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A Working Party Report on

**Microbiological Degradation
of Materials — and Methods
of Protection**

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by The Institute of Materials*

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European Federation of Corrosion Publications

Series Introduction

The EFC, incorporated in Belgium, was founded in 1955 with the purpose of promoting European co-operation in the fields of research into corrosion and corrosion prevention.

Membership is based upon participation by corrosion societies and committees in technical Working Parties. Member societies appoint delegates to Working Parties, whose membership is expanded by personal corresponding membership.

The activities of the Working Parties cover corrosion topics associated with inhibition, education, reinforcement in concrete, microbial effects, hot gases and combustion products, environment sensitive fracture, marine environments, surface science, physico-chemical methods of measurement, the nuclear industry, computer based information systems and corrosion in the oil and gas industry. Working Parties on other topics are established as required.

The Working Parties function in various ways, e.g. by preparing reports, organising symposia, conducting intensive courses and producing instructional material, including films. The activities of the Working Parties are co-ordinated, through a Science and Technology Advisory Committee, by the Scientific Secretary.

The administration of the EFC is handled by three Secretariats: DECHEMA e. V. in Germany, the Société de Chimie Industrielle in France, and The Institute of Materials in the United Kingdom. These three Secretariats meet at the Board of Administrators of the EFC. There is an annual General Assembly at which delegates from all member societies meet to determine and approve EFC policy. News of EFC activities, forthcoming conferences, courses etc. is published in a range of accredited corrosion and certain other journals throughout Europe. More detailed descriptions of activities are given in a Newsletter prepared by the Scientific Secretary.

The output of the EFC takes various forms. Papers on particular topics, for example, reviews or results of experimental work, may be published in scientific and technical journals in one or more countries in Europe. Conference proceedings are often published by the organisation responsible for the conference.

In 1987 the, then, Institute of Metals was appointed as the official EFC publisher. Although the arrangement is non-exclusive and other routes for publication are still available, it is expected that the Working Parties of the EFC will use The Institute of Materials for publication of reports, proceedings etc. wherever possible.

The name of The Institute of Metals was changed to The Institute of Materials with effect from 1 January 1992. This follows the agreement upon the merger of the Institute with The Plastics and Rubber Institute and The Institute of Ceramics. The complete integration of PRI and I. Ceram. within the Institute of Materials is expected by the end of 1992, though as at January 1992, both these bodies still exist independently. The address, main telephone and fax numbers and VAT numbers are unchanged.

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Series Introduction

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Foreword

Microbial Degradation of Materials and their Protection as an interdisciplinary field comprising microbiology and materials science has received increasing attention in recent years from scientists and engineers. In this study the state of the art and the desired development of R & D activities is analysed and presented. The study includes not only the microbial corrosion of all types of materials (metallic, inorganic and organic) but also desired effects such as leaching of ores and refinement of materials such as clay and carbon.

The chapters of this book have been prepared by members of the DECHEMA e. V. working party 'Microbial Materials Degradation and Protection', Frankfurt, and have been authorised by the EFC working party 'Microbial Corrosion'. Editors and authors are listed below.

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Introduction

Microorganisms can grow on materials of construction which may be metallic, ceramic, or organic — both natural and artificial — and also on “auxiliary” materials, i.e. those, such as paints, adhesives, plasters, hydrocarbons, used in assembling, treating or decorating construction materials. This growth may result in undesirable changes in the properties of the materials, sometimes leading to their destruction. This study treats microbiological destruction of materials as a whole. The microorganisms involved include bacteria, fungi, algae and lichens but higher organisms are not included. Similarly, the microbiological deterioration of food, drugs (pharmaceuticals) and cosmetics is not an objective of this study.

However, materials and raw materials can also be improved or obtained by microbiological activities and these aspects as well as the destructive effects of microbial action will be discussed. Thus, besides the involvement of microorganisms in the deterioration of materials it is equally important to recognise their use in naturally occurring processes, e.g. copper production by oxidation of CuS in heaps of low grade copper-ore which would be unsuitable for metallurgical processing. Leaching of low grade ores is of growing interest at the moment after having been neglected apart from in a few operational plants for many years. Ceramic materials like kaoline for china (porcelain) are often brown-coloured by iron oxides. Successful attempts have been made to eliminate the iron by leaching using iron-reducing or complexing agents produced by microorganisms. Carbonaceous components can be partially liquefied by the action of surface active substances produced by microbial action. The costs of transporting coal can be reduced by transforming the coal microbiologically into a pumpable suspension (see 4.8.4.). Sulphur removal from coal by microorganisms is also possible.

Microorganisms are omnipresent in an active or a quiescent condition, although they can be detected visually only if present in very high numbers. Their occurrence is restricted by lack of water or by temperatures below -10°C or above 110°C .

The diversity of metabolism makes microorganisms indispensable for mankind. A long time before the era of biotechnology, bacteria and fungi were used for the production of foodstuffs, luxuries and antibiotics as well as for leaching of low grade ores and the degradation of wastes and noxious residues.

Only bacteria and fungi take part in the natural carbon and nitrogen cycles in which plants and animals are eventually transformed into carbon dioxide, water, nitrate, phosphate, sulphate, and humic compounds. By the diversity of their biological activities microorganisms are able to populate materials and auxiliary materials, although metals and ceramic materials do not act as nutrients. On the other hand, organic matter can be attacked directly and destroyed (e.g. wood, paper, leather, some plastics) or damaged as a result of attack of additives (e.g. plasticisers) etc. It is difficult to estimate the economic losses resulting from microbiological deterioration of materials since any evaluation must consider not only the deterioration *per se* but also the financial costs incurred in the protection of materials. Indirect damage caused by the shutdown of production in plants must also be considered.

Research and development in the field of destruction and protection of materials requires close cooperation of several disciplines. First of all, microbiologists interested in applied sciences are needed, and then cooperation is required from all branches of the natural and technical sciences, e.g. physicists and engineers, chemists and architects with practical and

research experience. They have to recognise and to explain microbiologically influenced corrosion, identify the causes and establish remedial measures. The education and professional experience of microbiologists have little in common with that of those workers in other disciplines and there is a lot of scepticism among the latter. The usual approach follows the route: corrosion damage appears, microorganisms are recognised to be the cause, biocides are put to work, the responsible factors are eliminated and the plant continues to run at reasonable cost. Some problems can be solved in this way but — without question — no systematic materials protection scheme taking into account all the particular environmental conditions will have been used.

As for other interdisciplinary fields, discussions organised by scientific–technical societies and research institutions are very valuable since only in this way is it possible to cover efficiently this very complex field.

