations of calcium, zinc, and, more rarely, magnesium are sometimes used to balance formation pressures during various production operations. All can be corrosive because of dissolved oxygen or entrained air. In addition, such brines may be corrosive because of the acidity generated by the hydrolysis of the metallic ions, as illustrated in Eq 3:

$$Zn^{2+} + H_2O = ZnOH^+ + H^+ \qquad \text{(Eq 3)}$$

Corrosivity due to acidity is worst with dense zinc brines. More expensive calcium bromide brines are now often used at densities above about 1.7 g/cm$^3$ (14 lb/gal) (attainable with $CaBr_2$ brines) to avoid long-term exposure to $ZnCl_2$ brines.

## Stray-Current Corrosion

If an extraneous direct current (dc) in the earth is traversed by a conductor, part of the current will transfer to the lower-resistance path thus provided. Direct currents are much more destructive than alternating currents (ac); an equivalent ac current causes only about 1% of the damage of a dc current (Ref 15). Regions of current arrival (where electrons depart) will become cathodic, and those regions where the current departs will become anodic. With corrodible metals such as carbon and low-alloy steels, corrosion in the anodic areas is the result. For example, 1 A · yr can corrode 9 kg (20 lb) of steel.

Cathodic protection systems are the most likely present-day sources of stray dc currents in production operations. More detailed discussions are available in Ref 4 and 16. The section "General Corrosion" of the article "Forms of Corrosion in the Petrochemical Industry" in this Volume also contains information on the causes and mechanisms of stray-current corrosion.

## Under-Deposit (Crevice) Corrosion

This is a form of localized corrosion found almost exclusively (if not exclusively) in oxygen-containing systems. Such corrosion is usually most intense in chloride-containing systems. It is essential to have some form of shielding of an area on a metal such that it is wet by an electrolyte solution but is not readily accessible to oxygen, the diffusing corrosive species.

This type of attack is usually associated with small volumes of stagnant solution caused by surface deposits (sand, sludge, corrosion products, bacterial growth), crevices in joints, and gasket surfaces. Crevice corrosion is discussed in Ref 17, and a quantitative treatment of crevice corrosion (particularly of stainless steels) is provided in Ref 18 to 20.

The mechanism of crevice corrosion hinges upon the environmental conditions resulting from the loss of hydroxide production with cessation of the cathodic reaction when the initial oxygen in the shielded region is exhausted. Thus, in the shielded region, the anodic corrosion reaction continues because the corrosion potential is maintained by the reduction of oxygen on the outside surface. However, chloride or other anions now migrate into the developing anodic region to maintain electroneutrality. Thus, a relatively concentrated, essentially ferrous chloride solution accumulates in the shielded region. As a result of the hydrolysis of the ferrous ions, the pH drops to a value of 2 or 3.

At this point, the crevice corrosion type of localized attack is fully established. The anodic reaction continues in the shielded region because in the low-pH environment the ferrous ions go readily into solution and have little tendency to precipitate as an oxide or hydroxide on the surface and thus stifle the anodic reaction. Outside, the cathodic reaction continues unperturbed. Because of the large ratio of cathodic-to-anodic surface area, high rates of localized corrosion can be maintained with very modest cathodic current densities. The mechanisms of crevice corrosion are explained in greater detail in the section "Localized Corrosion" of the article "Forms of Corrosion in the Petrochemical Industry" in this Volume.

## Galvanic Corrosion

When two dissimilar metals are electrically coupled—both electronically by a metal bond and ionically through an electrolyte—the more active (electronegative) metal tends to become a sacrificial anode and supply cathodic protection to the more noble metal. Such situations are often encountered in heat exchangers in which carbon steel tubesheets are used with copper alloy tubes and at junctions between piping, fasteners, or corrosion-resistant sheeting with containers of another material.

Problems with galvanic corrosion are the most acute when the cathode-to-anode area ratio is large. Such situations are often encountered inadvertently. This has happened when the normal polarity difference between zinc and steel in a galvanized pipe reversed in a bicarbonate/chloride brine so that the steel pipe walls at pinholes in the galvanizing perforated rapidly while trying to protect the extensive adjacent galvanized area. Another situation is when plastic-coated steel is coupled to more noble metal. At any pinholes in

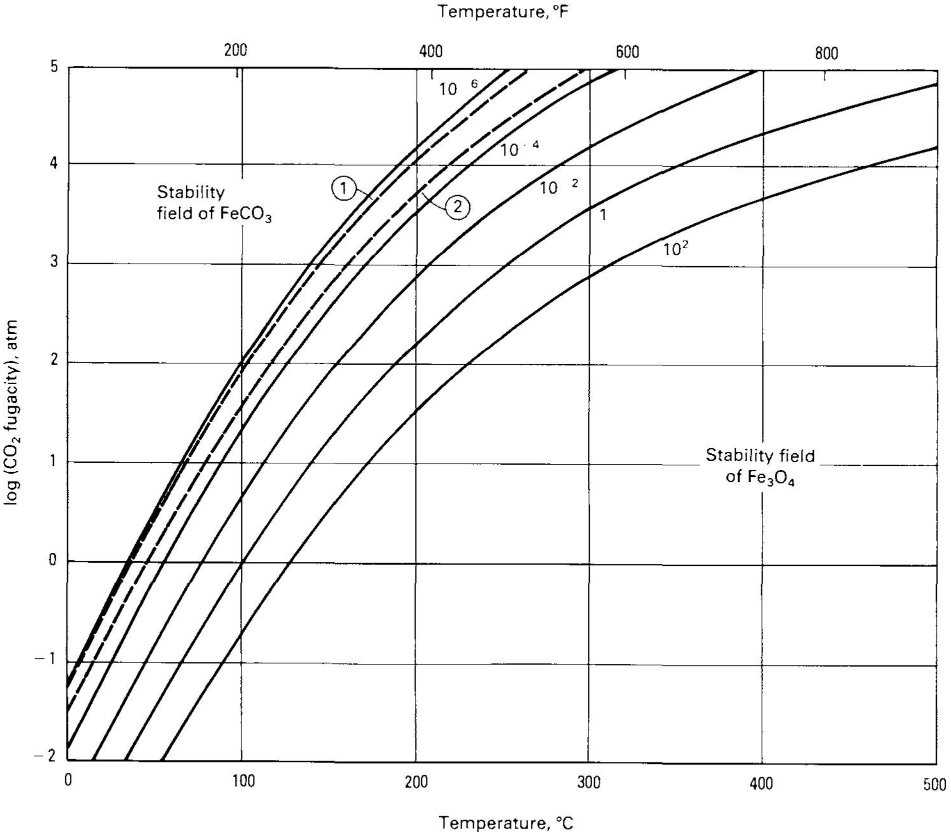

**Fig. 2** Effect of temperature and hydrogen fugacity on the stability of $FeCO_3$ and $Fe_3O_4$ in contact with aqueous $CO_2$. Equilibrium calculations determine boundaries (indicated by the iso-hydrogen fugacity curves, with fugacities given in atmospheres) between $FeCO_3$ and $Fe_3O_4$ stability fields in the produced fluid, which contained $CO_2$, water, and traces of hydrogen. Curves 1 and 2 locate boundaries for locations 5180 m (17,000 ft) deep and at the wellhead, respectively, of a 170,000 m$^3$/day (6,000,000-ft$^3$/day) well corroding at a rate of 0.75 mm/yr (30 mils/yr). Source: Ref 13

the coating, a very adverse area ratio will exist, and rapid corrosion rates can result. The section "General Corrosion" of the article "Forms of Corrosion in the Petrochemical Industry" in this Volume contains more information on this form of attack.

## Biological Effects

The most important biological effect on corrosion in oil and gas production is the generation of $H_2S$ by sulfate-reducing bacteria (SRB) (*Desulfovibrio Desulfuricans*). These are anaerobic bacteria that metabolize sulfate ions (using an organic carbon source) and produce hydrogen sulfide. They can thus introduce $H_2S$ and all its corrosive ramifications into normally $H_2S$-free systems.

Colonies of sulfate-reducing bacteria can also form deposits that are conducive to under-deposit corrosion. Contrary to previous beliefs, any resultant corrosion appears to be due to a mechanical shielding action, rather than any depolarizing action resulting from the metabolic processes of the SRB. However, this is not to deny that the introduction of $H_2S$ (whatever the source) into a crevice region could have an accelerating effect on corrosion, because $H_2S$ is known to be an anodic stimulant. More information on biological corrosion is available in the section "Localized Corrosion" of the article "Forms of Corrosion in the Petrochemical Industry" in this Volume.

## Mechanical and Mechanical/ Corrosive Effects

**Cavitation.** This metal removal— often grain by grain— is due to high-pressure shock wave impingement resulting from the rapid collapse of minute bubbles created under certain conditions in high-velocity fluid handling equipment. It is usually found on pump impellers operating with too low a suction pressure.

**Erosion.** Most commonly, this is direct metal removal by the cutting action of high-velocity abrasive particles. Erosion failures (washouts) are seen in drill pipe when leaks (loose connections or a corrosion fatigue crack) allow drilling mud to flow through the wall under a high-pressure gradient. Erosion of flow lines at bends and joints by produced sand is probably the other most common occurrence of erosion in oil and gas production.

**Erosion-Corrosion.** Strictly speaking, in erosion-corrosion, only the protective corrosion product film is removed by erosive forces; however, with the protective film absent, corrosion can occur at a greatly accelerated rate. Erosion-corrosion may play a role in CO2 corrosion (Ref 21), and sand, under mild flow conditions, may also cause erosion-corrosion. Erosion-corrosion has also been noted in heavy anchor chains where their use in an abrasive bottom mud allowed corrosion at contact regions to proceed at a rate of many hundreds of mils per year.

**Corrosion fatigue** results from subjecting a metal to alternating stresses in a corrosive environment. At points of greatest stress, the corrosion product film becomes damaged during cycling, thus allowing localized corrosion to take place. Eventually, this leads to crack initiation and crack growth by a combination of mechanical and corrosive action. Because of this combined action, damage per cycle is greater at low cycling rates, where corrosion can play a larger role. Also, in corrosion fatigue, a fatigue limit does not exist; rather than leveling out as in simple fatigue, the usable stress level continues to decrease with increasing cycles.

The greatest concern for corrosion fatigue arises in connection with highly stressed, submerged, offshore structures. Welded connections on drill ships and on drilling and production platforms are particularly susceptible to this form of structural impairment. More information on attack resulting from combined corrosion and mechanical effects is available in the section "Mechanically Assisted Degradation" of the article "Forms of Corrosion in the Petrochemical Industry" in this Volume.

## Environmental Stress Cracking

In corrosion-resistant alloy selection, environmental stress cracking normally requires the greatest portion of experimental effort. This follows from the use of high-strength alloys in environments in which there is relatively little experience with these alloys.

The problem is complicated by the fact that the lowest alloy content and the maximum reliable strength level are needed to achieve an economically viable choice. Because this involves design close to the limits of the material, it is necessary to define these limits as accurately as possible.

The presence of hydrogen sulfide and car-bon dioxide in hydrocarbon reservoirs can create significant materials problems. Materials degradation can take many forms, including sulfide-stress cracking, hydrogen-induced cracking, and stress-corrosion cracking. Each must be understood if appropriate measures are to be taken to minimize its effect in field operations.

### Sulfide-Stress Cracking (SSC)

Sulfide-stress cracking can occur when $H_2S$ is present in the reservoir and is in contact with high-strength steels commonly used in drilling, completing, and producing wells. Sulfide-stress cracking is an embrittlement phenomenon in which failures can occur at stresses well below the yield strength of the material. For SSC to occur, three conditions must be met. The first is that a surface tensile stress must be present. It is important to remember that tensile stresses can be both applied and residual. The second requirement is that the particular material must be susceptible. In oil- and gas-production environments, this includes some of the standard casing and tubing alloys, such as API 5AX, grade P-110. The third requirement is that an embrittling agent—in the case of SSC, hydrogen sulfide—must be present in the environment.

Sulfide-stress cracking is basically a hydrogen-embrittlement phenomenon. Atomic hydrogen enters the steel to cause cracking. Many mechanisms have been proposed to explain this occurrence (Ref 22, 23). The hydrogen is generated on the surface of the steel because of a corrosion reaction. Iron reacts with $H_2S$ to form iron sulfide and hydrogen (Ref 23). This hydrogen is generated in atomic form on the steel (or sulfide) surface, where it can either combine to form molecular hydrogen and leave the surface as bubbles or diffuse into the steel. This latter process may result in hydrogen embrittlement or SSC. Hydrogen sulfide prevents hydrogen recombination and thus promotes entry of atomic hydrogen into the steel. It is important to note that water must be present for this mechanism to occur; without it, SSC will not be observed, because the ionization of the hydrogen sulfide is required. Figure 3 shows an example of SSC in API grade L-80 downhole production tubing.

A number of factors influence the SSC resistance of steels. Some of these include $H_2S$ concentration, pH, temperature, strength level, and cold work.

**Effect of Hydrogen Sulfide Concentration.** In general, lower H2S concentrations take longer to promote cracking than higher concentrations; lower concentrations also require high-strength materials before SSC is observed. Figure 4 illustrates typical SSC data as a function of H2S concentration for alloy steels used in oil field tubular components. The data shown in Fig. 4 and 5 are for high-strength steels covered under the following American Petroleum Institute specifications:

- 5A: "Welded or Seamless Steel Pipe for Oil or Gas Well Casing, Tubing, or Drill Pipe"
- 5AC: "Welded or Seamless Steel Pipe with Restricted Yield-Strength Range for Oil or Gas Well Casing or Tubing"
- 5AX: "High-Strength Seamless Steel Pipe for Oil or Gas Well Casing, Tubing, or Drill Pipe"

Certain proprietary grades are also included.

The concentration of hydrogen sulfide in a produced fluid, for example, brine, is a function of the hydrogen sulfide partial pressure in the gas phase, which is a function of the total gas pressure. It should be noted that in reservoirs containing small

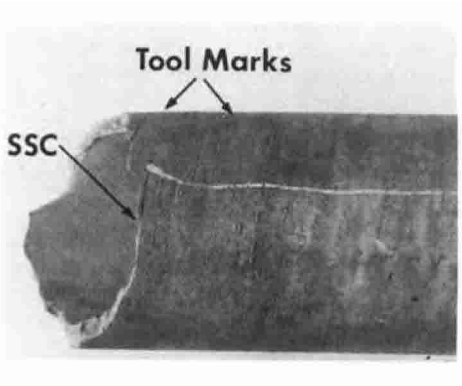

**Fig. 3** SSC of API grade L-80 oil well production tubing. SSC initiated at the tool marks on the tube OD. The well contained about 15% $H_2S$ and 4% $CO_2$ at 48 MPa (7000 psi). 0.3×. Courtesy of S.W. Ciaraldi, Amoco Corporation

amounts of $H_2S$ there may be some difficulty in obtaining an accurate analysis; the reaction of $H_2S$ with tubular goods and other components could result in a reading that is too low. Readings over several weeks, or even months, are sometimes required to obtain accurate results.

**Effect of pH.** The tendency toward SSC is a function of the pH of the system. With decreasing pH, the corrosion rate of the steel tends to increase, which causes more hydrogen to be produced. This causes more hydrogen to enter the steel and increases the susceptibility to cracking. It is generally agreed that increasing the pH above 8 is beneficial in reducing the tendency toward SSC. Although fluid pH control cannot be easily accomplished with produced fluids, control of drilling environments is common. During drilling operations in sour reservoirs, the pH is usually maintained in the 10 to 11 range, thus providing the opportunity to use high-strength steels.

**Effect of temperature** has been found to have a substantial effect on SSC resistance. As temperature increases, the resistance to SSC also increases. This is due to a reduction in the hydrogen-permeation rate at elevated temperatures (Ref 25). This effect allows materials that are susceptible to SSC at room temperature to be used at elevated temperatures. It has been found that SSC is most severe at room temperature; below room temperature, resistance to SSC again begins to increase. The influence of temperature on SSC is illustrated in Fig. 5.

The beneficial effect of temperature on SSC resistance is of practical significance in completing wells. For example, API, grade P-110, steel is susceptible to SSC at room temperature and therefore is not used in such applications. However, when the temperature is kept above about 80 °C (175 °F), P-110 can be successfully used. Therefore, this grade of steel is often used in the deeper portions of a well, where the temperatures are higher. However, caution must be exercised because SSC would be expected to occur if the temperature should ever decrease.

**Effect of Strength Level.** Various metallurgical variables can be controlled to maximize the resistance of a material to SSC. The strength level (commonly measured nondestructively by hardness) is probably the most widely used criterion in ensuring that steels and stainless steels do not fail by SSC. In most cases, carbon and low-alloy steels are used at hardnesses of 22 HRC or below. The exception is the quenched-and-tempered AISI 41*xx* series, which has been used at hardnesses to 26 HRC. Materials should be pretested in the anticipated service environment if there is any doubt about their suitability.

SCC resistance is influenced by steel microstructure, which in turn depends on steel composition and heat treatment. It has been observed that a martensitic structure provides better SSC resistance than other microstructures. Figure 6 illustrates this for a molybdenum-niobium modified AISI 4135 steel (compositions of the steels discussed in Fig. 6 to 8 are given in Table 1). The data in Fig. 6(a) were developed by using simple beam specimens strained in three-point bending

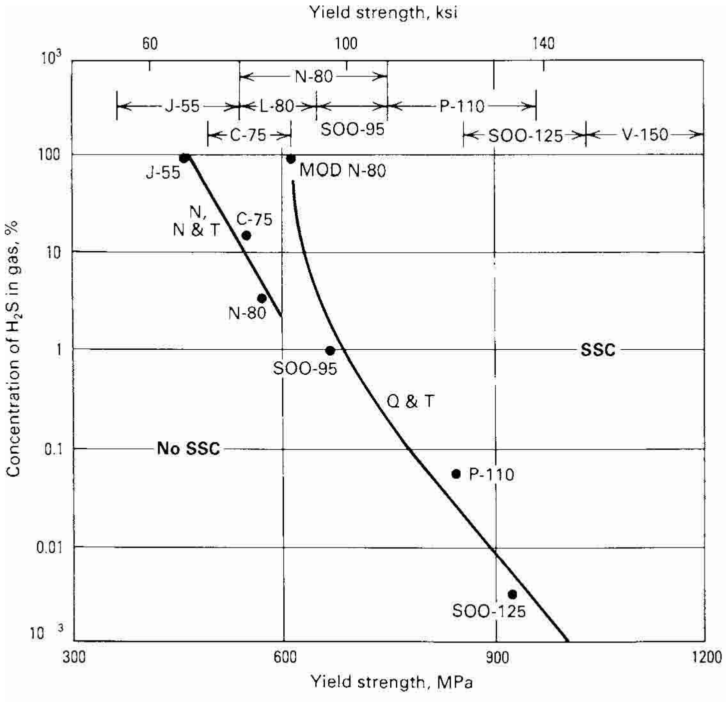

**Fig. 4** Effect of $H_2S$ concentration on SSC of high-strength steels. Source: Ref 24

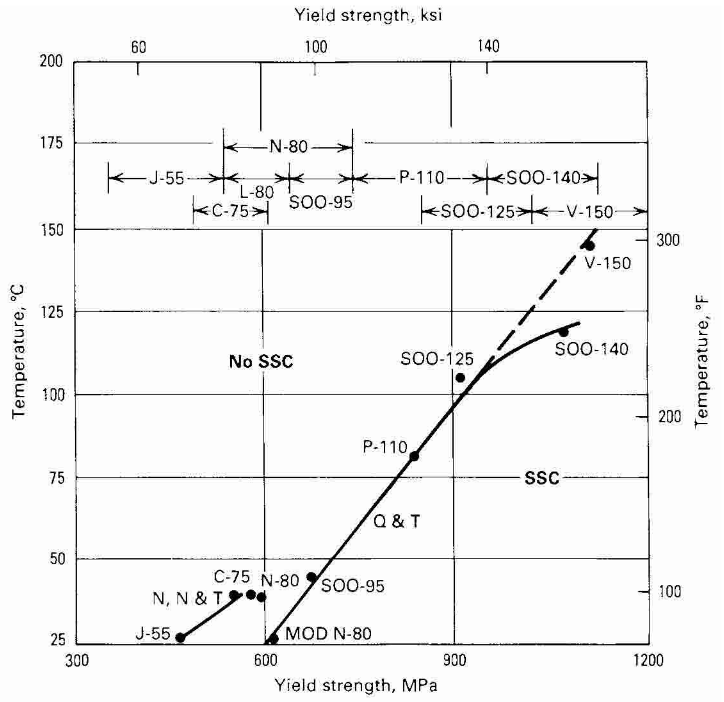

**Fig. 5** Effect of temperature on SSC of high-strength steels. N, normalized; N & T, normalized and tempered; Q & T, quenched and tempered. Source: Ref 24

**Table 1 Chemical compositions of the molybdenum-niobium modified 4130/4135 test steels discussed in Fig. 6 to 8**

| Steel code | Composition, wt% | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | C | Mn | Si | Cr | Mo | Nb | P | S | Al | N, ppm |
| A-2 | 0.34 | 0.74 | 0.39 | 1.06 | 0.60 | 0.035 | 0.030 | 0.022 | 0.12 | 208 |
| A-3 | 0.31 | 0.73 | 0.39 | 1.05 | 0.75 | 0.036 | 0.034 | 0.021 | 0.16 | 166 |
| A-4 | 0.32 | 0.74 | 0.39 | 1.04 | 0.85 | 0.035 | 0.027 | 0.026 | 0.16 | 138 |
| A-5 | 0.32 | 0.74 | 0.40 | 1.05 | 0.98 | 0.036 | 0.027 | 0.025 | 0.17 | 148 |
| A-9 | 0.34 | 0.68 | 0.38 | 1.00 | 0.75 | 0.034 | 0.025 | 0.027 | ND | 260 |
| A-10 | 0.36 | 0.68 | 0.29 | 1.03 | 0.74 | 0.033 | 0.017 | 0.014 | 0.078 | 151 |
| A-15 | 0.33 | 0.23 | 0.71 | 1.04 | 0.73 | 0.031 | 0.018 | 0.015 | 0.047 | 180 |

Source: Ref 26

for measuring a critical stress, $S_c$, and the data in Fig. 6(b) were obtained from double-cantilever beam specimens strained by wedge opening loading for measuring a threshold stress intensity, $K_{ISSC}$. Thus, it is important to select an alloy steel that has sufficient hardenability to achieve 100% martensite for a given application.

Furthermore, proper tempering of martensite is essential in order to maximize SSC resistance. Figure 7 illustrates the effects of tempering temperature on SSC behavior. It is evident that higher tempering temperatures improve SSC performance. The presence of untempered martensite, however, is extremely detrimental to SSC resistance. This is illustrated in Fig. 8, which shows the effect of tempering above the $Ac_1$ temperature for molybdenum-niobium modified 4130 steels containing two levels of silicon. Water quenching from above the $Ac_1$ temperature results in untempered martensite with a subsequent loss in SSC resistance. It has also been found that the development of a fine prior-austenite grain size and the use of accelerated cooling rates after tempering improve SSC resistance. The necessity for adequate hardenability is quite evident when considering alloy steels for heavy section wellhead components. Figure 9 shows how the SSC resistance of conventional steels used in wellhead equipment can be improved through modifications in composition, which increase hardenability.

It is common practice when quenching tubular products for this application to implement both inside-diameter and outside-diameter quenches to ensure that the entire cross section is transformed to martensite.

**Effect of Cold Work.** It is widely known that cold work can adversely affect the SSC resistance of materials. The hardness is locally increased, and residual stresses can also be generated. Hardnesses that greatly exceed 22 HRC (some as high as 40 HRC have been measured) can be produced by improper straightening and handling. Even identification stamping has been reported to cause enough cold work to initiate sulfide-stress cracks.

**Effect of a Stress.** Because SSC is a stress-dependent phenomenon, the actual stress to which the component is subjected will affect the SSC resistance of the material. It must be remembered that the total stress, which includes both applied and residual stresses, must be considered. It is generally agreed that there is a threshold stress below which SSC is not expected. The threshold stress is a function of the material as well as environmental parameters. However, it is difficult to design to this threshold stress because of the uncertainty of controlling the service conditions at all times. Another factor that contributes to high stresses and the initiation of sulfide-stress cracks is

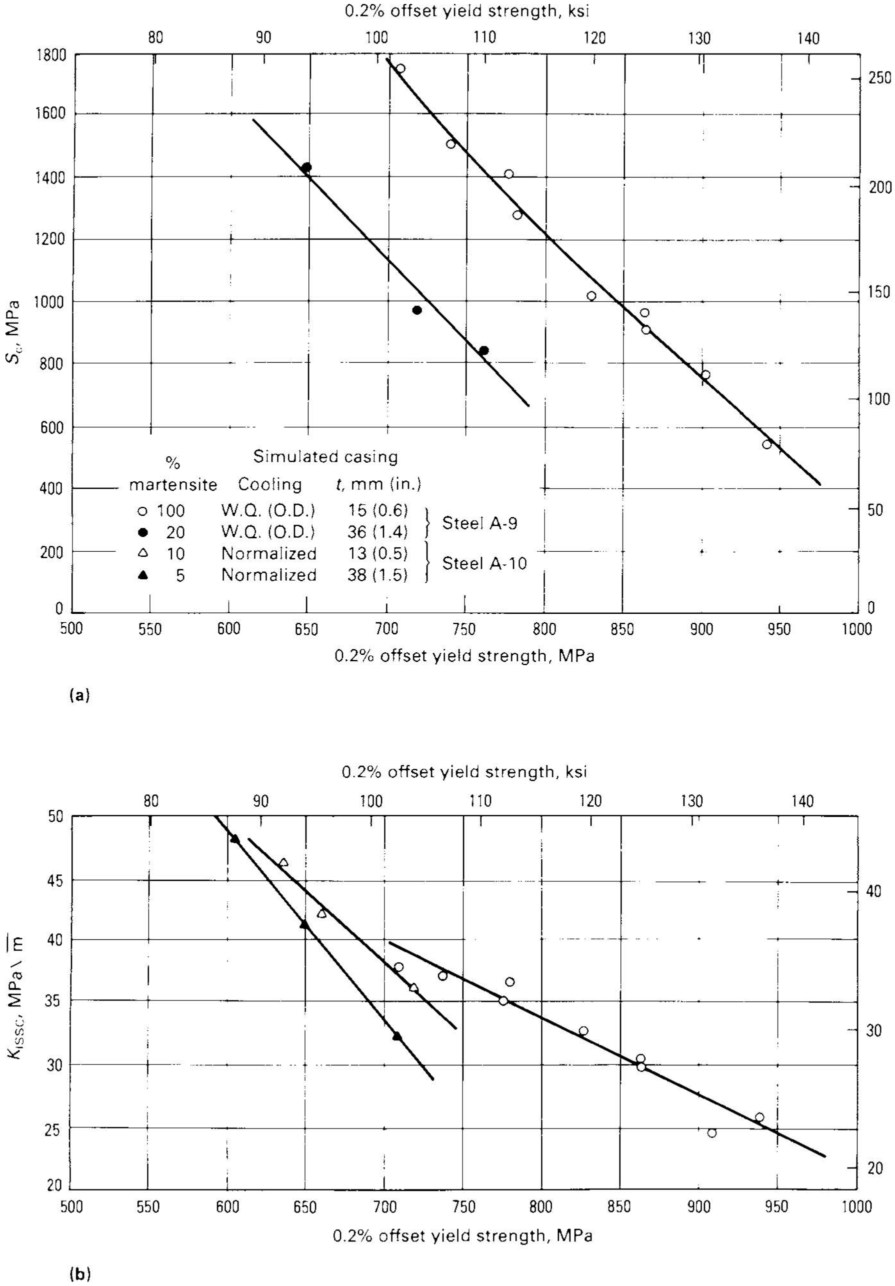

**Fig. 6** Effect of yield strength on the critical stress, $S_c$, and sulfide fracture toughness, $K_{ISSC}$, of molybdenum-niobium modified 4135 steel cooled from the austenitizing temperature at different rates to produce a wide range of martensite contents and then tempered. W.Q. (O.D.), externally water quenched. (a) Bent-beam test. (b) Double-cantilever beam test (without salt). See Table 1 for steel compositions. Source: Ref 26

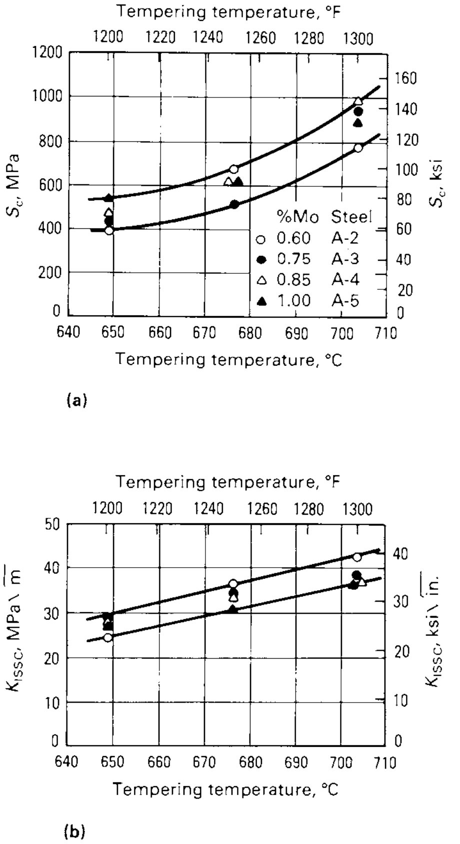

**Fig. 7** Effect of temperature of a 1-h temper on the critical stress, $S_c$, and sulfide fracture toughness, $K_{ISSC}$, of molybdenum-niobium modified 4130 steels. (a) Bent-beam test. (b) Double-cantilever beam test. See Table 1 for steel compositions. Source: Ref 26

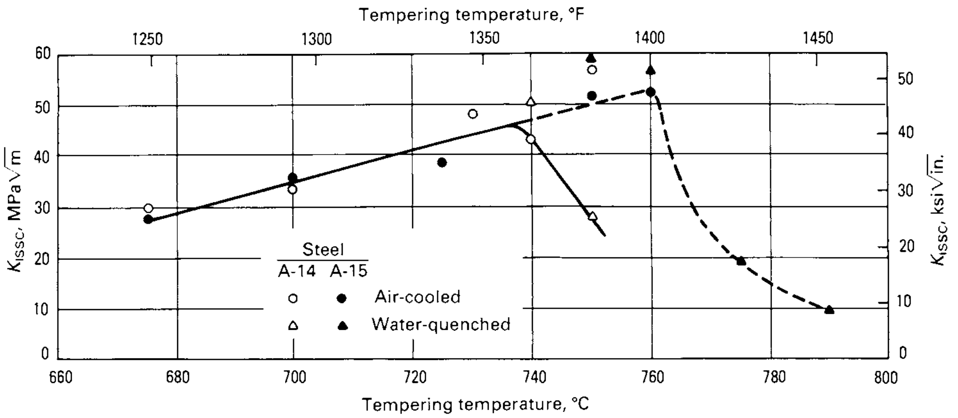

**Fig. 8** Effect of tempering temperature on sulfide fracture toughness, $K_{ISSC}$, of molybdenum-niobium modified 4130 steel A-14 and A-15. See Table 1 for steel compositions. Source: Ref 26

the presence of stress concentrations, such as those found in threaded connections.

## Hydrogen-Induced Cracking (HIC)

Hydrogen-induced cracking, also called stepwise cracking or blister cracking, is primarily found in lower-strength steels, typically with tensile strengths less than about 550 MPa (80 ksi). It is primarily found in line-pipe steels.

This type of degradation also begins with a reaction between steel and hydrogen sulfide in the presence of water. Again, hydrogen atoms enter the steel, but with HIC, as opposed to SSC, these hydrogen atoms combine to form hydrogen gas at internal defects. These internal discontinuities can be hard spots of low-temperature transformation products or laminations. However, manganese sulfide inclusions are the primary sites for this to occur. These inclusions tend to become elongated during pipe manufacture and give rise to high stresses at the tip of the inclusion when hydrogen gas forms there. As cracks initiate and propagate, they begin to link up with others, and a series of stepwise cracks can propagate through the material (Fig. 10). An applied stress is not required for this mechanism to occur.

Aside from reducing the amount of hydrogen being generated by reducing the corrosion reaction, another way of controlling HIC is through material processing. Shape control of sulfide inclusions is perhaps the best way to minimize the tendency toward HIC in line-pipe steels. Elongated manganese sulfide inclusions promote crack initiation and propagation due to the high stresses at the tips of the inclusions. However, the addition of calcium or rare earths to the steel makes the sulfides spherical, and because of their hardness, they remain spherical after processing. In addition, reduction of the sulfur content is also beneficial in reducing the susceptibility of steels to HIC. Other alloying additions that reduce hydrogen permeation, such as copper up to about 0.25%, are also beneficial (Ref 28).

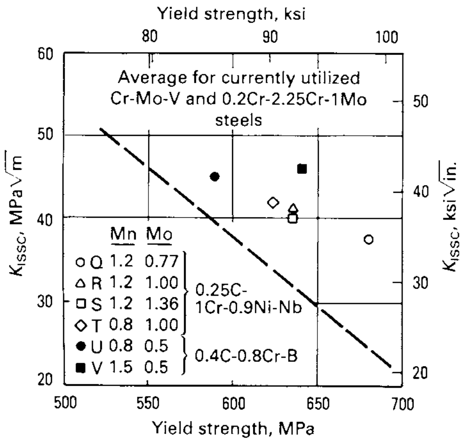

**Fig. 9** Effects of molybdenum and manganese content on the SSC resistance of manganese-nickel-chromium-molybdenum-niobium and manganese-chromium-molybdenum-boron steels. Open symbols are 400-mm (16-in.) section thickness; closed symbols are 250-mm (10-in.). Source: Ref 27

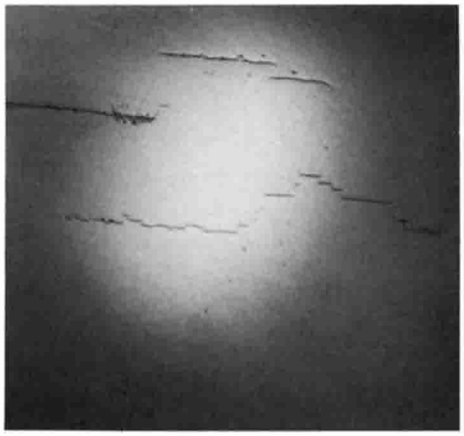

**Fig. 10** HIC of API, grade X-60, line-pipe steel after 28 days of exposure to ASTM seasalt brine, 20% $H_2S$, 20% $CO_2$, 1 atm, 24 °C

## Stress-Corrosion Cracking (SCC)

With this mechanism of degradation, a tensile stress is again required, together with a susceptible material and an environment that promotes cracking. In the oil and gas industries, the materials that are most generally found to be susceptible to SCC are the austenitic stainless steels and nickel-base alloys. Many different mechanisms have been proposed for SCC. The differences among these mechanisms depend upon the material and the environment, which would suggest that a single unified theory probably does not exist.

Austenitic stainless steels and nickel-base alloys are used in oil and gas production because they form protective films and therefore have very low corrosion rates. However, chloride ions (hence the term chloride stress-corrosion cracking), either in combination with hydrogen sulfide or alone, can attack this film, causing small pits to form. These small pits act as anodes, while the remainder of the oxide film acts as a cathode; the unfavorable area ratio causes the pit to grow. Also, the solution inside the pit is acidified because of the corrosion reaction, which also tends to increase the corrosion rate. Finally, a crack is initiated at the base of the pits because of the stress concentration, and propagation occurs because of the tensile stress. The crack often grows along grain boundaries because grain boundaries are electrochemically more active than the bulk grains. This is called active-path corrosion and is one of many possible mechanisms. Chloride SCC is usually observed at temperatures exceeding 65 to 95 °C (150 to 200 °F). Figure 11 shows an example of chloride SCC in an austenitic stainless steel. More information on SCC is available in the section "Environmentally Induced Cracking" of the article "Forms of Corrosion in the Petrochemical Industry" in this Volume.

There has been considerable interest in minimizing weight-loss corrosion in sour environments by using corrosion-resistant alloys. Corrosion-resistant alloys include nickel-base alloys, austenitic stainless steels, and duplex stainless steels. Use of these alloys is extremely attractive for offshore applications, where the corrosion inhibition of carbon and low-alloy steels may be difficult and expensive. Corrosion-resistant alloys possess very low corrosion rates because of the presence of a passivating oxide layer that protects the base metal from further corrosion. In general, it has been found that the risk of SCC of these alloys in production environments increases as temperature and chloride and hydrogen sulfide concentrations increase. In many cases, a synergism exists between $H_2S$ and chloride. Separately, each will not cause SCC, but together they promote it.

The presence of elemental sulfur also increases susceptibility to SCC. The reason for this is complicated, but it is probably due in part to a shift in potential into a range in which cracking is observed. If the pH is decreased, the material becomes more susceptible to SCC. The tendency of a material to exhibit SCC is also very temperature dependent. As temperature increases, susceptibility to SCC in production environments also increases. Unfortunately, this is where corrosion-resistant alloys are of most use, because corrosion inhibitors often become ineffective at elevated temperatures.

### Comparison of SSC and SCC

Stress-corrosion cracking is usually considered to be an anodic process, while SSC is considered to be a cathodic process. This can be very important in analyzing failures because the success of the method chosen to eliminate future failures may depend to a great extent on the determination of the proper failure mechanism. For example, it may have been decided that a particular failure was due to chloride SCC, and cathodic protection is being considered to increase the resistance of the material. However, if the actual failure mechanism is SSC, this remedy may actually worsen the situation because SSC is a cathodic process. The application of a cathodic-protection current will tend to add even more hydrogen to the lattice, which will increase the likelihood of another failure. It should be remembered that failures of low-alloy steels will most often be the result of SSC, while the high-temperature embrittlement of high-alloy stainless materials will most likely be due to SCC. Failure classification of intermediate alloys is sometimes more difficult.

Another important difference between SCC and SSC is the effect of temperature. Decreasing temperature usually causes a decrease in SCC susceptibility, while decreasing temperature causes an increase in SSC susceptibility. This can be useful when trying to determine the actual failure mechanism.

## Corrosion Control Methods

### Selection of Corrosion-Resistant Alloys

Traditionally, carbon and low-alloy steels were virtually the only metals used in the production of oil and gas. This was because large quantities of metal are required in petroleum production, and until a few years ago, crude oil and gas were relatively low-value products. In addition, insurmountable corrosion problems were not encountered.

This situation changed when gas and oil prices increased drastically and deeper wells were drilled that encountered corrosive environments of greatly increased severity. The final factor that made the current widespread use of corrosion-resistant alloy possible was the development of high-strength forms of these alloys. This allowed thinner pipe and vessel walls and greatly reduced the amount of material required.

The result of this situation is that essentially all high tonnage uses of corrosion-resistant alloy in oil and gas production involve alloys in high-strength form. Yield strengths typically span the range of 550 to 1250 MPa (80 to 180 ksi), but can reach nearly 1750 MPa (250 ksi) in wire lines. Table 2 lists the compositions of some corrosion-resistant alloys used in oil and gas production.

Alloy selection, from a corrosion standpoint, can be considered to be a three-step process. First, resistance to general corrosion must be ensured. This is primarily a function of the chromium content of the alloy. Second, resistance to localized attack also must be ensured. This is primarily a function of molybdenum content. Finally, resistance to environmental stress cracking is sought at the highest feasible strength level. Nickel content plays a principal role in this instance, particularly in providing resistance to anodic cracking.

The close correlation between pitting resistance and resistance to anodic cracking should be noted. This apparently results from the ease of crack initiation under the low-pH high-chloride conditions found in pits. Therefore, higher molybdenum can also increase resistance to anodic cracking.

With the procedures given below, regions of alloy applicability can be shown schematically as a qualitative function of environmental severity. This has been attempted in Fig. 12, in which an aqueous, $CO_2$-containing environment (hence low pH) has been assumed and the effects of temperature, chloride, and $H_2S$ concentration are illustrated. The effect of yield strength is not shown, but if environmental cracking is the limiting factor, reducing the yield strength should extend applicability to more severe environments.

The reader should be cautioned that a diagram such as Fig. 12 is really more of a guide to alloy qualification than to direct selection for a particular application. Therefore, it may aid in developing a more efficient approach to alloy testing.

### Testing for Resistance to Environmental Stress Cracking

The most directly applicable results are obtained by exposing samples of commercially produced alloys to an environment simulating as closely as possible that expected in actual production operations. Fortunately, an understanding of the principles involved allows considerable simplification to be made without significantly altering the value of the results.

Two simplifications can be readily made in the environmental parameters, as follows. First, only the $CO_2$ and $H_2S$ partial pressures are usually reproduced. The overburden of methane pressure to create the actual total pressure of the environment is dispensed with. This can substan-

**Fig. 11** SCC of AISI type 304 austenitic stainless steel. As-polished. 100×

**Table 2 Compositions of corrosion-resistant alloys**

| Alloy | UNS designation | Composition, %(a) C | Cr | Fe | Ni | Mo | Other |
|---|---|---|---|---|---|---|---|
| Hastelloy alloy C-276 | N10276 | 0.02 | 14.5-16.5 | 4-7 | bal | 15-17 | 2.5Co, 1.0Mn, 4.5W, 0.35V |
| Hastelloy alloy G | N06007 | 0.05 | 21-23.5 | 18-21 | bal | 5.5-7.5 | 2.5Nb, 2.5Co, 2.5Cu, 2.0Mn, 1W, 1Si |
| Haynes No. 20 Mod | N08320 | 0.05 | 21-23 | bal | 25-27 | 4-6 | 2.5Mn, 1Si, Ti-4 × C min |
| Sanicro 28 | N08028 | 0.03 | 26-28 | bal | 29.5-32.5 | 3-4 | 1.4Cu, 2.5Mn, 1Si |
| Inconel alloy 625 | N06625 | 0.10 | 20-23 | 5 | bal | 8-10 | 0.4Al, 4.15Nb, 0.5Mn, 0.4Ti |
| Incoloy alloy 825 | N08825 | 0.05 | 19.5-23.5 | bal | 38-46 | 2.5-3.5 | 0.2Al, 3Cu, 1Mn, 1.2Ti, 0.5Si |
| Monel alloy 400 | N04400 | 0.3 | ... | 2.5 | 63-70 | ... | bal Cu, 2Mn, 0.5Si |
| MP35N | R30035 | 0.025 | 19-21 | 1.0 | 33-37 | 9-10.5 | bal Co, 0.15Mn, 1Ti |
| Type 316 stainless steel | S31600 | 0.08 | 16-18 | bal | 10-14 | 2-3 | 2Mn, 1Si |
| Type 410 stainless steel | S41000 | 0.15 | 11.5-13.5 | bal | ... | ... | 1Si, 1Mn |
| Ferralium 255 | S32550 | 0.04 | 24-27 | bal | 4.5-6.5 | 2-4 | 2.5Cu, 1.5Mn, 0.25N, 1Si |

(a) Maximum unless range is given or otherwise indicated tially lower the pressure ratings of test vessels. Second, only the chloride content of the brine is typically reproduced, rather than trying to simulate the total ionic spectrum of the produced fluids. Often, no reliable analysis is available. Assumption of a saturated sodium chloride solution is then a relatively conservative approach.

A wide variety of test specimens are used, but for high-strength corrosion-resistant alloy tubulars, C-rings are particularly convenient. Double cantilever beam specimens are very attractive because they can provide a quantitative measure of fracture toughness, which can then be used in mechanical design. Other specimens that can be statically loaded include U-bend specimens, tensile bars, and bent beams. The most widely used dynamic test is the slow strain-rate test. The advantages and disadvantages of different test methods are reviewed in Ref 29.

U-bends are made from sheet and bent into a "U" shape to stress the material plastically. The specimen is usually held in this position by a bolt while taking care to ensure electrical isolation between the two if they are not of the same material. The technique is discussed in ASTM G 30 (Ref 30). Specimens are exposed to the environment for the desired time and then examined with metallographic techniques. This test provides information only on whether or not the material cracked during the exposure. The advantage of this test is that a large number of specimens can be run at the same time, which lends itself to the screening of various alloys.

Tensile bars, C-rings, and bent beams are all stressed to known values, which are usually reported as a percentage of yield strength. Use of any of the three of these specimen types results in a threshold stress below which cracking is not expected. This is a useful way of ranking materials; a material with a high threshold is assumed to perform better in field environments.

Of the three specimen types listed above, only the tensile bar is associated with a standard test method for sour environments. However, a NACE committee (T-1F-9) is currently developing suitable standards for all three specimen types.

A great deal of testing has been conducted using tensile bars in accordance with the NACE TM-01-77 test method (Ref 31). This method uses a test solution (called NACE solution) consisting of 5% NaCl, 0.5% acetic acid, and 1 atm $H_2S$ being bubbled through the solution at room temperature. The test is run for 720 h with the time-to-failure being plotted at various stress levels. From this plot, a threshold stress can be determined. The test specimens can be cut from almost any product form.