Influenced by the evident economic importance of the subject, the Committee for Scientific Research of the OECD initiated a research program in 1962 on the biological deterioration of materials. Mr. G. Becker (Bundesanstalt für Materialprüfung — BAM, Berlin) became leader of the German group. Between 1965 and 1970 five meetings were held supported by Deutsche Forschungsgemeinschaft (DFG) and these which led to the eventual production of the memorandum — “Applied Research: Organisms and Materials” — compiled by Mr. G. Becker and edited by DFG.

Since 1981 microbiologists in the field of microbiological deterioration of materials and materials protection have met regularly under the leadership of Prof. Dr. R. Schweisfurth. Their purpose was, and still is, to initiate advances in research and the awareness of biodeterioration of materials. At the occasion of a symposium supported by the VW-foundation and the BAM, this group was adopted as a subcommittee of DECHEMA’s biotechnology working parties. The objective of this subcommittee was to achieve, by involving microbiologists, the advancement of research in this field as well as the spreading of knowledge regarding microbiological deterioration of materials. The International Biodeterioration Research Group (IBRG) — based in the UK — was founded in the nineteen sixties as a group of experts of the OECD. Scientists and technologists engaged in problems of biologically influenced deterioration of materials were brought together. At the present time IBRG includes a number of groups: “Taxonomy/Ecology”, “Constructional Materials (except wood)”, “Problems of Industry”, “Cooling & Lubricating Agents”, “Corrosion by Microorganisms”, “Painting Materials”, and “Synthetic Materials”. The International Research Group on Wood-Preservation (IRGWP) was founded in 1969 to continue the activities started in the OECD-working group on wood preservation. Initially IRGWP had 22 members from 9 countries and the first chairman was G. Becker (BAM) from 1969 to 1973. A number of subgroups exist, e.g. “Biologically important problems in the study of wood preservation”, “Fundamentals of testing”, “Methods of treatments” etc.

The working party “Microbial Corrosion” of the European Federation of Corrosion under the chairmanship of Ken Tiller, Teddington, was founded in 1987 and has developed a number of activities in this field.

The National Association of Corrosion Engineers (NACE) from the USA has organised meetings and produced interesting publications in the field of biocorrosion of materials.

In Germany the journal *Material und Organismen* (i.e. “Materials and Organisms”) first appeared in 1966; another, *Dokumentation: Biologische Materialprüfung — Organismen und Werkstoffe* (Documentation: Biological Materials testing — Organisms and Materials”) appeared in 1981. Both are edited by Bundesanstalt für Materialprüfung, Fachgruppe Biologische Materialprüfung, Berlin. Single papers on microbiological deterioration of materials are published from time to time as special reviews, e.g. in *Werkstoffe und Korrosion*. One review in

that journal contains the results of the research program on “Corrosion and Corrosion Protection” of the BMFT, project management by DECHEMA, Frankfurt.

In the English speaking countries the review “Biofouling” (Harwood Academic publ.) has recently appeared. Contributions to microbiological materials deterioration appear also in the following: *Advances in Applied Microbiology*, *Applied and Environmental Microbiology*, *Developments in Industrial Microbiology and Materials Performance* (formerly *Materials Protection and Performance*), *Microbiology Abstracts* — Section A: Industrial and Applied Microbiology, Current Contents — Life Science, Agriculture, Biology Environmental Science also contain references.

In the UK the journal *International Biodeterioration* regularly publishes relevant papers.

The essential problems for microbiological research in this field are treated in section 8.

Knowledge of materials degradation and protection is directly related to environmental problems since what is not destroyed, will not have to be produced again.

Although the study was initiated and conducted in the Federal Republic of Germany, the phenomena investigated and the test methods and procedures used in combating the problem are clearly of international importance. For this reason, it was thought appropriate that an English language version should appear in the series of publications of the European Federation of Corrosion (EFC). Discussions with the chairman of the Microbial Corrosion Working Party of the EFC, of which some of the DECHEMA authors are members, resulted in agreement that the study should be published in the EFC series as a Working Party Report.

Microbiological Fundamentals

2.1. Microorganisms

2.1.1. Bacteria

Bacteria differ from other living organisms by their lack of a real membrane-coated nucleus (prokaryotes), by a chemically specific cell membrane structure, and by their small size (approx. 1 μm diameter). They are only poorly differentiated morphologically i.e. into cocci, straight and curved, ramified forms. Some are mobile by flagellae and can excrete slimes. Cyanobacteria contain blue-green pigments necessary for CO_2 -assimilation, as in the cases of green algae and plants. The majority of bacteria use organic matter as their carbon and energy source (heterotrophy). Other bacteria exist autotrophically, i.e. their energy source for the CO_2 assimilation that is required to build up cell material comes from the oxidation of inorganic compounds (lithotrophy).

2.1.2. Fungi and yeasts

Filamentous fungi contain a real nucleus and are eucaryotes. Their cell size is approximately 10 times that of bacteria, they form mycelia (cell networks) and are morphologically highly differentiated. They are heterotrophic and oxygen is necessary for their existence. Classification of fungi is based on the principal growth forms and by the method of sporulation in the conidiophores.

As a rule, yeasts form oval cells and propagate by budding. They do not form mycelia and can live even in anaerobic conditions.

2.1.3. Algae

Algae are mono-or multicellular phototrophic microorganisms of green, yellow, or brown colour with the pigments localised in chromatophores. Classification of algae is based on their pigments and morphology.

2.1.4. Lichens

Lichens result from a union of fungal hyphae with algae, forming a morphological and physiological unity. The algae present in lichens are monocellular or filamentous cyanobacteria or chlorophyceae. The fungi are almost exclusively ascomycetes and form lichens, although basidiomy participate. The configuration of lichens depends in some cases on the structure of the algae involved, but more frequently on that of the fungus.

Algae in lichens multiply only vegetatively and their cell size is greater than that of free living species.

Fungi in lichens develop a typical fruiting body (peritheziae and apotheziae).

2.2. Metabolism

2.2.1. Bacteria

Some groups of bacteria use inorganic reduced compounds as their energy source: CO , S^{2-} , S° , NO_2^- , NH_4^+ , Fe^{2+} , and H_2 .

These compounds are oxidised and the liberated energy is used to reduce carbon dioxide to organic compounds as well as for maintenance of metabolism (chemolithotrophy). Final products of this metabolism are CO_2 , SO_4^{2-} , NO_3^- , Fe^{3+} , and H_2O . Most bacteria of this group need oxygen (aerobes) and some can reduce NO_3^- , NO_2^- , N_2O , or CO_2 in the absence of oxygen (anaerobes).

The majority of chemolithotrophs grow with CO_2 or HCO_3^- as the carbon source (chemolithoautotrophy). They multiply independently of the presence of organic matter. They are often detected at unexpected locations as, for example, in waste water pipelines made of concrete in which they can produce sulphuric acid and liberate sand grains from concrete, or on natural stones where they can produce nitric acid and destroy the stone (see 4.2.).

Most species, genera and families of bacteria use organic compounds as their energy- and carbon source. They produce CO_2 and H_2O , and slowly degrade humic compounds although, depending on the species involved and on the substrate to be degraded, the final product will not necessarily be one of these. For example, some bacteria degrade cellulose to organic acids which can then be used by other bacteria so that communities of different species of micro-organisms are formed which are dependent on each other.

Sometimes the degradation of a substrate containing several types of organic compounds can occur only if bacteria and fungi are present together. The degradation of wood in soil (see 4.4.2.) is an example.

Bacteria and fungi are rarely specific in degrading only a single organic substrate. Thus, *Pseudomonas aeruginosa* uses sugar and alcohols as well as hydrocarbons. It is also able to use human proteins so becoming pathogenic to human beings. The use of different substrates is possible by enzymatic adaptation.

The number of degradable organic compounds is much higher than that of undegradable ones. It can be assumed that all natural compounds are degradable. This assumption is also true for most synthetic compounds. Degradation of some of these "xenobiotica" (foreign compounds) such as insecticides, pesticides or polychlorinated compounds is difficult, i.e. very slow. Polymers like polymethyl-methacrylate (plexiglas) are not degradable, but additives present in polymeric materials can be attacked (see 4.5.2.). Some of these materials which are difficult to degrade can be attacked only if a usable nutrient is present (co-metabolism).

The degradability of an organic compound is also dependent on the conditions under which degradation takes place, thus, pure hydrocarbons can be produced only if oxygen is present, unless the oxygen in other compounds for example, nitrate, is available as a hydrogen acceptor.

Multiplication of heterotrophic bacteria is influenced by the concentration of the compounds involved and depends on the species and concentrations of N, S, P, and also of trace elements. If nitrogen compounds and phosphate reach a minimum level of concentration the degradation of organic compounds can stop.

2.2.2. Fungi

Fungi use organic compounds — sometimes even trace amounts — for their energy and carbon needs. Several fungi produce organic acids. Single hyphae can leave etch tracks on sensitive

glass. Some fungi form highly specialised mycelia, e.g. the dry rot house fungus. These mycelia can convey water and salt from the cellar of a house right up to the roof infecting the whole of the woodwork. Some fungi proliferate at low water activity (a_w -value, see 2.4.2.1.).

2.2.3. Algae

Algae need inorganic nitrogen compounds as well as CO_2 to build up their cell substance. They occur in sea and fresh water as well as in soil layers exposed to light and on trees. Algae settle on plaster and varnishes giving to them a green–gray colour (see 4.6.2.). They excrete organic compounds and some ammonium compounds, which are used by other microorganisms.

2.2.4. Lichens

Lichens represent a symbiosis of algae and fungi. The fungus receives organic compounds synthesised by CO_2 fixation from the algae. The fungi supply water and minerals and probably prevent the drying out of the algae.

Lichens penetrate into stones and “lichenic acids” and metabolites with complexing properties are responsible for destruction of these materials.

2.3. Microbiologically Influenced Element Cycles

All materials and auxiliary materials are involved in natural element cycles. Destruction of organic material occurs by mechanisms similar to those involved in the natural degradation of stones.

The first important step in the corrosion of metals is the formation of a soluble compound, which then enters into an immobilising and mobilising cycle. All organic materials and synthetic substances, hydrocarbons included, are transformed by microbial attack into shorter chain compounds, until finally CO_2 , or under anaerobic conditions, CH_4 , is formed. Humic compounds are formed in low concentrations.

A survey of the principal reactions is presented in the following figures. Many specific reactions derive from them.

2.3.1. The carbon cycle

Figure 2.1. shows a generalised carbon cycle. Figure 2.2. shows the microbiological reactions at the boundary between aerobic and anaerobic metabolisms in the carbon cycle.

In a biofilm which causes microbiological corrosion of metals, the same reactions occur as e.g., in a cooling circuit.

2.3.2. The nitrogen cycle

Figure 2.3. (on page 8) shows the nitrogen cycle. The most important corrosion-relevant components are nitric acid (nitrate), nitrous acid (nitrite), and ammonia (ammonium salts).

2.3.3. The sulphur cycle

Figure 2.4. (on page 9) shows the sulphur cycle. Table 4.1. and Section 4.3. show examples of relevant parts for corrosion of metals.

Mobilising, immobilising, and valence changes of elements like Fe, Mn, and P by microorganisms play an important role in corrosion of metals: oxidation and reduction of iron by bacteria and fungi depends on pH and redox-potential (see Fig. 2.5. on page 10).

The phenomena are very complex and further elucidation is needed.