C-rings are made from tubular products and are bolt loaded to the desired stress level. ASTM G 38 (Ref 32) gives a procedure for making and stressing these samples. These specimens are usually placed in environments that more closely simulate field conditions than does the NACE solution. This requires the use of high-temperature and high-pressure autoclaves. The specimens are examined metallographically at the conclusion of the test for evidence of cracking. Again, a threshold stress can be determined for the exposure period in order to rank alloys.

Bent beams can be stressed in three-point or four-point bending. The stress level is again reported as a percentage of yield strength, and samples are tested in autoclaves to determine the susceptibility to cracking of the material over some particular time period. Beams can be machined from almost any product form.

Double-cantilever beam specimens are fracture mechanics specimens that allow development of crack-propagation data after the samples are exposed to the test environment (Ref 33). Other types of fracture mechanics specimens could be used, but the double-cantilever beam is the most common and probably the most convenient. These specimens are precracked by fatigue loading, then wedge-loaded to develop an initial stress intensity at the crack tip. If the crack propagates during the test, the stress intensity decreases, which reduces the driving force for further crack propagation. After a certain period of time, the crack is arrested. By measuring the length of the crack at arrest, a threshold value for the stress intensity can be calculated. This value is rarely used in minimum flaw tolerance design of drilling equipment. Instead, it provides a numerical value to be used for ranking alloys.

The slow strain-rate test, or constant extension rate test (CERT), is a technique that is used to determine the susceptibility of a material to cracking under dynamic loading conditions. The specimen is a tensile bar with a gauge diameter of about 2.5 mm (0.1 in.). A specimen is tested to failure in the environment of interest, and another is tested in an inert environment, such as air. Strain rates between $10^{-4}$ and $10^{-8}$ $s^{-1}$ can be used, with rates between $10^{-6}$ and $4 \times 10^{-6}$ $s^{-1}$ being common.

After the experiment, the fracture surface can be examined for evidence of embrittlement. Also, the ductility of the sample tested in the environment (measured by reduction of area of percent elongation) is compared to that of the test performed in air. A decrease in ductility is an indication that the material may be susceptible to embrittlement.

The slow strain-rate test is often considered to be a severe test because it will usually indicate embrittlement when other tests do not. This may be related to the fact that any passive films on the specimen surface are continually broken during the test, which exposes fresh surface to the environment. Detailed information on environmental cracking test specimens, procedures, and results can be found in the article "Evaluation of Stress-Corrosion Cracking" in Volume 13 of the *ASM Handbook*.

The National Association of Corrosion Engineers has published a procedure for testing steels to determine their hydrogen-reduced cracking (HIC) resistance. Standard TM-02-84 (Ref 34) calls for exposing unstressed coupons to a synthetic seawater solution saturated with hydrogen sulfide at ambient temperature at a pH between 4.8 and 5.4. The test is run for 96 h and is designed to accelerate the formation of cracks.

At the conclusion of the test, the samples are polished, and any cracks are measured at 100×. Crack thickness, length, and sensitivity ratios are calculated and are used to rank the various materials.

## Coatings

Internal protective coatings have been used to protect tubing, downhole equipment, wellhead components, Christmas trees (manifolds used to control the rate of production, receive the produced fluids under pressure, and direct the produced fluids to the gathering point), and various downstream flow lines and pressure vessels for

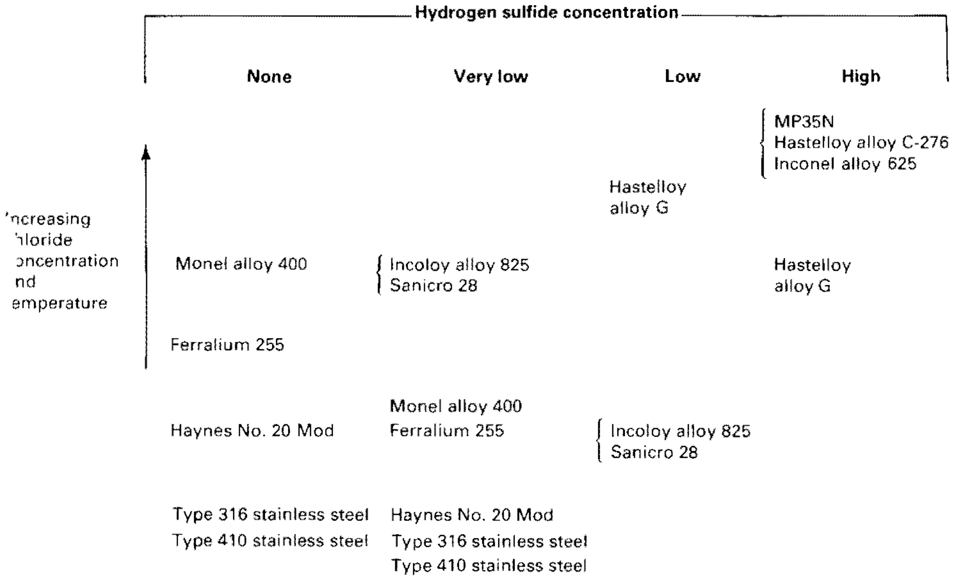

**Fig. 12** Schematic showing corrosion-resistant alloy selection for production environments containing aqueous $CO_2$ and $H_2S$

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more than 30 years. Because internal coatings are subject to damage, successful use is usually accompanied by chemical inhibition or cathodic protection as part of the entire protective program. Most of the coating use has been below 175 °C (345 °F).

**Tubing.** The benefits derived from coating tubing depend on the coating remaining intact. Because no coating can be applied and installed 100% holiday-free, inhibition programs are commonly employed to accommodate holidays and minor damage. The suitability of the service is dependent on specific testing and an effective quality control program.

Inhibitor and volume will not change even though an operator decides to use coated tubing rather than bare tubing. The use of coated tubing improves the protection in shielded areas that are inaccessible to inhibitors. The two greatest dangers to coated tubing are wireline damage and improper joint selection. Wireline damage can be minimized by adjusting running procedures to include wireline guides and to slow wireline speed (<0.5 m/s, or <100 ft/min). Inhibiting immediately after wireline work is good practice.

Proper joint selection involves choosing a joint that allows coating to be applied around the pin nose into the first few pin threads and from the first few coupling threads into the coupling body. The proper joint allows the coating to remain undamaged. Often, a corrosion barrier compression ring is used to accomplish this end. Metal-to-metal sealing joint designs are not joints that can be coated.

The coatings used for tubing protection are polyurethane, phenolformaldehyde, epoxized cresol novolac, and epoxy resins. Suitability for service is and should be based on laboratory testing using the specific environment proposed for the service.

The quality control parameters of concern are tubing surface finish/preparation, application techniques, coating thickness, holiday detection, joint condition, and inspection. Inspection is required to ensure the suitability of the other parameters. Quality control and surveillance are as much a part of a successful protective coating program as choosing the appropriate coating. The production coating must be applied in the same way the coating was applied to the test specimens.

Coated pipe and couplings must be carefully handled after coating, during shipping, in storage, and at the well site. The threads must be protected from impact with other pipe and objects.

Wireline work is necessary. These operations can be accomplished with a minimal amount of damage to the tubing if the wireline speeds are kept to 0.5 m/s (100 ft/min) or less, if all sharp edges are removed from the tools, if all tools are plastic coated or covered with a plastic sleeve, and if wheeled centralizers are used on all center hole jobs. Using the above precautions, many wireline trips can be made with little or no damage. The fact that coating should not be used because the wireline will cut the coating and cause accelerated corrosion in the wireline track is not true. When the wireline cuts uncoated tubing, it causes cold work. The wireline track then becomes anodic to the surrounding bare steel, and corrosion is accelerated. In coated tubing, the coating electrically insulates the cathodic areas so that the corrosion rate in the track is essentially the same as that for uncoated steel without wireline damage.

**Wellheads, Christmas Trees, and Downhole Equipment.** Exposed surfaces of wellhead equipment, Christmas trees, and downhole equipment must be coated or manufactured of corrosion-resistant materials. This starts with the tubing hanger, which is threaded onto the production tubing, and continues through the tubing bonnet (tubing adapter), the master valve(s), the tee or cross, and the wing and crown valve(s) and into the choke. Ring gasket grooves, valve seat pockets and other compression fitted parts must not be coated. These areas can be overlaid with corrosion-resistant alloys, and the coating can be applied over a transition area up to the corrosion-resistant alloy overlay. Valve internal cavities need not be coated.

Generally, tubing hangers are difficult to coat and are therefore made of corrosion-resistant alloys for corrosive service. Hangers without back pressure valve threads can be coated, but the cost of coating the carbon steel hanger may be equivalent to the cost of a corrosion-resistant alloy hanger.

Downhole equipment (nipples, polished bore receptacles, seal subs, tie backs, millout subs, packers, and so on) use the same stan-dards as tubing. Most downhole equipment is considered

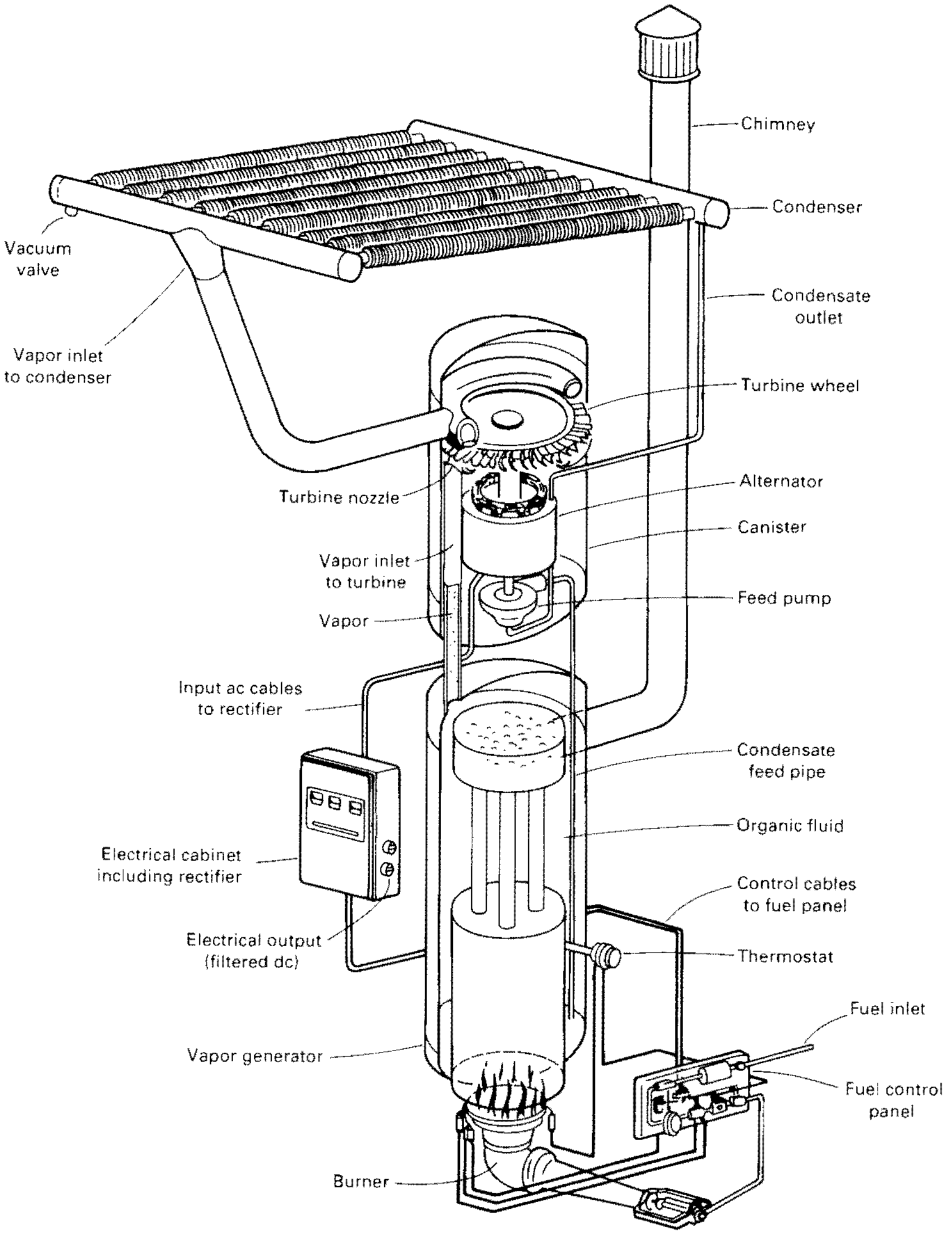

**Fig. 13** Thermoelectric generator used to power cathodic protection systems in remote locations. Source: Ref 39

# Corrosion in Petroleum Refining and Petrochemical Operations

# Corrosion in Petroleum Refining and Petrochemical Operations

CORROSION has always been an unavoidable part of petroleum refining and petrochemical operations. Although certain materials problems are caused by other factors, a predominant number are due to various aspects of corrosion. Corrosion problems increase operating and maintenance costs substantially. Scheduled and unscheduled shutdowns for repairing corrosion damage in piping and equipment can be extremely expensive, and anything that can be safely done to keep a process unit on stream for long periods of time will be of great benefit. A large proportion of corrosion problems are actually caused by shutdowns. When equipment is opened to the atmosphere for inspection and repair, metal surfaces covered with corrosion products will be exposed to air and moisture. This can lead to pitting corrosion and stress-corrosion cracking unless preventive measures are implemented. When equipment is washed with water during a shutdown, corrosion can be caused by pockets of water left to dry.

Most petroleum refining and petrochemical plant operations involve flammable hydrocarbon streams, highly toxic or explosive gases, and strong acids or caustics that are often at elevated temperatures and pressures. Among the many metals and alloys that are available, relatively few can be used for the construction of process equipment and piping (Ref 1). These include carbon steel; some cast irons; certain low-alloy steels and stainless steels; and, to a much lesser degree, aluminum, copper, nickel, titanium, and their alloys. This article will present the considerations and concerns involved in selecting materials for process equipment in refineries and petrochemical plants. In addition, specific information on mechanical properties, corrosion, stress-corrosion cracking (SCC), erosion, and corrosion control will be provided.

## Materials Selection

The selection of materials of construction has a significant impact on the operability, economics, and reliability of refining units and petrochemical plants. For this reason, materials selection should be a cooperative effort between the materials engineer and plant operations and maintenance personnel. Reliability can often be equated to predictable materials performance under a wide range of exposure conditions. Ideally, a material should provide some type of warning before it fails; materials that fracture spontaneously and without bulging as a result of brittle fracture or SCC should be avoided. Uniform corrosion of equipment can be readily detected by various inspection techniques. In contrast, isolated pitting is potentially much more serious because leakage can occur at highly localized areas that are difficult to detect. The effect of environment on the mechanical properties of a material can also be significant. Certain exposure conditions can convert a normally ductile material into a very brittle material that may fail without warning. A material must not only be suitable for normal process conditions but must also be able to handle transient conditions encountered during start-up, shutdown, emergencies, or extended standby. It is often during these time periods that equipment suffers serious deterioration or that failure occurs.

Of particular concern is what will happen to equipment during a fire. Unexpected exposure to elevated temperatures can not only affect mechanical properties but can also produce detrimental side effects. Although all possible precautions should be taken to minimize the probability of a fire, the engineer responsible for materials selection must recognize that a fire may occur and that the equipment is expected to retain its integrity in order to avoid fueling the fire. This limits the application of materials with low melting points or those that may become subject to damage by thermal shock when fire-fighting water is applied, particularly in the case of refinery piping and equipment used to handle highly flammable hydrocarbon streams. On the other hand, fire resistance need not be considered for cooling-water or instrument-air systems. Although petrochemical plants may include some processes that involve nonflammable or nonhazardous streams, most equipment must be resistant to fires. Lack of fire resistance rules out the use of plastic components in refineries and petrochemical plants despite their excellent resistance to many types of corrosives. In addition, plastic components tend to be damaged by steam-out during a shutdown; this is required in order to free components of hydrocarbon residues and vapor before inspection or maintenance operations. The final step in the materials selection process is a reliability review of the materials and the corrosion control techniques that were selected. There must be total assurance that a plant will provide reliable service under all conditions, including those that occur during start-ups, shutdowns, downtime, standby, and emergencies.

## Principal Materials

Materials selection criteria for a number of ferrous and nonferrous alloys used in petroleum-refining and petrochemical applications are presented in this section. Additional information on selecting the proper metal or alloy is available in the section "Materials Selection" in the article "Designing to Minimize Corrosion" in this Volume. Additional information on the corrosion characteristics of specific alloy systems is available in the article "Corrosion of Specific Alloy Systems" in Volume 13 of *ASM Handbook.*

**Carbon and Low-Alloy Steels.** Carbon steel is probably used for at least 80% of all components in refineries and petrochemical plants because it is inexpensive, readily available, and easily fabricated. Every effort is made to use carbon steel, even if process changes are required to obtain satisfactory service from carbon steel (Ref 2). For example, process temperatures can be decreased, hydrocarbon streams dried up, or additives injected in order to reduce potential corrosion problems with carbon steel (Ref 3). In refineries, fractionation towers, separator drums, heat-exchanger shells, storage tanks, most piping, and all structures are generally fabricated from carbon steel. Carbon molybdenum steels, primarily the C-0.5Mo grade, can offer substantial savings over carbon steels at temperatures between 425 and 540 °C (800 and 1000 °F). Because C-0.5Mo steel has better resistance than carbon steel to high-temperature hydrogen attack, it has been extensively used for reactor vessels, heat-exchanger shells, separator drums, and piping for processes involving hydrogen at temperatures above 260 °C (500 °F). Recently, however, questions have been raised regarding the effect of long-term hydrogen exposure on C-0.5Mo steel. As a result, low-alloy steels are preferred for new construction.

Low-alloy steels for refinery service are the chromium-molybdenum steels containing less than 10% Cr. These steels have excellent resistance to certain types of high-temperature sulfidic corrosion as well as to high-temperature hydrogen attack. To improve resistance to hydrogen stress cracking, low-alloy steels normally require postweld heat treatment. For refinery reactor vessels, which operate at high temperatures and pressures, 2.25Cr-1Mo steel is widely used. For improved corrosion resistance, these are often overlayed with stainless steel. Other applications for low-alloy steels are furnace tubes, heat-exchanger shells, and piping and separator drums.

**Stainless steels** are extensively used in petrochemical plants because of the highly corrosive nature of the catalysts and solvents that are often used. In refineries, stainless steels have been primarily limited to applications involving high-temperature sulfidic corrosion and other forms of high-temperature attack (Ref 4). Most stainless steels will pit in the presence of chlorides (Ref 5).

Martensitic stainless steels, such as type 410 (S41000), must be postweld heat treated after welding to avoid hydrogen stress cracking problems as a result of exposure to hydrogen sulfide containing environments. Typical applications include pump components, fasteners, valve trim, turbine blades, and tray valves and other tray components in fractionation towers. Low-carbon varieties of type 410 stainless steel (S41008) are preferred for furnace tubes and piping, often in combination with aluminizing. Ferritic stainless steels, such as type 405 (S40500), are not subject to hydrogen stress cracking and are therefore a better choice than type 410 (S41000) stainless steel for vessel linings that are attached by welding (Ref 6). Austenitic stainless steels, such as type 304 (S30400) or type 316 (S31600), have excellent corrosion resistance, but are subject to SCC by chlorides. If sensitized, they are also subject to SCC by polythionic acids (Ref 7, 8). Typical applications include linings and tray components in fractionation towers; piping; heat-exchanger tubes; reactor cladding; tubes and tube hangers in furnaces; various components for compressors, turbines, pumps, and valves; and reboiler tubes.

**Cast irons,** because of their brittleness and low strength, are normally not used for pressure-retaining components for handling flammable hydrocarbons. The main exceptions are pump and valve components, ejectors, jets, strainers, and fittings in which the high hardness of cast iron reduces the velocity effects of corrosion, such as impingement, erosion, and cavitation. High-silicon cast irons (with 14% Si) are extremely corrosion resistant because of a passive surface layer of silicon oxide that forms during exposure to many chemical environments (except hydrofluoric acid). Typical refinery and petrochemical plant applications include valve and pump components for corrosive service. High-nickel cast irons (with 13 to 36% Ni and up to 6% Cr) have excellent corrosion, wear, and high-temperature resistance because of the relatively high alloy content (Ref 9). Typical uses are valve components, pump components, dampers, diffusers, tray components, and compressor parts.

**Copper and aluminum alloys** are usually restricted to applications below 260 °C (500 °F) because of strength limitations. Admiralty metal (C44300) tubes have been extensively used in water-cooled condensers and coolers at most refineries, but have often performed poorly in overhead condensers, compressor aftercoolers, and other locations where high concentrations of hydrogen sulfide and ammonia are encountered in aqueous condensate. The usual failure modes are pitting, ammonia SCC, and dezincification. Aluminum alloys, at one time, were proposed for refinery use as a substitute for carbon steel and admiralty metal (C44300) heat-exchanger tubes in cooling-water service (Ref 10-12). Aluminum tubes were found to be highly resistant to aqueous sulfide corrosion in overhead condensers. Unfortunately, fouling and pitting corrosion on the water side have always been a problem, and except for certain limited applications, most refineries do not use aluminum tubes. The only other major refinery use of aluminum has been in vacuum towers, in which aluminum provides resistance to the naphthenic acid corrosion of tray components. Aluminum is also used, in the form of aluminized coatings, to protect low-alloy steels against high-temperature sulfidic corrosion.

**Nickel alloys** are especially resistant to sulfuric acid, hydrochloric acid, hydrofluoric acid, and caustic solutions, all of which can cause corrosion problems in certain refinery and petrochemical operations (Ref 13). As the nickel content is increased above 30%, austenitic alloys become, for all practical purposes, immune to chloride SCC. Nickel also forms the basis for many high-temperature alloys, but nickel alloys can be attacked and embrittled by sulfur-bearing gases at elevated temperatures. Alloy 400 (N04400) is extensively used as a lining for carbon steel equipment to prevent corrosion by hydrochloric acid and chloride salts (Ref 14). For the same reason, Alloy 400 (N04400) tubes have been used in overhead condensers. Alloy 400 (N04400) is also used against corrosion by hydrofluoric acid. High-nickel alloys, including alloy 625 (N06625) and alloy 825 (N08825), are used to reduce the polythionic acid corrosion of flare-stack tips. Alloy B-2 (N10665) is particularly well suited to handling hydrochloric acid at all concentrations and temperatures (including the boiling point), but is attacked if oxidizing salts are present (Ref 15, 16). Alloy B-2 (N10665), alloy C-4 (N10002), and alloy C-276 (N10276) have excellent resistance to all concentrations of sulfuric acid up to at least 95 °C (200 °F). Although expensive, these alloys are used for specific applications to overcome unusually severe corrosion problems.

**Titanium** is a relative newcomer to the refining industry, but it has been extensively used in certain petrochemical processes. Titanium is not a high-temperature metal; welding and cutting must be done under inert gas atmospheres to prevent embrittlement (Ref 17, 18). From a practical point of view, the use of titanium in refinery and petrochemical plant service is limited to temperatures below 260 °C (500 °F) (Ref 19, 20). If

**Table 1 Construction codes for refinery process equipment**

| Country | Issuing organization | Source document(s) |
|---|---|---|
| **Pressure Vessels** | | |
| United States | American Society of Mechanical Engineers/ American National Standards Institute | Boiler and Pressure Vessel Code, Section VIII |
| Great Britain | British Standards Institution | BS 1515: Fusion Welded Pressure Vessel for use in the Chemical, Petroleum and Allied Industries<br>BS 5500: Unfired Fusion Welded Pressure Vessels |
| Germany | Arbeitsgemeinschaft Druckbehalter (published by Carl Heymans Verlag KG) | A.D. Merkblatter |
| Italy | Associazione Nazionale per il Controllo della Combustione | ANCC Code |
| Netherlands | Dienst voor Stoomwezen | Regels Voor Toestellen (Rules for Pressure Vessels) |
| Sweden | Tryckkarlskomissionen (Swedish Pressure Vessel Commission) | Swedish Pressure Vessel Code |
| **Piping** | | |
| United States | American Society of Mechanical Engineers/ American National Standards Institute | B31.3 Code for Pressure Piping |
| Great Britain | British Standards Institution | BS 3351: Piping Systems for Petroleum Refineries and Petrochemical Plants |
| **Tanks** | | |
| United States | American Petroleum Institute | API 620: Recommended Rules for Design and Construction of Large Welded Low Pressure Storage Tanks<br>API 650: Welded Steel Tanks for Oil Storage |
| Great Britain | British Standards Institution | BS 2654: Vertical Steel Welded Storage Tanks for the Petroleum Industry |

**Table 2 ASTM standard specifications for refinery steels**

Carbon and alloy steel bolts and nuts covered by A193, A194, A320, A354, A449, A453, A540, A563

| Material | Pipes and tubes | Plates | Castings | Forgings |
|---|---|---|---|---|
| Carbon steel | A53, A106, A120, A134, A135, A139, A178, A179, A192, A210, A211, A214, A226, A333, A334, A369, A381(a), A524, A587, A671, A672, A691 | A283, A285, A299, A442, A455, A515, A516, A537, A570, A573(a) | A27(a), A216, A352 | A105, A181, A234, A268, A350, A372, A420, A508, A541 |
| C-0.5Mo steel | A161(a), A209, A250, A335, A369, A426, A672, A691 | A204, A302, A517, A533 | A217, A352, A487 | A182, A234, A336, A508, A541 |
| 1Cr-0.5Mo steel | A213, A335, A369, A426, A691 | A387, A517 | ... | A182, A234, A336 |
| 1.25Cr-0.5Mo steel | A199, A200(a), A213, A335, A369, A426, A691 | A387, A389(a), A517 | A217, A389(a) | A182, A234, A336, A541 |
| 2Cr-0.5Mo steel | A199, A200(a), A213, A369 | ... | ... | ... |
| 2.25Cr-1Mo steel | A199, A213, A335, A369, A426, A691 | A387, A542 | A217, A487 | A182, A234, A336, A541, A542 |
| 3Cr-1Mo steel | A199, A200(a), A213, A335, A369, A426, A691 | A387 | ... | A182, A336 |
| 5Cr-0.5Mo steel | A199, A200(a), A213, A335, A369, A426, A691 | A387 | A217 | A182, A234, A336 |
| 7Cr-0.5Mo steel | A199, A200(a), A213, A335, A369, A426 | A387 | ... | A182, A234 |
| 9Cr-1Mo steel | A199, A200(a), A213, A335, A369, A426 | A387 | A217 | A182, A234, A336 |
| Ferritic, martensitic, and austenitic stainless steel | A213, A249, A268, A269, A271(a), A312, A358, A376, A409, A430, A451, A452, A511(a) | A167, A176(a), A240, A412, A457 | A297(a), A351, A447(a) | A182, A336, A403, A473(a) |

(a) These specifications are not approved by either the ANSI/ASME Boiler and Pressure Vessel Code or by the ANSI/ASME Code for Pressure Piping B31.3.

hydrogen is present, temperatures should not exceed 175 °C (350 °F) in order to prevent embrittlement due to hydride formation. Titanium is fully resistant to many process streams. Tubes made from titanium grade 2 (R50400) are extensively used in overhead coolers and condensers on a number of refinery units to prevent corrosion by aqueous chlorides, sulfides, and sulfur dioxide. These tubes can corrode, however, beneath acidic deposits. Titanium tubes are often required when seawater or brackish water is used for cooling. Where underdeposit corrosion of pure titanium is a problem, titanium grade 12 (R53400), alloyed with nickel and molybdenum, should be used. Anodizing and high-temperature air oxidizing of titanium grade 2 (R50400) have been shown to be beneficial from a corrosion point of view (Ref 21).

## Codes and Standard Specifications

Rules for the design, fabrication, and inspection of pressure vessels, piping, and tanks are provided by codes that have been developed by industry and/or regulatory agencies in various countries, as shown by the listing in Table 1. In the United States, the ANSI/ASME Boiler and Pressure Vessel Code, Section VIII, which covers unfired pressure vessels, is used by most industries and fabricators. In most states, it is mandatory that the code be followed, and with the heightened concern over industrial safety, the number of states that require code compliance is increasing. Therefore, the first step in selecting materials of construction is to know what the code covers and what it does not.

The ANSI/ASME Boiler and Pressure Vessel Code also provides a list of acceptable steels and allowable stress values. The detailed specifications for these steels are provided in Sections II A and II B, which are based on ASTM standard specifications (Table 2). The code also provides the method for calculating the required minimum thickness of various components based on design temperature and pressure. The need for heat treating during fabrication and inspection requirements is also defined based on the alloy selected and the pressure-wall thickness. For welded pressure vessels, Section IX of the code defines the requirements for qualifying the welding process to be used.

The code does not consider the effect of process environment on the materials selected. The code recognizes that corrosion can and does occur, and it provides rules for including corrosion allowances in the calculation of the required pressure-wall thickness; but suitable values for the corrosion allowance must be specified by the designer. It is also the responsibility of the designer to specify any special heat treatments, hardness limitations, or other details that may be required as a result of environmental factors. Similarly, the designer must determine accurately the full range of likely operating conditions, including upsets, that may be encountered so that the design criteria are met.

## Mechanical Properties

**Elevated-Temperature Properties.** As mentioned in the preceding section, the applicable code will specify the allowable stress that is to be used for a particular steel in the design of a given piece of equipment. This allowable stress is based on the temperature to which the equipment will be exposed. Steels operating under normal plant conditions can be exposed to these temperatures for prolonged periods of time without adverse effects on their allowable strength if there is no corrosion. As working temperatures increase, the mechanical strength of most materials decreases. In actual practice, however, a material is more likely to fail at elevated temperatures by creep (elongation) or stress rupture than from a decrease in tensile or yield strength.

For example, Table 3 shows the short-term, elevated-temperature yield strengths of several carbon and low-alloy steels. As can be seen from the tabulated data, all three steels (carbon steel, C-0.5Mo steel, and 2.25Cr-1Mo steel) have satisfactory yield-strength values up to 480 °C (900 °F). These values do not, however, adequately represent the long-term resistance of the steels to creep when stressed at elevated temperatures. Instead, creep resistance values are a more accurate measure of elevated-temperature mechanical strength. Creep resistance values are obtained from creep and stress rupture tests at elevated temperatures over a period of 10 000 h and are usually extrapolated to 100 000 h. Table 4 shows creep resistance values for the three steels discussed above. The deterioration of creep resistance of carbon steel at 480 and 540 °C (900 and 1000 °F) is readily apparent, as is the marked improvement afforded by use of 2.25Cr-1Mo steel.

**Table 3 Short-term elevated-temperature yield strengths**

| Test temperature | | Carbon steel, 0.2% yield strength | | C-0.5Mo steel, 0.2% yield strength | | 2.25Cr-1Mo steel, 0.2% yield strength | |
|---|---|---|---|---|---|---|---|
| °C | °F | MPa | ksi | MPa | ksi | MPa | ksi |
| 25 | 80 | 248 | 36.0 | 276 | 40.0 | 272 | 39.5 |
| 150 | 300 | 208 | 30.2 | 241 | 34.9 | 247 | 35.8 |
| 260 | 500 | 192 | 27.8 | 212 | 30.7 | 238 | 34.5 |
| 370 | 700 | 175 | 25.4 | 190 | 27.6 | 234 | 34.0 |
| 480 | 900 | 148 | 21.5 | 175 | 25.4 | 193 | 28.0 |

Table 5 lists suggested maximum service temperatures for five different steels and alloys based on creep or rupture data. In some applications, such as furnace tubes, code-allowable stresses need not be followed, and equipment may be operated at temperatures and stresses that can lead to creep failure. In order to predict failure with greater accuracy, equipment operating in the creep range should be periodically inspected as the design life is approached.

**Hardness.** The hardness of steels is not considered by the code as a specified property. Whether it is the result of forming or welding operations, hardness has, however, a distinct effect on the suitability of a steel for a particular environment. Although carbon steel normally has low hardness values, cooling from elevated temperatures, such as those encountered during welding, may result in localized hard zones. If hardness values exceed 200 HB, carbon steel may become subject to cracking in aqueous sulfide environments. For this reason, it is often necessary to set a maximum hardness limit for carbon steel used in pressure vessels. In some cases, it is desirable to impose a uniform hardness limitation on all pieces of fabricated equipment because the originally intended service application might be changed at some future date to one in which the component would be exposed to an aqueous sulfide environment. A high hardness value is also indicative of an increase in tensile strength and a corresponding decrease in ductility. Steels with high hardness values can be expected to behave in a brittle manner. Low-alloy steels often require heat treatment after welding to reduce hardness in the weld area and to reduce the stresses associated with welding.

**Fatigue Strength.** Certain components, such as compressors or pumps, require materials with good fatigue resistance properties. Fatigue resistance also needs to be considered when bolting and piping materials are selected. Fatigue resistance is the ability of a load-carrying component to resist fracture from cycles of repeatedly applied forces, such as vibrational or rotational stresses. One common rule of thumb is to limit the average fatigue stress to approximately one-half the ultimate tensile strength of the material involved. Because fatigue involves crack formation, crack propagation, and residual strength, several mechanical properties are involved in determining fatigue resistance. Obviously, higher strength will help a material resist crack formation and final fracture. Other factors to be considered are the cleanliness of the material and whether it hardens or softens under plastic strain. Clean material with a low inclusion content and fine grains will improve fatigue resistance because inclusions can be a source for crack initiation, while fine grains will assist in allowing the crystallographic planes to slip without cracking.

**Low-Temperature Properties.** Carbon steel begins to lose its toughness and ductility as service temperatures decrease below ambient. Because most equipment in refineries and petrochemical plants is made of carbon steel, insufficient low-temperature toughness could represent a potentially serious problem. Fortunately, few operations are carried out at low temperatures and most equipment made of carbon steel operates at temperatures ranging from ambient to approximately 425 °C (800 °F). Refinery and petrochemical plant equipment and processes that may require special low-temperature toughness grades of steels include liquified-propane storage, ammonia storage, solvent dewaxing units, and liquified petroleum gas (LPG) processing. It is possible, by specifying certain additional requirements, to obtain carbon steels that are suitable for temperatures as low as –45 °C (–50 °F), depending on thickness. To resist brittle fracture at lowered temperatures, steels should be fully killed, fine grained, normalized, and should have received postweld heat treatment.

Typical American Society for Testing and Materials (ASTM) standard specifications for carbon steels with enhanced ability to perform at low temperatures are given in Table 6. Steels, alloyed with 2 to 9% Ni, and austenitic stainless steels can extend the range of available notch-tough steels to even lower temperatures. The simplest quality control test (although not always adequate) for ensuring proper notch toughness is the Charpy V-notch impact test carried out at the minimum design temperature, or lower. A minimum value of approximately 20.5 J (15 ft Ã lb) is the usual acceptance criterion. The Charpy test is designed to simulate failure of a pressure vessel, containing a fabrication- or service-induced cracklike defect, by rapid crack propagation (brittle failure) when stressed at low temperatures.

**Table 4 Creep resistance extrapolated to 100,000 h**

| Test temperature | | Carbon steel, stress for creep rate of 1% | | C-0.5Mo steel, stress for creep rate of 1% | | 2.25Cr-1Mo steel, stress for creep rate of 1% | |
|---|---|---|---|---|---|---|---|
| °C | °F | MPa | ksi | MPa | ksi | MPa | ksi |
| 425 | 800 | 95 | 13.8 | 150 | 21.8 | ... | ... |
| 480 | 900 | 41 | 6.0 | 98 | 14.2 | 152 | 22.0 |
| 540 | 1000 | 18 | 2.6 | 43 | 6.2 | 55 | 8.0 |

**Table 5 Suggested maximum temperatures for continuous service based on creep or rupture data**

| Material | Maximum temperature based on creep rate | | Maximum temperature based on rupture | |
|---|---|---|---|---|
| | °C | °F | °C | °F |
| Carbon steel | 450 | 850 | 540 | 1000 |
| C-0.5Mo steel | 510 | 950 | 595 | 1100 |
| 2.25Cr-1Mo steel | 540 | 1000 | 650 | 1200 |
| Type 304 stainless steel | 595 | 1100 | 815 | 1500 |
| Alloy C-276 nickel-base alloy | 650 | 1200 | 1040 | 1900 |

**Table 6 ASTM standard specifications for carbon steel with enhanced resistance to brittle fracture at lowered temperatures**

| Product form | Temperature | |
|---|---|---|
| | To –30 °C (–20 °F) | To –45 °C (–50 °F) |
| Plate | A516, normalized (may require impact testing) | A516 normalized, stress relieved and Charpy impact tested |
| Pipe | A524 | A333 grade 1 and grade 6 |
| Tube | A210 | A334 grade 1 and grade 6 |
| Forgings | A727 and A350 grade LF1 | A350 grade LF2 |
| Fittings | A420 WPL6 | A420 WPL6 |
| Castings | A352 grade LCA | A352 grade LCB and grade LCC |

**Embrittlement Phenomena.** There are a number of environmental effects on the mechanical properties of low-alloy steels and stainless steels used for refinery and petrochemical plant construction that need to be considered. In almost all cases, the effect is one of embrittlement due to an increase in hardness or a reduction in the notch ductility of the material. Detailed information on embrittlement mechanisms and the resulting fracture appearance can be found in the article "Visual Examination and Light Microscopy" in Volume 12 of *ASM Handbook*.

*Temper embrittlement* causes a significant increase in the brittle-to-ductile transition temperature of low-alloy steels containing 1 to 3% Cr that are exposed to above 370 to 540 °C (700 to 1000 °F) for some period of time. Brittle failure at weld defects can occur when process equipment made from these steels is fully pressurized during start-up or shutdown. Therefore, pressure should be limited to 25% of design when temperatures are below 150 °C (300 °F) (Ref 22). Ideally, equipment made from steels that have become temper embrittled should be preheated to above 120 °C (250 °F) before pressurization following a shutdown. Temper embrittlement is caused by the segregation of residual steel elements to the grain boundaries, and this greatly reduces the intercrystalline strength. Limiting the acceptance levels of such elements as manganese, silicon, phosphorus, tin, antimony, and arsenic can improve the temper embrittlement resistance of 2.25Cr-0.5Mo, 2.25Cr-1Mo, and 3Cr-1Mo steels. Frequent nondestructive testing of major weld seams is recommended to determine if equipment has become embrittled.

*885- °F (475- °C) Embrittlement.* Another embrittling phenomenon, referred to as 885 Embrittlement, occurs with ferritic stainless steels containing 12% or more chromium after long-term exposure to temperatures between 400 and

540 °C (750 and 1000 °F). Heat treatment at about 620 °C (1150 °F), followed by rapid cooling, will restore ductility to embrittled low-alloy and ferritic stainless steels.

*Sigma-phase embrittlement* can occur in austenitic stainless steels as well as in straight-chromium stainless steels. Of the austenitic stainless steels, the most susceptible compositions contain approximately 25% Cr and 20% Ni. The straight-chromium steels that are most susceptible to σ-phase formation contain 17% or more chromium. Sigma-phase formation increases room-temperature tensile strength and hardness while decreasing ductility to the point of extreme brittleness. As a result, cracks are very likely to develop during cooling from operating temperatures. Sigma-phase most commonly forms in equipment operating in a temperature range of 650 to 760 °C (1200 to 1400 °F). Because s-phase can be dissolved at temperatures above 980 °C (1800 °F), the original properties of stainless steels can be restored by a suitable heat treatment.

*Creep embrittlement* is the stress-dependent embrittlement of low-alloy steels operating in the creep range. The result is a reduction in the stress rupture ductility. Creep embrittlement is caused by the formation of precipitates within the grains and by elongated grain-boundary carbides. Detrimental effects can be eliminated by annealing the steel.

### Fabricability

With very few exceptions, process equipment and piping are fabricated by welding wrought steels. The shells of pressure vessels are usually made from rolled plate, while nozzles are forgings. This requires that the steels have sufficient ductility for forming and are readily weldable. Weldability of steels is important not only for initial fabrication but also for future field repairs or modifications. Weld repairs and postweld heat treatments can affect the mechanical properties of components that have been normalized or quenched and tempered.

Welding may result in certain other problems. Hydrogen dissolved in liquid weld metal can cause cracking during solidification, as well as embrittlement of the weld. The risk is reduced by the use of low-hydrogen electrodes, careful drying of electrodes, and close control of pre-and postweld heat treatments. Stress relief or reheat cracking is intergranular cracking in the weld heat-affected zone (HAZ). The HAZ cracking occurs when weldments are heated during postweld heat treatment, or it occurs by subsequent exposure to elevated service temperatures. Low-alloy steels are especially susceptible to the above phenomena, but hydrogen cracking can occur with any of the ferritic steels if proper care is not taken.

### Corrosion Resistance

The effects of the environment need to be considered when materials of construction are specified. General corrosion (uniform metal loss) is the easiest form of metal deterioration that can be considered in the design phase because additional metal can be provided in the form of a corrosion allowance. It is also the easiest form of corrosion that can be detected by nondestructive testing techniques. In the case of pitting corrosion, it is possible to provide a pitting allowance. Because metal loss due to general corrosion is often not significant under pitting conditions, this approach would represent a rather expensive method of protecting equipment. Instead, it would be more practical to avoid process conditions that produce pitting or to change to a material that will not pit. Stress-corrosion cracking is one of the most serious forms of metal deterioration because it can result in the complete fracture of equipment and considerable losses to an operating facility. Stress-corrosion cracks are very difficult to detect because they may occur during operation and because they are usually not uniformly distributed over the metal surfaces. Austenitic stainless steels are highly susceptible to SCC and consequently are usually avoided for the primary pressure boundary of components. However, they are used as protective, internal linings.

## Low- and High-Temperature Corrosion

For practical purposes, corrosion in refineries and petrochemical plants can be classified into low-temperature corrosion and high-temperature corrosion (Ref 23, 24). Low-temperature corrosion is considered to occur below approximately 260 °C (500 °F) in the presence of water. Carbon steel can be used to handle most hydrocarbon streams in this temperature range, except where aqueous corrosion by inorganic contamination, such as hydrogen chloride or hydrogen sulfide, necessitates selective application of more resistant alloys. High-temperature corrosion is considered to take place above approximately 260 °C (500 °F). The presence of water is not necessary, because corrosion occurs by the direct reaction between metal and environment.

### Low-Temperature Corrosion

Most corrosion problems in refineries are not caused by hydrocarbons that are processed but by various inorganic compounds, such as water, hydrogen sulfide, hydrochloric acid, hydrofluoric acid, sulfuric acid, and caustic (Ref 25). There are two principal sources of these compounds: feed-stock contaminants and process chemicals, including solvents, neutralizers, and catalysts. Generally, the same applies to corrosion problems in petrochemical plants except that corrosion is also caused by organic acids, such as acetic acid, that may be used as solvents. In addition, corrosion problems are caused by the atmosphere, cooling water, boiler feedwater, steam condensate, and soil.

### Low-Temperature Corrosion by Feed-Stock Contaminants

The major cause of low-temperature (and, for that matter, high-temperature) refinery corrosion is the presence of contaminants in crude oil as it is produced. Although some contaminants are removed during preliminary treating in the fields, most end up in refinery tankage, along with contaminants picked up in pipelines or marine tankers. In most cases, the actual corrosives are formed during initial refinery operations. For example, potentially corrosive hydrogen chloride evolves in crude preheat furnaces from relatively harmless calcium and magnesium chlorides entrained in crude oil (Ref 26). In petrochemical plants, certain corrosives may have been introduced from upstream refinery and other process operations. Other corrosives can form from corrosion products after exposure to air during shutdowns; polythionic acids fall into this category. The following discussion will focus on the most important crude oil contaminants that have caused corrosion problems.

**Air.** During shutdowns or turnarounds, most plant equipment is exposed to air. Air also can enter the suction side of pumps if seals or connections are not tight. In general, the air contamination of hydrocarbon streams has been more detrimental with regard to fouling than corrosion. However, air contamination has been cited as a cause of accelerated corrosion in vacuum transfer lines and vacuum towers of crude distillation units. Air contamination has supposedly increased the overhead corrosion of crude distillation towers, but this has been difficult to reconcile with the fact that oxygen in air reacts with hydrogen sulfide to form polysulfides, which tend to inhibit corrosion.

**Water.** Water is found in all crude oils and is difficult to remove completely. In addition, water originates with stripping steam for fractionation towers and is produced in hydrotreating operations. Water not only functions as an electrolyte but also hydrolyzes certain inorganic chlorides to hydrogen chloride, as noted above. Water is primarily responsible for various forms of corrosion in fractionation tower overhead systems. In general, whenever equipment can be kept dry through suitable process or equipment changes, corrosion problems will be minimized.

The combination of water and air can be especially detrimental. Moisture and air are drawn into storage tanks during normal breathing as a result of pumping and changes in temperature. Tank activity and corrosion are closely interrelated. Because crude and heavy oils form a protective oil film on the working areas of a tank shell, corrosion is generally limited to the top shell ring and the underside of the roof. Tank bottom corrosion occurs mostly with crude oil tanks and is caused by water and salt entrained in the crude oil. A layer of water usually settles out and can become highly corrosive. Alternate exposure to sour crude oils and salt water causes especially severe corrosion

(Ref 27). Mill scale tends to accelerate tank bottom corrosion because cracks in the mill scale form anodic areas that pit, while the remaining mill scale acts as the cathode.