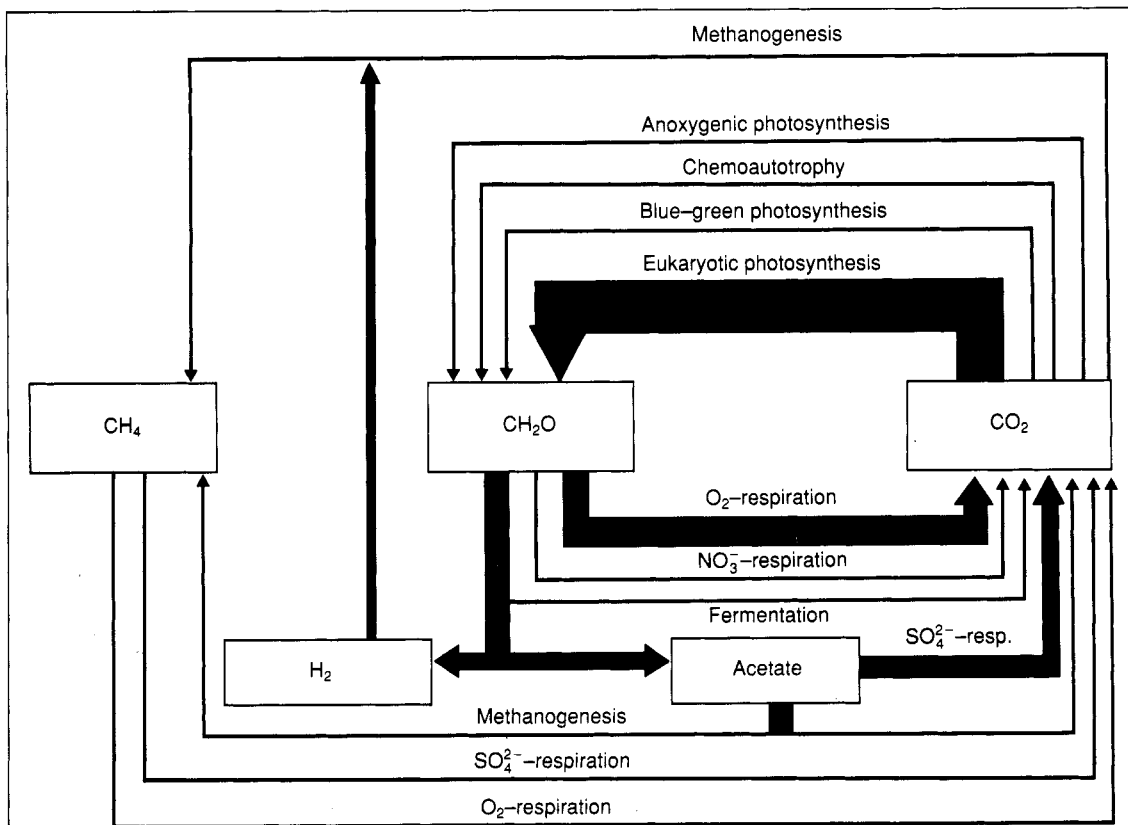


Fig. 2.1. Simplified carbon cycle [1].

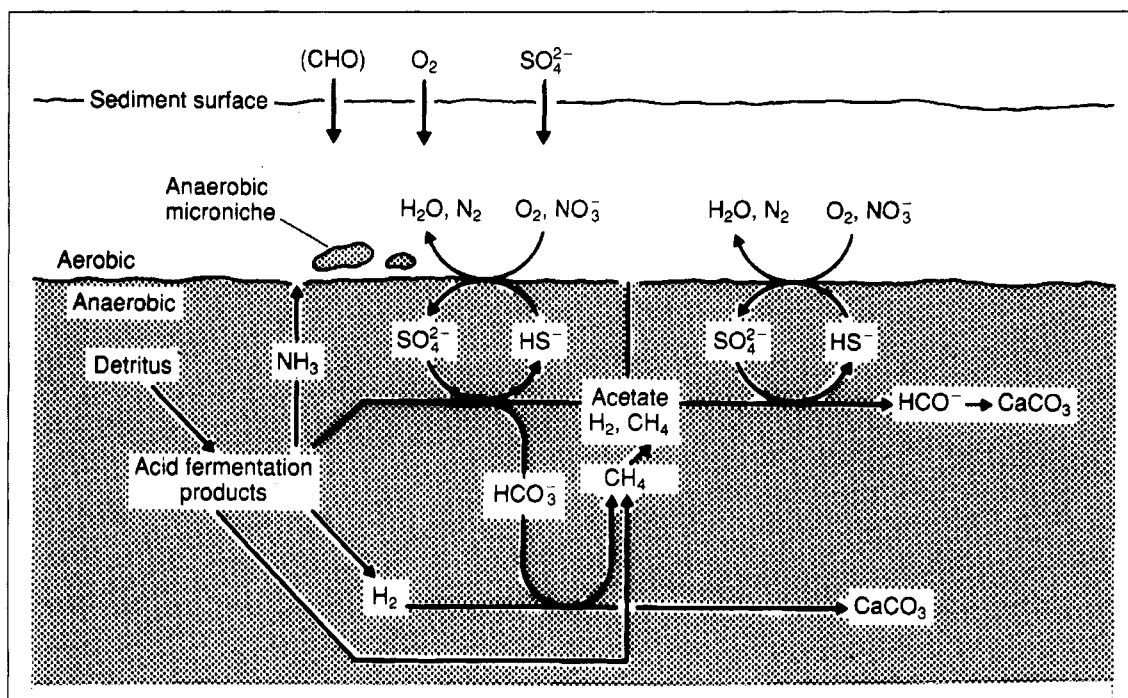


Fig. 2.2 Microbiological reactions at the boundary between aerobic and anaerobic conditions [1].

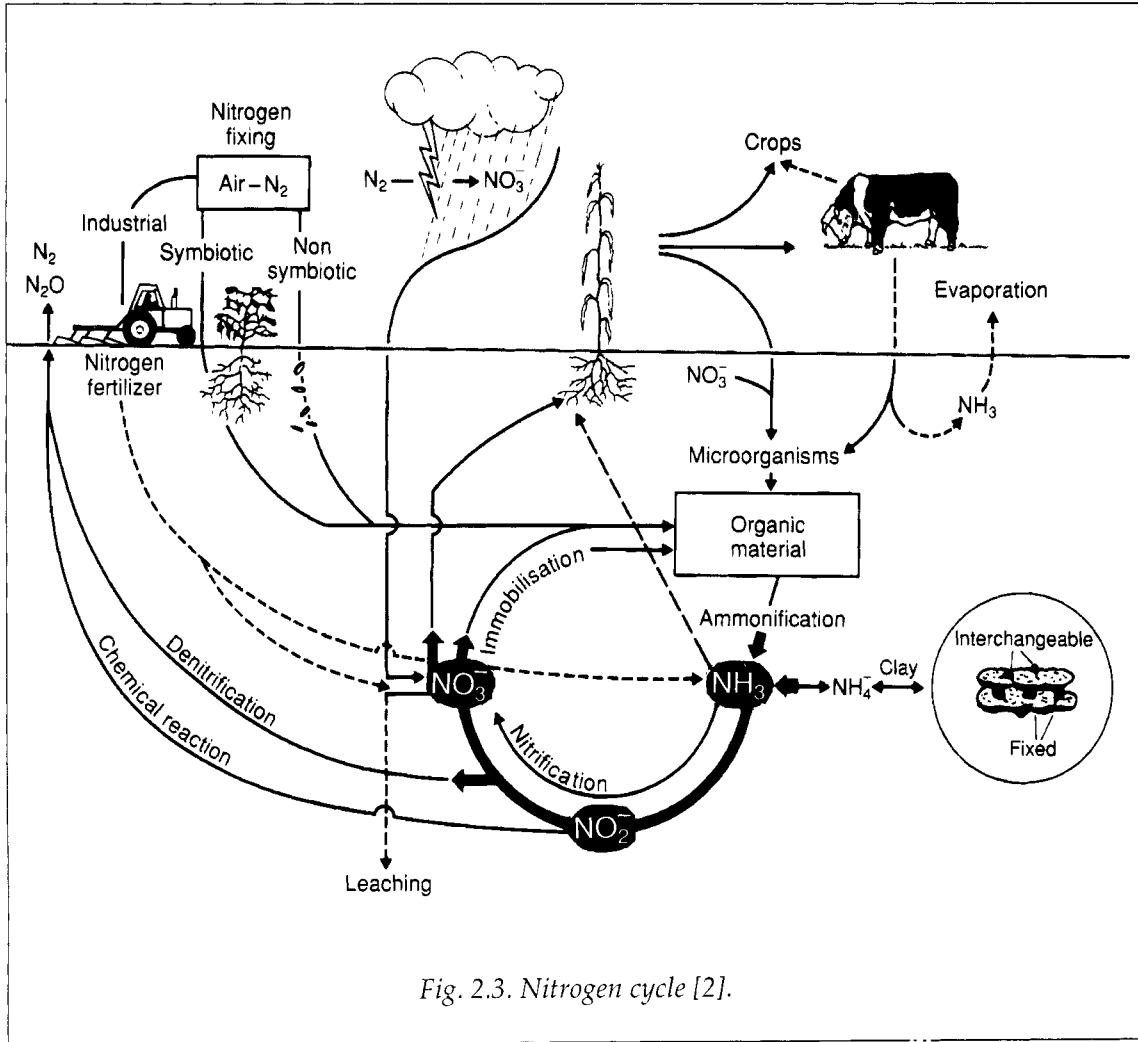


Fig. 2.3. Nitrogen cycle [2].

2.4. Growth and Proliferation of Microorganisms

2.4.1. Introduction

Knowledge of the growth requirements of microorganisms is very important for recognition and research on materials deterioration and protection. The most important parameters influencing growth of bacteria will be explained below.

2.4.2. Parameters of growth

2.4.2.1. WATER, WATER ACTIVITY

The demands of microorganisms for the water content of their substratum differ. The water activity a_w of the substrate is defined as:

$$a_w = \frac{p}{p_0}$$

where p is the pressure of the water vapour of the solution and p_0 is the vapour pressure of pure water at the same temperature.

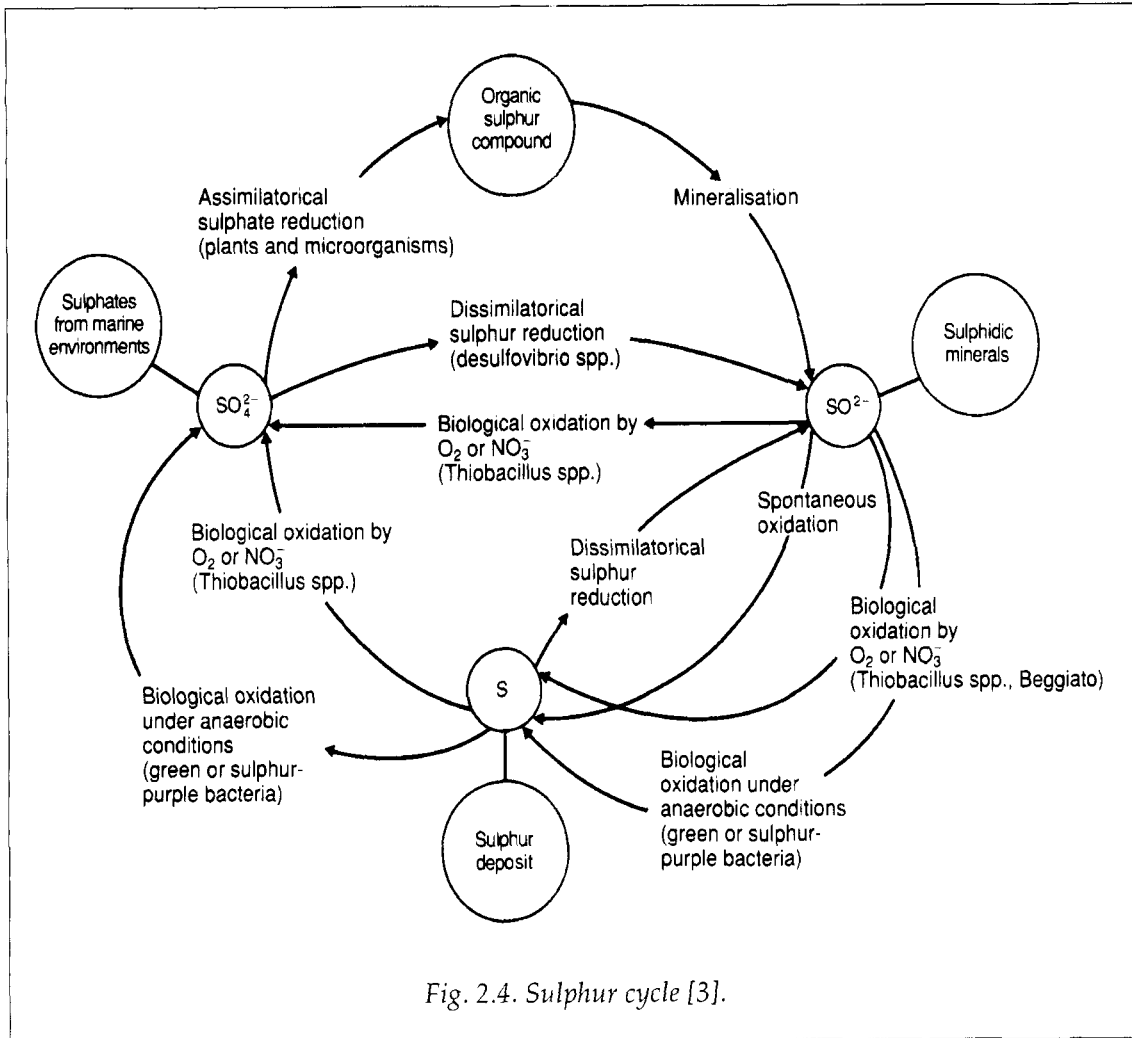


Fig. 2.4. Sulphur cycle [3].

Osmotolerant yeasts will still grow at an a_w -value of 0.6, moulds at an a_w -value of 0.8, but most bacteria need water activities of more than 0.98 [5, 6].