Light stocks do not form protective oil films, and corrosion occurs primarily at the middle shell rings because these are exposed to more wetting and drying cycles than other tank areas (Ref 28). Corrosion is in the form of pitting under globules of water that attach themselves to the tank wall. Pitting becomes so extensive that metal loss appears as more or less uniform corrosion. The rate of corrosion is proportional to the water and air content of light stocks. Contamination from chloride and hydrogen sulfide accelerates attack.

**Hydrogen Sulfide.** Sour crude oils and gases that contain hydrogen sulfide are handled by most refineries (Ref 29). Hydrogen sulfide is also present in some feed stocks handled by petrochemical plants. During processing at elevated temperatures, hydrogen sulfide is also formed by the decomposition of organic sulfur compounds that are present. Corrosion of steel by hydrogen sulfide forms the familiar black sulfide film seen in almost all refinery equipment (Ref 30). Hydrogen sulfide is the main constituent of refinery sour waters and can cause severe corrosion problems in overhead systems of certain fractionation towers, in hydrocracker and hydrotreater effluent streams, in the vapor recovery (light ends) section of fluid catalytic cracking units, in sour water stripping units, and in sulfur recovery units (Ref 31, 32). These will be discussed in greater detail in the section "Sour Water" in this article.

In general, carbon steel has fairly good resistance to aqueous sulfide corrosion because a protective iron sulfide film is formed (Ref 33). To avoid hydrogen stress cracking (sulfide cracking), hard welds (above 200 HB) must be avoided, if necessary, through suitable postweld heat treatment (Ref 34). Excessive localized corrosion in vessels has been resolved by selective lining with alloy 400 (N04400), but this alloy can be less resistant than carbon steel to aqueous sulfide corrosion at temperatures above 150 °C (300 °F). If significant amounts of chlorides are not present, lining vessels with type 405 (S40500) or type 304 (S30400) stainless steel can be considered. More recently, titanium grade 2 (R50400) tubes have been used as replacements for carbon steel tubes to control aqueous sulfide corrosion in heat exchangers at a number of units (Ref 35, 36).

**Hydrogen Chloride.** In refineries, corrosion by hydrogen chloride is primarily a problem in crude distillation units and, to a lesser degree, in reforming and hydrotreating units. In petrochemical plants, hydrogen chloride contamination can be present in certain feed stocks or can be formed by the hydrolysis of aluminum chloride catalyst.

In most production wells, chloride salts are found either dissolved in water that is emulsified in crude oil or as suspended solids. Salts also originate from brines injected for secondary recovery or from brines injected for secondary recovery or from seawater ballast in marine tankers. Typically, the salts in crude oils consist of 75% sodium chloride, 15% magnesium chloride, and 10% calcium chloride (Ref 37). When crude oils are charged to crude distillation units and heated to temperatures above approximately 120 °C (250 °F), hydrogen chloride is evolved from magnesium and calcium chloride, while sodium chloride is essentially stable up to roughly 760 °C (1400 °F). Hydrogen chloride evolution takes place primarily in crude preheat furnaces. Dry hydrogen chloride, especially in the presence of large amounts of hydrocarbon vapor or liquid, is not corrosive to carbon steel (Ref 38).

When steam is added, however, to the bottom of the crude tower to facilitate fractionation, dilute hydrochloric acid forms in the top of the tower and in the overhead condensing system. Severe aqueous chloride corrosion of carbon steel components can occur at temperatures below the initial water dew point (Ref 39). Corrosion rate increases with a decrease in pH value of overhead condensate water. Corrosion is mostly in the form of droplet-impingement attack at elbows of the overhead vapor line and at inlets of overhead condensers. Corrosion also occurs on condenser tubes that are at the temperatures where most of the water condenses out. Often, droplets of dilute hydrochloric acid become entrapped under deposits that are present on tower trays, in condenser shells, and at baffles. The resultant underdeposit corrosion is highly localized and usually quite severe.

Overhead condensing systems of both the crude and vacuum towers of crude distillation units are generally made from carbon steel. Coolers and condensers in cooling-water service usually use admiralty metal (C44300) tubes to reduce corrosion and fouling on the water side. Where aqueous chloride corrosion is a problem on the process side, titanium grade 2 (R50400) tubes should be considered. The top of the crude tower can be lined with alloy 400 (N04400), can be used for the upper five or so trays to combat aqueous chloride corrosion. Alloy 400 (N04400) and tray components made from alloy 400 (N04400) tubes usually have not been cost effective in overhead coolers and condensers, but alloy 400 (N04400) has been successfully used for selective strip lining of those areas of the overhead system where excessive corrosion occurs despite the implementation of other corrosion control measures.

To minimize aqueous chloride corrosion in the overhead system of crude towers, it is best to keep the salt content of the crude oil charge as low as possible, preferably below 1 pound per thousand barrels (PTB), corresponding to roughly 4 ppm. This is done by proper tank-settling, desalting, or, if necessary, double desalting (Ref 40-42). Another way to reduce overhead corrosion would be to inject caustic (sodium hydroxide) into the crude oil downstream of the desalter. Up to 3 PTB (10 ppm) caustic can usually be tolerated from a process point of view, while higher concentrations increase fouling of crude preheat exchangers, boiler corrosion by sodium vanadate (when reduced crude is burned as boiler fuel), or coking in lines and heaters of coking units (Ref 43). Caustic should not be used when reduced crude is charged directly to catalytic cracking or hydrotreating units, because of possible catalyst deactivation.

Neutralizers are injected into the overhead vapor line of the crude tower to maintain the pH value of stripping steam condensate between 5 and 6 (Ref 44-47). A pH value above 7 can increase corrosion with sour crudes, as well as fouling and underdeposit corrosion by neutralizer chloride salts. Where fouling becomes a problem, water should be injected, either intermittently or continuously, to dissolve salt deposits in those areas of the overhead system that are not exposed to stripping-steam condensate (Ref 48). Filming-amine corrosion inhibitors can be injected into the overhead vapor line to provide additional insurance against excessive corrosion (Ref 49-51).

In downstream refining equipment, chlorides accelerate corrosion by penetrating protective surface films, increasing electrolyte conductivity, or complexing with steel surfaces (Ref 52). In reforming units, organic chlorides are often used to regenerate reformer catalyst. Hydrogen chloride is stripped off the catalyst if excessive moisture is present in the reformer feed; this causes increased corrosion, not only in reforming units but also in hydrotreating units that use excess hydrogen (make-gas) from the reformer. As in the case of crude distillation units, water washing and injection of neutralizers and/or filming-amine corrosion inhibitors can be used to control fouling and corrosion by chloride salts. Hydrogen make-gas can be passed through a water scrubber to remove hydrogen chloride. Selective alloying with alloy 825 (N08825), alloy 400 (N04400), or titanium grade 2 (R50400) can be required to control chloride attack in heat exchangers and separator drums.

**Nitrogen Compounds.** Organic nitrogen compounds, such as indole, carbuzole, pyridine, or quinoline, are present in many crude oils, but do not contribute to corrosion problems unless converted to ammonia or hydrogen cyanide (Ref 53). This occurs primarily in catalytic cracking, hydrotreating, and hydrocracking operations where ammonia and hydrogen cyanide, in combination with hydrogen sulfide and other constituents, become the major constituents of sour water that can be highly corrosive to carbon steel (Ref 54).

Ammonia is also produced in ammonia plants to become a raw material for the manufacture of urea and other nitrogen-base fertilizers. Ammonia in synthesis gas at temperatures between 450 and 500 °C (840 and 930 °F) causes nitriding of steel components. When synthesis gas is compressed to up to 34.5 MPa (5000 psig) prior to conversion, corrosive ammonium carbonate is formed, requiring various stainless steels for critical components. Condensed ammonia is also corrosive and can cause SCC of stressed carbon steel and low-alloy steel components (Ref 55).

**Sour Water.** The term sour water denotes various types of process water containing primarily hydrogen sulfide, ammonia, and hydrogen cyanide, often in combination with certain other organic and inorganic compounds, including phenols, mercaptans, chlorides, and fluorides. Sour waters are removed from refining units by settling in overhead reflux drums, separator drums, water coalescer drums, and other specialized equipment. Depending on their exact composition, sour waters can become highly corrosive. Sour water corrosion is of particular concern in the vapor recovery (light ends) section of catalytic cracking units and in reactor effluent and light ends sections of hydrotreating and hydrocracking units, in which high concentrations of ammonia can saturate process water with ammonium bisulfide and cause serious corrosion of carbon steel components. Ammonium bisulfide will also rapidly attack admiralty metal (C44300) tubes. Sour water corrosion is a major problem at some sour water stripping units, in which exceptionally high concentrations of ammonium bisulfide build up in the thin film of condensed water on overhead condenser tubes. The resultant corrosion can be so severe that even tubes made from austenitic stainless steels are attacked, and only titanium grade 2 (R50400) tubes have sufficient resistance to be used in this service.

Normally, all components in the vapor recovery (light ends) sections of catalytic cracking units are made of carbon steel. Exceptions to this rule include tower internals made of type 405 (S40500) or 410 (S41000) stainless steel and tubes in overhead condensers and compressor aftercoolers made from admiralty metal (C44300), alloy 400 (N04400), or titanium grade 2 (R50400). Corrosion problems of carbon steel components are often closely associated with hydrogen blistering. Admiralty metal (C4430) tubes in overhead condensers may typically last only 5 years, with leaks finally occurring as a result of ammonia SCC. Depending on the particular process conditions, admiralty metal (C44300) tubes can also corrode by severe localized attack. Admiralty metal (C44300) tubes in compressor aftercoolers often need to be replaced with titanium grade 2 (R50400) tubes. The biggest recurring problem has been corrosion and hydrogen blistering of carbon steel in coolers, separator drums, absorber/stripper towers, and, occasionally, overhead condensers at a number of locations. These will be discussed in greater detail in the section "Hydrogen Blistering" in this article.

Components in hydrotreating and hydrocracking units that operate at temperatures below about 260 °C (500 °F) are typically made from carbon steel. Where aqueous ammonium bisulfide corrosion becomes a problem, generous corrosion allowances may have to be provided for carbon steel (Ref 56, 57). Selective alloying with alloy 825 (N08825), alloy 400 (N04400) or titanium grade 2 (R50400) may be required for heat exchangers and separator drums to control excessive corrosion. On some units, corrosion is accompanied by hydrogen blistering. Hydrotreating and hydrocracking units that experience fouling problems due to ammonium sulfide or ammonium chloride deposition may require intermittent or continuous water injection to dissolve these salt deposits. It is of prime importance, however, that sufficient coalescer capacity be available or provided in order to ensure that the injected water is removed. Otherwise, serious corrosion can occur when the water ends up in downstream equipment.

All equipment and piping of reforming units that operate at below approximately 260 °C (500 °F) are usually made from carbon steel. Although admiralty metal (C44300) tubes are often used in water-cooled effluent cooler and condensers, chloride attack may necessitate selective alloying with alloy 400 (N04400) or titanium grade 2 (R50400). In some cases, carbon steel tubes are superior to admiralty metal (C44300) tubes, provided the cooling water is properly treated. Similar considerations apply to water-cooled coolers and condensers in the overhead systems of prefractionator, splitter, debutanizer, and other fractionation towers. Filming-amine corrosion inhibitors can be used to help control overhead corrosion.

The principal material of construction for sour water stripping units is carbon steel. There are several varieties of sour water strippers, but nonacidified condensing and noncondensing strippers are most commonly used (Ref 58, 59). The stripping medium is primarily steam. Stripper towers are generally made from car-bon steel with type 316 (S31600) stainless steel, aluminum, or carbon steel internals, depending on corrosion experience. To control tower corrosion, a minimum top temperature of 80 °C (180 °F) is required. Below this temperature, hydrogen sulfide will concentrate in the upper part of the tower but will not be carried overhead. Feed charge pumps are usually made from cast iron or cast steel, including the impellers. Feed piping, bottoms piping, and the feed/bottoms heat exchanger can be made from carbon steel. Carbon steel has also been satisfactory for stripper reboilers that may be used instead of live stripping steam. Thermosyphon reboilers (with sour water in the tubes) are recommended over kettle reboilers because the latter are often prone to fouling and resultant underdeposit corrosion.

Most corrosion problems have been in overhead condensers of condensing sour water strippers (Ref 60). Although a variety of alloys have been used for overhead condenser tubes, only aluminum and titanium grade 2 (R50400) can be relied on to provide adequate resistance to the highly corrosive conditions encountered in many overhead systems. Carbon steel is usually satisfactory for the overhead vapor line, condenser shell, run down lines, accumulator drum, and reflux lines. All welds in these components should be postweld heat treated to avoid hydrogen stress cracking. Reflux pumps can be made of carbon steel or type 304 (S30400) stainless steel, but for optimum performance, alloy 20 (N08020) is recommended. Hydrogen blistering often accompanies corrosion in overhead condenser shells and reflux drums. Water-soluble filming-amine corrosion inhibitors can be injected into the overhead vapor line to help control both corrosion and hydrogen blistering. Few, if any, corrosion problems have been experienced with noncondensing sour water strippers.

Serious sour water corrosion of carbon steel components can occur in the overhead system of amine regenerators (strippers) of gas-treating or sulfur recovery units, especially if all of the water condensate is returned to the tower as reflux. Corrosion is usually accompanied by hydrogen blistering. Continuous or periodic blowdown of sour water to the sour water stripping unit should be employed to lower the concentrations of hydrogen sulfide, ammonia, and cyanide in the overhead water condensate. If this fails to control corrosion, carbon steel condenser tubes may have to be replaced with titanium grade 2 (R50400) tubes. In addition, corrosion can be minimized by operating the regenerator so that roughly 0.5% amine is taken overhead to act as a corrosion inhibitor.

**Polythionic Acids.** Combustion of $H_2S$ in refinery flares can produce polythionic acids of the type $H_2S_xO_y$ (including sulfurous acid) and cause severe intergranular corrosion of flare tips made of stainless steels and high-nickel alloys (Ref 61). Corrosion can be minimized by using nickel alloys, such as alloy 825 (N08825) or alloy 625 (N06625). Polythionic acids also cause SCC during shutdown, as discussed in the section "SCC and Embrittlement" in this article.

## Low-Temperature Corrosion by Process Chemicals

Severe corrosion problems can be caused by process chemicals, such as various alkylation catalysts, certain alkylation by-products, organic acid solvents used in certain petrochemical processes, hydrogen chloride stripped off reformer catalyst, and caustic and other neutralizers that, ironically, are added to control acid corrosion. Filming-amine corrosion inhibitors can be quite corrosive if injected undiluted (neat) into a hot vapor stream. Another group of process chemicals that are corrosive, or become corrosive, is solvents used in treating and gas-scrubbing operations.

**Acetic Acid.** Corrosion by acetic acid can be a problem in petrochemical process units for the manufacture of certain organic intermediates, such as terephthalic acid. Various types of austenitic stainless steels are used, as well as alloy C-4 (N06455), alloy C-276 (N10276), and titanium, to control corrosion by acetic acid in the presence of small amounts of hydrogen bromide or hydrogen chloride.

As a rule, even tenths of a percent of water in acetic acid can have a significant influence on corrosion. Type 304 (S30400) stainless steel usually has sufficient resistance to the lower concentrations of acetic acid up to the boiling point. Higher concentrations can also be handled by type 304 (S30400) stainless steel if the temperature is below about 90 °C (190 °F). Increasing the chromium and/or nickel content has little effect on resistance to acetic acid. Addition of molybdenum, however, markedly increases the resistance of austenitic stainless steels, and type 316 (S31600) and type 317 (S31700) stainless steels are used for the overwhelming majority of hot acetic acid applications. Corrosion by acetic acid increases with temperature. Bromide and chloride contamination causes pitting and SCC, while addition of oxidizing agents, including air, can reduce corrosion rates by several orders of magnitude.

**Aluminum Chloride.** Certain refining and petrochemical processes, such as butane isomerization, ethylbenzene production, and polybutene production, use aluminum chloride as a catalyst (Ref 62). Aluminum chloride is not corrosive if it is kept absolutely dry. If traces of water or water vapor are present in hydrocarbon streams, aluminum chloride hydrolyzes to hydrochloric acid, which can of course be highly corrosive. To control corrosion in the presence of aluminum chloride, feed is dried in calcium chloride dryers. During shutdowns, equipment should be opened for the shortest possible time. Upon closing, it should be dried with hot air, followed by inert gas blanketing. Equipment that is exposed to hydrochloric acid may require extensive lining with nickel alloys, such as alloy 400 (N04400), B-2 (N10665), C-4 (N06455), or C-276 (N10276) (Ref 63).

**Organic Chlorides.** Organic chlorides in crude oils will form various amounts of hydrogen chloride at the elevated temperatures of crude preheat furnaces, depending on the chlorides involved. Many crude oils contain small amounts of organic chlorides (5 to 50 ppm), but the major problem is contamination with organic chloride solvents during production. Although major producers are aware of the problem, some small operators may still use organic chloride solvents to remove wax deposits in oil field tankage and associated equipment and piping. Spent solvent is then simply added to the crude oil. Organic chloride solvents are also extensively used for metal-degreasing operations in and out of the refinery. Spent solvent is often discarded with slop oil, which is added to the crude oil and charged to the crude distillation unit.

Contaminated crude oils have been found to contain as much as 7000 ppm chlorinated hydrocarbons. Such crude oils not only cause severe corrosion in the overhead system of crude distillation towers but also affect reformer operations (Ref 64). Typical problems in the latter category include runaway cracking, rapid coke accumulation on the catalyst, and increased corrosion in fractionator overhead systems (Ref 65, 66). Obviously, every effort must be made to avoid charging contaminated crude oil. Organic chlorides cannot be removed by desalting. If contaminated crude oil must be run off, the usual approach is to blend it slowly into uncontaminated crude oil.

**Hydrogen Fluoride.** Some alkylation processes use concentrated hydrofluoric acid instead of sulfuric acid as the catalyst. In general, hydrofluoric acid is less corrosive than hydrochloric acid because it passivates most metals by the formation of protective fluoride films. If these films are destroyed by diluted acid, severe corrosion occurs. Therefore, as long as feed stocks are kept dry, carbon steel—with various corrosion allowances—can be used for vessels, piping, and valve bodies of hydrofluoric acid alkylation units. Alloy 400 (N04400) is used selectively at locations where excessive corrosion has been experienced. Hydrofluoric acid can cause hydrogen blistering of carbon steel equipment and hydrogen stress cracking of hardened bolts (Ref 67).

By following proper design practices and prescribed maintenance procedures and by diligently keeping feed stocks and equipment dry, there will be few corrosion problems. All carbon steel welds that contact hydrofluoric acid should be postweld heat treated (Ref 68). This applies especially to welds in various vessels. Vessels should be radiographed to check for slag inclusions in plates and welds; slag inclusions are attacked by hydrofluoric acid. Hydrofluoric acid has the capability of finding the smallest holes in welds or threads. During welding, each preceding pass must be properly cleaned. All threaded connections should be seal welded. Where leaks do show up after start-up, small holes can often be peened shut, or small bits of copper or lead can be peened into larger holes to seal a leak. Any subsequent repair welds should also be postweld heat treated.

Fractionation towers should have type 410 (S41000) stainless steel tray valves and bolting; alloy 400 (N04400) tray valves and bolting are preferred for the deisobutanizer tower. The acid rerun tower usually requires cladding with alloy 400 (N04400) and alloy 400 (N04400) tray components. To avoid SCC, alloy 400 (N04400) welds that contact hydrofluoric acid should be postweld heat treated. No asbestos gasketing should be used on trays. Soft iron gaskets are used on channel head-to-shell joints of heat exchangers. Spiral-wound alloy 400/Teflon gaskets are also used but are more expensive. Carbon steel U-tube bundles are preferred for all exchangers that contact hydrofluoric acid; alloy 400 (N04400) tubes have been found to offer few advantages (Ref 69). Tube ends and tubesheet holes should be carefully cleaned to ensure tube rolls that are tight against hydrofluoric acid. Seal welding of tubes may be required. Internal bolting should not be used in exchangers.

The piping is generally carbon steel with welded connections that have received postweld heat treatment. All taps should be self-draining and should have double block valves. Instrument connections should be made from the top. Valve bodies on gate and plug valves are usually carbon steel, with Teflon packing and Teflon seats. Relief valves should have alloy 400 (N04400) trim. Teflon tape sealing should be used on any threaded connections. Pumps in hydrofluoric acid service normally have carbon steel casings that are weld overlayed with alloy 400 (N04400). Impellers and sleeves should be alloy 400 (N04400); shafts should be alloy K500 (N05500).

Specific areas where corrosion is likely to occur include the bottom of the acid rerun tower, the feed inlet areas of the deisobutanizer and depropanizer towers, the overhead condensers of these towers, the reboiler of the propane stripper, and piping around the acid rerun tower (Ref 70). Trouble areas in vessels are often selectively strip lined with alloy 400 (N04400). Dimpling of tray valve caps during manufacture reduces their tendency to stick to trays because of corrosion products. Alloy 400 (N04400) piping is used to replace carbon steel piping, which corrodes at excessive rates; welds should be postweld heat treated.

Experience has shown that most corrosion problems in hydrofluoric acid alkylation units occur after shutdowns because pockets of water have been left in the equipment. This water is from the neutralization and washing operation required for personnel safety before the equipment can be opened for inspection. It is very important that equipment be thoroughly dried by draining all low spots and by circulating hydrocarbon before the introduction of hydrofluoric acid catalyst at start-up. Corrosion by hydrofluoric acid is occasionally accompanied by hydrogen blistering. Filming-amine corrosion inhibitors have been injected into the overhead systems of various towers, sometimes in conjunction with injection of dilute soda ash solutions. Because the primary goal of proper operations is to keep the unit as dry as possible, intentional addition of water in any form should be considered only as a last resort.

**Sulfuric Acid.** Certain alkylation units use essentially concentrated sulfuric acid as the catalyst; some of this sulfuric acid is entrained in reactor effluent and must be removed by neutralization with caustic and scrubbing with water. Acid removal may not be complete, however, and traces of acid—at various concentrations (in terms of water)—remain in the stream. Sulfuric acid can be highly corrosive to carbon steel, which is the principal material of construction for sulfuric acid alkylation units. Because the boiling point of sulfuric acid ranges from 165 to 315 °C (330 to 600 °F), depending on concentration, entrained acid usually ends up in the bottom of the first fractionation tower and reboiler following the reactor; this is where the entrained acid becomes concentrated.

Acid concentrations above 85% by weight are usually not corrosive to carbon steel if temperatures are below 40 °C (100 °F). Cold-worked metal (usually bends) should be stress relieved. Under ideal operating conditions, few, if any, corrosion and fouling problems occur (Ref 71, 72).

Carbon steel depends on a film of iron sulfate for corrosion resistance, and if its film is destroyed by high velocities and flow turbulence, corrosion can be quite severe. For this reason, flow velocities should be below 1.2 m/s (4 ft/s). Attack in the form of erosion-corrosion can occur at piping welds that have not received postweld heat treatment. This highly localized attack immediately downstream of piping welds has been attributed to a spheroidized structure; a normalizing postweld heat treatment at 870 °C (1600 °F) is required to minimize corrosion (Ref 73). Erosion-corrosion is also a problem at other locations of high turbulence or velocity (Ref 74). Alloy 20 (N08020) is more resistant than carbon steel to this type of corrosion. In extreme cases, however, even alloy 20 (N08020) will be damaged by erosion-corrosion, and the selective use of alloy B-2 (N10665) may be required.

Carbon steel valves usually require alloy 20 (N08020) internals or trim because even slight attack of carbon steel seating surfaces is sufficient to cause leakage (Ref 75). Pump internals and injection and mixing nozzles in concentrated or spent sulfuric acid service are often made of alloy 20 (N08020), alloy B-2 (N10665), and alloy C-4 (N10002) or C-276 (N10276). For hydrocarbon streams containing only traces of concentrated or dilute sulfuric acid, steel-body valves with type 316 (S31600) stainless steel trim can be used. In this service, steel pump casings that are weld overlayed with aluminum bronze have been successfully used. Pump impellers made from high-silicon cast iron are often used.

Piping for hydrocarbon/acid mixing lines ahead of the reactors may require alloy 20 (N08020), because water contamination of feed stocks can cause severe corrosion of car-bon steel. Alloy 400 (N04400) has been found to be useful for reactor effluent lines around the caustic and wash-water injection points. Valve trays in fractionation towers require type 405 (S40500) or 410 (S41000) stainless steel tray valves and bolting. In general, organic coatings are not resistant to concentrated sulfuric acid. Teflon has excellent resistance to sulfuric acid and is extensively used for gaskets, pump valve packing, and mixing nozzles.

In addition to sulfuric acid, reactor effluent contains traces of alkyl and dialkyl sulfates from secondary alkylation reactions (Ref 76). These esters decompose in reboilers to form sulfur dioxide and polymeric compounds (the latter are notorious foulants). Sulfur dioxide combines readily with water in the upper part and overhead system of fractionation towers; the resultant sulfurous acid can cause severe corrosion in overhead condensers. In some units, carbon steel or admiralty metal (C44300) tubes in overhead condensers, particularly those of the deisobutanizer tower, may have to be replaced with alloy 400 (N04400) or titanium grade 2 (R50400) tubes. As a rule, however, titanium is not resistant to sulfuric acid corrosion. Neutralizers can be injected into the overhead vapor lines of various towers to maintain the pH value of aqueous condensate near 7. Filming-amine corrosion inhibitors can also be injected.

**Caustic.** Sodium hydroxide is widely used in refinery and petrochemical plant operations to neutralize acidic constituents. At ambient temperature and under dry conditions, caustic can be handled in carbon steel equipment. Carbon steel is also satisfactory for aqueous caustic solutions between 50 and 80 °C (120 and 180 °F), depending on concentration. For caustic service above these temperatures but below approximately 95 °C (200 °F), carbon steel can also be used if it has been postweld heat treated to avoid SCC at welds. Austenitic stainless steels, such as type 304 (S30400), can be used up to approximately 120 °C (250 °F), while nickel alloys are required at higher temperatures.

Severe caustic corrosion of the crude transfer line, which is immediately downstream of the caustic injection point, can occur in crude distillation units when 40% (by weight) caustic solution is injected into hot, desalted crude oil to neutralize any remaining hydrogen chloride. Predilution of the caustic with water to form a 3% (by weight) solution minimizes this problem. Better dispersion of the more diluted solution in the hot crude oil prevents puddles of molten caustic from collecting along the bottom of the transfer line. If caustic is injected too close to an elbow of the transfer line, impingement by droplets of caustic can cause severe attack and hole-through at the elbow.

There are some unusual situations in which caustic corrosion is encountered. For example, traces of caustic can become concentrated in boiler feedwater and cause corrosion (gouging) and SCC (caustic embrittlement). This occurs in boiler tubes that alternate between wet and dry conditions (steam blanketing) because of overfiring. In some petrochemical processes, caustic gouging is found under deposits in heat exchangers that remove heat by generation of steam. For example, vertical heat exchangers for cracked gas in ethylene units are especially vulnerable if deposits are allowed to accumulate on the bottom tubesheet. Boiler feedwater permeates these deposits and evaporates, and this causes the caustic to concentrate in any liquid that is left behind. The caustic content of such trapped liquid can reach several percent, which is more than enough to destroy the normally protective iron oxide (magnetite) film on boiler steel and thus cause severe corrosion.

**Amines.** Corrosion of carbon steel by amines in gas-treating and sulfur recovery units can usually be traced to faulty plant design, poor operating practices, and solution contamination (Ref 77). In general, corrosion is most severe in systems removing only carbon dioxide and is least severe in systems removing only hydrogen sulfide. Systems handling mixtures of the two fall between these two extremes if the gases contain at least 1 vol% hydrogen sulfide. Corrosion in amine plants using monoethanolamine is more severe than in those using diethanolamine, because the former is more prone to degradation.

Corrosion is not caused by the amine itself, but is caused by dissolved hydrogen sulfide or carbon dioxide and by amine degradation products (Ref 78). Corrosion is most severe at locations where acid gases are desorbed or removed from rich amine solution. Here, temperatures and flow turbulence are highest. This includes the regenerator (stripper) reboiler and lower portions of the regenerator itself (Ref 79). Corrosion can also be a significant problem on the rich-amine side of the lean/rich-amine exchanger, in amine solution pumps, and in reclaimers. Hydrogen blistering has been a problem in the bottom of the contactor (absorber) tower and in regenerator overhead condensers and reflux drums (Ref 80).

The common material of construction for amine units is carbon steel. To prevent alkaline SCC, welds of components in both lean and rich-amine service should be postweld heat treated regardless of service temperature (Ref 81). Postweld heat treatment also protects against hydrogen stress cracking. On the whole, there have been relatively few corrosion problems in most amine units.

Operating guidelines usually set limits on amine concentration (20%), acid-gas loading (0.35 mol per mole of amine), and reboiler steam temperature (150 °C, or 300 °F) (Ref 82, 83). These guidelines should be followed to minimize corrosion. Sidestream filtration is also extremely beneficial. Filming-amine corrosion inhibitors are often ineffective. Several proprietary oxidizing corrosion inhibitors based on sodium metavanadate are available. These have been successfully used in certain cases, but licensing costs tend to be high for any but the smaller units.

Regenerator towers usually should be lined with type 405 (S40500) stainless steel, and tower internals are often made of type 304 (S30400) stainless steel. Where applicable, type 304 (S30400) stainless steel is required for the rich-amine pressure of the let-down valve, as well as for piping downstream of the let-down valve, to control corrosion accelerated by high flow turbulence.

Corrosion in the regenerator reboiler is usually in the form of pitting and groove-type corrosion of tubes and is caused by localized overheating inside baffle holes (Ref 84). If thermosyphon reboilers are undersized, part of the tube bundle will become vapor blanketed, and the tubes will overheat. Subsequent exposure of the hot tubes to amine solution will cause severe turbulence and velocity-accelerated corrosion. Vapor blanketing also occurs if tubes are allowed to fill partially with steam condensate; this reduces the amount of tube surface available for heat transfer and increases the heat flux through the remainder of the tubes. Unless faulty reboiler operation can be corrected, carbon steel tubes may have to be replaced with type 304 (S30400) or 316 (S31600) stainless steel tubes. Alloy 400 (N04400) reboiler tubes have been successfully used in amine units that handle only car-bon dioxide.

As a rule, carbon steel tubes are satisfactory for regenerator overhead condensers. As discussed in the section "Sour Water" in this article, high corrosion rates can occur at this location, and carbon steel tubes may have to be replaced with titanium grade 2 (R50400) tubes. Carbon steel tubes are used in reclaimers with proper neutralization of acidic constituents (Ref 85). Because the reclaimer can be taken out of service at any time, periodic retubing with carbon steel presents no problems. Cast iron pumps normally are used in low-pressure amine service. If corrosion problems occur, high-silicon cast iron impellers can be used. In high-pressure amine service type 316 (S31600) stainless steel pumps may be needed.

**Phenol.** Phenol (carbolic acid) is used in refineries to convert heavy, waxy distillates obtained by crude oil distillation into lubricating oils. As a rule, all components in the treating and raffinate recovery sections, except tubes in water-cooled heat exchangers, are made from carbon steel. If water is not present, few significant corrosion problems can be expected to occur in these sections. In the extract recovery section, however, severe corrosion can occur, especially where high flow turbulence is encountered. As a result, certain components require selective alloying with type 316 (S31600) stainless steel. Typically, stainless steel liners are required for the top of the dryer tower, the entire phenol flash tower, and various condenser shells and separator drums that handle phenolic water. Tubes and headers in the extract furnace should also be made of type 316 (S31600) stainless steel, with U-bends sleeved

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with alloy C-4 (N06455) on the outlet side to minimize velocity-accelerated corrosion.

## High-Temperature Corrosion

High-temperature corrosion problems in refineries are of considerable importance (Ref 86). Equipment failures can have serious consequences because processes at high temperatures usually involve high pressures as well. With hydrocarbon streams, there is always the danger of fire when ruptures occur. On a more positive note, high-temperature refinery corrosion is primarily caused by various sulfur compounds originating with crude oil. Over the years, extensive research has been done to establish the mechanism of various forms of high-temperature sulfide corrosion. Corrosion rate correlations are available; therefore, equipment life can be predicted with some degree of reliability.

**Sulfidic Corrosion.** Corrosion by various sulfur compounds at temperatures between 260 and 540 °C (500 and 1000 °F) is a common problem in many petroleum-refining processes and, occasionally, in petrochemical processes. Sulfur compounds originate with crude oils and include polysulfides, hydrogen sulfide, mercaptans, aliphatic sulfides, disulfides, and thiophenes (Ref 87). With the exception of thiophenes, sulfur compounds react with metal surfaces at elevated temperatures, forming metal sulfides, certain organic molecules, and hydrogen sulfide (Ref 88, 89). The relative corrosivity of sulfur compounds generally increases with temperature. Depending on the process particulars, corrosion is in the form of uniform thinning, localized attack, or erosion-corrosion. Corrosion control depends almost entirely on the formation of protective metal sulfide scales that exhibit parabolic growth behavior (Ref 90). In general, nickel and nickel-rich alloys are rapidly attacked by sulfur compounds at elevated temperatures, while chromium-containing steels provide excellent corrosion resistance (as does aluminum). The combination of hydrogen sulfide and hydrogen can be particularly corrosive, and as a rule, austenitic stainless steels are required for effective corrosion control.

**Sulfidic Corrosion Without Hydrogen Present.** This type of corrosion occurs primarily in various components of crude distillation units, catalytic cracking units, and hydrotreating and hydrocracking units upstream of the hydrogen injection line. Crude distillation units that process mostly sweet crude oils (less than 0.6% total sulfur, with essentially no hydrogen sulfide) experience relatively few corrosion problems. Preheat-exchanger tubes, furnace tubes, and transfer lines are generally made from carbon steel, as is corresponding equipment in the vacuum distillation section. The lower shell of distillation towers, where temperatures are above 230 °C (450 °F), is usually lined with stainless steel containing 12% Cr, such as type 405 (S40500). This prevents impingement attack under the highly turbulent flow conditions encountered, for example, near downcomers. For the same reason, trays are made of stainless steel containing 12% Cr. Even with low corrosion rates of carbon steel, certain tray components, such as tray valves, may fail in a short time because attack occurs from both sides of a relatively thin piece of metal.

Crude distillation units that process mostly sour crude oils require additional alloy protection against high-temperature sulfidic corrosion. The extent of alloying needed also depends on the design and the operating practices of a given unit. Typically, such units require low-alloy steels containing a minimum of 5% Cr for furnace tubes, headers and U-bends, and elbows and tees in transfer lines. In vacuum furnaces, tubes made from chromium steels containing 9% Cr are often used. Distillation towers are similar to those of units that process mostly sweet crude oils. Where corrosion problems persist, upgrading with steels containing a greater amount of chromium is indicated.

The high processing temperatures encountered in the reaction and catalyst regeneration section of catalytic cracking units require extensive use of refractory linings to protect all carbon steel components from oxidation and sulfidic corrosion. Refractory linings also provide protection against erosion by catalyst particles, particularly in cyclones, risers, standpipes, and slide valves. Stellite hardfacing is used on some components to protect against erosion. When there are no erosion problems and when protective linings are impractical, austenitic stainless steels, such as type 304 (S30400), can be used. Cyclone diplegs, air rings, and other internals in the catalyst regenerator are usually made from type 304 (S30400) stainless steel, as is piping for regenerator flue gas. Reactor feed piping is made from low-alloy steel, such as 5Cr-0.5Mo or 9Cr-1Mo, to control high-temperature sulfidic corrosion.

The main fractionation tower is usually made of carbon steel, with the lower part lined with stainless steel containing 12% Cr, such as type 405 (S40500) (Ref 91). Slurry piping between the bottom of the main fractionation tower and the reactor may receive an additional corrosion allowance as protection against excessive erosion. As a rule, there are few corrosion problems in the reaction, catalyst regeneration, and fractionation sections (Ref 92).

Hydrocracking and hydrotreating units usually require alloy protection against both high-temperature sulfidic corrosion and high-temperature hydrogen attack (Ref 93, 94). Low-alloy steels may be required for corrosion control ahead of the hydrogen injection line.

The so-called McConomy curves can be used to predict the relative corrosivity of crude oils and their various fractions (Ref 95). Although this method relates corrosivity to total sulfur content, and thus does not take into account the variable effects of different sulfur compounds, it can provide reliable corrosion trends if certain corrections are applied. Plant experience has shown that the McConomy curves, as originally published, tend to predict excessively high corrosion rates. The curves apply only to liquid hydrocarbon streams containing 0.6 wt% S (unless a correction factor for sulfur content is applied) and do not take into account the effects of vaporization and flow regime. The curves can be particularly useful, however, for predicting the effect of operational changes on known corrosion rates.

Over the years, it has been found that corrosion rates predicted by the original McConomy curves should be decreased by a factor of roughly 2.5, resulting in the modified curves shown in Fig. 1. The curves demonstrate the beneficial effects of alloying steel with chromium in order to reduce corrosion rates. Corrosion rates are roughly halved when the next higher grade of low-alloy steel (for example, 2.25Cr-1Mo, 5Cr-0.5Mo, 7Cr-0.5Mo, or 9Cr-1Mo steel) is selected. Essentially, no corrosion occurs with stainless steels containing 12% or more chromium. Although few data are available, plant experience has shown that corrosion rates start to decrease as temperatures exceed 455 °C (850 °F). Two explanations frequently offered for this phenomenon are the possible decomposition of reactive sulfur compounds and the formation of a protective coke layer.

Metal skin temperatures, rather than stream temperatures, should be used to predict corrosion rates when significant differences between the two arise. For example, metal temperatures of furnace tubes are typically 85 to 100 °C (150 to 200 °F) higher than the temperature of the hydrocarbon stream passing through the tubes. Furnace tubes normally corrode at a higher rate on the hot side (fire side) than on the cool side (wall side), as shown in Fig. 2. Convective-section tubes often show accelerated corrosion at contact areas with tube hangers because of locally increased temperatures. Similarly, replacement of bare convective-section tubes with finned or studded tubes can further increase tube metal temperatures by 85 to 110 °C (150 to 200 °F).

Correction factors for process streams with various total sulfur contents, averages of those proposed originally by McConomy, are shown in

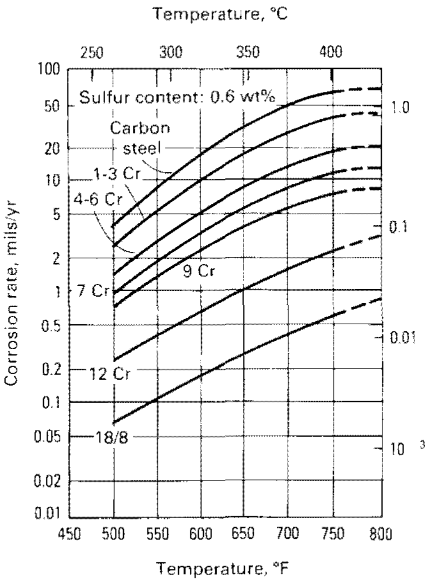

**Fig. 1** Modified McConomy curves showing the effect of temperature on high-temperature sulfidic corrosion of various steels and stainless steels. Source: Ref 96

# Corrosion of Petroleum and Petrochemical Pipelines

# Corrosion of Petroleum and Petrochemical Pipelines

PIPELINES play an extremely important role throughout the world as a means of transporting gases and liquids over long distances from their sources to the ultimate consumers. The general public is not aware of the number of pipelines that are continually in service as a primary means of transportation. A buried operating pipeline is rather unobtrusive and rarely makes its presence known except at valves, pumping or compressor stations, or terminals. Because pipelines are hidden from view, they are not as noticeable as drilling rigs, refineries, or gas-processing plants.

At present, there are approximately 460,000 km (285,000 miles) of common carrier pipelines transporting about 46% of all the crude oil and refined products moved in the United States. In 1984, there were more than $1.6 \times 10^6$ km ($10^6$ miles) of natural gas pipelines in service in the United States; about 25% of this was in interstate service. At that time, there were approximately 280,000 km (174,000 miles) of pipeline carrying liquids in interstate service in the United States. Construction continues to add more miles of pipelines. In 1986, 9800 km (6090 miles) of natural gas pipeline were constructed, along with 5740 km (3567 miles) of crude oil pipelines and 2660 km (1652 miles) of pipeline for refined products. With this vast network of constantly functional pipelines in use moving natural resources and end products to locations where they are utilized, it becomes apparent that keeping them in service through the prevention of corrosion is technologically and economically advantageous.

Corrosion control of pipelines throughout the world is accomplished in the vast majority of cases through the use of cathodic protection combined with a suitable dielectric coating. The cathodic protection system applies protective current to the outer surface of the pipeline steel where it is exposed to the adjacent soils at imperfections in the coating system. The coating system serves to reduce greatly the total amount of protective current required during the operating life of the pipeline. Corrosion control considerations should begin in the design phase of a pipeline and should be continued through the construction phase and the entire economic life of the pipeline.

**Table 1 Practical galvanic series of metals and alloys in neutral soils and water**

| Metal or alloy | Potential, V(a) |
|---|---|
| **Most active** | |
| Commercially pure magnesium | −1.75 |
| Magnesium alloy (Mg-6Al-3Zn-0.15Mn) | −1.16 |
| Zinc | −1.1 |
| Aluminum alloy (5% Zn) | −1.05 |
| Commercially pure aluminum | −0.8 |
| Low-carbon steel (clean and shiny) | −0.5 to −0.8 |
| Low-carbon steel (rusted) | −0.2 to −0.5 |
| Cast iron (not graphitized) | −0.5 |
| Lead | −0.5 |
| Low-carbon steel in concrete | −0.2 |
| Copper, brass, bronze | −0.2 |
| High-silicon cast iron | −0.2 |
| Mill scale on steel | −0.2 |
| Carbon, graphite, coke | +0.3 |
| **Most noble** | |

(a) Typical potential normally observed in neutral soils and water, measured with respect to copper sulfate reference electrode. Source: Ref 1

## Causes of Pipeline Corrosion

**Dissimilar Soils.** A buried pipeline, even one of a relatively short length, will almost inevitably encounter soils that have varying compositions. There can be variations of a physical nature (for example, differences in coarseness and grain size) as well as variations in type (for example, rock, loam, and clays). Additional variations can be of a chemical nature, such as pH and chemical constituents.

When a pipeline traverses dissimilar soils, the pipeline steel in a particular soil electrolyte will often assume a galvanic potential that is somewhat different from the potential of portions of the same pipeline traversing dissimilar soils elsewhere along the pipeline route. Such galvanic potential differences between different areas of a single pipeline can occur on a macroscale (that is, over many miles in the route of the pipeline) or on a microscale (within inches of each other or even over shorter distances).

**Differential Aeration.** A pipeline traversing soils that have varying levels of oxygen concentration will be subject to corrosion cell activity where the portion of the pipeline steel in the area of lowest oxygen concentration is anodic to other areas of the pipeline where there is a greater concentration of oxygen. This form of corrosion activity is also referred to as a concentration cell.

**Dissimilar Metals.** Pipelines having dissimilar materials of construction (for example, carbon steel pipe with brass cocks or valves) that are in contact with a common electrolyte with no electrical isolation between the two metals can be subject to intense corrosion (see the section "General Corrosion" of the article "Forms of Corrosion in the Petrochemical Industry" in this Volume). The metal that is highest in the galvanic series (Table 1) will be anodic to metals lower in the series. An example of dissimilar-metal corrosion is the use of magnesium alloys, aluminum alloys (in seawater), and zinc as galvanic (sacrificial) anodes for the protection of carbon steel structures such as pipelines.

**New and Old Steel Pipe.** As indicated in Table 1, the potential of steel located in a neutral electrolyte as measured against a copper-copper sulfate reference electrode can vary within a range of −0.2 to −0.8 V. The potential of a particular piece or section of steel is largely determined by the condition of the steel surface that contacts the electrolyte. Bright, new steel or old steel that has been mechanically restored to a shiny pristine surface condition will exhibit a potential between −0.5 and −0.8 V. Old, rusty steel will have a potential from −0.2 to −0.5 V. With bright, new steel pipe that is electrically connected to older or superficially rusted steel pipe in an electrolyte, galvanic potential differences as great as 0.5 V can exist in which the new pipe is anodic to the older, rusty pipe.

**Bacteriological Corrosion.** Microorganisms existing in a pipeline trench can affect the control of corrosion either directly or indirectly. Anaerobic bacteria, which thrive in the absence of oxygen, are sulfate-reducing organisms that consume hydrogen and cause a loss of polarization at the steel pipe surface. This loss of polarization can make the attainment of successful cathodic protection much more difficult.

Other bacteria that oxidize sulfur can exist in aerated environments. These bacteria (*Thiobacillus Thioxidans*) consume oxygen and oxidize sulfides into sulfates, such as sulfuric acid ($H_2SO_4$). By their metabolic processes, these bacteria can create concentrations of $H_2SO_4$ as high as 10%. Such an environment can be particularly hazardous to pipeline steel. Microbiological corrosion activity is discussed at length in the section "Localized Corrosion" of the article

"Forms of Corrosion in the Petrochemical Industry" in this Volume.

**Interference-current effects** are also referred to as stray-current effects. They usually occur when the direct currents associated with a foreign metallic system (one not directly associated with the pipeline of concern) use the pipeline steel as a preferential conductor in returning to their source. When this occurs, the currents will couple to the pipeline steel from the soil and flow longitudinally on the steel to a location or locations where they discharge from the steel to the adjacent soils in order to complete their circuit.

The hazard to the affected pipeline is primarily to the steel in the locations where current discharges to the earth; in so doing, it is in essence creating anodic areas with the attendant loss of pipe metal. Current pickup locations can also be hazardous to the corrosion control system of the affected pipeline if the current density being collected is of sufficient magnitude to incur hydrogen overvoltage conditions. The formation of gaseous hydrogen at dielectric coating imperfections can cause coating damage and can create hydrogen cracking effects on certain higher-strength steels. There are generally two types of interference-current activity: steady state and transient.

*Steady State.* In this type of interference-current activity, the magnitude of the interference current is essentially a constant. Such currents are usually incurred by the operation of other nearby impressed-current cathodic protection systems. Because all of the systems involved (the affected pipeline and the other cathodic protection system) are fixed with regard to location, the stray-current flow patterns are constant, and analysis through field testing is relatively straightforward.

*Transient.* In this type, the source of the stray current is the operation of a traction system (electrified railroad, subway, mining equipment) that uses direct current (dc) series motors for propulsion and the rail system as the return leg to their dc power source (for example, a substation). Such traction equipment will often have the positive feed to the vehicle motor through an overhead catenary wire or third rail. The negative return leg consisting of the surface-mounted rails can allow the return currents to couple at least partially to buried metallic shunt conductors, such as pipelines and buried metallic sheath cables.

A rail system with poorly bonded rails can represent a high-resistance intended current path. This current path can multiply the resultant stray-current magnitude picked up on adjacent pipelines, cables, and other subsurface metallic structures.

Again, the major hazard caused by a dc traction system to a buried pipeline is the area or areas where the stray current discharges from the pipeline to the adjacent soil to return to its source. In addition, the magnitude of these stray traction currents can be hundreds or even thousands of amperes.

Assessment of these stray traction currents can be very difficult because their magnitude varies as a function of the accelerating and loading demands on all the individual dc motors in the system. Because the stray-current sources are usually moving vehicles, their locations, and therefore the locations at which the stray-current couples initially to earth, can be a constantly shifting pattern. More information on this phenomenon is available in the section "General Corrosion" of the article "Forms of Corrosion in the Petrochemical Industry" in this Volume.

## Corrosion Control and Prevention

**Materials Selection.** The selection of materials for pipeline construction is limited when all of the aspects of safety, structural integrity, operating life, and economic considerations are taken into account and acted upon.

Carbon steel is the almost exclusive choice of pipeline designers. This is true for pipeline systems that are used to gather or collect the natural gas, crude oil, or water; it is also true for those pipelines that are used to transport substances over distances of hundreds of feet to hundreds of miles. It is also the case for piping systems that are used to distribute natural gas, water, water-refined liquids, and so on, to the end user.

Cast iron is extensively used in water and natural gas distribution systems. In recent years, nonmetallic materials have found application in natural gas distribution systems as carrier vehicles and as liners for restoring failed metallic piping to service without the need for trenching and replacement.

Carbon steels and, in certain types of service or environmental conditions, alloy steels are by far the most commonly used pipeline materials of construction. Table 2 lists compositions of some standard pipe steels.

**Protective (Dielectric) Coatings.** The function and desired characteristics of a dielectric-type pipeline coating are covered in NACE RP-01-69 (Ref 2). This specification states that the function of such coatings is to control corrosion by isolating the external surface of the underground or submerged piping from the environment, to reduce cathodic protection requirements, and to improve (protective) current distribution. Coatings must be properly selected and applied, and the coated piping must be carefully installed to fulfill these functions. Different types of coatings can accomplish the desired functions. The desired characteristics of the coatings are:

- Effective electrical insulation. For preventing the electrolytic discharge of current from the steel surface of the pipe, the coating must have the characteristics of an effective dielectric material
- Effective moisture barrier. The permeation of a coating material by soil moisture would significantly reduce its dielectric properties
- Application considerations. The coating must be capable of being readily applied to the pipe, and it must not of itself or through required ap-

**Table 2 Typical compositions of ASTM and API pipe steels**

| Steel | Composition, % | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | C | Mn | Si | P | S | Cr | Mo | Nb | V | Ti | Al | B |
| A106, Grade A | 0.25 max | 0.27-0.93 | 0.10 min | 0.048 max | 0.058 max | ... | ... | ... | ... | ... | ... | ... |
| A106, Grade B | 0.30 max | 0.29-1.06 | 0.10 min | 0.048 max | 0.058 max | ... | ... | ... | ... | ... | ... | ... |
| A335, Grade P2 | 0.10-0.20 | 0.30-0.61 | 0.10-0.30 | 0.045 max | 0.045 max | 0.50-0-0.81 | 0.44-0.65 | ... | ... | ... | ... | ... |
| A335, Grade P5 | 0.15 max | 0.30-0.60 | 0.50 max | 0.030 max | 0.030 max | 4-6 | 0.45-0.65 | ... | ... | ... | ... | ... |
| A335, Grade P7 | 0.15 max | 0.30-0.60 | 0.50-1 | 0.030 max | 0.030 max | 6-8 | 0.44-0.65 | ... | ... | ... | ... | ... |
| A335, Grade P11 | 0.15 max | 0.30-0.60 | 0.50-1 | 0.030 max | 0.030 max | 1-1.50 | 0.44-0.65 | ... | ... | ... | ... | ... |
| A335, Grade P22 | 0.15 max | 0.30-0.60 | 0.50 max | 0.030 max | 0.030 max | 1.90-2.60 | 0.87-1.13 | ... | ... | ... | ... | ... |
| A381, Class Y52 | 0.26 max | 1.40 max | ... | 0.040 max | 0.050 max | ... | ... | ... | ... | ... | ... | ... |
| API 5L-X46 | 0.30 max | 1.35 max | ... | 0.04 max | 0.05 max | ... | ... | ... | ... | ... | ... | ... |
| API 5L-X60 | 0.26 max | 1.35 max | ... | 0.04 max | 0.05 max | ... | ... | 0.05 min | 0.02 min | 0.03 min(a) | ... | ... |
| API 5L, Grade X52 | 0.21 | 0.90 | 0.26 | 0.015 max | 0.015 max | ... | ... | ... | 0.09 | ... | 0.030 | ... |
| API 5A, Grade K-55 | 0.45 | 1.30 | 0.26 | 0.015 max | 0.015 max | ... | ... | ... | ... | ... | 0.007 | ... |
| API 5AX, Grade N-80 | 0.28 | 1.48 | 0.26 | 0.015 max | 0.015 max | 0.20 | 0.10 | ... | ... | ... | 0.007 | ... |
| API 5AX, Grade P-110 | 0.28 | 1.48 | 0.26 | 0.015 max | 0.015 max | 0.22 | 0.23 | ... | ... | ... | 0.007 | ... |
| API 5AC, Grade C-90 | 0.29 | 0.50 | 0.26 | 0.015 max | 0.015 max | 1.08 | 0.33 | ... | 0.03 | ... | ... | 0.0015 min |
| API 5L, Grade A | 0.17 | 0.50 | ... | 0.020 | 0.020 | ... | ... | ... | ... | ... | ... | ... |
| API 5L, Grade X60 | 0.05 | 1.11 | 0.017 | 0.007 | 0.006 | ... | ... | 0.045 | ... | ... | 0.045 | ... |

(a) Niobium, vanadium, and titanium are used at manufacturer's option.

plication procedures adversely affect the properties of the pipe. In addition, the coating system must be capable of application to the pipe with a minimum of defects

- Good adhesion to the pipe surface is required to prevent soil moisture migration between the pipe steel surface and the coating inner surface
- Ability to resist holidays with time. With a pipeline in place and backfilled, soil stress and soil contaminants—two primary considerations—can cause coating degradation. Soil stress, which can be brought about by seasonal variations in soil moisture content, can create significant forces on the coating that can wrinkle, tear, or thin areas of the coating. Contaminants in the soils adjacent to the coating can also seriously affect its long-term performance. Such contaminants can be chemical, such as solvents from leaks in a product pipeline. Microorganisms in the soil can also have a marked effect, as described in the section "Bacteriological Corrosion" in this article
- Ability to resist damage during handling, storage, and installation
- Ability to maintain substantially constant electrical resistivity over time. Because the corrosion control systems of most pipelines consist of the combination of coating and cathodic protection, it is desirable that the dielectric properties of the coating deteriorate at the minimum rate possible. Significant deterioration of the coating with time would otherwise result in a constant requirement for additional cathodic protection current, which would be both a technical and economic burden on the pipeline operator
- Resistance to disbonding. With the cathodic protection current applied and collecting on those portions of the pipeline steel exposed to the soil at coating holidays, there is the possibility of generation of gaseous hydrogen at the steel surface. The gaseous hydrogen can lift the coating edge adjacent to the holiday, thus worsening a bad situation. Therefore, resistance to electrically induced disbondment is an important coating property
- Resistance to chemical degradation
- Ease of repair
- Retention of physical characteristics

**Types of Coatings.** The pipe coating systems currently in use include the following generic types. Detailed information on paint and coating formulation and application for corrosion protection is available in the article "Organic Coatings and Linings" in Volume 13 of the *ASM Handbook.*

*Bituminous enamels* are formulated from coal tar pitches or petroleum asphalts and have been widely used as protective coatings for more than 65 years. Coal tar and asphalt enamels are available in summer or winter grades. These enamels are the corrosion coating; they are combined with various combinations of fiberglass and/or felt to obtain mechanical strength for handling. The enamel coatings have been the workhorse coatings of the industry, and when properly selected and applied, they can provide efficient long-term corrosion protection.

Enamel systems can be designed for installation and use within an operating temperature range of 1 to 82 °C (30 to 180 °F). When temperatures fall below 4.4 °C (40 °F), added precautions should be taken to prevent cracking and disbonding of the coating during field installation. Enamels are affected by ultraviolet rays and should be protected by kraft paper or whitewash. Enamels are also affected by hydrocarbons, and the use of a barrier coat is recommended when known contamination exists. Bituminous enamel coatings are available for all sizes of pipe. In recent years, the use of enamels has declined for the following reasons:

- Reduced number of suppliers
- Restrictive environmental and health standards from the Occupational Safety and Health Administration, the Environmental Protection Agency, and the Food and Drug Administration
- Increased acceptance of plastic coating materials
- Alternative use of coating raw materials as fuels

*Asphalt mastic* pipe coating is a dense mixture of sand, crushed limestone, and fiber bound together with a select air-blown asphalt. These materials are proportioned to secure a maximum density of approximately 2.1 g/cm$^3$ (132 lb/ft$^3$). This mastic material is available with various types of asphalt. Selection is based on operating temperature and climatic conditions to obtain maximum flexibility and operating characteristics. This coating is a thick (12.7 to 16 mm, or ½ to ⅝ in.) extruded mastic that results in a seamless corrosion coating.

Extruded asphalt mastic pipe coating has been in use for more than 50 years. It is the thickest of the corrosion coatings and is cost effective for offshore installations.

Asphalt mastic systems can be designed for installation and use within an operating temperature range of 4.4 to 88 °C (40 to 190 °F). Precautionary measures should be taken when handling asphalt mastics in freezing temperatures. Whitewash is used to protect it from ultraviolet rays, and this should be maintained when in storage. This system is not intended for use above ground or in hydrocarbon-contaminated soils. This coating is available on 11.4- to 122-cm (4½- to 48-in.) outside diameter pipe.

*Liquid Epoxies and Phenolics.* Many different liquid systems are available that cure by heat and/or chemical reaction. Some are solvent types, and others are 100% solids. These systems are primarily used on larger-diameter pipe when conventional systems may not be available or when they may offer better resistance to operation temperatures in the 95 °C (200 °F) range.

Generally, epoxies have an amine or a polyamide curing agent and require a near-white blast-cleaned surface (NACE No. 2 or SSPC SP10). Coal tar epoxies have coal tar pitch added to the epoxy resin. A coal tar epoxy cured with a low molecular weight amine is especially resistant to an alkaline environment, such as that which occurs on a cathodically protected structure. Some coal tar epoxies become brittle when exposed to sunlight.

*Extruded plastic coatings* fall into two categories based on the method of extrusion, with additional variations resulting from the selection of adhesive. The two methods of extrusion are the crosshead or circular die and the side extrusion or T-shaped die. The four types of adhesives are asphalt-rubber blend, polyethylene copolymer, butyl rubber adhesive, and polyolefin rubber blend.

To date, of the polyolefins available, polyethylene has found the widest use, with polypropylene being used on a limited basis for its higher operating temperature. It is a recognized fact that the perfect pipe coating system does not exist. Each type or variation of adhesive and method of extrusion offers different characteristics based on the degree of importance to the user of certain measurable properties.

*Fusion-bonded epoxy coatings* are heat-activated, chemically cured coating systems. The epoxy coating is furnished in powdered form and, with the exception of the welded field joints, its plant applied to preheated pipe, special sections, connections, and fittings using fluid bed, air spray, or electrostatic spray methods.

Fusion-bonded epoxy coatings were introduced in 1959 and were first used as an exterior pipe coating in 1961. These coatings are applied to preheated pipe surfaces at 218 to 244 °C (425 to 475 °F). Some systems may require a primer system, and some require postheating for complete cure. A NACE No. 2 (SSPC SP10) near-white blast-cleaned surface is required. The coating is applied to a minimum thickness of 0.3 mm (12 mils); in some applications, coating thicknesses range to 0.64 mm (25 mils), with the restriction not to bend pipe coated with a film thickness greater than 0.4 mm (16 mils). The epoxy coatings exhibit good mechanical and physical properties and are the most resistant to hydrocarbons, acids, and alkalies.

A primary advantage of the fusion-bonded pipe coatings is that they cannot hide apparent steel defects; therefore, the steel surface can be inspected after it is coated. The number of holidays that occur is a function of the surface condition and the thickness of the coating specified. Increasing the thickness minimizes this problem, and the excellent resistance to the electrically induced disbondment of these coatings has resulted in their frequent use as pipeline coatings.

*Mill-applied tape systems* have been in use for more than 30 years on pipelines. For normal construction conditions, prefabricated cold-applied tapes are applied as a three-layer system consisting of a primer, corrosion-preventive tape (inner layer), and a mechanically protective tape (outer layer). Tape systems are available on 5- to 305-cm (2- to 120-in.) outside diameter pipe.

The function of the primer is to provide a bonding medium between the pipe surface and the adhesive or sealant on the inner layer. The inner layer tape consists of a plastic backing and an adhesive. This layer is the corrosion-protective coating; therefore, it must provide a high electrical resistivity, low moisture absorption and permeability, and an effective bond to the primed steel surface. The minimum thickness is usually 3.7 mm (145 mils), with the total system being a minimum of 10 mm (400 mils) thick. The outer layer tape consists of a plastic film and an adhesive composed of the same types of materials used in the inner tape or materials that are compatible with the inner layer tape. The purpose of the outer layer tape is to provide mechanical protection to the inner layer tape and to be resistant to the elements during outdoor storage. The outer layer tape is usually a minimum of 0.64 mm (25 mils) in thickness.

The cold-applied multilayer tape systems are designed for plant coating operations and result in a uniform, reproducible, holiday-free coating over the entire length of any size pipe. The multiple-layer system allows the coating thickness to be custom designed to meet specific environmental conditions. These systems have been engineered to withstand normal handling, outdoor weathering, storage, and shipping conditions.

*Waxes.* Wax coatings have been in use for more than 48 years and are still employed on a limited basis. Microcrystalline wax coatings are usually used with a protective overwrap. The wax serves to waterproof the pipe, and the wrapper protects the wax coating from contact with the soil and affords some mechanical protection. The most prevalent use of wax coating is the over-the-ditch application with a combination machine that cleans, coats, wraps, and lowers into the ditch in one operation. The lack of objectionable or toxic fumes or smoke should make this system more acceptable.

*Polyurethane Thermal Insulation.* Efficient pipeline insulation has grown increasingly important as a means of operating hot and cold service pipelines. This is a system for controlling heat transfer in above- or belowground and marine pipelines. Polyurethane insulation is generally used in conjunction with a corrosion coating, but if the proper moisture vapor barrier is used over the polyurethane foam, effective corrosion protection is attained.

*Concrete.* Mortar linings and coatings have the longest history of use in protecting steel or wrought iron from corrosion. When steel is encased in concrete, a protective iron oxide film forms. As long as the alkalinity is maintained and the concrete is impermeable to chlorides and oxygen, corrosion protection is obtained.

The use of concrete as a corrosion coating is currently limited to internal lining. External application is usually employed over a corrosion-resistant coating for armor protection and negative buoyancy in marine environments.

**Metallic (Galvanic) Coatings.** Pipe coated with a galvanic coating, such as zinc (galvanizing) or cadmium, should not be utilized in direct burial service. Such metallic coatings are intended for the mitigation of atmospheric-type corrosion activity on the substrate steel.

**Cathodic Protection.** Some of the mechanisms or circumstances that can create anodic and cathodic areas on a steel pipeline or can make areas on the steel pipeline anodic to adjacent buried metallic structures were discussed in the section "Causes of Pipeline Corrosion" in this article. At the anodic areas on a pipeline, the electrochemical phenomenon known as corrosion causes metallic ions to be lost to the electrolyte in an irreversible manner. At the anodic areas, the conventional current discharges from the pipeline steel flow through the electrolyte to cathodic areas or structures.

The magnitude of the corrosion cell current is proportional to the driving potential between the anodic and cathodic areas and is inversely proportional to the resistance of the total path along which it flows. The total path resistance consists of the anode/electrolyte (soil) interface, the electrolyte itself, the electrolyte/cathodic interface, and the longitudinal resistance of the metallic paths traversed.

Two principal methods are used to eliminate, or at least significantly reduce, the corrosion current flow. The first approach involves increasing the resistance of the circuit over which the corrosion cell potential is impressed. Dielectric coatings attempt to accomplish this, but because holidays in a coating are inevitable in the case of a soil-buried pipeline, the corrosion circuit or circuits retain a finite resistance path.

The second approach consists of eliminating the open-circuit potential differences between anodic and cathodic areas. When there is no driving potential across the corrosion cell circuits, no corroding current can flow. Cathodic protection can be used to accomplish this method of control. Cathodic protection is obtained by causing a direct current to flow from a source external to the pipeline, through the electrolyte, and to the pipeline steel surface in contact with the electrolyte.

If all of the steel surface is collecting current from the adjacent electrolyte, no current can be discharging from the previously anodic areas of the pipeline; therefore, corrosion activity ceases on the pipeline steel. In essence, if the application of the protective current causes all exposed steel surfaces to become cathodes, cathodic protection has been properly established.

To establish a cathodic protection system for a pipeline, the protective current is discharged into the electrolyte from its source. This source consists of objects, usually metallic, that are properly located in the electrolyte and commonly referred to as anodes or a ground bed. These devices are correctly referred to as anodes because, in discharging the protective current to the electrolyte, they are consumed through the irreversible loss of metallic ions.

There are two primary methods of establishing a cathodic protection system for a pipeline. One is to use anodes made of metals or alloys that, by virtue of their place in the galvanic series of metals, will be anodic to the steel when connected to the pipeline electrically and located in the same electrolyte. Such anodes are known as galvanic anodes or sacrificial anodes. Common anode metals for land or marine pipelines are high-purity zinc and certain magnesium alloys. For marine pipelines, a number of aluminum alloys are also used.

In the second method of establishing cathodic protection for pipelines, the current for the anode system is provided by an external source. The most common source used for the protective current is a transformer-rectifier system in an appropriate housing. The input of the source is commercial alternating current (ac) that is transformed down to the required level and then rectified to a dc voltage of that level. The dc voltage output, when applied between the pipeline steel and the anode system through insulated conductors, creates a protective current flow. Such powered cathodic protection systems are commonly referred to as impressed-current systems.

The materials used for the anodes in impressed-current systems are usually selected for their low consumption rates, that is, relatively low amounts of metal consumed per ampere of current discharged per year. Such materials include graphite, high-silicon cast iron, a thin layer of platinum overlaying a titanium or niobium substrate, certain ferrites, certain conductive polymers, and carbon steel pipe or rails. Steel does not have a low consumption rate, but is usually used when availability of the pipe or rails has economic benefit.

Alternative power sources for impressed-current systems include engine-driven generators, photovoltaic arrays, fuel cells, thermoelectric generators, and wind-powered generators. As a general rule, galvanic anodes are used where relatively low amounts of protective current are required from an individual protective system. Impressed-current installations can provide hundreds of amperes each, but for pipeline applications, typical dc output ratings for individual installations would range from 10 to 60 A at 10 to 70 V. More information on equipment and applications for cathodic protection is available in the section "Cathodic Protection" of the article "Corrosion in Petroleum Production Operations" in this Volume. The cathodic protection of marine pipelines is discussed in the section "Anodic and Cathodic Protection" of the article "Corrosion Protection Methods for the Petrochemical Industry" in this Volume.

**Design Considerations.** Proper corrosion control of a pipeline is most effectively and economically begun during the design stage of the pipeline. Factors affecting the efficacy of the corrosion control program for the pipeline are discussed below.

*The terrain, soils, and waters* in which the pipeline will be located should be considered in order to determine the most effective and most durable coating system for the pipeline. These factors also have a direct bearing on the type and amount of cathodic protection that will be required for corrosion control. Harsher and more aggressively corrosive soils can require protective current densities to be raised, thus increasing total current requirements for a given pipeline system.

*Adjacent or crossing pipeline systems* to the proposed pipeline right-of-way must also be considered. The greater the number of nearby or crossing foreign pipeline systems relative to the proposed pipeline, the greater the chance for interference-current activity. This includes both steady-state interference current and transient current exchange between pipelines.

*Urban Environments.* The potential for damage to the pipeline coating or the pipeline itself from construction activity will usually be much greater in an urban environment. Therefore, the total current requirements for cathodic protection should be generously rated during design to provide for future increases beyond that which would be considered for normal coating degradation.

*Adjacent overhead electric circuits* can cause induced or conductive couplings between the electric circuit and the pipeline steel. Such couplings, if of sufficient transient or steady-state magnitude, can result in ac potentials on the pipeline steel that are injurious to personnel, pipeline equipment, or the pipeline dielectric coating. Although not strictly a corrosion consideration, such analysis is usually performed by corrosion/cathodic protection personnel because they are best equipped to make such analyses.

*Electrical isolation* must be established for those portions of the pipeline system intended for cathodic protection. Electrical isolation of the pipeline segments that will be placed under cathodic protection is required for two reasons. First, it minimizes the total amount of protective current needed to establish overall protection, and second, it enhances the ability of personnel to obtain and interpret field survey data relative to the levels of protection being attained.

The best time to analyze the system for the determination of electrical isolation requirements is during the design phase. This allows required isolation devices to be available for installation during pipeline construction and avoids retrofit requirements. Electrical isolation devices include flange insulation kits, insulating couplings, insulating unions, and other devices that block the flow of longitudinal current.

*Test stations* should be established for conducting electrical field surveys intended to determine the performance of the cathodic protection system. Test stations are devices that are similar to electric junction boxes in which insulated electric wires connected to the pipeline steel are terminated. These flush or aboveground stations permit cathodic protection personnel to analyze electrically the operation of the cathodic protection system.

With regard to electrical isolation equipment, there is economic justification for having such test stations and their pipe-connected test wires installed during pipeline construction before the pipe in the trench is backfilled. The number and type of test stations will usually be determined primarily by the type of pipeline system (transmission, distribution, and so on) and the area in which the pipeline will be located.

**Construction Techniques.** Corrosion control of a pipeline system is normally accomplished through the synergistic effects of cathodic protection and dielectric coatings. Corrosion cell activity is halted by the application of current components in proper densities at pipe steel exposed to the electrolyte. The coating system reduces, by many orders of magnitude in most cases, the total current output required to achieve full protection. Throughout a pipeline service life of, for example, 25 years, any factor that operates to minimize total current requirements can provide significant benefit in terms of operating costs.

Therefore, the pipeline system operator should use a high-quality coating that is well suited to the conditions and location in which the pipeline will operate. In addition, significant care and attention should be paid to ensure that the integrity of the coating is as close to perfect as possible.

Therefore, the primary corrosion considerations in terms of construction are careful handling and transporting of the pipe from the time the coating is applied to the point at which the pipe is backfilled in place. Extreme care in handling, loading, unloading, burying, and backfilling the pipe are paramount concerns. Most pipeline companies follow the practice of locating holidays in the coating by using a high-voltage detector just before or while the pipe is being lowered into the trench. Any holidays detected in this manner are repaired with techniques appropriate to the type of coating used. The purpose of this method is to optimize coating quality immediately before the coating becomes inaccessible.

## Corrosion of Specific Types of Pipelines

**Transmission Pipelines.** Mitigation of corrosion in onshore transmission pipelines is primarily accomplished by the combination of cathodic protection and dielectric coating systems. The design of such cathodic protection systems is reasonably straightforward, because the corrosion engineer can often predict the distance at which protective current application from a remote anode bed will effectively protect the pipeline in both directions from a current drain point attached to the pipeline steel. The distance of effective full protection can be estimated if the pipeline diameter, steel type, wall thickness, soil characteristics, and general coating quality are known. This is so because a pipeline has an attenuation characteristic to current pickup from the electrolyte and longitudinal flow that is analogous to a leaky electric transmission line.

It is interesting to note that it is possible to protect the pipeline to a greater distance from a given anode location on a larger-diameter pipeline than on a pipeline with a smaller diameter. This is because the resistance of the longitudinal pipe steel current path is lower per unit length in proportion to the pipe diameter.

In establishing anode beds for transmission pipelines, an attempt is usually made to place the anodes at remote earth relative to the pipeline. Remote earth in most soils can be a minimum distance of 60 to 150 m (200 to 500 ft) from the pipeline. The higher the resistivity of the indigenous soil, the farther the anode bed must be from the nearest point on the pipeline to be at remote earth.

A remote earth anode bed placement is desirable because it results in the maximum spread of protective current in each direction from an individual anode bed. On larger-diameter (75 to 90 cm, or 30 to 36 in.) pipelines, corrosion can be controlled on 33 to 66 km (30 to 40 miles) of pipeline, assuming a reasonably satisfactory dielectric coating is in place. Remote anode beds are established in primarily two types of installations: surface anode beds and deep anode beds.

*Surface anode beds* are typically installations in which a multiple number of cylindrical anodes 7.5 cm (3 in.) in diameter and 152 cm (60 in.) long are installed vertically to a depth of 4.5 m (15 ft) at 6-m (20-ft) centers. The individual anodes are connected in parallel to the positive-polarity output terminal of a suitably rated transformer-rectifier unit by an insulated anode header cable.

*Deep anode beds* are often used where right-of-way, urban buildup in the area, or soil resistivity conditions dictate their necessity. A deep anode is a vertical installation in which the individual anodes such as those described above are installed in a vertical array in a 20-cm (8-in.) hole drilled to a depth of 30 to 90 m (100 to 300 ft). The intent with a deep anode is usually to attain a remote earth installation without the necessity of departing a long distance from the pipeline right-of-way or attaining a lower electrical resistance (greater operating efficiency) anode installation by placing the anodes in lower resistivity, subsurface soil horizons.

Where localized protection of discrete areas on a transmission pipeline is required, either properly sized galvanic anode arrays or distributed impressed-current anode systems are usually used. Distributed impressed-current anode systems consist of one or more cylindrical anodes installed relatively close to the pipeline (7 to 30 m, or 25 to 100 ft) such that a modest current discharge from each anode will couple to the exposed pipeline steel in its vicinity.

**Distribution Pipelines.** Cathodic protection of distribution pipelines is accomplished with the same techniques and systems as those cited for transmission pipelines, that is, galvanic anodes or impressed-current systems. However, the installation, surveillance, and maintenance of distribution pipeline cathodic protection systems can be much more complex than with a transmission pipeline, which is often a simple buried, coated steel cylinder running between points A and B.

Distribution pipeline systems are often installed in a grid configuration conforming to the roadways fronting the individual structures that the system services. Whether rural or urban, they are usually in place in commercial areas, often under paved roadways and in close proximity to other buried piping and electrical and telephone systems.

In addition, distribution pipeline systems serve multiple delivery points, all of which require the installation and maintenance of electric isolation devices, which are often not in readily accessible locations, such as building basements. Failure or inadvertent short circuiting of just one such electric insulation device, out of a total of perhaps hundreds, can render a well-designed cathodic protection system ineffective.

For this reason, many distribution pipeline operators sectionalize their distribution pipeline systems into discrete areas of electrically continuous piping. This protects against the possibility of one short-circuited isolation device disabling a large portion of the cathodic protection system.

**Fig. 1** Hydrogen-induced cracking in a linepipe steel. 30×

**Fig. 2** Appearance of fracture surface of line pipe that failed by SCC. Actual size. See also Fig. 3 to 5.

By virtue of the close proximity of a distribution piping system to adjacent buried metallic structures that may not be cathodically protected (for example, cast iron water or sewer systems), inadvertent contact to such systems can also disable an otherwise effective cathodic protection system. In heavily trafficked urban areas, such contacts can be extremely difficult to locate and to clear. In addition, assessment of the continuing effectiveness of a distribution pipeline cathodic protection system through electrical test techniques is also difficult because the system is usually located under paved surfaces.

Despite all of the difficulties cited above, distribution pipeline systems are protected against corrosion activity. Both galvanic anode and impressed-current systems are used by system operators. The most prevalent type of design is the distributed anode type, often with galvanic anodes installed at specific intervals that are a function of the diameter of the pipeline. Impressed-current systems are also used, but with their typically higher operating voltages and protective current magnitudes, they are more susceptible to interference-current effects from adjacent buried metallic systems.

**Oil and Gas Transmission.** The transmission of oil and gas involves consideration of the corrosion problems associated with linepipe steels. In addition to carbon steels, high-strength low-alloy steels are often used in pipeline service.

*Hydrogen-Induced Cracking.* Linepipe steels can be susceptible to a specialized form of hydrogen damage when $H_2S$ is present in oil and gas. This type of embrittlement, known as hydrogen-induced cracking, results from the accumulation of hydrogen at internal surfaces within the steel. Examples include interfaces at nonmetallic inclusions and at microstructure constituents that differ significantly from the surrounding matrix. Martensite islands in a ferrite-pearlite matrix would be typical. Microcracks that form at these interfaces grow in a stepwise fashion toward the surface of the pipe, with the result being failure. Figure 1 illustrates an example of this type of cracking.

Very few failures due to hydrogen-induced cracking have been reported. However, they can be catastrophic, and considerable investigative work has been done to understand the nature of the problem and to develop preventive measures. Hydrogen-induced cracking can usually be prevented by control of the environment—for example, dehydration to remove water and through chemical inhibition. A number of metallurgical factors have also been identified that influence resistance to hydrogen-induced cracking and offer a means of reducing the susceptibility of linepipe steels to this form of embrittlement.

Two factors that influence the susceptibility of linepipe steels to hydrogen-induced cracking are steel cleanliness and degree of alloying element segregation. This might be expected, because the degree of steel cleanliness affects the volume fraction of nonmetallic inclusions present and therefore the number of interfaces available for the accumulation of hydrogen. Segregation of alloying elements can lead to the formation of low-temperature austenite decomposition products, thus providing additional sites for hydrogen accumulation.

Hydrogen-induced cracking has been found to be associated with manganese sulfide inclusions that have become elongated during hot rolling. Elongated silicate inclusions also provide interfaces for hydrogen accumulation. Laboratory tests have shown that reduction in the sulfur level of a linepipe steel reduces susceptibility to hydrogen-induced cracking. Reducing the sulfur content to levels of 0.002% or less can result in a significant improvement in resistance to hydrogen-induced cracking. It has also been observed that resistance to hydrogen-induced cracking can be improved through the use of sulfide shape control techniques. Calcium or rare-earth metals are added to the steel to form calcium or rare-earth sulfides. These inclusions are not plastic at hot working temperatures and therefore do not elongate during hot rolling.

The effects of various alloying elements on resistance to hydrogen-induced cracking are uncertain and somewhat controversial. The alloying element that has received the most attention is copper. Laboratory results have shown that copper can significantly reduce susceptibility to hydrogen-induced cracking. Apparently, the benefits of copper are realized only in environments with a pH of 4.5 to 4.8 and above. At pH levels less than this, copper has no effect on resistance to hydrogen-induced cracking.

*Stress-Corrosion Cracking.* Figure 2 shows the fracture surface of a stress-corrosion crack in line pipe. Failures of this type have primarily occurred

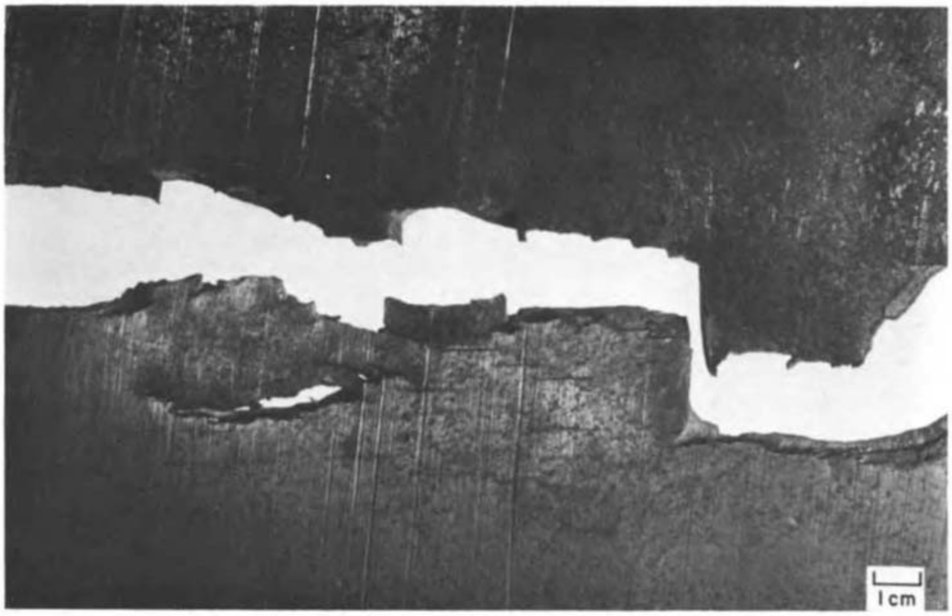

**Fig. 3** Secondary cracking in pipe surface adjacent to stress-corrosion cracks shown in Fig. 2. Actual size. See also Fig. 4 and 5.

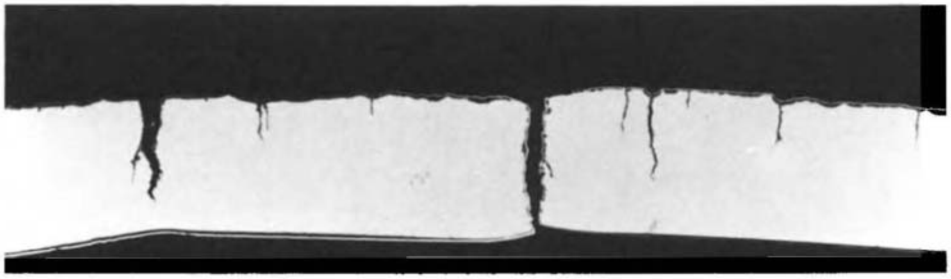

**Fig. 4** Macrograph of unetched section through stress-corrosion cracks in line pipe. See also Fig. 2, 3, and 5.

on gas-transmission pipelines immediately downstream of compressor stations, where the pipe temperatures are the highest. The characteristic feature is a series of elliptical crack shapes, which initiated from the outside surface. Normally, a black oxide layer can be observed on the elliptical crack surfaces. Also, the cracks frequently overlap in the axial direction and link together. Figure 3 shows secondary cracks on the pipe surface. Information on the pipe-to-soil cathodic-potential level, pipe temperature, pressure, and pressure fluctuations in the pipeline should be obtained.

The investigation should begin with a low-power examination of the fracture surface to select locations for metallographic sections. The nature of the cracks can be determined by preparing several matched metallographic sections across the fracture surface. Also, analysis of any corrosion product on the elliptical crack surface using an energy-dispersive x-ray spectrometer may be helpful in defining the corrosive medium. In a high percentage of the failures, iron carbonate or bicarbonate has been detected on the crack surface (this environment is produced at a pore in the pipe coating as the hydroxide created by the cathodic potential is converted by the $CO_2$ in the soil to a carbonate-bicarbonate environment). Scanning electron microscopy examination of the fracture surface can also be helpful in identifying whether the fracture is transgranular or intergranular.

Usually, the fracture surfaces are primarily intergranular, and a number of branched secondary fractures are often evident in the metallographic sections (Fig. 4). Figure 5 shows an unetched section of a stress-corrosion crack that illustrates the branching and intergranular nature of the fracture.

The conditions that have been responsible for a high percentage of the stress-corrosion cracks in line pipe are the carbonate-bicarbonate environment, the pipe surface in the critical potential range for cracking (–0.6 to –0.7 V versus the saturated calomel electrode, SCE, for a carbonate-bicarbonate environment), and the applied tensile stress.

The carbonate-bicarbonate environment is believed to be formed by the cathodic potential at pores in the coating where the current penetrates to the pipe surface. The cathodic potential also creates the critical potential for SCC. The hoop stress in the circumferential direction of the pipe is created by the internal pressure in the pipe.

There is no simple control for external SCC, because one of the three conditions necessary for cracking must be prevented. This means keeping the cathodic potential outside of the critical range for cracking, which is difficult, if not impossible, at all points on a long pipeline.

Keeping the temperature as low as possible slows the reaction rate, which helps to prevent cracking. Many of the pipeline failures have been located in the first 16 km (10 miles) downstream of a gas compressor station, which is the high-temperature region on a gas pipeline. Applying a good coating to the pipe surface is also a deterrent, as is shot peening the pipe surface to remove mill scale and to provide a good surface for coating bonding. Small pressure fluctuations have been found to promote cracking. Thus, pressure control is helpful, but is difficult to achieve in most situations.

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**Fig. 5** Polished section through stress-corrosion cracks showing branching and intergranular cracking. See also Fig. 2 to 4.

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# Case Histories in Failure Analysis: Corrosion of Petroleum and Petrochemical Pipelines

# Rapid Pitting Failure of Type 304 Stainless Steel Pipework*

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*Several hundred leaks were reported in the type 304 stainless steel pipelines, vessels, and tanks of a chemical plant at a tropical location within a few weeks after startup. Investigation of the failure involved a site visit, metallographic examination and analysis of the material, analysis of hydrotest waters, and microbiological examination of slime that had formed in certain pipework sections. It was determined that the failure resulted from microbially induced corrosion promoted by the use of poor-quality hydrotest water and uncontrolled hydrotesting practice. Use of appropriate hydrotesting procedures was recommended to prevent similar failures.*

**Key Words**

Austenitic stainless steels, corrosion
Chemical processing equipment, corrosion
Bacterial corrosion
Leakage
Piping, corrosion

**Alloys**

Austenitic stainless steel—304

## Background

The type 304 stainless steel pipelines, vessels, and tanks of a chemical plant at a tropical location developed several hundred leaks soon after startup.

## *Applications*

Hydrotesting of new pipework and reservoirs in the petroleum industry and in chemical processing plants is conveniently achieved by using water pressure. A pump is used to force water through the pipes to a valve that controls the fluid pressure and flow. Drops in pressure over a set period of time, as well as visual inspection, can reveal unsound joints and welds.

Locally available water is commonly used for hydrotesting. Subsequently, the water is often resident in the pipes and vessels for an extended period, until the process plant comes "on stream." In the case of mild steel pipework, hydrotest/storage waters are commonly treated with a corrosion-preventative hydrotest package that contains an oxygen scavenger, a biocide, and, frequently, a corrosion inhibitor. Such treatments are not generally used in the case of stainless steel pipelines and vessels.

## *Circumstances leading to failure*

The case history detailed here concerns rapid pitting damage to a new chemical plant constructed at a tropical location (Fig. 1). The extensive stainless steel pipework was not expected to suffer corrosion in the process liquors. It was built by a European company according to a well-established design.

The pipework, tanks and reservoirs were hydrotested using local mountain borehole water, which was stored in an open pond prior to use. The water was considered potable (that is, nonsaline) by the contractor and was resident in the plant for 3 months. Leaks at a few locations were discovered during the later stages of this period and were stopped by external clamping (Fig. 2). Shortly after chemical process startup, several hundred leaks were reported. The leaks showed no correlation to the type of process liquor (for example, dodecylbenzene sulfonate, fatty acids, synthetic and natural fatty alcohols, triethanolamine, sodium silicate, sodium carbonate, and others). All stainless steel pipelines and many vessels and tanks were affected.

The plant was subsequently shut down after only a few weeks of operation. By this time, leaks were so numerous that they were no longer recorded systematically by the operator.

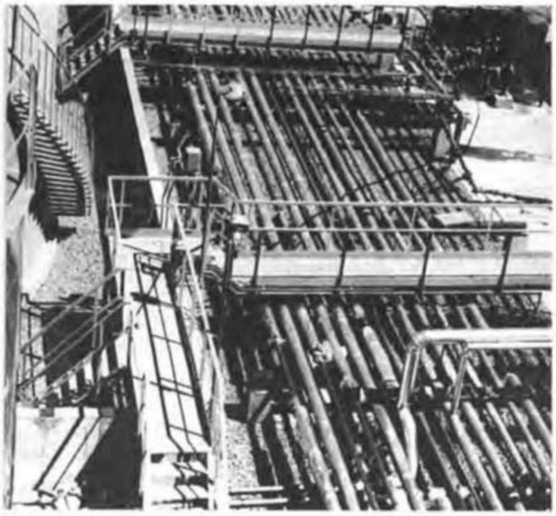

**Fig. 1** View of new stainless steel chemical plant

## *Performance of other parts in same or similar service*

The chemical plant was one of three similar complexes constructed from AISI type 304 stainless steel in the same general location. The two other plants were in the process of hydrotesting at the time that failure occurred.

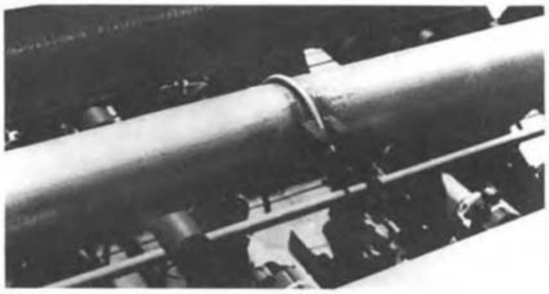

**Fig. 2** External clamping used to stop leaks

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*Originally published in *Corrosion*, 3rd ed., Shreir, Jarman, and Burstein, Ed., Butterworth-Heinemann. Reprinted with permission.

### *Specimen selection*

The stainless steel lines in the tankfarm area were affected most severely. These lines had been constructed by two separate companies. However, all such stainless steel lines had been affected. Sections of damaged 150 mm (6 in.) and 75 mm (3 in.) diam stainless steel line were available for investigation. Ring sections around the actual pit sites were cut for laboratory analysis.

Water samples were collected for on-site and laboratory analysis. Sampling conformed to ASTM D 3370. Although samples of the actual hydrotest water were not available, samples of borehole water were taken from various sites at the plant.

## Examination of General Physical Features

Stainless steel samples of pipework were analyzed using spark spectrographic analysis. A typical composition is given in Table 1. Although the material complied with the chemical requirements for AISI type 304 austenitic stainless steel, chromium was at the very lowest allowable level. Examination of the microstructure in metallographic sections revealed no abnormalities.

The composition of the hydrotest water is shown in Table 2.

It was not truly potable because of its elevated chloride content and exceptionally high bacterial loading.