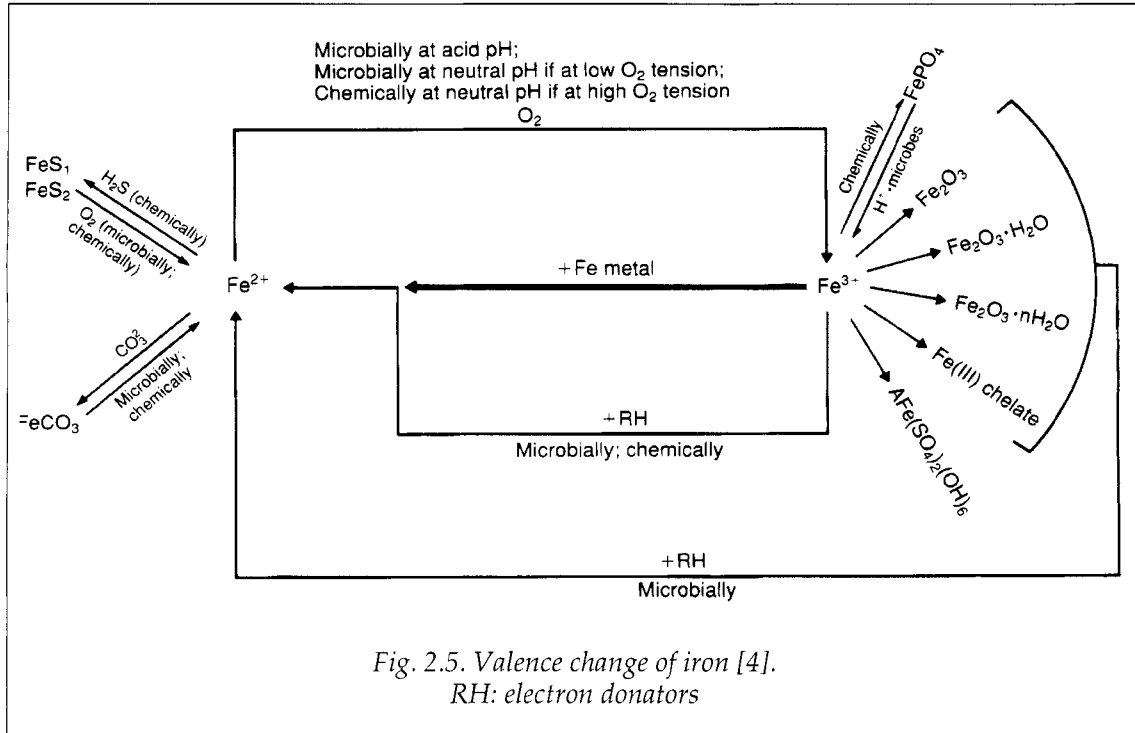
Periods of total dryness can be overcome by sporulation. Vegetative cells may use other mechanisms, e.g. formation of slimes.

Water always contains inorganic and organic compounds which are usable as nutrients. Bidistilled or deionised water contain sufficient inorganic and organic nutrients for limited growth of bacteria and algae.

Cooling water, as used for example, in industrial plant, is cooled by air streams and the intimate contact of water with the air can lead to solution of some compounds present in the air. The dissolved compounds are sufficient to permit buildup of biofilms in the cooling systems. In this case proliferation of microorganisms can occur more readily than in laboratory systems using batch cultures.

2.4.2.2. NUTRIENTS

The elemental analysis of microbial biomass shows that C, O, H, N, S, P, K, Ca, Mg, and Fe are present in all microorganisms. Trace elements like Mn, Mo, Zn, Cu, Co, Ni, V, B, Cl, Na, Se, Si and W are not needed by all microorganisms. We may assume that trace elements are always



present naturally and that only in cases of massive proliferation of bacteria or fungi (e.g. in the case of an accidental presence of excessive amounts of hydrocarbons in the soil) will N, P, or a trace element reach a minimum value that will slow down or even stop further microbial growth.

Some microorganisms are not able to synthesise vitamins, aminoacids, purines or pyrimidines. These must be present in the biotope, for instance via formation by other microorganisms. Vitamin solutions for laboratory cultures may contain biotine, nicotinic acid, thoamine, 4-aminobenzoate, panthotenate, pyridoxamine and cyanocobalamine.

Under natural conditions in which materials deterioration occurs we always have mixed cultures. The populations of microorganisms will contain producers and users e.g. vitamins. This means that not only the characteristics of the biotope but also the actual microorganisms are important in determining the composition of a biofilm.

The carbon source (see 2.3.1.) for chemolithotrophic bacteria and also for phototrophic bacteria and algae is CO_2 or HCO_3^- . All other bacteria and fungi need organic compounds as carbon and energy sources. Some bacteria are in an intermediate position: *Desulphovibrio vulgaris* uses carbon dioxide and acetate as carbon source and obtain energy by oxidation of hydrogen only. This use of hydrogen makes this organism important in the anaerobic corrosion of metals.

Nitrogen sources are N_2 , NO_3^- , NH_4^+ , and organic nitrogen compounds. Fixation of nitrogen from air or water is achieved only by bacteria.

The bacteria of interest here can grow aerobically (*Azotobacter*, *Azomonas*, *Azospirillum*, *Cyanobacteria*) or anaerobically (*Clostridium*). Nitrogen fixation in soil occurs primarily by bacteria living in symbiosis with leguminoses or with certain other plants. Nodules are formed on the roots of these plants, where nitrogen fixing bacteria live in small tuberculi. Sulphur and phosphorus are picked up as sulphate and phosphate and built into the cell substance. The hypothetical general formula of a bacterial cell ($C_{106} H_{203} N_{16} P$) indicate that absence of phosphorus or of nitrogen can cause inhibition of growth.

Oligotrophic bacteria need only low concentrations of organic carbon- and energy sources as well as of organic nitrogen compounds in their biotope. In the laboratory they can be grown in the presence of as little as 1–5 mg/l of an organic substance [7].

2.4.2.3. TEMPERATURE

Many bacteria show optimal growth at temperatures between 20 and 42°C (mesophilic bacteria). This statement is made very often, but not necessarily true. The experimental data on which it is based are generally obtained using pure cultures under laboratory conditions, i.e. conditions which are not encountered in natural conditions. In the latter situation we often lack information about the composition and proliferation rate of the species.

The physico-chemical rule about doubling of the reaction speed by a rise in temperature of 10°C may be true for enzymatic reactions within close limits, but it becomes irrelevant for populations of microorganisms. Increasing the temperature at a particular location in which there are a number of bacterial species, will lead to proliferation of the more thermophilic. In this case the species composition but not necessarily their quality will also change.

Bacteria also grow at lower temperatures (+20 to -10°C). Porous rocks around water pipelines of a constant temperature of +10°C may contain up to 10⁵ bacteria per gram dry weight. Cultivation of arctic soil samples at +2°C provides up to 10⁵ bacteria per gram dry weight. Antarctic permafrost soils contain living bacteria even at a depth of 40 cm.

The temperature limits are not always reliably known. It may be assumed that some microorganisms grow only at the temperature of their location, e.g. +10°C and do not grow at higher temperatures. Other microorganisms from cold locations can be cultivated and show optimal proliferation at temperatures of 20°C or even 28°C.

Microorganisms can multiply even at temperatures higher than 44°C (thermophilic microorganisms) and extremely thermophilic bacteria can show optimum growth up to 105°C.

2.4.2.4. OXYGEN, REDOX POTENTIAL

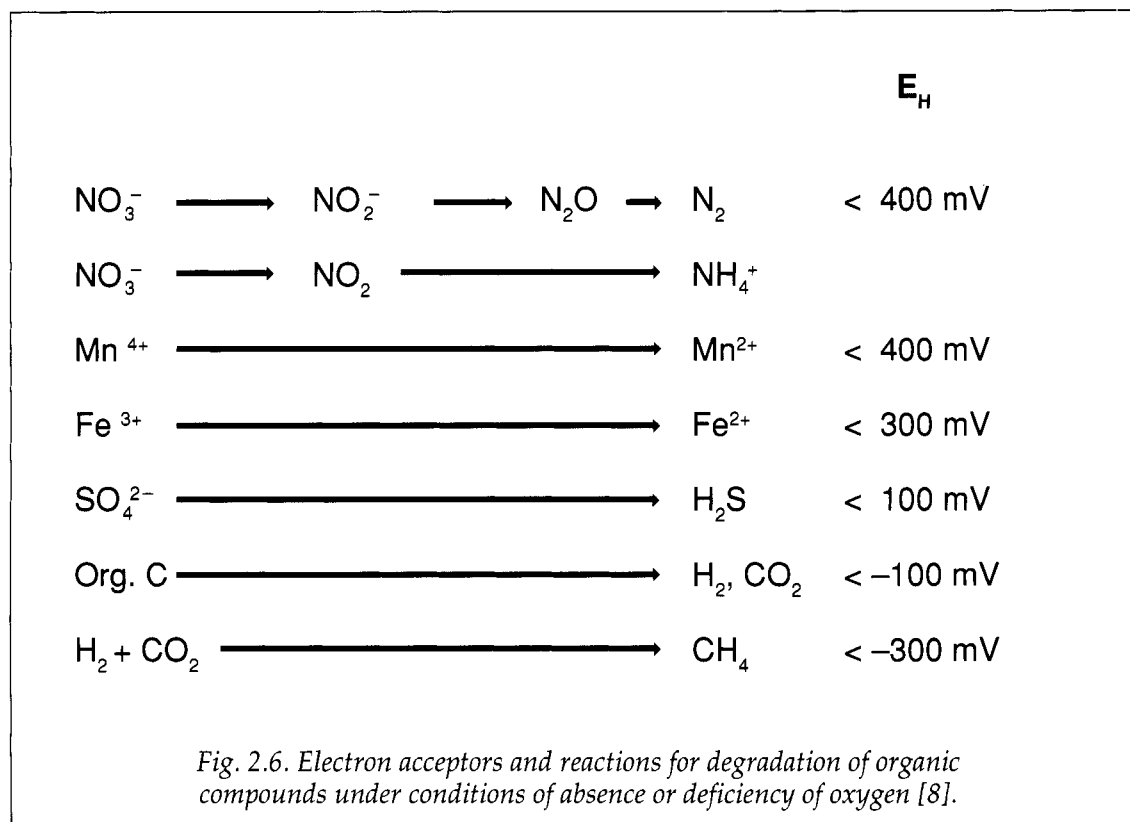
Many bacteria including all cyanobacteria as well as fungi and algae are aerobic organisms, i.e. they grow only if free oxygen in the atmosphere or dissolved in water, is present. Most species of bacteria can be designated as "facultatively anaerobic", because they can multiply with or without oxygen present although anaerobic multiplying can slow down the growth rate. Qualitative and quantitative changes of the excreted metabolites can also occur. "Obligate anaerobic bacteria" proliferate only when oxygen is absent.

Under conditions of oxygen deficiency or under anaerobic conditions aerobic bacteria, facultatively anaerobic, and anaerobic bacteria, as well as some fungi are able to reduce inorganic compounds. The similarity with aerobic metabolism is maintained, but the hydrogen, which is usually transferred to free oxygen with formation of H₂O is now transferred to other electron acceptors such as nitrate or sulphate, i.e. containing chemically bound oxygen, which is then reduced. In either case the resulting product is water. Some of the reduced electron acceptors may be used again if oxygen enters the system (see Fig. 2.6. on page 12).

If E_H-values of 0 mV are measured in a biotope it must be assumed not only that oxygen is absent but that microorganisms have formed and eliminated reducing agents. E_H and pH values are closely related, alkaline conditions favouring oxidation and acidic conditions favouring reduction.

These reactions allow the conclusion to be drawn that, for instance, manganese or iron reduction will occur only after the nitrate content of the biotope has been consumed, i.e. the nitrate has been transformed into N₂ or NH₄⁺.

The location of the reactions is quite irrelevant. They may occur in a sediment, in a filtering river bank strip for winning of drinking water, in the water and/or the sediment of a lake, in a cooling pipe with a biolayer (biofilm) growth on its inner surface, or in a waste deposit. The processes in these various situations are essential for the maintenance of the carbon, nitrogen and sulphur cycle (see 2.3.).



The redox potential (E_H -value) depends on the redox systems present in the biotope, especially oxygen. The E_H value is a determining factor for the activity of microorganisms. Water containing dissolved oxygen shows an E_H -value of about +400mV.

Usually mobilising of iron, which is insoluble as Fe^{3+} , occurs microbiologically. Figure 2.7. shows a thermodynamically calculated stability diagram.

It is recommended that pH and E_H values measured in experimental work should always be quoted. Ions such as sulphate and hydrogen carbonate can however modify the redox behaviour of metal species.