**Table 1 Composition of stainless steel**

| | Composition, % | |
|---|---|---|
| Element | Pipe sample | Type 304 stainless steel (ASTM A276-88)(a) |
| Carbon | 0.03 | 0.08 (max) |
| Silicon | 0.47 | 1.00 (max) |
| Manganese | 1.59 | 2.00 (max) |
| Phosphorus | 0.031 | 0.045 (max) |
| Sulfur | 0.015 | 0.030 (max) |
| Chromium | 18.0 | 18.00-20.00 |
| Molybdenum | 0.33 | NR |
| Nickel | 8.8 | 8.00-10.50 |
| Copper | 0.18 | NR |
| Vanadium | 0.04 | NR |
| Aluminum | <0.05 | NR |
| Niobium | <0.05 | NR |
| Titanium | <0.02 | NR |
| Nitrogen | ... | 0.10 (max) |

(a) NR, no requirement

**Table 2 Composition of hydrotest water**

| Parameter | Measured values | Acceptable levels (U.S.)(a) |
|---|---|---|
| pH | 7.3 | 6.5-8.5 |
| Chloride | 1260 ppm | 250 mg/L |
| Sulfate | 160 ppm | 250 mg/L |
| Nitrate | 40 ppm | 10.0 (as N) |
| Bicarbonate | 350 ppm as $CaCO_3$ | ... |
| Calcium hardness | 390 ppm as $CaCO_3$ | ... |
| Magnesium hardness | 311 ppm as $CaCO_3$ | ... |
| Dissolved iron | 0 ppm (very high suspended iron) | 0.3 mg/L |
| Oxygen | <1 ppm | ... |
| Temperature | 35 °C (95 °F) at time of sampling | ... |
| Total viable bacteria (heterotrophs) | $>10^7$/mL | ... |
| Sulfate-reducing bacteria | $10^4$/mL | ... |
| Iron bacteria (*Gallionella*) | Very abundant | ... |

(a) Per "Prevention and Control of Water-Caused Problems in Building Potable Water Systems," TPC Publ. 7, National Association of Corrosion Engineers

## Testing Procedure and Results

### *Surface examination*

Because the hydrotest water was implicated in the failures, the hydrotesting regime history was provided. This covered a total period of 5 months. All pipework was hydrotested using untreated borehole water supplied to the site through 17 km (11 mi), 115 mm (4.5 in.) diam carbon steel pipework. The borehole water was resident in the pipelines for 2 months, but no water quality/corrosion monitoring was undertaken.

All tanks were hydrotested using potable (rain) water brought in by tanker. This potable water was resident in the tanks for 3 months. Leaks in the tank walls were neither noted nor found. Areas of iridescent staining and light corrosion around welds in an accessible tank were investigated. Although pitting could be found near welds in a stainless steel heating coil (serpentine) in the bottom of this tank, no pitting could be found in the tank walls. It was noted that a type 316 stainless steel bracket had been welded to the type 304 serpentine support frame.

### *Metallography*

**Microstructural Analysis.** The microstructure of the pipe was fairly typical of a rolled/drawn austenitic stainless steel. It consisted of relatively fine equiaxed austenitic grains, some of which exhibited twins. No other second phases were observed in the microstructure.

The stainless steel was riddled with flask-shaped pits of the type shown in Fig. 3. The majority of such pits were in the "six o'clock" position. Electron probe microanalysis revealed that these pits were filled with sulfide and, to a lesser extent, chloride at elevated concentrations.

### *Chemical analysis/identification*

**Associated Environment.** Certain sections of pipework that were still filled with hydrotest water (resident for 3 months) were opened and were found to be completely blocked with a brown, gelatinous mass of slime, which was later identified as iron bacteria of the genus *Gallionella* (Fig. 4). Sulfate-reducing bacteria were present in high numbers close to the stainless steel surface.

## Discussion

Type 304 stainless steel is the minimum grade of austenitic stainless steel. It is susceptible to localized pitting by either sulfide or chloride ions under conditions in which repassivation is hindered. Normally, it is protected by a passive oxide layer. However, chloride ions have the power to penetrate the oxide film, causing local breakdown of passivity and the formation of an anodic site. Repassivation occurs by the formation of fresh oxide by reaction of the metal with dissolved oxygen or with water molecules. The former—that is, the less energetic reaction—is preferred.

In this case, microbiological activity had reduced dissolved oxygen, and the solid deposits restricted access of fresh dissolved oxygen. Hence, the corrosion reaction at a sulfide or chloride ion-induced anodic site under a deposit was supported by a cathodic reaction at the edges of the deposits, followed by the initiation of pits. Once the pits were established, the anodic reaction within the confines of each pit produced increased acidity and an accelerating corrosion rate, which contributed to the frequency of flask-shaped pits (Fig. 3). The influence of solid deposits accounted for the frequency of pits in the six o'clock position, where deposits naturally settle out.

**Fig. 3** Flask-shaped pit

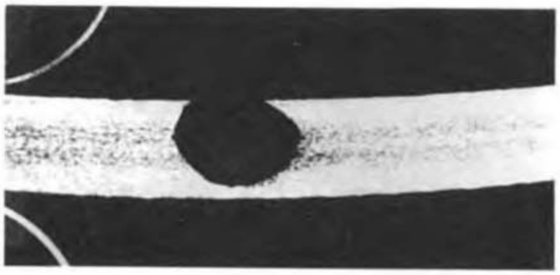


**Fig. 4** Iron bacteria of genus *Gallionella*

## Conclusion and Recommendations

### Most probable cause

The corrosion problem was one of environment, rather than material. The type 304 stainless steel pipework experienced widespread pitting corrosion attack because of poor-quality hydrotest water and uncontrolled hydrotesting practices.

The aggressiveness of the water was due to the relatively high concentration of both chloride and sulfide ions, combined with massive insoluble stagnant deposits caused by microbiological activity. Such activity was encouraged by the high local ambient temperatures.

It appeared that the main producers of deposits and tubercules in the pipework were iron bacteria of the genus *Gallionella*. Sulfate-reducing bacteria of the genus *Desulfovibrio*, which often cause severe problems in industrial situations, were a secondary component in this instance. These sulfate-reducing bacteria produced hydrogen sulfide by anaerobic reduction of sulfate beneath the deposits.

### Remedial action

The remedial actions outlined below are critical at sites with poor-quality water. To ensure the successful operation of the two other plants in the same general location, it was imperative that these remedial measures be instituted quickly:

- Conduct the hydrotest using potable water with less than 400 ppm chloride. The water should not contain significant amounts of suspended solids, sulfides, or excessive bacterial contamination. Filter water to the highest standard practicable.
- Following the hydrotest, excess water should be blown out using dry warm air. Heat, up to approximately 60 °C (140 °F), should be applied to the pipes. Drying should be assisted by flushing with methanol, if possible.
- If the system cannot be completely drained, then the hydrotest should be conducted by using either clean steam condensate or demineralized water, or by using potable water followed by a demineralized water rinse to give an effluent chloride level of less than 5 ppm. If this cannot be achieved, then trisodium phosphate equal to five times the chloride concentration should be added.
- If any carbon steel is present in the system, then a mixture of sodium nitrite/sodium borate should be dissolved in the hydrotest water to give a final concentration of 500 ppm for each substance.
- A proprietary biocide, such as 50% gluteraldehyde solution, should be dosed at 250 ppm in all cases.

### *How failure could have been prevented*

When the remedial actions described above were instituted at the other two plants in the same general location, no damage was reported. Thus, these procedures were deemed effective in preventing the type of damage that occurred at the first plant. The stainless steel pipework at that plant required nearly complete replacement.

# Corrosion Data

The data compiled in this section provide a point of entry into the vast literature on materials in corrosive environments. The information in this section has been organized into three groups:

- Steel Specifications and Compositions
- Resistance of Materials to Selected Corrosive Media
- Properties of Selected Nonmetallic Materials

The materials and corrosive media presented here were selected for their importance to the petrochemical industry; however, this compilation does not include every corrosive medium encountered in this industry, nor does it include all of the properties and corrosion rates for the listed materials. For a more complete presentation on the resistance of metals to corrosive media, the reader is referred to ASM's *Handbook of Corrosion Data.* Additional data are available in *Corrosion Data Survey*, 5th Edition, NACE, 1985. Information on the compositions, properties, and selection of metallic materials is available in Volumes 1 and 2 of *ASM Handbook.* Information on nonmetallic materials can be found in ASM's four-volume *Engineered Materials Handbook* and in Raymond B. Seymour, *Polymers for Engineering Applications*, ASM International, 1987.

# Steel Specifications and Compositions

## Table 1 SAE-AISI system of designations

| Numerals and digits | Type of steel and nominal alloy content, % |
|---|---|
| **Carbon steels** | |
| 10*xx*(a) | Plain carbon (Mn 1.00 max) |
| 11*xx* | Resulfurized |
| 12*xx* | Resulfurized and rephosphorized |
| 15*xx* | Plain carbon (max Mn range: 1.00-1.65) |
| **Manganese steels** | |
| 13*xx* | Mn 1.75 |
| **Nickel steels** | |
| 23*xx* | Ni 3.50 |
| 25*xx* | Ni 5.00 |
| **Nickel-chromium steels** | |
| 31*xx* | Ni 1.25; Cr 0.65 and 0.80 |
| 32*xx* | Ni 1.75; Cr 1.07 |
| 33*xx* | Ni 3.50; Cr 1.50 and 1.57 |
| 34*xx* | Ni 3.00; Cr 0.77 |
| **Molybdenum steels** | |
| 40*xx* | Mo 0.20 and 0.25 |
| 44*xx* | Mo 0.40 and 0.52 |
| **Chromium-molybdenum steels** | |
| 41*xx* | Cr 0.50, 0.80, and 0.95; Mo 0.12, 0.20, 0.25, and 0.30 |
| **Nickel-chromium-molybdenum steels** | |
| 43*xx* | Ni 1.82; Cr 0.50 and 0.80; Mo 0.25 |
| 43BV*xx* | Ni 1.82; Cr 0.50; Mo 0.12 and 0.25; V 0.03 min |
| 47*xx* | Ni 1.05; Cr 0.45; Mo 0.20 and 0.35 |
| 81*xx* | Ni 0.30; Cr 0.40; Mo 0.12 |
| 86*xx* | Ni 0.55; Cr 0.50; Mo 0.20 |
| 87*xx* | Ni 0.55; Cr 0.50; Mo 0.25 |
| 88*xx* | Ni 0.55; Cr 0.50; Mo 0.35 |
| 93*xx* | Ni 3.25; Cr 1.20; Mo 0.12 |
| 94*xx* | Ni 0.45; Cr 0.40; Mo 0.12 |
| 97*xx* | Ni 0.55; Cr 0.20; Mo 0.20 |
| 98*xx* | Ni 1.00; Cr 0.80; Mo 0.25 |
| **Nickel-molybdenum steels** | |
| 46*xx* | Ni 0.85 and 1.82; Mo 0.20 and 0.25 |
| 48*xx* | Ni 3.50; Mo 0.25 |
| **Chromium steels** | |
| 50*xx* | Cr 0.27; 0.40, 0.50, and 0.65 |
| 51xx | Cr 0.80, 0.87, 0.92, 0.95, 1.00, *and 1.05* |
| **Chromium (bearing) steels** | |
| 50*xxx* | Cr 0.50; C 1.00 min |
| 51*xxx* | Cr 1.02; C 1.00 min |
| 52*xxx* | Cr 1.45; C 1.00 min |
| **Chromium-vanadium steels** | |
| 61*xx* | Cr 0.60, 0.80, and 0.95; V 0.10 and 0.15 min |
| **Tungsten-chromium steel** | |
| 72*xx* | W 1.75; Cr 0.75 |
| **Silicon-manganese steels** | |
| 92*xx* | Si 1.40 and 2.00; Mn 0.65, 0.82, and 0.85; Cr 0 and 0.65 |
| **High-strength low-alloy steels** | |
| 9*xx* | Various SAE grades |
| **Boron steels** | |
| *xx*B*xx* | B denotes boron steel |
| **Leaded steels** | |
| *xx*L*xx* | L denotes leaded steel |

(a) The *xx* in the last two digits of these designations indicates that the carbon content (in hundredths of a percent) is to be inserted.

**Table 2 Carbon steel compositions**

Applicable to semifinished products for forging, hot-rolled and cold-finished bars, wire rods, and seamless tubing

| UNS number | SAE-AISI number | Cast or heat chemical ranges and limits, %(a) | | | |
|---|---|---|---|---|---|
| | | C | Mn | P max | S max |
| G10050 | 1005 | 0.06 max | 0.35 max | 0.040 | 0.050 |
| G10060 | 1006 | 0.08 max | 0.25-0.40 | 0.040 | 0.050 |
| G10080 | 1008 | 0.10 max | 0.30-0.50 | 0.040 | 0.050 |
| G10100 | 1010 | 0.08-0.13 | 0.30-0.60 | 0.040 | 0.050 |
| G10120 | 1012 | 0.10-0.15 | 0.30-0.60 | 0.040 | 0.050 |
| G10130 | 1013 | 0.11-0.16 | 0.50-0.80 | 0.040 | 0.050 |
| G10150 | 1015 | 0.13-0.18 | 0.30-0.60 | 0.040 | 0.050 |
| G10160 | 1016 | 0.13-0.18 | 0.60-0.90 | 0.040 | 0.050 |
| G10170 | 1017 | 0.15-0.20 | 0.30-0.60 | 0.040 | 0.050 |
| G10180 | 1018 | 0.15-0.20 | 0.60-0.90 | 0.040 | 0.050 |
| G10190 | 1019 | 0.15-0.20 | 0.70-1.00 | 0.040 | 0.050 |
| G10200 | 1020 | 0.18-0.23 | 0.30-0.60 | 0.040 | 0.050 |
| G10210 | 1021 | 0.18-0.23 | 0.60-0.90 | 0.040 | 0.050 |
| G10220 | 1022 | 0.18-0.23 | 0.70-1.00 | 0.040 | 0.050 |
| G10230 | 1023 | 0.20-0.25 | 0.30-0.60 | 0.040 | 0.050 |
| G10250 | 1025 | 0.22-0.28 | 0.30-0.60 | 0.040 | 0.050 |
| G10260 | 1026 | 0.22-0.28 | 0.60-0.90 | 0.040 | 0.050 |
| G10290 | 1029 | 0.25-0.31 | 0.60-0.90 | 0.040 | 0.050 |
| G10300 | 1030 | 0.28-0.34 | 0.60-0.90 | 0.040 | 0.050 |
| G10350 | 1035 | 0.32-0.38 | 0.60-0.90 | 0.040 | 0.050 |
| G10370 | 1037 | 0.32-0.38 | 0.70-1.00 | 0.040 | 0.050 |
| G10380 | 1038 | 0.35-0.42 | 0.60-0.90 | 0.040 | 0.050 |
| G10390 | 1039 | 0.37-0.44 | 0.70-1.00 | 0.040 | 0.050 |
| G10400 | 1040 | 0.37-0.44 | 0.60-0.90 | 0.040 | 0.050 |
| G10420 | 1042 | 0.40-0.47 | 0.60-0.90 | 0.040 | 0.050 |
| G10430 | 1043 | 0.40-0.47 | 0.70-1.00 | 0.040 | 0.050 |
| G10440 | 1044 | 0.43-0.50 | 0.30-0.60 | 0.040 | 0.050 |
| G10450 | 1045 | 0.43-0.50 | 0.60-0.90 | 0.040 | 0.050 |
| G10460 | 1046 | 0.43-0.50 | 0.70-1.00 | 0.040 | 0.050 |
| G10490 | 1049 | 0.46-0.53 | 0.60-0.90 | 0.040 | 0.050 |
| G10500 | 1050 | 0.48-0.55 | 0.60-0.90 | 0.040 | 0.050 |
| G10530 | 1053 | 0.48-0.55 | 0.70-1.00 | 0.040 | 0.050 |
| G10550 | 1055 | 0.50-0.60 | 0.60-0.90 | 0.040 | 0.050 |
| G10590 | 1059 | 0.55-0.65 | 0.50-0.80 | 0.040 | 0.050 |
| G10600 | 1060 | 0.55-0.65 | 0.60-0.90 | 0.040 | 0.050 |
| G10640 | 1064 | 0.60-0.70 | 0.50-0.80 | 0.040 | 0.050 |
| G10650 | 1065 | 0.60-0.70 | 0.60-0.90 | 0.040 | 0.050 |
| G10690 | 1069 | 0.65-0.75 | 0.40-0.70 | 0.040 | 0.050 |
| G10700 | 1070 | 0.65-0.75 | 0.60-0.90 | 0.040 | 0.050 |
| G10740 | 1074 | 0.70-0.80 | 0.50-0.80 | 0.040 | 0.050 |
| G10750 | 1075 | 0.70-0.80 | 0.40-0.70 | 0.040 | 0.050 |
| G10780 | 1078 | 0.72-0.85 | 0.30-0.60 | 0.040 | 0.050 |
| G10800 | 1080 | 0.75-0.88 | 0.60-0.90 | 0.040 | 0.050 |
| G10840 | 1084 | 0.80-0.93 | 0.60-0.90 | 0.040 | 0.050 |
| G10850 | 1085 | 0.80-0.93 | 0.70-1.00 | 0.040 | 0.050 |
| G10860 | 1086 | 0.80-0.93 | 0.30-0.50 | 0.040 | 0.050 |
| G10900 | 1090 | 0.85-0.98 | 0.60-0.90 | 0.040 | 0.050 |
| G10950 | 1095 | 0.90-1.03 | 0.30-0.50 | 0.040 | 0.050 |

(a) When silicon ranges or limits are required for bar and semifinished products, the values in Table 1 apply. For rods, the following ranges are commonly used: 0.10 max; 0.07-0.15%; 0.10-0.20%; 0.15-0.35%; 0.20-0.40%; and 0.30-0.60%. Steels listed in this table can be produced with additions of lead or boron. Leaded steels typically contain 0.15-0.35% Pb and are identified by inserting the letter L in the designation (10L45); boron steels can be expected to contain 0.0005-0.003% B and are identified by inserting the letter B in the designation (10B46). Source: Chemical Compositions of SAE Carbon Steels, SAE J403, *1989 SAE Handbook*, Vol 1, *Materials*, Society of Automotive Engineers, p 1.08

**Table 3 Carbon steel compositions**

Applicable only to structural shapes, plates, strip, sheets, and welded tubing

| UNS number | SAE-AISI number | Cast or heat chemical ranges and limits, %(a) C | Mn | P max | S max |
|---|---|---|---|---|---|
| G10060 | 1006 | 0.08 max | 0.45 max | 0.040 | 0.050 |
| G10080 | 1008 | 0.10 max | 0.50 max | 0.040 | 0.050 |
| G10090 | 1009 | 0.15 max | 0.60 max | 0.040 | 0.050 |
| G10100 | 1010 | 0.08-0.13 | 0.30-0.60 | 0.040 | 0.050 |
| G10120 | 1012 | 0.10-0.15 | 0.30-0.60 | 0.040 | 0.050 |
| G10150 | 1015 | 0.12-0.18 | 0.30-0.60 | 0.040 | 0.050 |
| G10160 | 1016 | 0.12-0.18 | 0.60-0.90 | 0.040 | 0.050 |
| G10170 | 1017 | 0.14-0.20 | 0.30-0.60 | 0.040 | 0.050 |
| G10180 | 1018 | 0.14-0.20 | 0.60-0.90 | 0.040 | 0.050 |
| G10190 | 1019 | 0.14-0.20 | 0.70-1.00 | 0.040 | 0.050 |
| G10200 | 1020 | 0.17-0.23 | 0.30-0.60 | 0.040 | 0.050 |
| G10210 | 1021 | 0.17-0.23 | 0.60-0.90 | 0.040 | 0.050 |
| G10220 | 1022 | 0.17-0.23 | 0.70-1.00 | 0.040 | 0.050 |
| G10230 | 1023 | 0.19-0.25 | 0.30-0.60 | 0.040 | 0.050 |
| G10250 | 1025 | 0.22-0.28 | 0.30-0.60 | 0.040 | 0.050 |
| G10260 | 1026 | 0.22-0.28 | 0.60-0.90 | 0.040 | 0.050 |
| G10300 | 1030 | 0.27-0.34 | 0.60-0.90 | 0.040 | 0.050 |
| G10330 | 1033 | 0.29-0.36 | 0.70-1.00 | 0.040 | 0.050 |
| G10350 | 1035 | 0.31-0.38 | 0.60-0.90 | 0.040 | 0.050 |
| G10370 | 1037 | 0.31-0.38 | 0.70-1.00 | 0.040 | 0.050 |
| G10380 | 1038 | 0.34-0.42 | 0.60-0.90 | 0.040 | 0.050 |
| G10390 | 1039 | 0.36-0.44 | 0.70-1.00 | 0.040 | 0.050 |
| G10400 | 1040 | 0.36-0.44 | 0.60-0.90 | 0.040 | 0.050 |
| G10420 | 1042 | 0.39-0.47 | 0.60-0.90 | 0.040 | 0.050 |
| G10430 | 1043 | 0.39-0.47 | 0.70-1.00 | 0.040 | 0.050 |
| G10450 | 1045 | 0.42-0.50 | 0.60-0.90 | 0.040 | 0.050 |
| G10460 | 1046 | 0.42-0.50 | 0.70-1.00 | 0.040 | 0.050 |
| G10490 | 1049 | 0.45-0.53 | 0.60-0.90 | 0.040 | 0.050 |
| G10500 | 1050 | 0.47-0.55 | 0.60-0.90 | 0.040 | 0.050 |
| G10550 | 1055 | 0.52-0.60 | 0.60-0.90 | 0.040 | 0.050 |
| G10600 | 1060 | 0.55-0.66 | 0.60-0.90 | 0.040 | 0.050 |
| G10640 | 1064 | 0.59-0.70 | 0.50-0.80 | 0.040 | 0.050 |
| G10650 | 1065 | 0.59-0.70 | 0.60-0.90 | 0.040 | 0.050 |
| G10700 | 1070 | 0.65-0.76 | 0.60-0.90 | 0.040 | 0.050 |
| G10740 | 1074 | 0.69-0.80 | 0.50-0.80 | 0.040 | 0.050 |
| G10750 | 1075 | 0.69-0.80 | 0.40-0.70 | 0.040 | 0.050 |
| G10780 | 1078 | 0.72-0.86 | 0.30-0.60 | 0.040 | 0.050 |
| G10800 | 1080 | 0.74-0.88 | 0.60-0.90 | 0.040 | 0.050 |
| G10840 | 1084 | 0.80-0.94 | 0.60-0.90 | 0.040 | 0.050 |
| G10850 | 1085 | 0.80-0.94 | 0.70-1.00 | 0.040 | 0.050 |
| G10860 | 1086 | 0.80-0.94 | 0.30-0.50 | 0.040 | 0.050 |
| G10900 | 1090 | 0.84-0.98 | 0.60-0.90 | 0.040 | 0.050 |
| G10950 | 1095 | 0.90-1.04 | 0.30-0.50 | 0.040 | 0.050 |

(a) When silicon ranges or limits are required, the following ranges and limits are commonly used: up to SAE 1025 inclusive, 0.10% max, 0.10-0.25%, or 0.15-0.35%. Over SAE 1025, 0.10-0.25% or 0.15-0.35%. Source: Chemical Compositions of SAE Carbon Steels, SAE J403, *1989 SAE Handbook*, Vol 1, *Materials*, Society of Automotive Engineers, p 1.09

## Table 4 Chemical compositions for typical low-alloy steels

| | Composition, wt%(a) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| **Steel** | **C** | **Si** | **Mn** | **P** | **S** | **Ni** | **Cr** | **Mo** | **Other** |
| **Low-carbon quenched and tempered steels** | | | | | | | | | |
| A 514/A 517 grade A | 0.15-0.21 | 0.40-0.80 | 0.80-1.10 | 0.035 | 0.04 | ... | 0.50-0.80 | 0.18-0.28 | 0.05-0.15 Zr(b)<br>0.0025 B |
| A 514/A 517 grade F | 0.10-0.20 | 0.15-0.35 | 0.60-1.00 | 0.035 | 0.04 | 0.70-1.00 | 0.40-0.65 | 0.40-0.60 | 0.03-0.08 V<br>0.15-0.50 Cu<br>0.0005-0.005 B |
| A 514/A 517 grade R | 0.15-0.20 | 0.20-0.35 | 0.85-1.15 | 0.035 | 0.04 | 0.90-1.10 | 0.35-0.65 | 0.15-0.25 | 0.03-0.08 V |
| A 533 type A | 0.25 | 0.15-0.40 | 1.15-1.50 | 0.035 | 0.04 | ... | ... | 0.45-0.60 | ... |
| A 533 type C | 0.25 | 0.15-0.40 | 1.15-1.50 | 0.035 | 0.04 | 0.70-1.00 | ... | 0.45-0.60 | ... |
| HY-80 | 0.12-0.18 | 0.15-0.35 | 0.10-0.40 | 0.025 | 0.025 | 2.00-3.25 | 1.00-1.80 | 0.20-0.60 | 0.25 Cu<br>0.03 V<br>0.02 Ti |
| HY-100 | 0.12-0.20 | 0.15-0.35 | 0.10-0.40 | 0.025 | 0.025 | 2.25-3.50 | 1.00-1.80 | 0.20-0.60 | 0.25 Cu<br>0.03 V<br>0.02 Ti |
| **Medium-carbon ultrahigh-strength steels** | | | | | | | | | |
| 4130 | 0.28-0.33 | 0.20-0.35 | 0.40-0.60 | ... | ... | ... | 0.80-1.10 | 0.15-0.25 | ... |
| 4340 | 0.38-0.43 | 0.20-0.35 | 0.60-0.80 | ... | ... | 1.65-2.00 | 0.70-0.90 | 0.20-0.30 | ... |
| 300M | 0.40-0.46 | 1.45-1.80 | 0.65-0.90 | ... | ... | 1.65-2.00 | 0.70-0.95 | 0.30-0.45 | 0.05 V min |
| D-6a | 0.42-0.48 | 0.15-0.30 | 0.60-0.90 | ... | ... | 0.40-0.70 | 0.90-1.20 | 0.90-1.10 | 0.05-0.10 V |
| **Carburizing bearing steels** | | | | | | | | | |
| 4118 | 0.18-0.23 | 0.15-0.30 | 0.70-0.90 | 0.035 | 0.040 | ... | 0.40-0.60 | 0.08-0.18 | ... |
| 5120 | 0.17-0.22 | 0.15-0.30 | 0.70-0.90 | 0.035 | 0.040 | ... | 0.70-0.90 | ... | ... |
| 3310 | 0.08-0.13 | 0.20-0.35 | 0.45-0.60 | 0.025 | 0.025 | 3.25-3.75 | 1.40-1.75 | ... | ... |
| **Through-hardened bearing steels** | | | | | | | | | |
| 52100 | 0.98-1.10 | 0.15-0.30 | 0.25-0.45 | 0.025 | 0.025 | ... | 1.30-1.60 | ... | ... |
| A 485 grade 1 | 0.90-1.05 | 0.45-0.75 | 0.95-1.25 | 0.025 | 0.025 | 0.25 | 0.90-1.20 | 0.10 | 0.35 Cu |
| A 485 grade 3 | 0.95-1.10 | 0.15-0.35 | 0.65-0.90 | 0.025 | 0.025 | 0.25 | 1.10-1.50 | 0.20-0.30 | 0.35 Cu |

(a) Single values represent the maximum allowable. (b) Zirconium may be replaced by cerium. When cerium is added, the cerium/sulfur ratio should be approximately 1.5/1, based on heat analysis.

## Table 5 Compositions of AISI standard grades of stainless steels

| UNS designation | AISI type | Composition, %(a) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | C | Mn | P | S | Si | Cr | Ni | Mo | Others |
| **Austenitic grades** | | | | | | | | | | |
| S20100 | 201 | 0.15 | 5.60-7.50 | 0.06 | 0.03 | 1.00 | 16.00-18.00 | 3.50-5.50 | … | 0.25N |
| S20200 | 202 | 0.15 | 7.50-10.0 | 0.06 | 0.03 | 1.00 | 17.00-19.00 | 4.00-6.00 | … | 0.25N |
| S20500 | 205 | 0.12-0.25 | 14.00-15.50 | 0.03 | 0.03 | 0.50 | 16.50-18.00 | 1.00-1.75 | … | 0.32-0.40N |
| S30100 | 301 | 0.15 | 2.00 | 0.045 | 0.03 | 1.00 | 16.00-18.00 | 6.00-8.00 | … | … |
| S30200 | 302 | 0.15 | 2.00 | 0.045 | 0.03 | 1.00 | 17.00-19.00 | 8.00-10.00 | … | … |
| | 302B | 0.15 | 2.00 | 0.045 | 0.03 | 2.00-3.00 | 17.00-19.00 | 8.00-10.00 | … | … |
| S30300 | 303 | 0.15 | 2.00 | 0.2 | 0.15 | 1.00 | 17.00-19.00 | 8.00-10.00 | 0.60 | … |
| | 303Se | 0.15 | 2.00 | 0.2 | 0.06 | 1.00 | 17.00-19.00 | 8.00-10.00 | … | 0.15Se min |
| S30400 | 304 | 0.08 | 2.00 | 0.045 | 0.03 | 1.00 | 18.00-20.00 | 8.00-10.50 | … | … |
| S30403 | 304L | 0.03 | 2.00 | 0.045 | 0.03 | 1.00 | 18.00-20.00 | 8.00-12.00 | … | … |
| S30430 | S30430 | 0.08 | 2.00 | 0.045 | 0.03 | 1.00 | 17.00-19.00 | 8.00-10.00 | … | 3.00-4.00Cu |
| | 304N | 0.08 | 2.00 | 0.045 | 0.03 | 1.00 | 18.00-20.00 | 8.00-10.50 | … | 0.10-0.16N |
| S30500 | 305 | 0.12 | 2.00 | 0.045 | 0.03 | 1.00 | 17.00-19.00 | 10.50-13.00 | … | … |
| S30800 | 308 | 0.08 | 2.00 | 0.045 | 0.03 | 1.00 | 19.00-21.00 | 10.00-12.00 | … | … |
| S30900 | 309 | 0.2 | 2.00 | 0.045 | 0.03 | 1.00 | 22.00-24.00 | 12.00-15.00 | … | … |
| | 309S | 0.08 | 2.00 | 0.045 | 0.03 | 1.00 | 22.00-24.00 | 12.00-15.00 | … | … |
| S31000 | 310 | 0.25 | 2.00 | 0.045 | 0.03 | 1.50 | 24.00-26.00 | 19.00-22.00 | … | … |
| | 310S | 0.08 | 2.00 | 0.045 | 0.03 | 1.50 | 24.00-26.00 | 19.00-22.00 | … | … |
| S31400 | 314 | 0.25 | 2.00 | 0.045 | 0.03 | 1.50-3.00 | 23.00-26.00 | 19.00-22.00 | … | … |
| S31600 | 316 | 0.08 | 2.00 | 0.045 | 0.03 | 1.00 | 16.00-18.00 | 10.00-14.00 | 2.00-3.00 | … |
| | 316F | 0.08 | 2.00 | 0.2 | 0.10 min | 1.00 | 16.00-18.00 | 10.00-14.00 | 1.75-2.50 | … |
| S31603 | 316L | 0.03 | 2.00 | 0.045 | 0.03 | 1.00 | 16.00-18.00 | 10.00-14.00 | 2.00-3.00 | … |
| | 316N | 0.08 | 2.00 | 0.045 | 0.03 | 1.00 | 16.00-18.00 | 10.00-14.00 | 2.00-3.00 | 0.10-0.16N |
| S31700 | 317 | 0.08 | 2.00 | 0.045 | 0.03 | 1.00 | 18.00-20.00 | 11.00-15.00 | 3.00-4.00 | … |
| S31703 | 317L | 0.03 | 2.00 | 0.045 | 0.03 | 1.00 | 18.00-20.00 | 11.00-15.00 | 3.00-4.00 | … |
| S32100 | 321 | 0.08 | 2.00 | 0.045 | 0.03 | 1.00 | 17.00-19.00 | 9.00-12.00 | … | Ti:5 × C min |
| | 329 | 0.10 | 2.00 | 0.04 | 0.03 | 1.00 | 25.00-30.00 | 3.00-6.00 | 1.00-2.00 | … |
| | 330 | 0.08 | 2.00 | 0.04 | 0.03 | 0.75-1.50 | 17.00-20.00 | 34.00-37.00 | … | 0.10Ta, 0.20Nb |
| S34700 | 347 | 0.08 | 2.00 | 0.045 | 0.03 | 1.00 | 17.00-19.00 | 9.00-13.00 | … | Nb:10 × C min |
| S34800 | 348 | 0.08 | 2.00 | 0.045 | 0.03 | 1.00 | 17.00-19.00 | 9.00-13.00 | … | Nb:10 × C min |
| | 384 | 0.08 | 2.00 | 0.045 | 0.03 | 1.00 | 15.00-17.00 | 17.00-19.00 | … | … |
| **Ferritic grades** | | | | | | | | | | |
| S40500 | 405 | 0.08 | 1.00 | 0.04 | 0.03 | 1.00 | 11.50-14.50 | … | … | 0.10-0.30Al |
| S40900 | 409 | 0.08 | 1.00 | 0.045 | 0.045 | 1.00 | 10.50-11.75 | … | … | Ti:6 × C-0.75 |
| S42900 | 429 | 0.12 | 1.00 | 0.04 | 0.03 | 1.00 | 14.00-16.00 | … | … | … |
| S43000 | 430 | 0.12 | 1.00 | 0.04 | 0.03 | 1.00 | 16.00-18.00 | … | … | … |
| | 430F | 0.12 | 1.25 | 0.06 | 0.15 | 1.00 | 16.00-18.00 | … | 0.60 | … |
| | 430FSe | 0.12 | 1.25 | 0.06 | 0.06 | 1.00 | 16.00-18.00 | … | … | 0.15Si min |
| S43400 | 434 | 0.12 | 1.00 | 0.04 | 0.03 | 1.00 | 16.00-18.00 | … | 0.75-1.25 | … |
| S43600 | 436 | 0.12 | 1.00 | 0.04 | 0.03 | 1.00 | 16.00-18.00 | … | 0.75-1.25 | Nb:5 × C-0.70 |
| S44200 | 442 | 0.20 | 1.00 | 0.04 | 0.03 | 1.00 | 18.00-23.00 | … | … | … |
| S44400 | 444 | 0.25 | 1.00 | 0.04 | 0.03 | 1.00 | 17.50-19.50 | … | … | (Ti + Nb):0.2 + 4(C + N)-0.8 |
| S44600 | 446 | 0.20 | 1.50 | 0.04 | 0.03 | 1.00 | 23.00-27.00 | … | … | 0.25N |
| **Martensitic grades** | | | | | | | | | | |
| S40300 | 403 | 0.15 | 1.00 | 0.04 | 0.03 | 0.50 | 11.50-13.00 | … | … | … |
| S41000 | 410 | 0.15 | 1.00 | 0.04 | 0.03 | 1.00 | 11.50-13.50 | … | … | … |
| S41400 | 414 | 0.15 | 1.00 | 0.04 | 0.03 | 1.00 | 11.50-13.50 | 1.25-2.50 | … | … |
| S41600 | 416 | 0.15 | 1.25 | 0.06 | 0.15 min | 1.00 | 12.0-14.00 | … | 0.60 | … |
| | 416Se | 0.15 | 1.25 | 0.06 | 0.06 | 1.00 | 12.00-14.00 | … | … | 0.15Se min |
| S42000 | 420 | 0.15 min | 1.00 | 0.04 | 0.03 | 1.00 | 12.00-14.00 | … | … | … |
| | 420F | 0.15 min | 1.25 | 0.06 | 0.15 min | 1.00 | 12.00-14.00 | … | 0.60 | … |
| S42200 | 422 | 0.20-0.25 | 1.00 | 0.025 | 0.025 | 0.75 | 11.00-13.00 | 0.50-1.00 | 0.75-1.25 | 0.15-0.30V, 0.75-1.25W |
| S43100 | 431 | 0.20 | 1.00 | 0.04 | 0.03 | 1.00 | 15.00-17.00 | 1.25-2.50 | … | … |
| | 440A | 0.60-0.75 | 1.00 | 0.04 | 0.03 | 1.00 | 16.00-18.00 | … | 0.75 | … |
| | 440B | 0.75-0.95 | 1.00 | 0.04 | 0.03 | 1.00 | 16.00-18.00 | … | 0.75 | … |
| | 440C | 0.95-1.20 | 1.00 | 0.04 | 0.03 | 1.00 | 16.00-18.00 | … | 0.75 | … |
| **Precipitation-hardening grades** | | | | | | | | | | |
| S13800 | S13800 | 0.05 | 0.20 | 0.010 | 0.008 | 0.10 | 12.25-13.25 | 7.50-8.50 | 2.00-2.50 | 0.90-1.35Al, 0.01*N* |
| S15500 | S15500 | 0.07 | 1.00 | 0.04 | 0.03 | 1.00 | 14.00-15.50 | 3.50-5.50 | … | 2.50-4.50Cu, 0.15-0.45Nb |
| S17400 | S17400 | 0.07 | 1.00 | 0.04 | 0.03 | 1.00 | 15.50-17.50 | 3.00-5.00 | … | 3.00-5.00Cu, 0.15-0.45Nb |
| S17700 | S17700 | 0.09 | 1.00 | 0.04 | 0.04 | 0.04 | 16.00-18.00 | 6.50-7.75 | … | 0.75-1.50Al |

(a) Maximum unless otherwise indicated; all compositions include balance of iron.

**Table 6 Compositions of some proprietary and nonstandard stainless steels**

| UNS designation | Common name | Composition, %(a) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | C | Mn | P | S | Si | Cr | Ni | Mo | Others |
| **Austenitic grades** | | | | | | | | | | |
| S24100 | 18Cr-2Ni-12Mn | 0.15 | 11.0-14.0 | 0.060 | 0.03 | 1.00 | 16.50-19.50 | 0.5-2.50 | ... | 0.2-0.45N |
| S20910 | Nitronic 50 (22-13-5) | 0.06 | 4.0-6.0 | 0.040 | 0.03 | 1.00 | 20.50-23.50 | 11.50-13.50 | 1.50-3.00 | 0.1-0.3Nb, 0.2-0.4N, 0.1-0.3V |
| S30345 | 303Al MODIFIED | 0.15 | 2.00 | 0.050 | 0.11-0.16 | 1.00 | 17.00-19.00 | 8.00-10.00 | 0.40-0.60 | 0.60-1.00Al |
| | 303BV(b) | 0.11 | 1.75 | 0.03 | 0.14 | 0.35 | 17.75 | 9.00 | 0.50 | 0.75Al |
| | 302HQ-FM | 0.06 | 2.00 | 0.04 | 0.14 | 1.00 | 16.00-19.00 | 9.00-11.00 | ... | 1.3-2.4Cu |
| S30430 | 302HQ | 0.10 | 2.00 | 0.045 | 0.03 | 1.00 | 17.00-19.00 | 8.00-10.00 | ... | 3.0-4.0Cu |
| S30453 | 304LN | 0.03 | 2.00 | 0.045 | 0.03 | 1.00 | 18.00-20.00 | 8.00-12.00 | ... | 0.1-0.16N |
| S31653 | 316LN | 0.03 | 2.00 | 0.045 | 0.03 | 1.00 | 16.00-18.00 | 10.00-14.00 | 2.00-3.00 | 0.1-0.16N |
| S31753 | 317LN | 0.03 | 2.00 | 0.045 | 0.30 | 1.00 | 18.00-20.00 | 11.00-15.00 | 3.00-4.00 | 0.1-0.2N |
| S31725 | 317LM | 0.03 | 2.00 | 0.045 | 0.03 | 0.075 | 18.00-20.00 | 13.00-17.00 | 4.00-5.00 | 0.1N, 0.75Cu |
| | 317LMN | 0.03 | 2.00 | 0.045 | 0.03 | 0.075 | 18.00-10.00 | 13.00-17.00 | 4.00-5.00 | 0.1-0.2N |
| N08904 | 904L | 0.02 | 2.00 | 0.045 | 0.035 | 1.00 | 19.00-23.00 | 23.0-28.0 | 4.00-5.00 | 1.0-2.0Cu |
| N08700 | JS700 | 0.04 | 2.00 | 0.04 | 0.03 | 1.00 | 19.00-23.00 | 24.0-26.0 | 4.3-5.0 | 0.5Cu, Nb:(8 × C) –1.00, 0.005Pb, 0.035Sn |
| | JS777 | 0.025 | 1.70 | 0.03 | 0.03 | 0.50 | 19.00-23.00 | 24.0-26.0 | 4.00-5.00 | 2.10Cu, 0.25Nb |
| N08020 | 20Cb-3 | 0.07 | 2.00 | 0.045 | 0.035 | 1.00 | 19.00-21.00 | 32.00-38.00 | 2.00-3.00 | 3.0-4.0Cu, (8 × C)Nb |
| N08024 | 20Mo-4 | 0.03 | 1.00 | 0.035 | 0.035 | 0.50 | 22.5-25.00 | 35.00-40.00 | 3.50-5.00 | 0.5-1.5Cu, 0.15-0.35Nb |
| N08026 | 20Mo-6 | 0.03 | 1.00 | 0.03 | 0.03 | 0.50 | 22.00-26.00 | 33.00-37.20 | 5.00-6.70 | 2.0-4.0Cu |
| N08028 | Alloy 28 | 0.03 | 2.50 | 0.03 | 0.03 | 1.00 | 26.00-28.00 | 29.5-32.5 | 3.0-4.0 | 0.6-1.4Cu |
| N08367 | AL-6 × N | 0.03 | 2.0 | 0.04 | 0.03 | 1.00 | 20.0-22.0 | 23.50-25.50 | 6.0-7.0 | 0.18-0.25N |
| S31254 | 254SMO | 0.02 | 1.00 | 0.03 | 0.01 | 0.80 | 19.50-20.50 | 17.50-18.50 | 6.0-6.5 | 0.5-1.0Cu, 0.18-0.22N |
| **Ferritic grades** | | | | | | | | | | |
| S44627 | E-Brite | 0.01 | 0.40 | 0.02 | 0.02 | 0.40 | 25.0-27.0 | 0.50 | 0.75-1.50 | 0.05-0.2Nb, 0.2Cu, 0.015N |
| S44635 | MONIT | 0.025 | 1.00 | 0.04 | 0.03 | 0.75 | 24.5-26.0 | 3.50-4.50 | 3.50-4.50 | 0.035N, Nb + Ti:0.20 + 4(C + N)-0.80 |
| S44660 | Sea-Cure | 0.025 | 1.00 | 0.04 | 0.03 | 1.00 | 25.0-27.0 | 1.50-3.50 | 2.50-3.50 | 0.035N, Nb + Ti:0.20 + 4(C + N)-0.80 |
| S44735 | AL-29-4C | 0.03 | 1.00 | 0.04 | 0.03 | 1.00 | 28.0-30.0 | 1.00 | 3.60-4.20 | 0.045N, Nb + Ti:6(C + N) |
| S44735 | Usinor 290 Mo | 0.03 | 1.00 | 0.04 | 0.03 | 1.00 | 28.0-30.0 | 1.00 | 3.60-4.20 | 0.045N, Nb + Ti:6(C + N) |
| S44800 | AL-29-4-2 | 0.01 | 0.30 | 0.025 | 0.02 | 0.20 | 28.0-30.0 | 2.0-2.5 | 3.50-4.20 | 0.15Cu, 0.02N, C + N:0.025 max |
| **Duplex grades** | | | | | | | | | | |
| S31803 | 2205 | 0.03 | 2.00 | 0.03 | 0.02 | 1.00 | 21.0-23.0 | 4.50-6.50 | 2.50-3.50 | 0.08-0.2N |
| S31200 | 44LN | 0.03 | 2.00 | 0.045 | 0.03 | 1.00 | 24.0-26.0 | 5.50-6.50 | 1.20-2.00 | 0.14-0.2N |
| S31260 | DP-3 | 0.03 | 1.00 | 0.03 | 0.03 | 0.75 | 24.0-26.0 | 5.50-7.50 | 2.50-3.50 | 0.2-0.8Cu, 0.1-0.3N |
| S31500 | 3RE60 | 0.03 | 1.20-2.00 | 0.03 | 0.03 | 1.4-2.0 | 18.0-19.0 | 4.25-5.25 | 2.50-3.00 | ... |
| S32550 | Ferralium 255 | 0.04 | 1.50 | 0.04 | 0.03 | 1.00 | 24.0-27.0 | 4.50-6.50 | 2.00-4.00 | 1.5-2.5Cu, 0.1-0.25N |
| S32950 | 7Mo-PLUS | 0.03 | 2.00 | 0.035 | 0.01 | 0.60 | 26.0-29.0 | 3.50-5.20 | 1.00-2.50 | 0.15-0.35N |
| **Martensitic grades** | | | | | | | | | | |
| S41040 | XM-30 | 0.15 | 1.00 | 0.04 | 0.03 | 1.00 | 11.50-13.50 | ... | ... | 0.05-0.2Nb |
| S41610 | XM-6 | 0.15 | 2.50 | 0.06 | 0.15 | 1.00 | 12.00-14.00 | ... | 0.60 | ... |
| **Precipitation-hardening grades** | | | | | | | | | | |
| S31800 | PH13-8Mo | 0.05 | 0.20 | 0.01 | 0.008 | 0.10 | 12.25-13.25 | 7.50-8.50 | 2.00-2.50 | 0.90-1.35Al, 0.01N |
| S45000 | Custom 450 | 0.05 | 1.00 | 0.03 | 0.03 | 1.00 | 14.00-16.00 | 5.00-7.00 | 0.5-1.00 | 1.25-1.75Cu, Nb:8 × C min |
| S45500 | Custom 455 | 0.05 | 0.50 | 0.04 | 0.03 | 0.50 | 11.00-12.50 | 7.50-9.50 | 0.50 | 0.1-0.5Nb, 1.50-2.50Cu, 0.8-1.40Ti |

(a) Maximum unless otherwise indicated; all compositions contain balance of iron. (b) Nominal composition

Table 7 Compositions and typical microstructures of ACI corrosion-resistant cast steels

| ACI type | Wrought alloy type(a) | ASTM specifications | Most common end-use microstructure | Composition, %(b) C | Mn | Si | Cr | Ni | Others(c) |
|---|---|---|---|---|---|---|---|---|---|
| **Chromium steels** | | | | | | | | | |
| CA-15 | 410 | A 743, A 217, A 487 | Martensite | 0.15 | 1.00 | 1.50 | 11.5-14.0 | 1.0 | 0.50Mo(d) |
| CA-15M | ... | A 743 | Martensite | 0.15 | 1.00 | 0.65 | 11.5-14.0 | 1.0 | 0.15-1.00Mo |
| CA-40 | 420 | A 743 | Martensite | 0.40 | 1.00 | 1.50 | 11.5-14.0 | 1.0 | 0.5Mo(d) |
| CA-40F | ... | A 743 | Martensite | 0.2-0.4 | 1.00 | 1.50 | 11.5-14.0 | 1.0 | ... |
| CB-30 | 431, 442 | A 743 | Ferrite and carbides | 0.30 | 1.00 | 1.50 | 18.0-22.0 | 2.0 | ... |
| CC-50 | 446 | A 743 | Ferrite and carbides | 0.30 | 1.00 | 1.50 | 26.0-30.0 | 4.0 | ... |
| **Chromium-nickel steels** | | | | | | | | | |
| CA-6N | ... | A 743 | Martensite | 0.06 | 0.50 | 1.00 | 10.5-12.5 | 6.0-8.0 | ... |
| CA-6NM | ... | A 743, A 487 | Martensite | 0.06 | 1.00 | 1.00 | 11.5-14.0 | 3.5-4.5 | 0.4-1.0Mo |
| CA-28MWV | ... | A 743 | Martensite | 0.20-0.28 | 0.50-1.00 | 1.00 | 11.0-12.5 | 0.50-1.00 | 0.9-1.25Mo; 0.9-1.25W; 0.2-0.3V |
| CB-7Cu-1 | ... | A 747 | Martensite, age hardenable | 0.07 | 0.70 | 1.00 | 15.5-17.7 | 3.6-4.6 | 2.5-3.2Cu; 0.20-0.35Nb; 0.05N max |
| CB-7Cu-2 | ... | A 747 | Martensite, age hardenable | 0.07 | 0.70 | 1.00 | 14.0-15.5 | 4.5-5.5 | 2.5-3.2Cu; 0.20-0.35 Nb; 0.05N max |
| CD-4MCu | ... | A 351, A 743, A744, A 890 | Austenite in ferrite, age hardenable | 0.04 | 1.00 | 1.00 | 25.0-26.5 | 4.75-6.0 | 1.75-2.25Mo; 2.75-3.25Cu |
| CE-30 | 312 | A 743 | Ferrite in austenite | 0.30 | 1.50 | 2.00 | 26.0-30.0 | 8.0-11.0 | ... |
| CF-3(e) | 304L | A 351, A 743, A 744 | Ferrite in austenite | 0.03 | 1.50 | 2.00 | 17.0-21.0 | 8.0-12.0 | ... |
| CF-3M(e) | 316L | A 351, A 743, A 744 | Ferrite in austenite | 0.03 | 1.50 | 2.00 | 17.0-21.0 | 8.0-12.0 | 2.0-3.0Mo |
| CF-3MN | ... | A 743 | Ferrite in austenite | 0.03 | 1.50 | 1.50 | 17.0-21.0 | 9.0-13.0 | 2.0-3.0Mo, 0.10-0.20N |
| CF-8(e) | 304 | A 351, A 743, A 744 | Ferrite in austenite | 0.08 | 1.50 | 2.00 | 18.0-21.0 | 8.0-11.0 | ... |
| CF-8C | 347 | A 351, A 743, A 744 | Ferrite in austenite | 0.08 | 1.50 | 2.00 | 18.0-21.0 | 9.0-12.0 | Nb(f) |
| CF-8M | 316 | A 351, A 743, A 744 | Ferrite in austenite | 0.08 | 1.50 | 2.00 | 18.0-21.0 | 9.0-12.0 | 2.0-3.0Mo |
| CF-10 | ... | A 351 | Ferrite in austenite | 0.04-0.10 | 1.50 | 2.00 | 18.0-21.0 | 8.0-11.0 | ... |
| CF-10M | ... | A 351 | Ferrite in austenite | 0.04-0.10 | 1.50 | 1.50 | 18.0-21.0 | 9.0-12.0 | 2.0-3.0Mo |
| CF-10MC | ... | A 351 | Ferrite in austenite | 0.10 | 1.50 | 1.50 | 15.0-18.0 | 13.0-16.0 | 1.75-2.25Mo |
| CF-10SMnN | ... | A 351, A 743 | Ferrite in austenite | 0.10 | 7.00-9.00 | 3.50-4.50 | 16.0-18.0 | 8.0-9.0 | 0.08-0.18N |
| CF-12M | 316 | ... | Ferrite in austenite or austenite | 0.12 | 1.50 | 2.00 | 18.0-21.0 | 9.0-12.0 | 2.0-3.0Mo |
| CF-16F | 303 | A 743 | Austenite | 0.16 | 1.50 | 2.00 | 18.0-21.0 | 9.0-12.0 | 1.50Mo max; 0.20-0.35Se |
| CF-20 | 302 | A 743 | Austenite | 0.20 | 1.50 | 2.00 | 18.0-21.0 | 8.0-11.0 | ... |
| CG-6MMN | ... | A 351, A 743 | Ferrite in austenite | 0.06 | 4.00-6.00 | 1.00 | 20.5-23.5 | 11.5-13.5 | 1.50-3.00Mo; 0.10-0.30Nb; 0.10-30V; 0.20-40N |
| CG-8M | 317 | A 351, A 743, A 744 | Ferrite in austenite | 0.08 | 1.50 | 1.50 | 18.0-21.0 | 9.0-13.0 | 3.0-4.0Mo |
| CG-12 | ... | A 743 | Ferrite in austenite | 0.12 | 1.50 | 2.00 | 20.0-23.0 | 10.0-13.0 | ... |
| CH-8 | ... | A 351 | Ferrite in austenite | 0.08 | 1.50 | 1.50 | 22.0-26.0 | 12.0-15.0 | ... |
| CH-10 | ... | A 351 | Ferrite in austenite | 0.04-0.10 | 1.50 | 2.00 | 22.0-26.0 | 12.0-15.0 | ... |
| CH-20 | 309 | A 351, A 743 | Austenite | 0.20 | 1.50 | 2.00 | 22.0-26.0 | 12.0-15.0 | ... |
| CK-3MCuN | ... | A 351, A 743, A 744 | Ferrite in austenite | 0.025 | 1.20 | 1.00 | 19.5-20.5 | 17.5-19.5 | 6.0-7.0V; 0.18-0.24N; 0.50-1.00Cu |
| CK-20 | 310 | A 743 | Austenite | 0.20 | 2.00 | 2.00 | 23.0-27.0 | 19.0-22.0 | ... |
| **Nickel-chromium steels** | | | | | | | | | |
| CN-3M | ... | A 743 | Austenite | 0.03 | 2.00 | 1.00 | 20.0-22.0 | 23.0-27.0 | 4.5-5.5Mo |
| CN-7M | ... | A 351, A 743, A 744 | Austenite | 0.07 | 1.50 | 1.50 | 19.0-22.0 | 27.5-30.5 | 2.0-3.0Mo; 3.0-4.0Cu |
| CN-7MS | ... | A 743, A 744 | Austenite | 0.07 | 1.50 | 3.50(g) | 18.0-20.0 | 22.0-25.0 | 2.5-3.0Mo; 1.5-2.0Cu |
| CT-15C | ... | A 351 | Austenite | 0.05-0.15 | 0.15-1.50 | 0.50-1.50 | 19.0-21.0 | 31.0-34.0 | 0.5-1.5V |

(a) Type numbers of wrought alloys are listed only for nominal identification of corresponding wrought and cast grades. Composition ranges of cast alloys are not the same as for corresponding wrought alloys; cast alloy designations should be used for castings only. (b) Maximum unless a range is given. The balance of all compositions is iron. (c) Sulfur content is 0.04% in all grades except: CG-6MMN, 0.030% S (max); CF-10SMnN, 0.03% S (max); CT-15C, 0.03% S (max); CK-3MCuN, 0.010% S (max); CN-3M, 0.030% S (max), CA-6N, 0.020% S (max); CA-28MWV, 0.030% S (max); CA-40F, 0.20-0.40% S; CB-7Cu-1 and -2, 0.03% S (max). Phosphorus content is 0.04% (max) in all grades except: CF-16F, 0.17% P (max); CF-10SMnN, 0.060% P (max); CT-15C, 0.030% P (max); CK-3MCuN, 0.045% P (max); CN-3M, 0.030% P (max); CA-6N, 0.020% P (max); CA-28MWV, 0.030% P (max); CB-7Cu-1 and -2, 0.035% P (max). (d) Molybdenum not intentionally added. (e) CF-3A, CF-3MA, and CF-8A have the same composition ranges as CF-3, CF-3M, and CF-8, respectively, but have balanced compositions so that ferrite contents are at levels that permit higher mechanical property specifications than those for related grades. They are covered by ASTM A 351. (f) Nb, 8 × %C min (1.0% max); or Nb + Ta × %C (1.1% max). (g) For CN-7MS, silicon ranges from 2.50 to 3.50%.

# Resistance of Materials to Selected Corrosive Media

## Carbon Dioxide

Carbon dioxide, $CO_2$, also known as carbonic anhydride and carbonic acid gas, is a colorless, odorless gas that liquifies at −65 °C (−86 °F) and solidifies in dry ice at −78.2 °C (−107 °F). It is soluble in water, alcohol, and most alkaline solutions. In a relatively slow reaction, carbon dioxide hydrates in water to become carbonic acid and is corrosive. In petroleum production, the velocity of the carbon dioxide gas can increase the corrosion rate to very high levels, with the presence of salts becoming unimportant. Carbon dioxide is used in preparing carbonated beverages, fire extinguishers, dry ice refrigerants, and as a raw material in the production of sodium carbonate and sodium bicarbonate using the Solvay procedure.

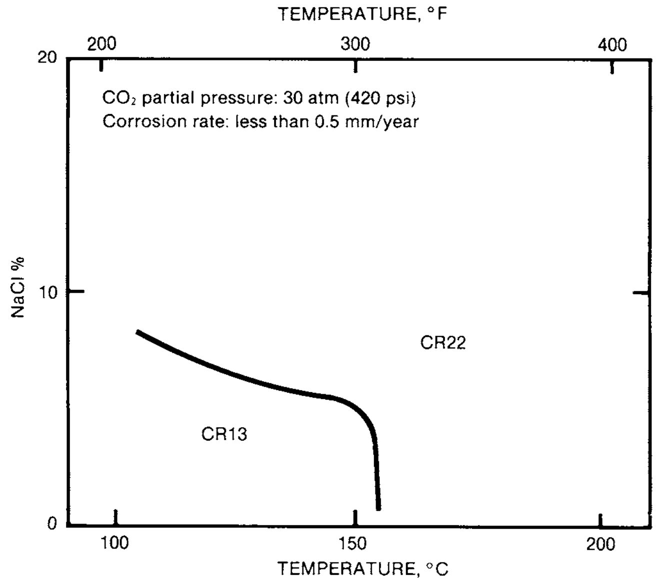


**Fig. 1** Relative corrosion resistance of 13% chromium stainless steel and duplex stainless steel (Cr 22) in carbon dioxide as a function of temperature and sodium chloride content. Source: Nippon Kokan K.K.

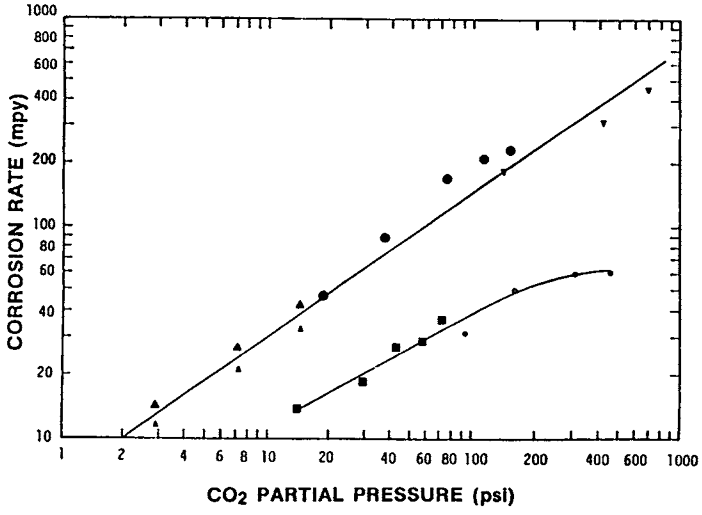


**Fig. 2** Corrosion rate of steel as a function of carbon dioxide partial pressure. Source: D.W. De Berry and W.S. Clark, "Corrosion Due to Use of $CO_2$ for Enhanced Oil Recovery," U.S. Department of Energy, DOE/MC/08442-T1, 1979

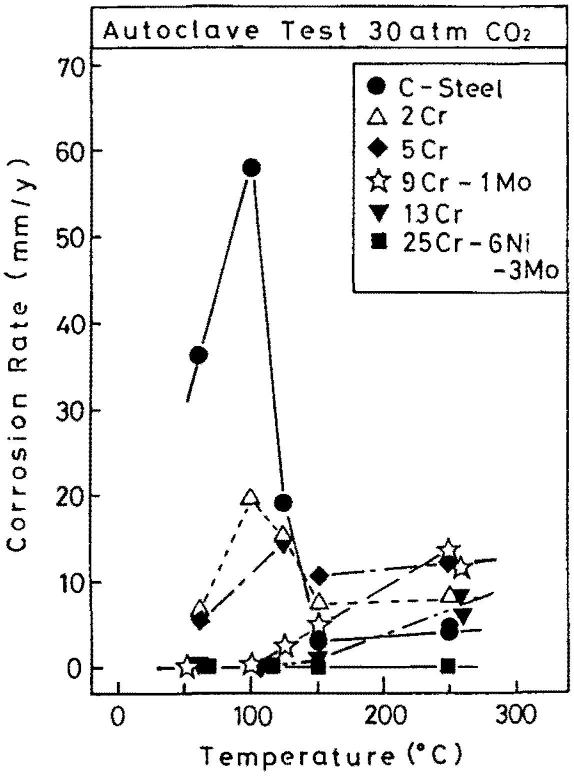


**Fig. 3** Corrosion of chromium steels in high-pressure wet carbon dioxide as a function of temperature. Source: A. Ikeda, S. Mukai, and M. Ueda, $CO_2$ Corrosion Behavior of Carbon and Chromium Steels, *Sumitomo Search*, Vol 31, 1985, p 91-102

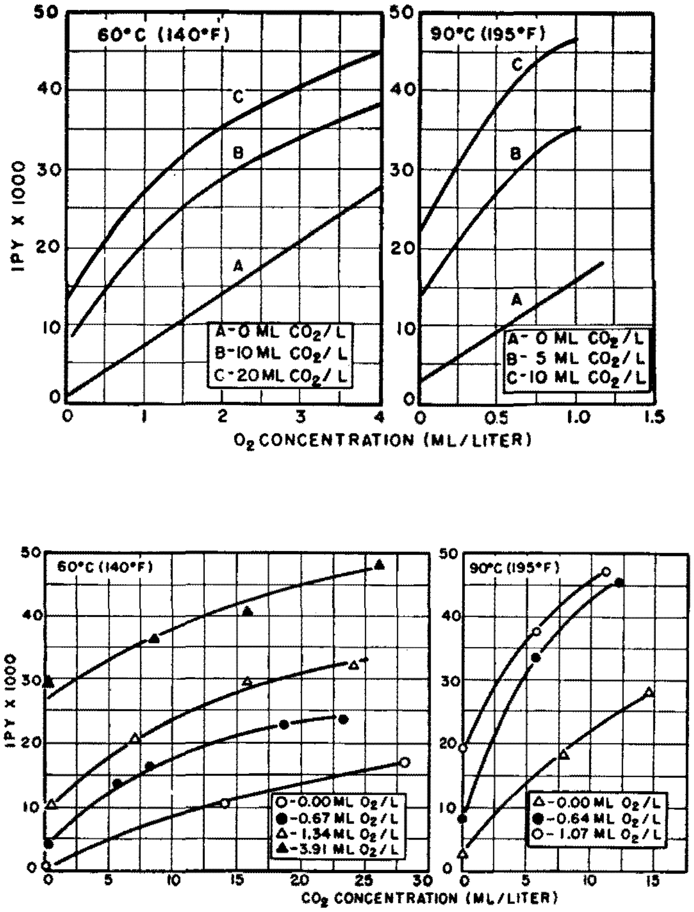


**Fig. 4** Corrosion of mild steel (0.15% carbon) as a function of dissolved carbon dioxide and oxygen concentration during a 5-h test; velocity, 45 cm (0.025 ft) per min; specimen size, 6.3 × 2.5 × 0.318 cm (2.5 × 1 × ⅛ in.). Source: H.H. Uhlig, Iron and Steel, in *The Corrosion Handbook*, H.H. Uhlig, Ed., John Wiley & Sons, New York, 1948, p 128

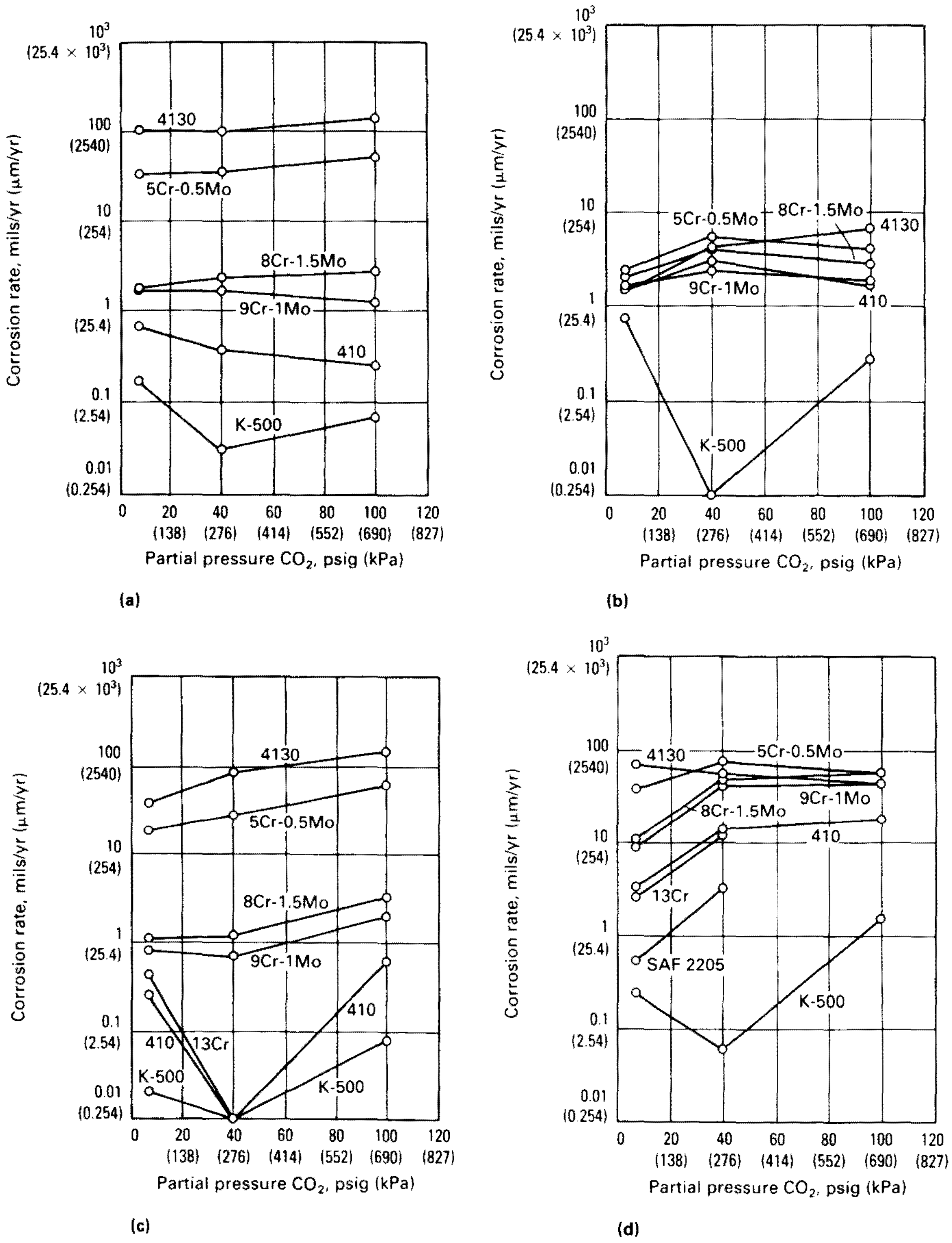


**Fig. 5** Effect of partial pressure of carbon dioxide on the corrosion rates of various alloy steels. (a) 0% chlorides at 65 °C (150 °F). (b) 0% chlorides at 175 °C (350 °F). (c) 15.2% chlorides at 65 °C (150 °F). (d) 15.2% chlorides at 175 °C (350 °F). Source: *ASM Handbook*, Vol 13, *Corrosion*, ASM International, 1987, p 536

## Chlorides

All metallic chlorides, except silver chloride and mercurous chloride, are soluble in water. Lead chloride, cuprous chloride, and thallium chloride are only slightly soluble in water. Alkali chlorides are more volatile than the corresponding alkali oxides, nitrates, or sulfates. Metallic chlorides melt when heated and volatilize or decompose. For example, sodium chloride melts at 804 °C (1480 °F), magnesium chloride crystals decompose to yield magnesium oxide residue and hydrogen chloride, and cupric chloride yields cuprous chloride and chlorine. Sodium, calcium, strontium, and barium metals are produced by electrolyzing the molten metallic chloride.

**Table 1 How various alloys rate in tests in different types of chloride solutions**
Results of short-term (1 to 10 day) tests. Long-term results may be different.

| | Successful alloy tests in chloride solutions | | | | | | |
|---|---|---|---|---|---|---|---|
| | | | | Alloy 20 (% Ni > 30) | | | |
| Chloride solution | Carbon steel | Duplex 255 SS | Ferritic 26-1 SS | 2-3% Mo | 6-9% Mo | Alloy C-276 | Titanium Grade 2 |
| Alkaline | Seawater<br>pH = 8<br>50 °C | Seawater<br>pH = 8<br>50 °C | 26% NaCl<br>+ $Na_2CO_3$<br>pH = 11 boiling | Seawater<br>pH = 8<br>NR at 25 °C(a) | Saturated NaCl<br>pH = 8.5-10<br>120 °C | Saturated NaCl<br>pH = 8.5-10<br>120 °C | Seawater<br>pH = 8<br>Boiling |
| Neutral pH | 22% NaCl<br>25 °C | 26% NaCl<br>200 °C | 2/% NaCl<br>25 °C | No data | 26% NaCl<br>200 °C | Saturated NaCl<br>125 °C | 26% NaCl<br>113 °C |
| Acidic | NR | 4% NaCl + 280 ppm $Fe^{+3}$<br>pH = 2<br>35 °C | 6% $FeCl_3$<br>pH = 1<br>25 °C | 4% NaCl + 280 ppm $Fe^{+3}$<br>pH = 2<br>15 °C | 4% NaCl + 280 ppm $Fe^{+3}$<br>pH = 2<br>25 °C | 40% $MgCl_2$<br>pH=0.5-1.0<br>Boiling | 20% $MgCl_2$<br>100 °C |
| Oxidizing | NR | 6% $FeCl_3$<br>25 °C | 10% $FeCl_3$<br>38 °C | 6% $FeCl_3$<br>Below –5 °C | 4% NaCl + 280 ppm $Fe^{+3}$<br>pH = 2<br>25 °C | 15% $FeCl_3$<br>25 °C | 40% $FeCl_3$<br>Boiling |
| Hypochlorite | NR | No data | 5.25% NaOCl<br>70 °C | NR | 10% NaOCl + 2% NaOH<br>30 °C | 10% NaOCl<br>25 °C | 16% NaOCl<br>25 °C |

Note: SS, stainless steel; NR, not recommended. (a) Alloy 20Cb-3 pits in seawater at 25 °C. Source: G.N. Kirby, Selecting Alloys for Chloride Service, *Chemical Engineering* 92, Feb 1985, p 82

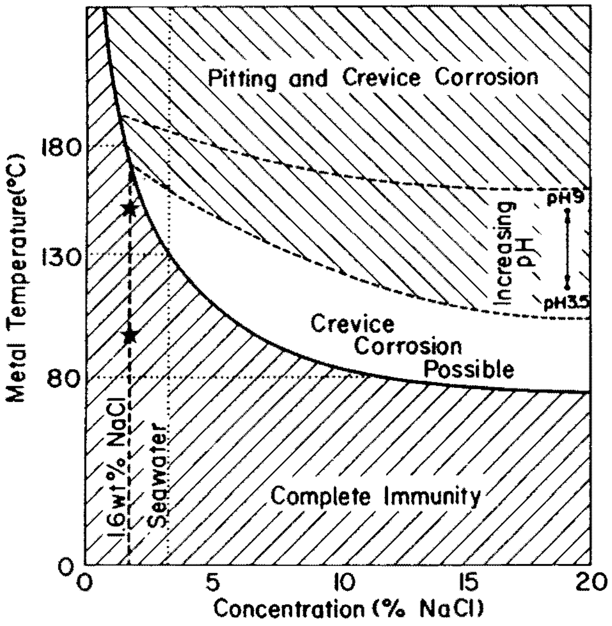


**Fig. 6** Effect of temperature, chloride concentration, and pH on the localized corrosion of unalloyed titanium. Data on crevice corrosion of grade 2 titanium in 1.6 wt% sodium chloride are included for comparison. Source: P. McKay and D.B. Mitton, "An Electrochemical Investigation of Localized Corrosion on Titanium in Chloride Environments," *Corrosion*, Vol 41, Jan 1985, p 61

## Chlorine

Chlorine (Cl) melts at −101 °C and boils at −34.1 °C. Chlorine gas is about 2½ times heavier than air and is poisonous and irritating to the eyes and throat. Chlorine is used in the manufacture of PVC, solvents, insecticides, and many non-chlorine-containing compounds. It is also used in bleaching of paper and pulp, in household and commercial bleaches, and in treatment of municipal and industrial water supplies.

Dry chlorine is not corrosive to steels, stainless steels, or nickel alloys at ambient temperature. Steel is usable up to about 150 °C (300 °F) and possibly higher under certain conditions. Stainless steels are usable up to about 300 °C (570 °F), and nickel is commonly used up to about 500 °C (930 °F). However, many industrial chlorine environments contain substantial water, particularly those encountered in the manufacture of chlorine prior to the drying operation. Wet chlorine gas is extremely corrosive at temperatures below the dew point, because the condensate is a very acidic and oxidizing mixture.

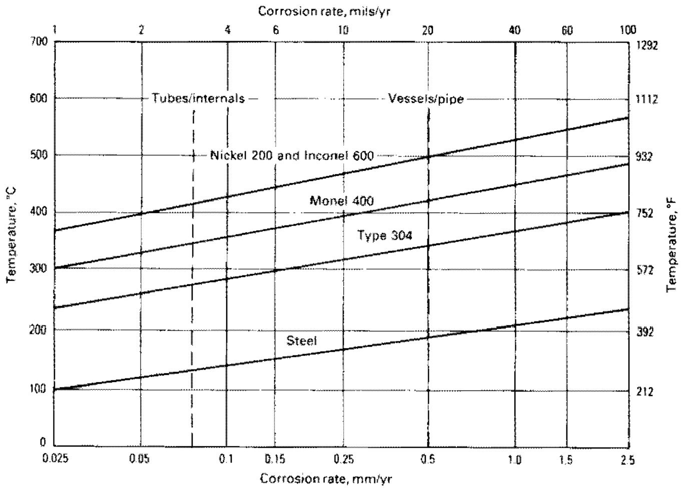


**Fig. 7** Corrosion resistance of various alloys exposed to dry chlorine

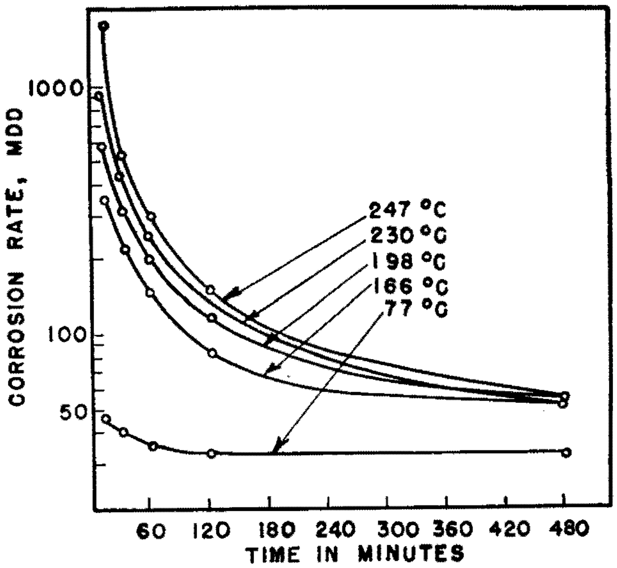


**Fig. 8** Rate of corrosion (weight loss) of mild carbon steel in contact with commercial chlorine (0.005% moisture) as a function of time. Source: H.H. Uhlig, "Iron and Steel," in *The Corrosion Handbook*, H.H. Uhlig, Ed., John Wiley & Sons, New York, 1948, p 142

## Hydrochloric Acid

Hydrochloric acid, HCl, also known as muriatic acid, is a poisonous, corrosive, hazardous liquid that reacts with most metals to form explosive hydrogen gas and causes severe burns and irritation of eyes and mucous membranes. It is made by absorbing hydrogen chloride in water. Most acid is the by-product of chlorination. Pure acid is produced by burning chlorine and hydrogen. Hydrochloric acid is available in technical, recovered, food-processing, and reagent grades. Frequently, the commercial grades are slightly yellow as a result of impurities, notably dissolved iron. Reagent grade, which normally contains about 37.1% hydrochloric acid, is perfectly clear and colorless.

Hydrochloric acid is an important mineral acid with many uses, including acid pickling of steel, acid treatment of oil wells, chemical cleaning and processing, ore reduction, production of numerous chlorides, production of chlorine, and food processing.

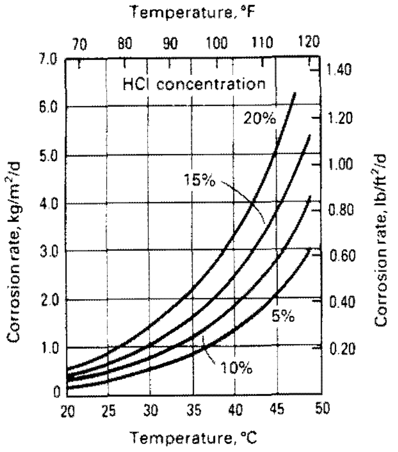


**Fig. 9** Effect of temperature on corrosion of low-carbon steel in uninhibited hydrochloric acid

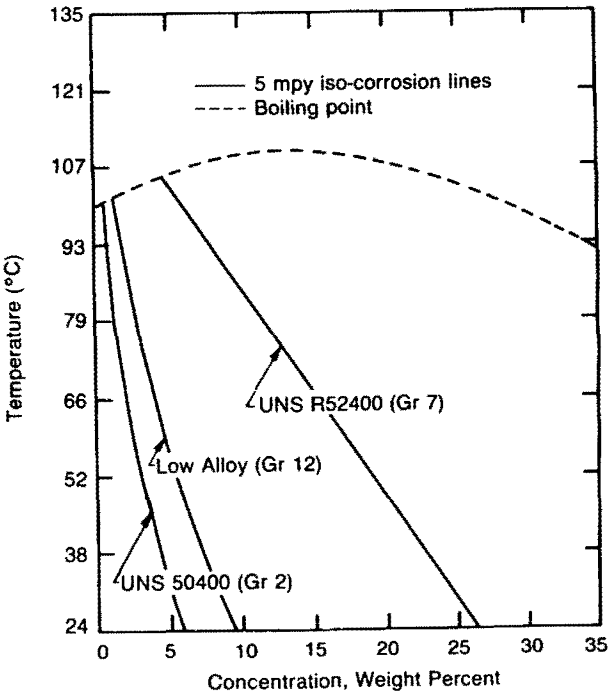


**Fig. 10** Corrosion of titanium alloys in naturally aerated hydrochloric acid solutions. Source: T.F. Degnan, "Materials Construction for Hydrochloric Acid," in *Process Industries Corrosion*, B.J. Moniz and W.I. Pollock, Ed., National Association of Corrosion Engineers, Houston, 1986, p 170

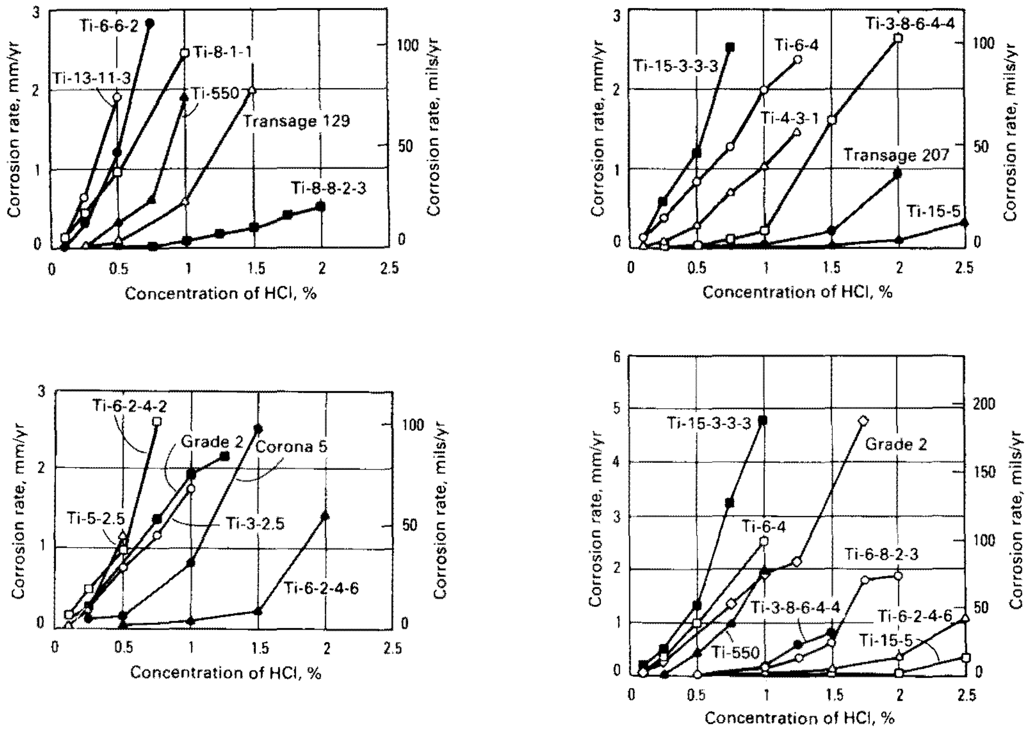
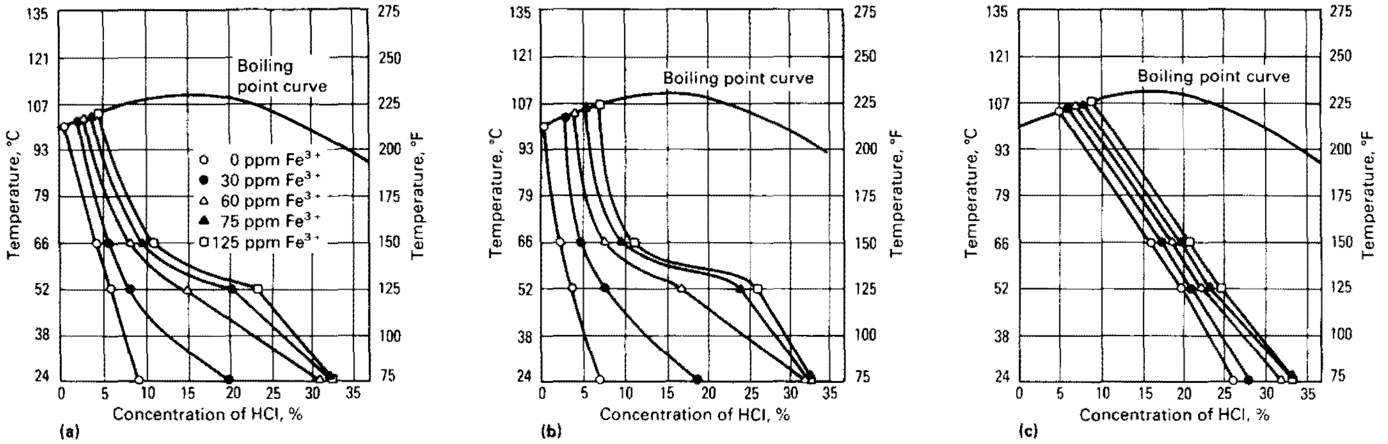


**Fig. 11** General corrosion of annealed titanium alloys in naturally aerated hydrochloric acid solution. Source: *ASM Handbook*, Vol 13, *Corrosion*, ASM International, 1987, p 680



(a) (b) (c)

**Fig. 12** Effect of minute ferric ion concentrations on the useful corrosion resistance of grade 2 titanium (a), grade 12 titanium (b), and grade 7 titanium (c) in naturally aerated hydrochloric acid solutions. 0.127-mm/yr (5-mils/yr) isocorrosion lines are shown. Source: *ASM Handbook*, Vol 13, *Corrosion*, ASM International, 1987, p 683

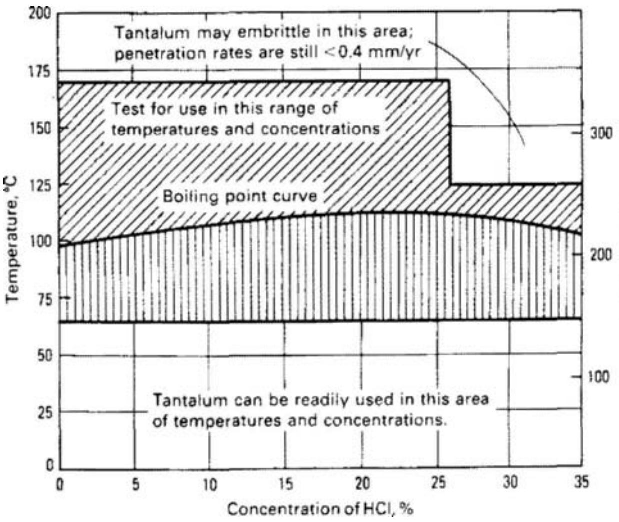


**Fig. 13** Corrosion of tantalum in hydrochloric acid at various concentrations and temperatures. Source: M. Stern and C.R. Bishop, Corrosion and Electrochemical Behavior, in *Columbium and Tantalum*, F.T. Sisco and E. Epremian, Ed., John Wiley & Sons, New York, 1963, and "Tantalum, Corrosion Data, Comparative Charts and Coating Characteristics," General Technologies Corporation

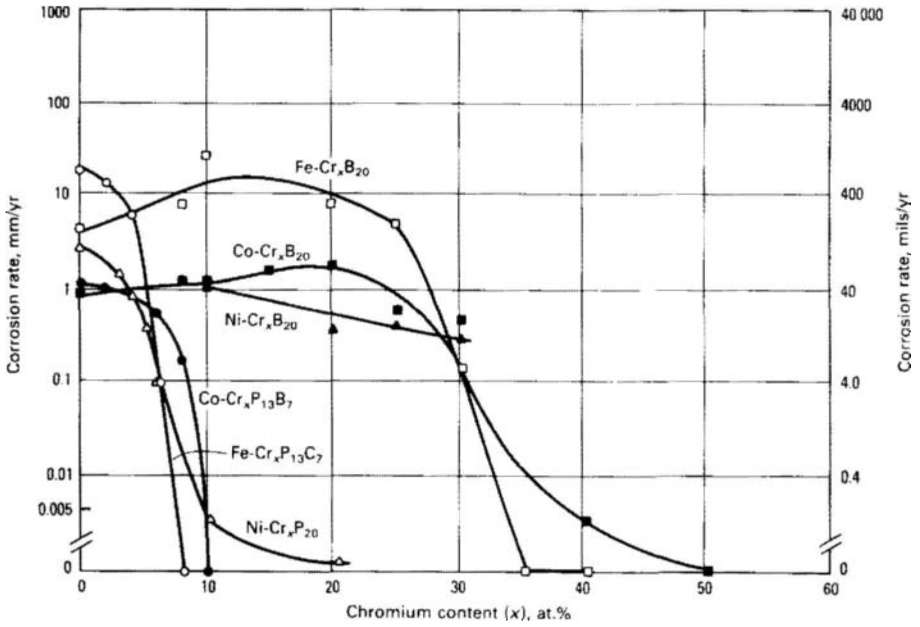


**Fig. 14** The influence of chromium content on the corrosion rates of iron-, cobalt-, and nickel-base amorphous alloys in 1 *N* hydrochloric acid. Source: *ASM Handbook*, Vol 13, *Corrosion*, ASM International, 1987, p 867

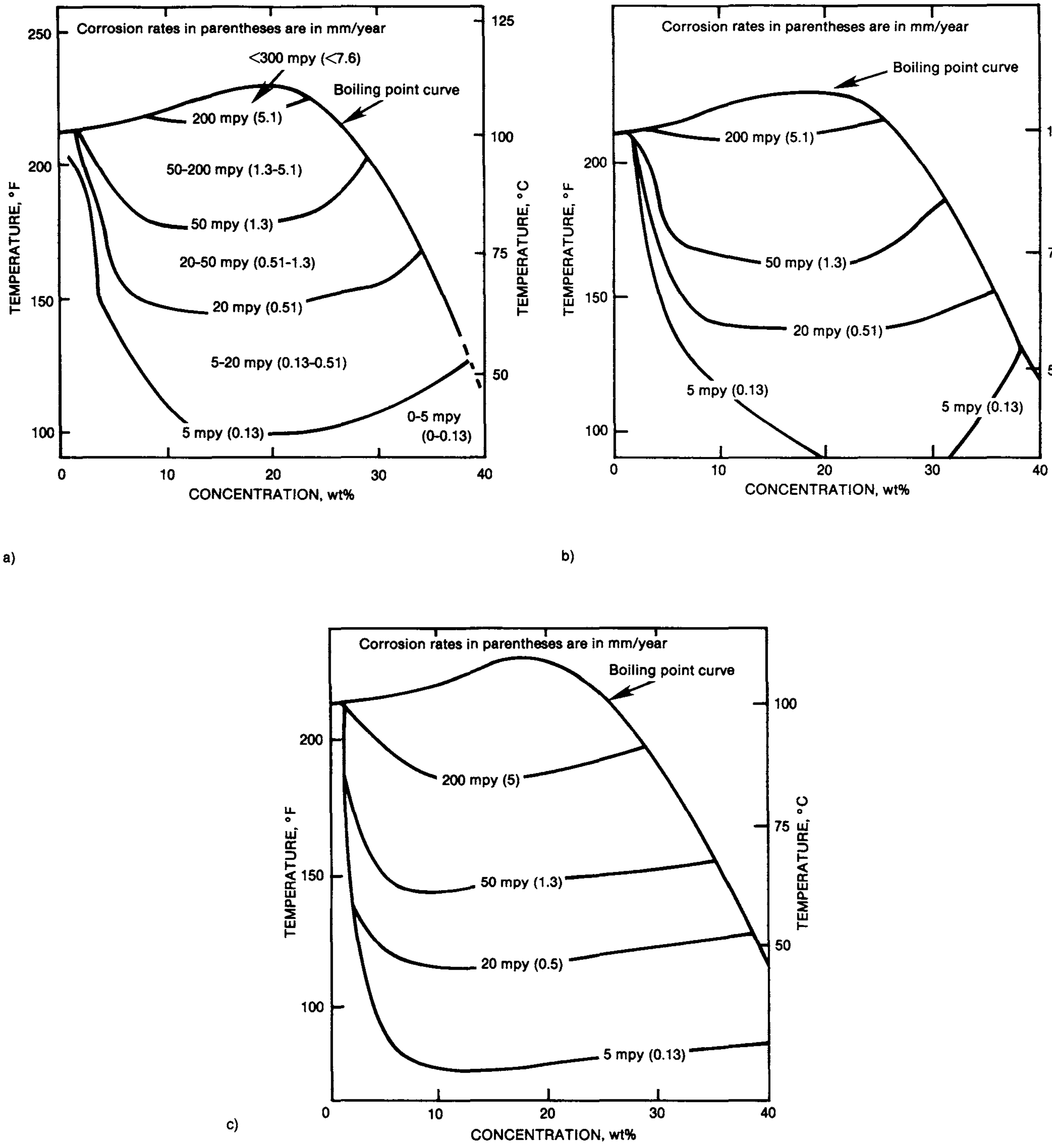


**Fig. 15** Resistance of nickel alloys to hydrochloric acid. (a) Hastelloy C-4, test specimens were solution heat-treated at 1066 °C (1950 °F), rapid quenched and in the unwelded condition. (b) Hastelloy C-22, test specimens were solution heat-treated and in the unwelded condition. (c) Hastelloy G-30, test specimens were heat-treated at 1177 °C (2150 °F), rapid quenched and in the unwelded condition. Source: Haynes International

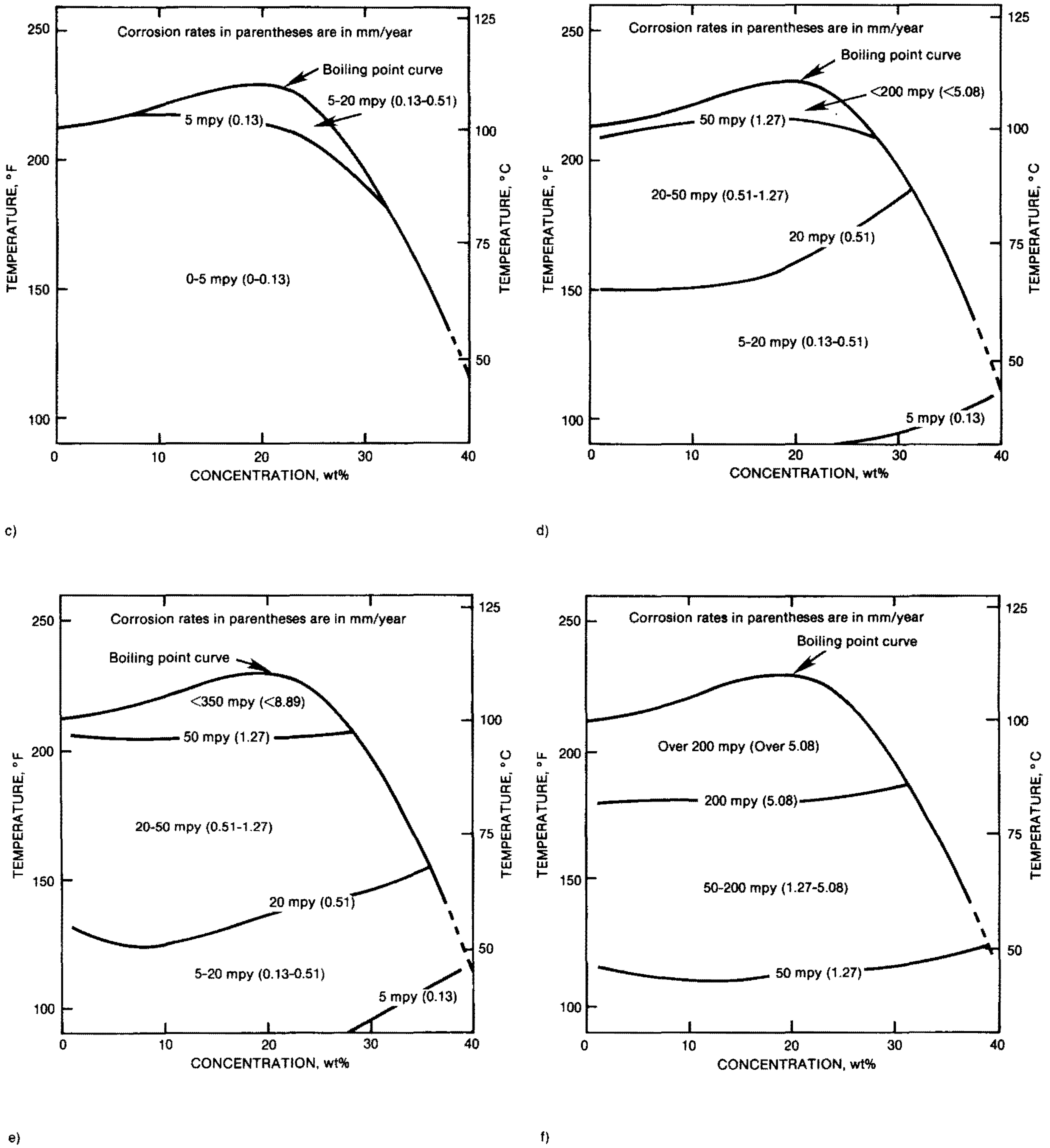
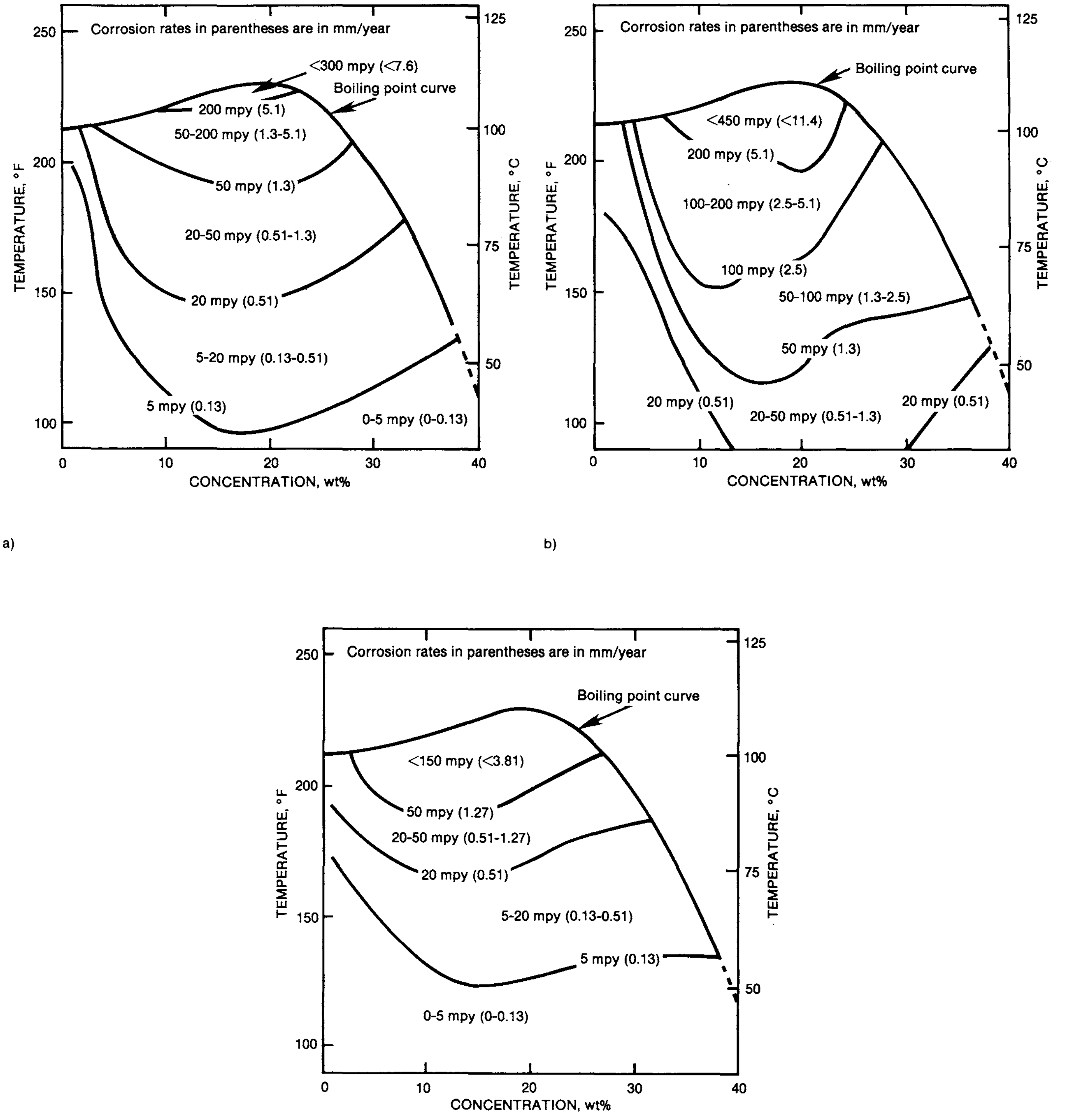


**Fig. 16** Resistance of Hastelloy B-2 to (a) hydrochloric acid, (b) hydrochloric acid purged with oxygen, (c) hydrochloric acid purged with nitrogen, (d) hydrochloric acid with 50 ppm ferric ions, (e) hydrochloric acid with 100 ppm ferric ions, and (f) hydrochloric acid with 500 ppm ferric ions. All test specimens were solution heat-treated and in the unwelded condition. Source: Haynes International, 1984



a)

b)

c)

**Fig. 17** Resistance of Hastelloy C-276 to (a) hydrochloric acid, (b) hydrochloric acid purged with oxygen, and (c) hydrochloric acid purged with nitrogen. Test specimens for (a) and (b) were heat treated at 1121 °C (2050 °F), rapid quenched, and in the unwelded condition; for (c) test specimens were solution heat-treated and in the unwelded condition. Source: Haynes International, 1984

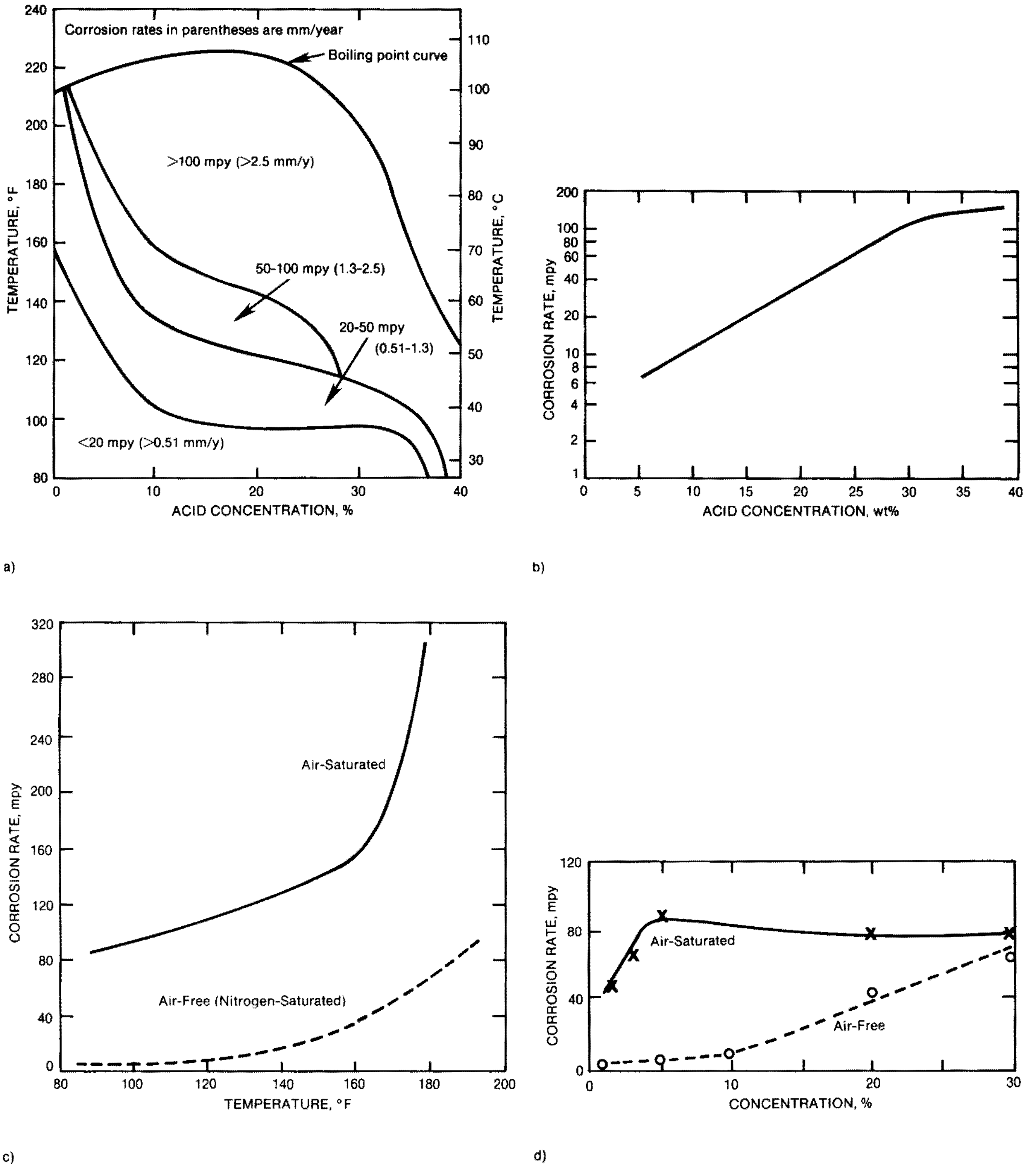


**Fig. 18** Corrosion rates for nickel alloys in hydrochloric acid for (a) Incoloy alloy 825, based on laboratory tests in pure acid; (b) Inconel alloy 600, at room temperature; (c) Monel alloy 400 in 5% hydrochloric acid; and (d) Nickel 200 in hydrochloric acid at 86 °F (the air-free samples were nitrogen saturated). Source: Inco Alloys International

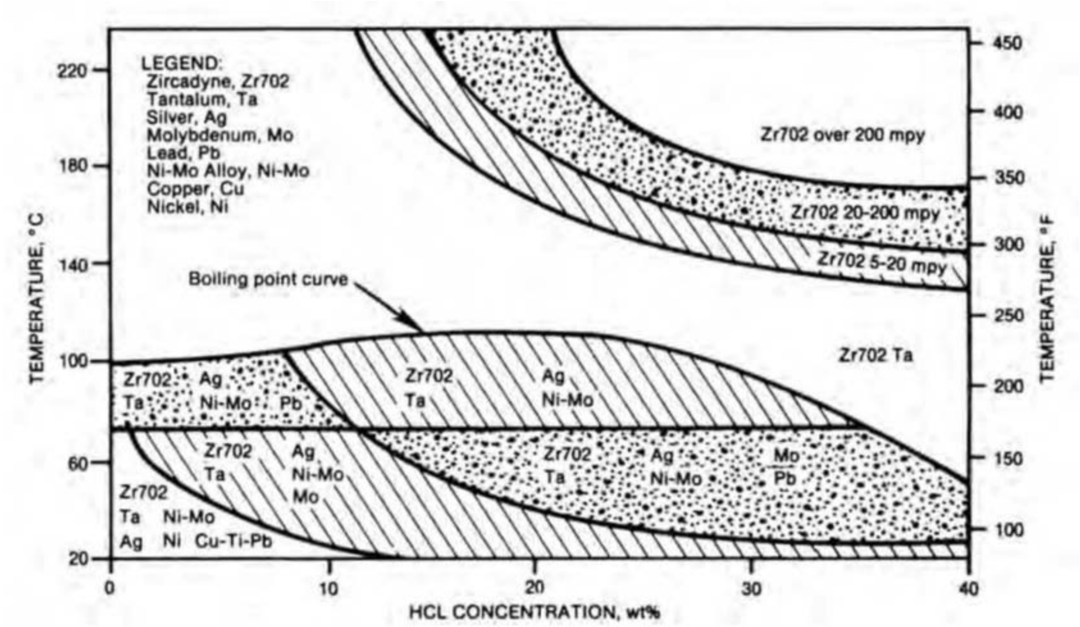


**Fig. 19** Corrosion resistance of various materials to hydrochloric acid. These materials exhibit a corrosion rate of less than 20 mils/yr, except for zirconium and tantalum, which have corrosion rates of less than 5 mils/yr. Source: Teledyne Wah Chang Albany

## Hydrofluoric Acid and Hydrogen Fluoride

Anhydrous hydrogen fluoride (AHF) and hydrofluoric acid (aqueous hydrogen fluoride) are of great industrial importance. Hydrofluoric acid (HF), a colorless, fuming, poisonous, highly corrosive, extremely reactive liquid, is used in large quantities for pickling of stainless steels and other metals, acid treating of wells, and etching of glass. Other uses include production of aluminum fluoride and synthetic cryolite for aluminum production; production of fluorinated organics such as aerosol propellants, special-purpose solvents, refrigerants, and plastics; formulation of atomic-energy feed materials; manufacture of elemental fluorine; preparation of fluorides and fluoborates; dissolving of ores; and cleaning of stone and brick.

### Table 2 Corrosion of nickel stainless steels and chromium-nickel-molybdenum-iron alloys in aqueous hydrofluoric acid

| Concentration HF, % | Temperature | | Test duration, days | Corrosion rate | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | Type 304 | | Type 316 | | Type 309Cb | | Alloy 20Cb-3 | | Incoloy 825 | |
| | °C | °F | | mm/yr | mils/yr | mm/yr | mils/yr | mm/yr | mils/yr | mm/yr | mils/yr | mm/yr | mils/yr |
| 0.05 | 60 | 140 | 10 | 0.3 | 12 | ... | ... | 0.25 | 10 | ... | ... | ... | ... |
| 0.1 | 60 | 140 | 10 | 0.64 | 25 | ... | ... | 0.69 | 27 | ... | ... | ... | ... |
| 0.15 | 60 | 140 | 10 | 1.2 | 47 | ... | ... | 1.1 | 44 | ... | ... | ... | ... |
| 0.2 | 60 | 140 | 10 | 1.6 | 62 | ... | ... | 1.4 | 54 | ... | ... | ... | ... |
| 10 | 16 | 60 | 30 | 0.01 | 0.4 | <0.002 | <0.1 | ... | ... | ... | ... | ... | ... |
| 20 | 102 | 215 | 3 | ... | ... | ... | ... | ... | ... | ... | ... | 1.04 | 41 |
| 38 | 110 | 230 | 2 | ... | ... | 51 | 2000 | ... | ... | ... | ... | ... | ... |
| 38 | Boiling | Boiling | 4 | ... | ... | ... | ... | ... | ... | ... | ... | 0.25 | 10 |
| 48 | Boiling | Boiling | 4 | ... | ... | ... | ... | ... | ... | ... | ... | 0.23 | 9 |
| 50 | 60 | 140 | 35 | ... | ... | ... | ... | ... | ... | ... | ... | 0.05 | 2 |
| 65 | 60 | 140 | 35 | ... | ... | ... | ... | ... | ... | ... | ... | 0.13 | 5 |
| 70 | 60 | 140 | 35 | ... | ... | ... | ... | ... | ... | ... | ... | 0.13 | 5 |
| 70 | 21 | 70 | 42 | ... | ... | 1.24 | 49 | ... | ... | 0.38 | 15 | 0.35 | 14 |
| 90 | 4 | 40 | 0.2 | 0.9 | 35 | ... | ... | ... | ... | ... | ... | ... | ... |
| 90 | 21 | 70 | 1 | 0.76 | 30 | ... | ... | ... | ... | ... | ... | ... | ... |
| 90 | 21 | 70 | 1 | 0.28 | 11(a) | ... | ... | ... | ... | ... | ... | ... | ... |
| 98 | 34-44 | 95-110 | 3.5 | ... | ... | 0.05 | 2 | ... | ... | ... | ... | ... | ... |

(a) Velocity: 0.14 to 0.43 m/s (0.4 to 1.4 ft/s). Source: T.F. Degnan, "Materials of Construction for Hydrofluoric Acid and Hydrogen Fluoride," in *Process Industries Corrosion*, B.J. Moniz and W.I. Pollock, Ed., National Association of Corrosion Engineers, Houston, 1986

### Table 3 Corrosion of Hastelloy alloys in aqueous hydrofluoric acid

| Concentration HF, % | Temperature °C (°F) | Corrosion rate | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | Hastelloy B | | Hastelloy C | | Hastelloy D | | Hastelloy F | |
| | | mm/yr | mils/yr | mm/yr | mils/yr | mm/yr | mils/yr | mm/yr | mils/yr |
| 5 | Room | 0.1 | 4 | 0.025 | 1 | 0.025 | 1 | 0.05 | 2 |
| 25 | Room | 0.13 | 5 | 0.13 | 5 | 0.15 | 6 | 0.3 | 12 |
| 40 | Room | 0.07 | 2.6 | 0.074 | 2.9 | 0.025 | 1 | ... | ... |
| 40 | 54 (130) | 0.025 | 1 | 0.025 | 10 | 0.07 | 2.6 | ... | ... |
| 45 | Room | 0.076 | 3 | 0.15 | 6 | 0.1 | 4 | 0.38 | 15 |
| 50 | Boiling (95 °C, or 205 °F) | ... | ... | 4.6 | 180 | ... | ... | ... | ... |
| 60 | Room | 0.04 | 1.6 | 0.09 | 3.6 | 0.06 | 2.4 | ... | ... |
| 65 | Boiling (70 °C, or 160 °F) | ... | ... | 0.43 | 17 | ... | ... | ... | ... |
| 98 | 34-44 (95-110) | 0.1 | 4 | 0.025 | 1 | ... | ... | ... | ... |

Source: T.F. Degnan, "Materials of Construction for Hydrofluoric Acid and Hydrogen Fluoride," in *Process Industries Corrosion*, B.J. Moniz and W.I. Pollock, Ed., National Association of Corrosion Engineers, Houston, 1986

### Table 4 Corrosion of metals and alloys in hydrofluoric acid gas

| Alloy | Corrosion rate | |
|---|---|---|
| | mm/yr | mils/yr |
| Hastelloy C | 0.008 | 0.3 |
| Inconel 600 | 0.018 | 0.7 |
| Hastelloy B | 0.05 | 2 |
| Nickel 200 | 0.23 | 9 |
| Nickel 201 | 0.36 | 14 |
| Monel 400 | 0.33 | 13 |
| Monel K-500 | 0.4 | 16 |
| 70-30 copper-nickel | 0.4 | 16 |

Source: T.F. Degnan, "Materials of Construction for Hydrofluoric Acid and Hydrogen Fluoride," in *Process Industries Corrosion*, B.J. Moniz and W.I. Pollock, Ed., National Association of Corrosion Engineers, Houston, 1986

## Table 5 Corrosion of metals and alloys in anhydrous hydrogen fluoride

| | Corrosion rate at temperature, °C (°F) | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 15-25 (60-80) | | 25-40 (80-100) | | 40-95 (100-200) | | 55 (130) | | 70 (160) | | 80-90 (180-190) | |
| Metal | mm/yr | mils/yr | mm/yr | mils/yr | mm/yr | mils/yr | mm/yr | mils/yr | mm/yr | mils/yr | mm/yr | mils/yr |
| Carbon steel | 0.07 | 2.8 | 0.16 | 6.2 | ... | ... | 0.35 | 14 | ... | ... | 2.3 | 89 |
| Low-alloy steel | 0.15 | 6 | 0.14 | 5.9 | ... | ... | ... | ... | ... | ... | 2 | 78 |
| Austenitic stainless steel | 0.16 | 6.2 | 0.12 | 4.8 | ... | ... | ... | ... | ... | ... | 0.06 | 2.4 |
| Monel 400 | 0.08 | 3.2 | 0.02 | 0.9 | 0.12 | 4.7 | ... | ... | ... | ... | ... | ... |
| Copper | 0.33 | 12.9 | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... |
| Nickel 200 | 0.06 | 2.5 | ... | ... | ... | ... | ... | ... | 0.12 | 4.6 | ... | ... |
| 70-30 copper-nickel | ... | ... | 0.05 | 2 | ... | ... | 0.008 | 0.3 | ... | ... | 0.25 | 10 |
| 80-20 copper-nickel | ... | ... | 0.13 | 5.2 | ... | ... | ... | ... | ... | ... | ... | ... |
| Red brass | 0.76 | 30 | 0.4 | 16 | ... | ... | ... | ... | ... | ... | 1.3 | 50 |
| Admiralty brass | 0.25 | 10 | 0.33 | 12.8 | ... | ... | 0.01 | 0.4 | ... | ... | 0.5 | 20 |
| Aluminum-bronze | 0.37 | 14.4 | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... |
| Phosphorus-bronze | 0.5 | 20 | 0.48 | 18.8 | ... | ... | ... | ... | ... | ... | 1.5 | 60 |
| Inconel 600 | ... | ... | 0.067 | 2.6 | ... | ... | ... | ... | ... | ... | ... | ... |
| Duriron | ... | ... | 1.1 | 45 | ... | ... | ... | ... | ... | ... | ... | ... |
| Aluminum | 0.52 | 20.4 | ... | ... | ... | ... | ... | ... | ... | ... | 24.8 | 976 |
| Magnesium | 0.13 | 5.2 | 0.43 | 17.1 | ... | ... | nil | nil | ... | ... | nil | nil |

Source: T.F. Degnan, "Materials of Construction for Hydrofluoric Acid and Hydrogen Fluoride," in *Process Industries Corrosion*, B.J. Moniz and W.I. Pollock, Ed., National Association of Corrosion Engineers, Houston, 1986

## Table 6 Corrosion of metals and alloys by gaseous anhydrous hydrofluoric acid at elevated temperatures

| | Corrosion rate at temperature, °C (°F) | | | | | |
|---|---|---|---|---|---|---|
| | 500 (930) | | 550 (1020) | | 600 (1110) | |
| Metal | mm/yr | mils/yr | mm/yr | mils/yr | mm/yr | mils/yr |
| Nickel 200 | 0.9 | 36 | ... | ... | 0.9 | 36 |
| Monel 400 | 1.2 | 48 | 1.2 | 48 | 1.8 | 72 |
| Copper | 1.5 | 60 | ... | ... | 1.2 | 48 |
| Inconel 600 | 1.5 | 60 | ... | ... | 1.5 | 60 |
| Aluminum alloy 1100 | 4.9 | 192 | ... | ... | 14.6 | 576 |
| Magnesium G | 13.8 | 542 | ... | ... | ... | ... |
| 1020 steel | 15.5 | 612 | 14.6 | 576 | 7.6 | 300 |
| Type 430 stainless steel | 1.5 | 60 | 9.1 | 360 | 11.6 | 456 |
| Type 304 stainless steel | ... | ... | ... | ... | 13.4 | 528 |
| Type 347 stainless steel | 183 | 7200 | 457 | 18 000 | 177 | 6960 |
| Type 309Cb stainles steel | 5.8 | 228 | 42.7 | 1680 | 168 | 6600 |
| Type 310 stainless steel | 12.2 | 480 | 100.6 | 3960 | 305 | 12 000 |

Source: T.F. Degnan, "Materials of Construction for Hydrofluoric Acid and Hydrogen Fluoride," in *Process Industries Corrosion*, B.J. Moniz and W.I. Pollock, Ed., National Association of Corrosion Engineers, Houston, 1986

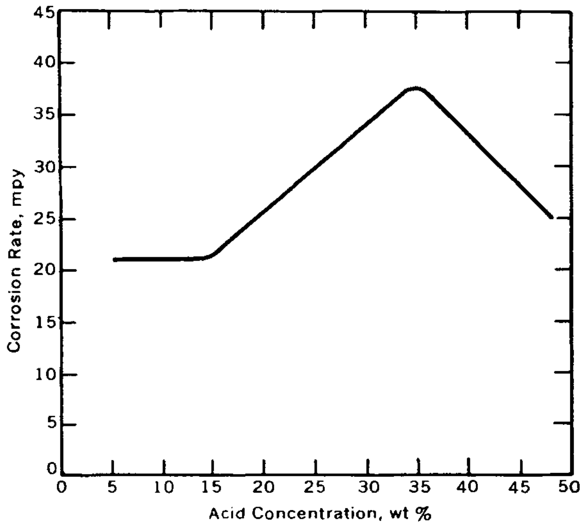


**Fig. 20** Corrosion rates for Inconel 600 in hydrofluoric acid at 75 °C (167 °F). Source: Inco Alloys International, 1962

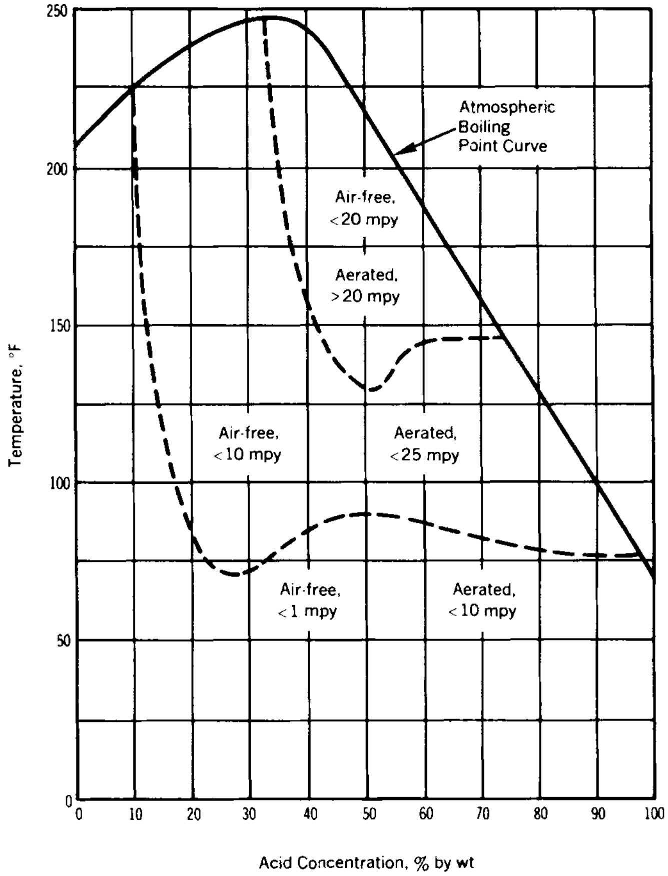
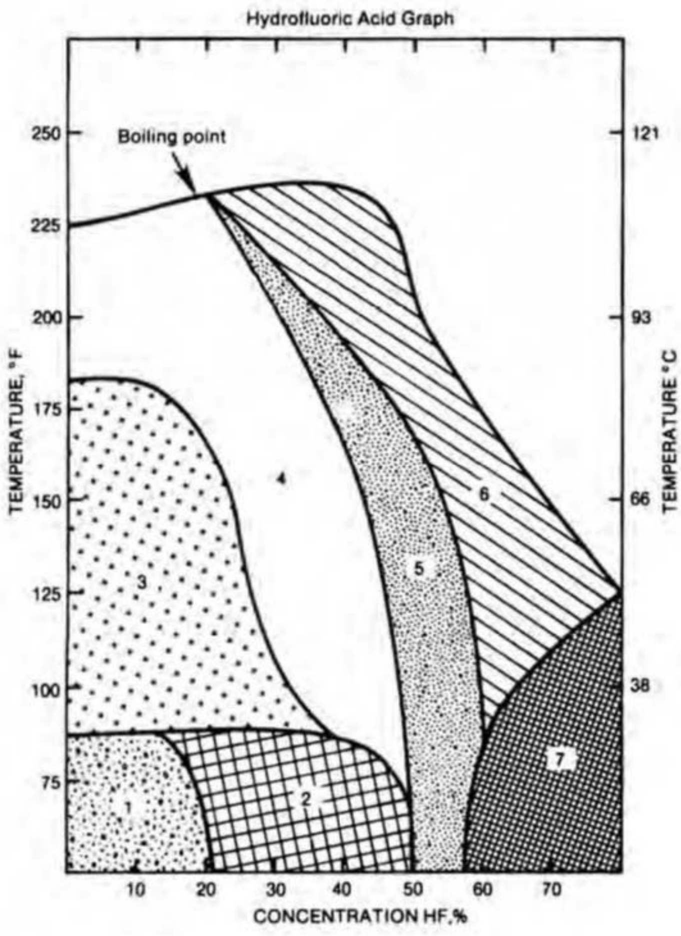


**Fig. 21** Isocorrosion charts of Monel 400 in hydrofluoric acid. Source: Inco Alloys International, 1984



CODE FOR HYDROFLUORIC ACID GRAPH

Materials in shaded zone have reported corrosion rate of >20 mpy

**ZONE 1**
20Cr 30Ni
25Cr 20 Ni steel
70Cu 30Ni[1]
66Ni 32Cu[1]
54Ni 15Cr 16Mo
Copper[1]
Gold
Lead[1]
Nickel[1]
Nickel cast iron
Platinum Silver

**ZONE 2**
20Cr 30 Ni
70Cu 30 Ni1
54Ni 15Cr 16Mo
66Ni 32Cu[1]
Copper[1]
Gold
Lead[1]
Nickel[1]
Platinum
Silver

**ZONE 3**
20Cr 30Ni
70Cu 30Ni[1]
54Ni 15Cr 16Mo
66Ni 32Cu[1]
Copper[1]
Gold
Lead[1]
Platinum
Silver

**ZONE 4**
70Cu 30Ni[1]
66Ni 32Cu[1]
54Ni 15Cr 16Mo
Gold
Lead[1]
Platinum
Silver

**ZONE 5**
70Cu 30Ni[1]
6Ni 32Cu[1]
54Ni 15Cr 16Mo
Gold
Lead[1]
Platinum
Silver

**ZONE 6**
66Ni 32Cu[1]
54Ni 15Cr 16Mo
Gold
Platinum
Silver

**ZONE 7**
66Ni 32Cu[1]
54Ni 15Cr 16Mo
Gold
Platinum
Silver

[1] No air

**Fig. 22** Corrosion of selected metals and alloys in boiling 48% hydrofluoric acid. Source: T.F. Degnan, "Materials of Construction for Hydrofluoric Acid and Hydrogen Fluoride," in *Process Industries Corrosion*, B.J. Moniz and W.I. Pollock, Ed., National Association of Corrosion Engineers, Houston, 1986

## Hydrogen

Hydrogen, $H_2$, is a tasteless, colorless, odorless gas that may be liquified by cooling under pressure. Hydrogen is used in welding, in the production of ammonia, methanol, and other chemicals, for the hydrogenation of oil and coal, and for the reduction of metallic oxide ores. It is obtained by the dissociation of water and as a by-product in the electrolysis of brine solutions. Molecular hydrogen at ambient temperature is relatively innocuous to most metals. However, atomic hydrogen is detrimental to most metals.

**Table 7 Relative resistance to hydrogen embrittlement of various alloys in high-pressure hydrogen at room temperature**

| Alloy | Stress concentration factor, $K_t$ | Pressure | | Ratio $H_2$/He(a) |
|---|---|---|---|---|
| | | MPa | ksi | |
| 250 maraging steel | 8 | 69 | 10 | 0.12 |
| Type 410 stainless steel | 8 | 69 | 10 | 0.22 |
| 1042 steel (quenched and tempered) | 8 | 69 | 10 | 0.22 |
| 17-7PH (TH1050) | 8 | 69 | 10 | 0.23 |
| HP9-4-20 alloy steel | 8 | 69 | 10 | 0.24 |
| H-11 high-strength steel | 8 | 69 | 10 | 0.25 |
| Inconel alloy X-750 | 6.3 | 48 | 7 | 0.26 |
| René 41 | 8 | 69 | 10 | 0.27 |
| ED nickel | 8 | 69 | 10 | 0.31 |
| 4140 steel | 8 | 69 | 10 | 0.40 |
| Inconel alloy 718 | 8 | 69 | 10 | 0.46 |
| MP35N | 6.3 | 69 | 10 | 0.50 |
| Type 440C stainless steel | 8 | 69 | 10 | 0.50 |
| Ti-6Al-4V (solution treated and aged) | 8 | 69 | 10 | 0.58 |
| Monel alloy 400 | 6.3 | 48 | 7 | 0.65 |
| D-979 stainless steel | 6.3 | 48 | 7 | 0.69 |
| Nickel 270 | 8 | 69 | 10 | 0.70 |
| CG27 stainless steel | 6.3 | 48 | 7 | 0.72 |
| ASTM A515, grade 70 | 8 | 69 | 10 | 0.73 |
| HY-100 steel | 8 | 69 | 10 | 0.73 |
| ASTM A372, type IV | 8 | 69 | 10 | 0.74 |
| 1042 steel (normalized) | 8 | 69 | 10 | 0.75 |
| Inconel alloy 625 | 8 | 34 | 5 | 0.76 |
| ASTM A517, grade F | 8 | 69 | 10 | 0.77 |
| ASTM A533, type B | 8 | 69 | 10 | 0.78 |
| Waspaloy | 6.3 | 48 | 7 | 0.78 |
| Ti-6Al-4V (annealed) | 8 | 69 | 10 | 0.79 |
| 1020 steel | 8 | 69 | 10 | 0.79 |
| HY-80 steel | 8 | 69 | 10 | 0.80 |
| Inconel alloy 706 | 6.3 | 48 | 7 | 0.80 |
| Ti-5Al-2.5Sn | 8 | 69 | 10 | 0.81 |
| ARMCO iron | 8 | 69 | 10 | 0.86 |
| P/M Inconel alloy 718 | 6.3 | 48 | 7 | 0.86 |
| Type 304 stainless steel | 8 | 69 | 10 | 0.87 |
| Type 321 stainless steel | 8 | 34 | 5 | 0.87 |
| Hastelloy alloy X | 8 | 34 | 5 | 0.87 |
| Type 305 stainless steel | 8 | 69 | 10 | 0.89 |
| Astroloy | 8 | 34 | 5 | 0.90 |
| Type 347 stainless steel | 8 | 34 | 5 | 0.91 |
| Haynes alloy 188 | 6.3 | 48 | 7 | 0.92 |
| Type 304N stainless steel | 6.3 | 103 | 15 | 0.93 |
| Type 310 stainless steel | 8 | 69 | 10 | 0.93 |
| Beryllium-copper | 8 | 69 | 10 | 0.93 |
| RA330 | 6.3 | 48 | 7 | 0.95 |
| A-286 | 8 | 69 | 10 | 0.97 |
| 21-6-9 stainless steel | 6.3 | 48 | 7 | 0.97 |
| Aluminum alloy 7075-T73 | 8 | 69 | 10 | 0.98 |
| Incoloy alloy 802 | 6.3 | 48 | 7 | 0.99 |
| Aluminum alloy 6061-T6 | 8 | 69 | 10 | 1.00 |
| Copper (C10100) | 8 | 69 | 10 | 1.00 |
| Type 316 stainless steel | 8 | 69 | 10 | 1.00 |
| Incoloy alloy 903 | 8 | 34 | 5 | 1.00 |

(a) Ratio of notched strength in hydrogen to notched strength in helium

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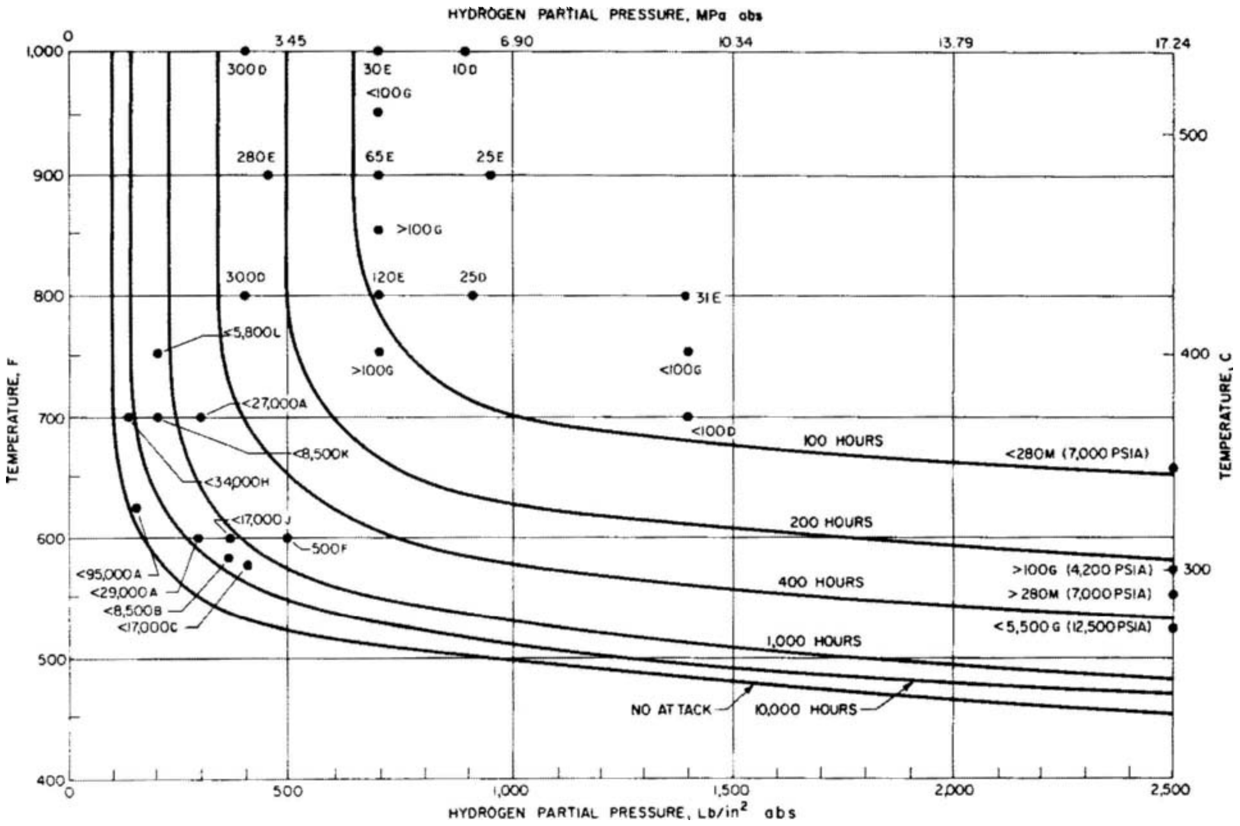

**Fig. 23** Time for incipient attack of carbon steel in hydrogen service. Source: *Corrosion Data Survey: Metals Section*, 6th ed., National Association of Corrosion Engineers, Houston, 1985, p 174

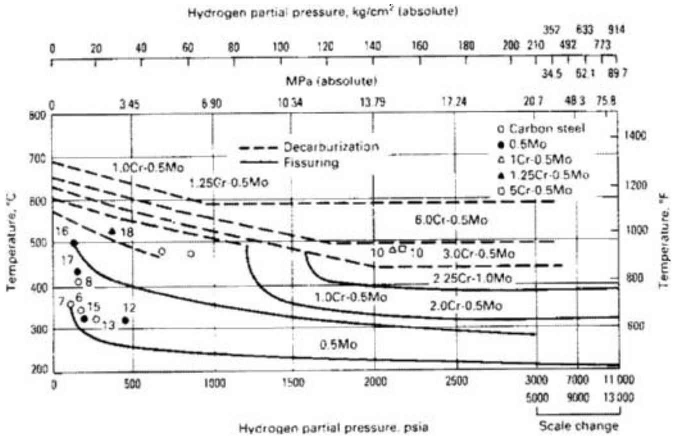

**Fig. 24** Nelson curve defining safe upper limits for steels in hydrogen service. Source: G.R. Prescott, "Materials Problems in the Hydrogen-Carbon Processing Industries," in *Alloys for the Eighties*, Climax Molybdenum Company, p 303-315

# Glossary of Terms

## A

**absorption.** A process in which fluid molecules are taken up by a liquid or solid and distributed throughout the body of that liquid or solid. Compare with *adsorption.*

**accelerated corrosion test.** Method designed to approximate, in a short time, the deteriorating effect under normal long-term service conditions.

**acid.** A chemical substance that yields hydrogen ions ($H^+$) when dissolved in water. Compare with *base.*

**acid embrittlement.** A form of *hydrogen embrittlement* that may be induced in some metals by acid.

**activation.** The changing of a passive surface of a metal to a chemically active state. Contrast with *passivation.*

**active.** The negative direction of *electrode potential.* Also used to describe corrosion and its associated potential range when an electrode potential is more negative than an adjacent depressed corrosion rate (passive) range.

**active metal.** A metal ready to corrode, or being corroded.

**active potential.** The *potential* of a corroding material.

**activity.** A measure of the *chemical potential* of a substance, where chemical potential is not equal to concentration, that allows mathematical relations equivalent to those for ideal systems to be used to correlate changes in an experimentally measured quantity with changes in chemical potential.

**activity (ion).** The ion concentration corrected for deviations from ideal behavior. Concentration multiplied by activity coefficient.

**activity coefficient.** A characteristic of a quantity expressing the deviation of a solution from ideal thermodynamic behavior; often used in connection with electrolytes.

**addition agent.** A substance added to a solution for the purpose of altering or controlling a process. Examples include wetting agents in acid pickles, brighteners or antipitting agents in plating solutions, and inhibitors.

**adsorption.** The surface retention of solid, liquid, or gas molecules, atoms, or ions by a solid or liquid. Compare with *absorption.*

**aeration.** (1) Exposing to the action of air. (2) Causing air to bubble through. (3) Introducing air into a solution by spraying, stirring, or a similar method. (4) Supplying or infusing with air, as in sand or soil.

**aerobic.** Having to do with or occurring in the presence of atmospheric oxygen. Contrasted with anaerobic.

**alkali metal.** A metal in group 1A of the periodic system—namely, lithium, sodium, potassium, rubidium, cesium, and francium. They form strongly alkaline hydroxides, hence the name.

**alkaline.** (1) Having properties of an alkali. (2) Having a pH greater than 7.

**alkaline cleaner.** A material blended from alkali hydroxides and such alkaline salts as borates, carbonates, phosphates, or silicates. The cleaning action may be enhanced by the addition of surface-active agents and special solvents.

**alkylation.** (1) A chemical process in which an alkyl radical is introduced into an organic compound by substitution or addition. (2) A refinery process for chemically combining isoparaffin with olefin hydrocarbons.

**ammeter.** An instrument for measuring the magnitude of electric current flow.

**amorphous solid.** A rigid material whose structure lacks crystalline periodicity; that is, the pattern of its constituent atoms or molecules does not repeat periodically in three dimensions.

**amphoteric.** A term applied to oxides and hydroxides which can act basic toward strong acids and acidic toward strong alkalis. Substances which can dissociate electrolytically to produce hydrogen or hydroxyl ions according to conditions.

**anaerobic.** Free of air or uncombined oxygen.

**anion.** A negatively charged ion that migrates through the electrolyte toward the *anode* under the influence of a potential gradient. See also *cation.*

**annealing.** A generic term denoting a treatment, consisting of heating to and holding at a suitable temperature, followed by cooling at a suitable rate, used primarily to soften metallic materials, but also to simultaneously produce desired changes in other properties or in microstructure. The purpose of such changes may be, but is not confined to, improvement of machinability, facilitation of cold work, improvement of mechanical or electrical properties, and/or increase in stability of dimensions. When the term is used by itself, full annealing is implied. When applied only for the relief of stress, the process is properly called stress relieving or stress-relief annealing.

**anode.** The electrode of an electrolyte cell at which oxidation occurs. Electrons flow away from the anode in the external circuit. It is usually at the electrode that corrosion occurs and metal ions enter solution. Contrast with *cathode.*

**anode corrosion.** The dissolution of a metal acting as an *anode.*

**anode corrosion efficiency.** The ratio of the actual corrosion (weight loss) of an *anode* to the theoretical corrosion (weight loss) calculate by *Faraday's law* from the quantity of electricity that has passed.

**anode effect.** The effect produced by polarization of the *anode* in electrolysis. It is characterized by a sudden increase in voltage and a corresponding decrease in amperage due to the anode becoming virtually separated from the electrolyte by a gas film.

**anode efficiency.** Current efficiency at the *anode.*

**anode film.** (1) The portion of solution in immediate contact with the *anode*, especially if the concentration gradient is steep. (2) The outer layer of the anode itself.

**anodic cleaning.** Electrolytic cleaning in which the work is the anode. Also called reverse-current cleaning.

**anodic coating.** A film on a metal surface resulting from an electrolytic treatment at the *anode.*

**anodic inhibitor.** A chemical substance or mixture that prevents or reduces the rate of the anodic or oxidation reaction. See also *inhibitor.*

**anodic polarization.** The change of the electrode potential in the noble (positive) direction due to current flow.

**anodic protection.** (1) A technique to reduce the corrosion rate of a metal by polarizing it into its passive region, where dissolution rates are low. (2) Imposing an external electrical potential to protect a metal from corrosive attack. (Applicable only to metals that show active-passive behavior.) Contrast with *cathodic protection.*

**anodic reaction.** Electrode reaction equivalent to a transfer of positive charge from the electronic to the ionic conductor. An anodic reaction is an oxidation process. An example common in corrosion is: $\text{Me} \rightarrow \text{Me}^{n+} + ne^-$.

**anti-fouling.** Intended to prevent fouling of underwater structures, such as the bottoms of ships.

**antipitting agent.** An addition agent for electroplating solutions to prevent the formation of pits or large pores in the electrodeposit.

**aqueous.** Pertaining to water; an aqueous solution is made by using water as a solvent.

**atmospheric corrosion.** The gradual degradation or alteration of a material by contact with substances present in the atmosphere, such as oxygen, carbon dioxide, water vapor, and sulfur and chlorine compounds.

**austenite.** A solid solution of one or more elements in face-centered cubic iron. Unless otherwise designated (such as nickel austenite), the solute is generally assumed to be carbon.

**austenitizing.** Forming austenite by heating a ferrous alloy into the transformation range (partial austenitizing) or above the transformation range (complete austenitizing). When used without qualification, the term implies complete austenitizing.

## B

**backfill.** Material placed in a drilled hole to fill space around anodes, vent pipe, and buried components of a cathodic protection system.

**base.** A chemical substance that yields hydroxyl ions ($OH^-$) when dissolved in water. Compare with *acid*.

**base metal.** (1) The metal present in the largest proportion in an alloy; brass, for example, is a copper-base alloy. (2) An *active metal* that readily oxidizes, or that dissolves to form ions. (3) The metal to be brazed, cut, soldered, or welded. (4) After welding, that part of the metal which was not melted.

**beach marks.** Macroscopic progression marks on a fatigue fracture or stress-corrosion cracking surface that indicate successive positions of the advancing crack front. The classic appearance is of irregular elliptical or semielliptical rings, radiating outward from one or more origins. Beach marks (also known as clamshell marks or arrest marks) are typically found on service fractures where the part is loaded randomly, intermittently, or with periodic variations in mean stress or alternating stress.

**biological corrosion.** Deterioration of metals as a result of the metabolic activity of microorganisms.

**bipolar electrode.** An *electrode* in an *electrolytic cell* that is not mechanically connected to the power supply, but is so placed in the electrolyte, between the *anode* and *cathode*, that the part nearer the anode becomes cathodic and the part nearer the cathode becomes anodic. Also called intermediate electrode.

**blister.** A raised area, often dome shaped, resulting from (1) loss of adhesion between a coating or deposit and the base metal or (2) delamination under the pressure of expanding gas trapped in a metal in a near-subsurface zone. Very small blisters may be called pinhead blisters or pepper blisters.

**blow down.** (1) Injection of air or water under high pressure through a tube to the anode area for the purpose of purging the annular space and possibly correcting high resistance caused by gas blocking. (2) In connection with boilers or cooling towers, the process of discharging a significant portion of the aqueous solution in order to remove accumulated salts, deposits, and other impurities.

**brackish water.** (1) Water having salinity values ranging from approximately 0.5 to 17 parts per thousand. (2) Water having less salt than seawater, but undrinkable.

**breakdown potential.** The least noble potential where *pitting* or *crevice corrosion*, or both, will initiate and propagate.

**brine.** Seawater containing a higher concentration of dissolved salt than that of the ordinary ocean.

## C

**cathode.** The *electrode* of an *electrolytic cell* at which reduction is the principal reaction. (Electrons flow toward the cathode in the external circuit.) Typical cathodic processes are cations taking up electrons and being discharged, oxygen being reduced, and the reduction of an element or group of elements from a higher to a lower valence state. Contrast with *anode*.

**cathode efficiency.** Current efficiency at the *cathode*.

**cathode film.** The portion of solution in immediate contact with the *cathode* during *electrolysis*.

**cathodic cleaning.** *Electrolytic cleaning* in which the work is the *cathode*.

**cathodic corrosion.** Corrosion resulting from a cathodic condition of a structure usually caused by the reaction of an amphoteric metal with the alkaline products of *electrolysis*.

**cathodic inhibitor.** A chemical substance or mixture that prevents or reduces the rate of the cathodic or reduction reaction.

**cathodic pickling.** Electrolytic pickling in which the work is the *cathode*.

**cathodic polarization.** The change of the *electrode potential* in the active (negative) direction due to current flow.

**cathodic protection.** (1) Reduction of corrosion rate by shifting the *corrosion potential* of the electrode toward a less oxidizing potential by applying an external *electromotive force*. (2) Partial or complete protection of a metal from corrosion by making it a *cathode*, using either a galvanic or an impressed current. Contrast with *anodic protection*.

**cathodic reaction.** Electrode reaction equivalent to a transfer of negative charge from the electronic to the ionic conductor. A cathodic reaction is a reduction process. An example common in corrosion is: $\text{Ox} + ne^- \rightarrow \text{Red}$.

**cation.** A positively charged ion that migrates through the electrolyte toward the *cathode* under the influence of a potential gradient. See also *anion*.

**caustic.** (1) Burning or corrosive. (2) A hydroxide of a light metal, such as sodium hydroxide or potassium hydroxide.

**caustic dip.** A strongly alkaline solution into which metal is immersed for etching, for neutralizing acid, or for removing organic materials such as greases or paints.

**caustic embrittlement.** An obsolete historical term denoting a form of *stress-corrosion cracking* most frequently encountered in carbon steels or iron-chromium-nickel alloys that are exposed to concentrated hydroxide solutions at temperatures of 200 to 250 °C (400 to 480 °F).

**cavitation.** The formation and instantaneous collapse of innumerable tiny voids or cavities within a liquid subjected to rapid and intense pressure changes. Cavitation produced by ultrasonic radiation is sometimes used to effect violent localized agitation. Cavitation caused by severe turbulent flow often leads to *cavitation damage*.

**cavitation corrosion.** A process involving conjoint *corrosion* and *cavitation*.

**cavitation damage.** The degradation of a solid body resulting from its exposure to *cavitation*. This may include loss of material, surface deformation, or changes in properties or appearance.

**cavitation-erosion.** Progressive loss of original material from a solid surface due to continuing exposure to *cavitation*.

**cell.** Electrochemical system consisting of an *anode* and a *cathode* immersed in an *electrolyte*. The anode and cathode may be separate metals or dissimilar areas on the same metal. The cell includes the external circuit, which permits the flow of electrons from the anode toward the cathode. See also *electrochemical cell*.

**Charpy test.** An impact test in which a V-notched, keyhole-notched, or U-notched specimen, supported at both ends, is struck behind the notch by a striker mounted at the lower end of a bar that can swing as a pendulum. The energy that is absorbed in fracture is calculated from the height to which the striker would have risen had there been no specimen and the height to which it actually rises after fracture of the specimen.

**checking.** The development of slight breaks in a coating that do not penetrate to the underlying surface.

**checks.** Numerous, very fine cracks in a coating or at the surface of a metal part. Checks may appear during processing or during service and are most often associated with thermal treatment or thermal cycling. Also called check marks, *checking*, or *heat checks*.

**chelate.** (1) A molecular structure in which a heterocyclic ring can be formed by the unshared electrons of neighboring atoms. (2) A *coordination compound* in which a heterocyclic ring is formed by a metal bound to two atoms of the associated *ligand*. S

**chelating agent.** (1) An organic compound in which atoms form more than one coordinate bond with metals in solution. (2) A substance used in metal finishing to control or eliminate certain metallic ions present in undesirable quantities.

**chelation.** A chemical process involving formation of a heterocyclic ring compound that contains at least one metal cation or hydrogen ion in the ring.

**chemical potential.** In a thermodynamic system of several constituents, the rate of change of the Gibbs function of the system with respect to the change in the number of moles of a particular constituent.

**clad metal.** A composite metal containing two or more layers that have been bonded together. The bonding may have been accomplished by co-rolling, co-extrusion, welding, diffusion bonding, casting, heavy chemical deposition, or heavy electroplating.

**conductivity.** The ratio of the electric current density to the electric field in a material. Also called electrical conductivity or specific conductance.

**contact corrosion.** A term primarily used in Europe to describe *galvanic corrosion* between dissimilar metals.

**contact plating.** A metal plating process wherein the plating current is provided by galvanic action between the work metal and a second metal, without the use of an external source of current.

**contact potential.** The potential difference at the junction of two dissimilar substances.

**corrosion.** The chemical or electrochemical reaction between a material, usually a metal, and its environment that produces a deterioration of the material and its properties.

**corrosion effect.** A change in any part of the *corrosion system* caused by *corrosion*.

**corrosion embrittlement.** The severe loss of ductility of a metal resulting from corrosive attack, usually *intergranular* and often not visually apparent.

**corrosion-erosion.** See *erosion-corrosion*.

**corrosion fatigue.** The process in which a metal fractures prematurely under conditions of simultaneous corrosion and repeated cyclic loading at lower stress levels or fewer cycles than would be required in the absence of the corrosive environment.

**corrosion fatigue strength.** The maximum repeated stress that can be endured by a metal without failure under definite conditions of corrosion and fatigue and for a specific number of stress cycles and a specified period of time.

**corrosion inhibitor.** See *inhibitor*.

**corrosion potential.** ($E_{corr}$).The *potential* of a corroding surface in an electrolyte, relative to a *reference electrode*. Also called rest potential, open-circuit potential, or freely corroding potential.

**corrosion product.** Substance formed as a result of *corrosion*.

**corrosion protection.** Modification of a *corrosion system* so that corrosion damage is mitigated.

**corrosion rate.** *Corrosion effect* on a metal per unit of time. The type of corrosion rate used depends on the technical system and on the type of corrosion effect. Thus, corrosion rate may be expressed as an increase in corrosion depth per unit of time (penetration rate, for example, mils/yr) or the mass of metal turned into corrosion products per unit area of surface per unit of time (weight loss, for example, $g/m^2/yr$). The corrosion effect may vary with time and may not be the same at all points of the corroding surface. Therefore, reports of corrosion rates should be accompanied by information on the type, time dependency, and location of the corrosion effect.

**corrosion resistance.** Ability of a metal to withstand *corrosion* in a given *corrosion system*.

**corrosion system.** System consisting of one or more metals and all parts of the environment that influence *corrosion*.

**corrosivity.** Tendency of an environment to cause *corrosion* in a given *corrosion system*.

**cracking (of coating).** Breaks in a coating that extend through to the underlying surface.

**crazing.** A network of checks or cracks appearing on the surface.

**crevice corrosion.** *Localized corrosion* of a metal surface at, or immediately adjacent to, an area that is shielded from full exposure to the environment because of close proximity between the metal and the surface of another material.

**critical pitting potential.** ($E_{cp}$, $E_p$, $E_{pp}$). The lowest value of oxidizing potential at which pits nucleate and grow. It is dependent on the test method used.

**current.** The net transfer of electric charge per unit time. Also called electric current.

**current density.** The current flowing to or from a unit area of an electrode surface.

## D

**deactivation.** The process of prior removal of the active corrosive constituents, usually oxygen, from a corrosive liquid by controlled corrosion of expendable metal or by other chemical means, thereby making the liquid less corrosive.

**dealloying.** The selective corrosion of one or more components of a solid solution alloy. Also called parting or selective leaching.

**deep groundbed.** One or more *anodes* installed vertically at a nominal depth of 15 m (50 ft) or more below the earth's surface in a drilled hole for the purpose of supplying *cathodic protection* for an underground or submerged metallic structure. See also *groundbed*.

**deoxidizing.** (1) The removal of oxygen from molten metals by use of suitable deoxidizers. (2) Sometimes refers to the removal of undesirable elements other than oxygen by the introduction of elements or compounds that readily react with them. (3) In metal finishing, the removal of oxide films from metal surfaces by chemical or electrochemical reaction.

**deposit corrosion.** Corrosion occurring under or around a discontinuous deposit on a metallic surface. Also called poultice corrosion.

**descaling.** Removing the thick layer of oxides formed on some metals at elevated temperatures.

**dielectric shield.** In a *cathodic protection* system, an electrically nonconductive material, such as a coating, plastic sheet, or pipe, that is placed between an *anode* and an adjacent *cathode* to avoid current wastage and to improve current distribution, usually on the cathode.

**diffusion.** (1) Spreading of a constituent in a gas, liquid, or solid, tending to make the composition of all parts uniform. (2) The spontaneous movement of atoms or molecules to new sites within a material.

**duplex stainless steels.** Stainless steels having a fine-grained mixed microstructure of ferrite and austenite (Fig. 140) with a composition centered around 26Cr-6.5Ni. The corrosion resistance of duplex stainless steels is like that of austenitic stainless steels. However, duplex stainless steels possess higher tensile and yield strengths and improved resistance to stress-corrosion cracking than their austenitic counterparts.

## E

**electrical conductivity.** See *conductivity*.

**electrical isolation.** The condition of being electrically separated from other metallic structures or the environment.

**electrical resistivity.** The electrical resistance offered by a material to the flow of current, times the cross-sectional area of current flow and per unit length of current path; the reciprocal of the conductivity. Also called resistivity or specific resistance.

**electrochemical admittance.** The inverse of *electrochemical impedance*.

**electrochemical cell.** An electrochemical system consisting of an *anode* and a *cathode* in metallic contact and immersed in an *electrolyte*. (The anode and cathode may be different metals or dissimilar areas on the same metal surface.)

**electrochemical corrosion.** Corrosion that is accompanied by a flow of electrons between cathodic and anodic areas on metallic surfaces.

**electrochemical equivalent.** The weight of an element or group of elements oxidized or reduced at 100% efficiency by the passage of a unit quantity of electricity. Usually expressed as grams per coulomb.

**electrochemical impedance.** The frequency-dependent complex-valued proportionality factor ($\Delta E/\Delta i$) between the applied potential or current and the response signal. This factor is the total opposition ($\Omega$ or $\Omega \cdot \text{cm}^2$) of an electrochemical system to the passage of charge. The value is related to the *corrosion rate* under certain circumstances.

**electrochemical potential.** The partial derivative of the total electrochemical free energy of a constituent with respect to the number of moles of this constituent where all factors are kept constant. It is analogous to the *chemical potential* of a constituent except that it includes the electric as well as chemical contributions to the free energy. The *potential* of an electrode in an electrolyte relative to a *reference electrode* measured under open circuit conditions.

**electrochemical series.** Same as *electromotive force series*.

**electrode.** (1) An electronic conductor used to establish electrical contact with an electrolytic part of a circuit. (2) An electronic conductor in contact with an ionic conductor.

**electrode polarization.** Change of *electrode potential* with respect to a reference value. Often the *free corrosion potential* is used as the reference value. The change may be caused, for example, by the application of an external electrical current or by the addition of an oxidant or reductant.

**electrode potential.** The *potential* of an *electrode* in an *electrolyte* as measured against a *reference electrode*. The electrode potential does not include any resistance losses in potential in either the solution or external circuit. It represents the reversible work to move a unit charge from the electrode surface through the solution to the reference electrode.

**electromotive force series (emf series).** A list of elements arranged according to their standard *electrode* potentials, with "noble" metals such as gold being positive and "active" metals such as zinc being negative.

**embrittlement.** The severe loss of *ductility* or *toughness* or both, of a material, usually a metal or alloy. Many forms of embrittlement can lead to *brittle fracture*. Many forms can occur during thermal treatment or elevated-temperature service (thermally induced embrittlement). Some of these forms of embrittlement, which affect steels, include *blue brittleness*, *475 °C (885 °F) embrittlement*, *quench-age embrittlement*, *sigma-phase embrittlement*, *strain-age embrittlement*, *temper embrittlement*, *tempered martensite embrittlement*, and *thermal embrittlement*. In addition, steels and other metals and alloys can be embrittled by environmental conditions (environmentally assisted embrittlement). The forms of environmental embrittlement include *acid embrittlement*, *caustic embrittlement*, *corrosion embrittlement*, *creep-rupture embrittlement*, *hydrogen embrittlement*, *liquid metal embrittlement*, *neutron embrittlement*, *solder embrittlement*, *solid metal embrittlement*, *and stress-corrosion cracking*.

**emulsion.** (1) A two-phase liquid system in which small droplets of one liquid (the internal phase) are immiscible in, and are dispersed uniformly throughout, a second continuous liquid phase (the external phase). The internal phase is sometimes described as the dispense phase. (2) A stable dispersion of one liquid in another, generally by means of an emulsifying agent that has affinity for both the continuous and discontinuous phases. The emulsifying agent, discontinuous phase, and continuous phase can together produce another phase that serves as an enveloping (encapsulating) protective phase around the discontinuous phase.

**environment.** The surroundings or conditions (physical, chemical, mechanical) in which a material exists.

**environmental cracking.** *Brittle fracture* of a normally ductile material in which the corrosive effect of the environment is a causative factor. Environmental cracking is a general term that includes *corrosion fatigue*, *high-temperature hydrogen attack*, *hydrogen blistering*, *hydrogen embrittlement*, *liquid metal embrittlement*, *solid metal embrittlement*, *stress-corrosion cracking*, *and sulfide stress cracking*. The following terms have been used in the past in connection with environmental cracking, but are becoming obsolete: caustic embrittlement, delayed fracture, season cracking, static fatigue, stepwise cracking, sulfide corrosion cracking, and sulfide stress-corrosion cracking. See also *embrittlement*.

**erosion.** Destruction of metals or other materials by the abrasive action of moving fluids, usually accelerated by the presence of solid particles or matter in suspension. When corrosion occurs simultaneously, the term *erosion-corrosion* is often used.

**erosion-corrosion.** A conjoint action involving *corrosion* and *erosion* in the presence of a moving corrosive fluid, leading to the accelerated loss of material.

**exfoliation.** Corrosion that proceeds laterally from the sites of initiation along planes parallel to the surface, generally at grain boundaries, forming corrosion products that force metal away from the body of the material, giving rise to a layered appearance.

## F

**failure.** A general term used to imply that a part in service (1) has become completely inoperable, (2) is still operable but is incapable of satisfactorily performing its intended function, or (3) has deteriorated seriously, to the point that it has become unreliable or unsafe for continued use.

**fatigue.** The phenomenon leading to fracture under repeated or fluctuating stresses having a maximum value less than the tensile strength of the material. Fatigue fractures are progressive and grow under the action of the fluctuating stress.

**ferrite.** (1) A solid solution of one or more elements in body-centered cubic iron. Unless otherwise designated (for instance, as chromium ferrite), the solute is generally assumed to be carbon. On some equilibrium diagrams, there are two ferrite regions separated by an austenite area. The lower area is alpha ferrite; the upper, delta ferrite. If there is no designation, alpha ferrite is assumed. (2) In the field of magnetics, substances having the general formula: $M^{2+}O \cdot M_2^{3+}O_3$, the trivalent metal often being iron.

**flame spraying.** *Thermal spraying* in which a coating material is fed into an oxyfuel gas flame, where it is melted. Compressed gas may or may not be used to atomize the coating material and propel it onto the substrate.

**fouling.** An accumulation of deposits. This term includes accumulation and growth of marine organisms on a submerged metal surface and also includes the accumulation of deposits (usually inorganic) on heat exchanger tubing.

**fouling organism.** Any aquatic organism with a sessile adult stage that attaches to and fouls underwater structures of ships.

## G

**galvanic anode.** A metal which, because of its relative position in the galvanic series, provides *sacrificial protection* to metals that are more noble in the series, when coupled in an electrolyte.

**galvanic cell.** A cell in which chemical change is the source of electrical energy. It usually consists of two dissimilar conductors in contact with each other and with an electrolyte, or of two similar conductors in contact with each other and with dissimilar electrolytes.

**galvanic corrosion.** Accelerated corrosion of a metal because of an electrical contact with a more noble metal or nonmetallic conductor in a corrosive electrolyte.

**galvanic couple.** A pair of dissimilar conductors, commonly metals, in electrical contact. See also *galvanic corrosion.*

**galvanic couple potential.** See *mixed potential.*

**galvanic current.** The electric current that flows between metals or conductive nonmetals in a *galvanic couple.*

**galvanic series.** A list of metals and alloys arranged according to their relative corrosion potentials in a given environment. Compare with *electromotive force series.*

**galvanize.** To coat a metal surface with zinc using any of various processes.

**gaseous corrosion.** Corrosion with gas as the only corrosive agent and without any aqueous phase on the surface of the metal. Also called dry corrosion.

**gamma iron.** The face-centered cubic form of pure iron, stable from 910 to 1400 °C (1670 to 2550 °F).

**general corrosion.** See *uniform corrosion.*

**Gibbs free energy.** The thermodynamic function $\Delta G = \Delta H - T\Delta S$, where $H$ is enthalpy, $T$ is absolute temperature, and $S$ is entropy. Also called free energy, free enthalpy, or Gibbs function.

**grain.** An individual crystal in a polycrystalline metal or alloy; it may or may not contain twinned regions and subgrains.

**grain boundary.** A narrow zone in a metal corresponding to the transition from one crystallographic orientation to another, thus separating one *grain* from another; the atoms in each grain are arranged in an orderly pattern.

**grain-boundary corrosion.** Same as intergranular corrosion.

**graphitic corrosion.** Deterioration of gray cast iron in which the metallic constituents are selectively leached or converted to corrosion products leaving the graphite intact. The term *graphitization* is commonly used to identify this form of corrosion, but is not recommended because of its use in metallurgy for the decomposition of carbide to graphite. See also *dealloying* and *selective leaching.*

**gray iron.** A broad class of ferrous casting alloys (*cast irons*) normally characterized by a microstructure of flake graphite in a ferrous matrix. Gray irons usually contain 2.5 to 4% C, 1 to 3% Si, and additions of manganese, depending on the desired microstructure (as low as 0.1% Mn in ferritic gray irons and as high as 1.2% in pearlitics). Sulfur and phosphorus are also present in small amounts as residual impurities.

**groundbed.** A buried item, such as junk steel or graphite rods, that serves as the *anode* for the *cathodic protection* of pipelines or other buried structures. See also *deep groundbed.*

## H

**hardfacing.** Depositing filler metal on a surface by welding, spraying, or braze welding to increase resistance to abrasion, erosion, wear, galling, impact, or cavitation damage.

**hardness.** A measure of the resistance of a material to surface indentation or abrasion; may be thought of as a function of the *stress* required to produce some specified type of surface deformation. There is no absolute scale for hardness; therefore, to express hardness quantitatively, each type of test has its own scale of arbitrarily defined hardness. Indentation hardness can be measured by *Brinell*, *Knoop*, *Rockwell*, *Scleroscope*, and *Vickers hardness tests.*

**hard water.** Water that contains certain salts, such as those of calcium or magnesium, which form insoluble deposits in boilers and form precipitates with soap.

**heat-affected zone (HAZ).** That portion of the base metal that was not melted during brazing, cutting, or welding, but whose microstructure and mechanical properties were altered by the heat.

**hematite.** (1) An iron mineral crystallizing in the rhombohedral system; the most important ore of iron. (2) An iron oxide, $Fe_2O_3$, corresponding to an iron content of approximately 70%.

**high-temperature hydrogen attack.** A loss of strength and ductility of steel by high-temperature reaction of absorbed hydrogen with carbides in the steel resulting in *decarburization* and internal fissuring.

**holidays.** Discontinuities in a coating (such as porosity, cracks, gaps, and similar flaws) that allow areas of base metal to be exposed to any corrosive environment that contacts the coated surface.

**hoop stress.** The circumferential stress in a material of cylindrical form subjected to internal or external pressure.

**hot corrosion.** An accelerated corrosion of metal surfaces that results from the combined effect of oxidation and reactions with sulfur compounds and other contaminants, such as chlorides, to form a molten salt on a metal surface that fluxes, destroys, or disrupts the normal protective oxide. See also *gaseous corrosion.*

**hydrogen-assisted cracking (HAC).** See *hydrogen embrittlement.*

**hydrogen-assisted stress-corrosion cracking (HSCC).** See *hydrogen embrittlement.*

**hydrogen blistering.** The formation of blisters on or below a metal surface from excessive internal hydrogen pressure. Hydrogen may be formed during cleaning, plating, corrosion, and so forth.

**hydrogen damage.** A general term for the embrittlement, cracking, blistering, and hydride formation that can occur when hydrogen is present in some metals.

**hydrogen embrittlement.** A process resulting in a decrease of the *toughness* or *ductility* of a metal due to the presence of atomic hydrogen. Hydrogen embrittlement has been recognized classically as being of two types. The first, known as internal hydrogen embrittlement, occurs when the hydrogen enters molten metal which becomes supersaturated with hydrogen immediately after solidification. The second type, environmental hydrogen embrittlement, results from hydrogen being absorbed by solid metals. This can occur during elevated-temperature thermal treatments and in service during electroplating, contact with maintenance chemicals, corrosion reactions, cathodic protection, and operating in high-pressure hydrogen. In the absence of residual stress or external loading, environmental hydrogen embrittlement is manifested in various forms, such as blistering, internal cracking, hydride formation, and reduced ductility. With a tensile stress or stress-intensity factor exceeding a specific threshold, the atomic hydrogen interacts with the metal to induce subcritical crack growth leading to fracture. In the absence of a corrosion reaction (polarized cathodically), the usual term used is hydrogen-assisted cracking (HAC) or hydrogen stress cracking (HSC). In the presence of active corrosion, usually as pits or crevices (polarized anodically), the cracking is generally called *stress-corrosion cracking (SCC)*, but should more properly be called hydrogen-assisted stress-corrosion cracking (HSCC). Thus, HSC and electrochemically anodic SCC can operate separately or in combination (HSCC). In some metals, such as high-strength steels, the mechanism is believed to be all, or nearly all, HSC. The participating mechanism of HSC is not always recognized and may be evaluated under the generic heading of SCC.

**hydrogen-induced cracking (HIC).** Same as *hydrogen embrittlement.*

**hydrogen stress cracking (HSC).** See *hydrogen embrittlement.*

**hydrophilic.** Having an affinity for water. Contrast with *hydrophobic.*

**hydrophobic.** Lacking an affinity for, repelling, or failing to absorb or adsorb water. Contrast with *hydrophilic.*

**hygroscopic.** (1) Possessing a marked ability to accelerate the condensation of water vapor; applied to condensation nuclei composed of salts that yield aqueous solutions of a very low equilibrium vapor pressure compared with that of pure water at the same temperature. (2) Pertaining to a substance whose physical characteristics are appreciably altered by effects of water vapor. (3) Pertaining to water absorbed by dry soil minerals from the atmosphere; the amounts depend on the physicochemical character of the surfaces, and increase with rising relative humidity.

## I

**immunity.** A state of resistance to corrosion or anodic dissolution of a metal caused by thermodynamic stability of the metal.

**impingement corrosion.** A form of *erosion-corrosion* generally associated with the local impingement of a high-velocity, flowing fluid against a solid surface.

**impressed current.** Direct current supplied by a device employing a power source external to the electrode system of a *cathodic protection* installation.

**inclusions.** Particles of foreign material in a metallic matrix. The particles are usually compounds (such as oxides, sulfides, or silicates), but may be of any substance that is foreign to (and essentially insoluble in) the matrix.

**incubation period.** A period prior to the detection of corrosion while the metal is in contact with a corrodent.

**industrial atmosphere.** An atmosphere in an area of heavy industry with soot, fly ash, and sulfur compounds as the principal constituents.

**inert anode.** An *anode* that is insoluble in the *electrolyte* under the conditions prevailing in the *electrolysis*.

**inhibitor.** A chemical substance or combination of substances that, when present in the environment, prevents or reduces corrosion without significant reaction with the components of the environment.

**inorganic.** Being or composed of matter other than hydrocarbons and their derivatives, or matter that is not of plant or animal origin. Contrast with *organic*.

**intergranular.** Between crystals or grains. Also called intercrystalline. Contrast with *transgranular*.

**intergranular corrosion.** Corrosion occurring preferentially at grain boundaries, usually with slight or negligible attack on the adjacent grains. Also called intercrystalline corrosion.

**intergranular cracking.** Cracking or fracturing that occurs between the grains or crystals in a polycrystalline aggregate. Also called intercrystalline cracking. Contrast with *transgranular cracking*.

**intergranular fracture.** Brittle fracture of a metal in which the fracture is between the grains, or crystals, that form the metal. Also called intercrystalline fracture. Contrast with *transgranular fracture*.

**intergranular stress-corrosion cracking (IGSCC).** *Stress-corrosion cracking* in which the cracking occurs along grain boundaries.

**internal oxidation.** The formation of isolated particles of corrosion products beneath the metal surface. This occurs as the result of preferential oxidation of certain alloy constituents by inward diffusion of oxygen, nitrogen, sulfur, and so forth.

**isocorrosion diagram.** A graph or chart that shows constant corrosion behavior with changing solution (environment) composition and temperature.

## K

**$K_{ISCC}$.** Abbreviation for the critical value of the plane strain *stress-intensity factor* that will produce crack propagation by *stress-corrosion cracking* of a given material in a given environment.

**knife-line attack.** *Intergranular corrosion* of an alloy, usually stabilized stainless steel, along a line adjoining or in contact with a weld after heating into the sensitization temperature range.

## L

**lignite.** A brownish-black coal in which decomposition of vegetable matter has proceeded farther than in peat but not so far as in bituminous coal. Also called brown coal.

**limiting current density.** The maximum current density that can be used to obtain a desired electrode reaction without undue interference such as from *polarization*.

**liquid metal embrittlement.** Catastrophic brittle failure of a normally ductile metal when in contact with a liquid metal and subsequently stressed in tension.

**localized corrosion.** Corrosion at discrete sites, for example, *crevice corrosion*, *pitting*, and *stress-corrosion cracking*.

## M

**macroscopic.** Visible at magnifications to 25×.

**macrostructure.** The structure of metals as revealed by macroscopic examination of the etched surface of a polished specimen.

**magnetite.** Naturally occurring magnetic oxide of iron ($Fe_3O_4$).

**martensite.** A generic term for microstructures formed by diffusionless phase transformation in which the parent and product phases have a specific crystallographic relationship. Martensite is characterized by an acicular pattern in the microstructure in both ferrous and nonferrous alloys. In alloys where the solute atoms occupy interstitial positions in the martensitic lattice (such as carbon in iron), the structure is hard and highly strained; but where the solute atoms occupy substitutional positions (such as nickel in iron), the martensite is soft and ductile. The amount of high-temperature phase that transforms to martensite on cooling depends to a large extent on the lowest temperature attained, there being a rather distinct beginning temperature ($M_s$) and a temperature at which the transformation is essentially complete ($M_f$).

**microstructure.** The structure of a prepared surface of a metal as revealed by a microscope at a magnification exceeding 25×.

**mill scale.** The heavy oxide layer formed during hot fabrication or heat treatment of metals.

## N

**noble.** The positive direction of *electrode potential*, thus resembling noble metals such as gold and platinum.

**noble metal.** (1) A metal whose *potential* is highly positive relative to the hydrogen electrode. (2) A metal with marked resistance to chemical reaction, particularly to oxidation and to solution by inorganic acids. The term as often used is synonymous with *precious metal*.

## O

**oleum.** A solution of sulfur trioxide and concentrated sulfuric acid, used as an agent in chemical processes. Oleum is also known as fuming sulfuric acid, because this kind of sulfuric acid fumes when exposed to air.

**organic.** Being or composed of hydrocarbons or their derivatives, or matter of plant or animal origin. Contrast with *inorganic*.

**organic acid.** A chemical compound with one or more carboxyl radicals (COOH) in its structure; examples are butyric acid, $CH_3(CH_2)_2COOH$; maleic acid, HOOCCH-CHCOOH; and benzoic acid, $C_6H_5COOH$.

**oxidation.** (1) A reaction in which there is an increase in valence resulting from a loss of electrons. Contrast with *reduction*. (2) A corrosion reaction in which the corroded metal forms an oxide; usually applied to reaction with a gas containing elemental oxygen, such as air.

## P

**passivation.** (1) A reduction of the anodic reaction rate of an electrode involved in corrosion. (2) The process in metal corrosion by which metals become *passive*. (3) The changing of a chemically active surface of a metal to a much less reactive state. Contrast with *activation*.

**passivator.** A type of *inhibitor* that appreciably changes the potential of a metal to a more noble (positive) value.

**passive.** (1) A metal corroding under the control of a surface reaction product. (2) The state of the metal surface characterized by low corrosion rates in a potential region that is strongly oxidizing for the metal.

**passive-active cell.** A corrosion cell in which the *anode* is a metal in the *active* state and the *cathode* is the same metal in the *passive* state.

**passivity.** A condition in which a piece of metal, because of an impervious covering of oxide or other compound, has a *potential* much more positive than that of the metal in the active state.

**patina.** The coating, usually green, that forms on the surface of metals such as copper and copper alloys exposed to the atmosphere. Also used to describe the appearance of a weathered surface of any metal.

**pH.** The negative logarithm of the hydrogen-ion activity; it denotes the degree of acidity or basicity of a solution. At 25 °C (77 °F), 7.0 is the neutral value. Decreasing values below 7.0 indicate increasing acidity; increasing values above 7.0, increasing basicity.

**pickle.** A solution or process used to loosen or remove corrosion products such as scale or tarnish.

**pickling.** Removing surface oxides from metals by chemical or electrochemical reaction.

**pitting.** *Localized corrosion* of a metal surface, confined to a point or small area, that takes the form of cavities.

**pitting factor.** Ratio of the depth of the deepest pit resulting from corrosion divided by the average penetration as calculated from weight loss.

**potential-pH diagram.** See *Pourbaix (potential-pH) diagram.*

**Pourbaix (potential-pH) diagram.** A plot of the *redox potential* of a corroding system versus the pH of the system, compiled using thermodynamic data and the *Nernst equation.* The diagram shows regions within which the metal itself or some of its compounds are stable.

**primer.** The first coat of paint applied to a surface. Formulated to have good bonding and wetting characteristics; may or may not contain inhibiting pigments.

## R

**redox potential.** The *potential* of a reversible oxidation-reduction electrode measured with respect to a *reference electrode*, corrected to the hydrogen electrode, in a given *electrolyte*.

**reducing agent.** A compound that causes *reduction*, thereby itself becoming oxidized.

**reduction.** A reaction in which there is a decrease in valence resulting from a gain in electrons. Contrast with *oxidation*.

**relative humidity.** The ratio, expressed as a percentage, of the amount of water vapor present in a given volume of air at a given temperature to the amount required to saturate the air at that temperature.

**Rockwell hardness number, HR.** A number derived from the net increase in the depth of impression as the load on an indenter is increased from a fixed minor load to a major load and then returned to the minor load. Rockwell hardness numbers are always quoted with a scale symbol representing the penetrator, load, and dial used.

**Rockwell hardness test.** An indentation hardness test using a calibrated machine that utilizes the depth of indentation, under constant load, as a measure of hardness. Either a 120° diamond cone with a slightly rounded point or a 1.6- or 3.2-mm ($^{1}/_{16}$- or $^{1}/_{8}$-in.) diam steel ball is used as the indenter.

**rust.** A visible corrosion product consisting of hydrated oxides of iron. Applied only to ferrous alloys. See also *white rust.*

## S

**sacrificial protection.** Reduction of corrosion of a metal in an *electrolyte* by galvanically coupling it to a more anodic metal; a form of *cathodic protection.*

**selective leaching.** Corrosion in which one element is preferentially removed from an alloy, leaving a residue (often porous) of the elements that are more resistant to the particular environment. Also called *dealloying* or parting.

**sensitizing heat treatment.** A heat treatment, whether accidental, intentional, or incidental (as during welding), that causes precipitation of constituents at grain boundaries, often causing the alloy to become susceptible to *intergranular corrosion* or *intergranular stress-corrosion cracking.* See also *sensitization.*

**sensitization.** In austenitic stainless steels, the precipitation of chromium carbides, usually at grain boundaries, on exposure to temperatures of about 550 to 850 °C (about 1000 to 1550 °F), leaving the grain boundaries depleted of chromium and therefore susceptible to preferential attack by a corroding (oxidizing) medium.

**siderite.** An iron ore occurring in various forms and colors and crystalline with perfect rhombohedral cleavage. Formula: $FeCO_3$.

**sigma phase.** A hard, brittle, nonmagnetic intermediate phase with a tetragonal crystal structure, containing 30 atoms per unit cell, space group $P4_2/mnm$, occurring in many binary and ternary alloys of the transition elements. The composition of this phase in the various systems is not the same and the phase usually exhibits a wide range in homogeneity. Alloying with a third transition element usually enlarges the field of homogeneity and extends it deep into the ternary section.

**sigma-phase embrittlement.** *Embrittlement* of iron-chromium alloys (most notably austenitic stainless steels) caused by precipitation at grain boundaries of the hard, brittle intermetallic *sigma phase* during long periods of exposure to temperatures between approximately 560 and 980 °C (1050 and 1800 °F). Sigma-phase embrittlement results in severe loss in *toughness* and *ductility*, and can make the embrittled material susceptible to *intergranular corrosion.* See also *sensitization.*

**slow strain rate technique.** An experimental technique for evaluating susceptibility to *stress-corrosion cracking*. It involves pulling the specimen to failure in uniaxial tension at a controlled slow strain rate while the specimen is in the test environment and examining the specimen for evidence of stress-corrosion cracking.

**soft water.** Water that is free of magnesium or calcium salts.

**solvent.** The component of either a liquid or *solid solution* that is present to a greater or major extent; the component that dissolves the *solute.*

**sour gas.** A gaseous environment containing hydrogen sulfide and carbon dioxide in hydrocarbon reservoirs. Prolonged exposure to sour gas can lead to *hydrogen damage*, *sulfide-stress cracking*, and/or *stress-corrosion cracking* in ferrous alloys.

**sour water.** Waste waters containing fetid materials, usually sulfur compounds.

**stray current.** Current flowing through paths other than the intended circuit.

**stray-current corrosion.** Corrosion resulting from direct current flow through paths other than the intended circuit. For example, by an extraneous current in the earth.

**stress.** The intensity of the internally distributed forces or components of forces that resist a change in the volume or shape of a material that is or has been subjected to external forces. Stress is expressed in force per unit area and is calculated on the basis of the original dimensions of the cross section of the specimen. Stress can be either direct (tension or compression) or shear.

**stress concentration factor ($K_t$).** A multiplying factor for applied stress that allows for the presence of a structural discontinuity such as a notch or hole; $K_t$ equals the ratio of the greatest stress in the region of the discontinuity to the nominal stress for the entire section. Also called theoretical stress concentration factor.

**stress-corrosion cracking (SCC).** A cracking process that requires the simultaneous action of a corrodent and sustained tensile stress. This excludes corrosion-reduced sections that fail by fast fracture. It also excludes intercrystalline or transcrystalline corrosion, which can disintegrate an alloy without applied or residual stress. Stress-corrosion cracking may occur in combination with *hydrogen embrittlement*.

**stress-intensity factor.** A scaling factor, usually denoted by the symbol $K$, used in *linear-elastic fracture mechanics* to describe the intensification of applied stress at the tip of a crack of known size and shape. At the onset of rapid crack propagation in any structure containing a crack, the factor is called the critical stress-intensity factor, or the *fracture toughness*. Various subscripts are used to denote different loading conditions or fracture toughnesses:

- $K_c$. Plane-stress fracture toughness. The value of stress intensity at which crack propagation becomes rapid in sections thinner than those in which plane-strain conditions prevail.
- $K_I$. Stress-intensity factor for a loading condition that displaces the crack faces in a direction normal to the crack plane (also known as the opening mode of deformation).
- $K_{Ic}$. Plane-strain fracture toughness. The minimum value of $K_c$ for any given material and condition, which is attained when rapid crack propagation in the opening mode is governed by plane-strain conditions.
- $K_{Id}$. Dynamic fracture toughness. The fracture toughness determined under dynamic loading conditions; it is used as an approximation of $K_{Ic}$ for very tough materials.
- $K_{ISCC}$. Threshold stress-intensity factor for stress-corrosion cracking. The critical plane-strain stress intensity at the onset of stress-corrosion cracking under specified conditions.
- $K_Q$. Provisional value for plane-strain fracture toughness.
- $K_{th}$. Threshold stress intensity for stress-corrosion cracking. The critical stress intensity at the onset of stress-corrosion cracking under specified conditions.
- $\Delta K$. The range of the stress-intensity factor during a fatigue cycle.

**stress-intensity factor range, $\Delta K$.** In fatigue, the variation in the *stress-intensity factor* in a cycle, that is, $K_{max} - K_{min}$.

**stress raisers.** Changes in contour or discontinuities in structure that cause local increases in stress.

**sulfidation.** The reaction of a metal or alloy with a sulfur-containing species to produce a sulfur compound that forms on or beneath the surface on the metal or alloy.

**sulfide stress cracking (SSC).** Brittle failure by cracking under the combined action of *tensile stress* and *corrosion* in the presence of water and hydrogen sulfide. See also *environmental cracking*.

## T

**tarnish.** Surface discoloration of a metal caused by formation of a thin film of corrosion product.

**transgranular.** Through or across crystals or grains. Also called intracrystalline or transcrystalline.

**transgranular cracking.** Cracking or fracturing that occurs through or across a crystal or grain. Also called transcrystalline cracking. Contrast with *intergranular cracking*.

**tuberculation.** The formation of *localized corrosion* products scattered over the surface in the form of knoblike mounds called tubercules.

## U, V

**uniform corrosion.** (1) A type of corrosion attack (deterioration) uniformly distributed over a metal surface. (2) Corrosion that proceeds at approximately the same rate over a metal surface. Also called general corrosion.

**voids.** A term generally applied to paints to describe *holidays*, holes, and skips in a *film*. Also used to describe shrinkage in castings and welds.

## W

**weld cracking.** Cracking that occurs in the weld metal.

**weld decay.** *Intergranular corrosion*, usually of stainless steels or certain nickel-base alloys, that occurs as the result of *sensitization* in the *heat-affected zone* during the welding operation.

**white rust.** Zinc oxide; the powdery product of corrosion of zinc or zinc-coated surfaces.

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