2.4.2.5. pH VALUE

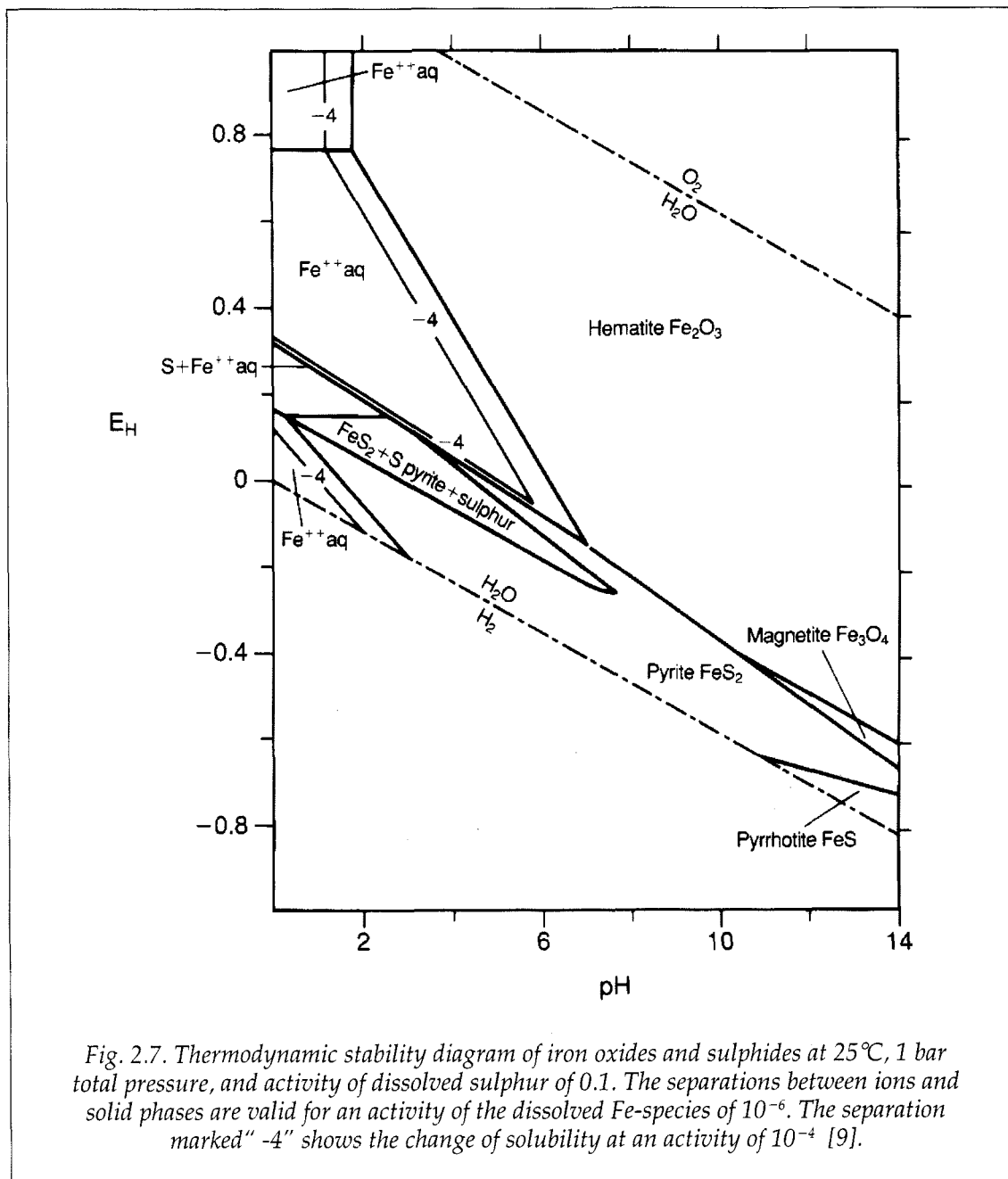
Most bacteria and algae prefer a pH-value near to neutral, i.e. between 6 and 8. Fungi prefer pH-values around 5 — at least in the laboratory cultures — although values between 2 and 12 may be tolerated.

In certain natural and artificial locations microorganisms can show optimum development at very acidic and very alkaline pH values.

Thiobacillus ferrooxidans, for example, is a chemolithoautotrophic bacterium and needs a pH of below 3. It oxidises S^{2-} to sulphuric acid and can be used to leach low grade copper or uranium ores. Under such conditions a heterotrophic flora or bacteria and fungi can also grow (see 4.8.3.).

2.4.3. Kinetics of growth

In the laboratory, pure cultures of microorganisms develop rapidly or slowly depending on species and genus. In optimum conditions cell division may occur every 20–30 minutes. In a certain volume of an optimum nutrient solution microorganisms will behave as follows: first,



the resting cells multiply their enzymes, they then reach the maximum cell division rate; because of a new resting period which is reached in a few hours of days as a result of total consumption of the nutrients or accumulation of inhibitors and finally a period of variable length in which the bacteria die off.

These optimum conditions do not necessarily occur in the case of the microbiologically influenced deterioration of materials since under both natural and artificial conditions a continuous, (slow, or rapid) input of nutrients or output of metabolites will be taking place — provided they are not used by adjoining bacteria. The population then represents a flow culture, and this can be reproduced in the laboratory.

A shortage of nutrients is of little influence, because usually the population is fixed in a biofilm that is provided with nutrients (see 2.4.4.). Bacteria and fungi multiplying in aqueous solutions (e.g. cooling–lubricating fluids, see 4.7.4.) reach very high cell numbers (10^8 /ml), because of the regular supply of fresh lubricant into the system.

Microbiological corrosion of ceramic or metallic materials is in most cases a process that will require a long time. It may be the case that without microorganisms the process would not take place at all or would progress much more slowly. For example, an underground steel-pipeline protected with an external layer of bitumen can be corroded by microorganisms within months or within years depending on the rate of nutrient supply whereas consumption of the nutrient in a cooling lubricating emulsion will take place in a few hours or days.

2.4.4. Growth forms: biofilm formation

Because of their small size (0.5 to 1–2 μ m) bacteria are able to penetrate pores of ceramic materials. That is why as much as 2/3 of the number of heterotrophic bacteria found in the 2 cm thick surface layer [10] can still be found 12–14 cm from the surface of sandstone.

On metallic materials bacteria can settle on the surface to form a biofilm. If the nutrient source is a natural or artificial organic compound then fungi, in particular, will penetrate into it. Plastics placed for 3 months in water become coated with a deposit of some mm thickness (see 4.5.). Biofilms are of special interest because they represent the living form of microbial communities.

In nature bacteria grow on all surfaces. Some evaluations have established that up to 90% of bacterial activity takes place in biofilms. Bacteria settle on the surface of materials of very different compositions and therefore, it would appear that there is no single mechanism of adhesion. In this complex system a lot of questions are still unanswered [11].

In the case of an unsterile contact between a liquid medium and a solid, bacteria will practically always adhere to the latter. This is also true for the contact between humid air and surfaces. The nature of the adherence is determined by three factors:

- (a) those relating to the microorganism (e.g. species, composition of the mixed population, growth phase, nutritional condition, surface charge, hydrophobicity);
- (b) those relating to the surface (e.g. chemical composition, surface energy, surface charge, surface tension, hydrophobicity, roughness);
- (c) those relating to the water (e.g. temperature, pH, oxygen concentration, content of organic and inorganic compounds, viscosity, surface tension, hydrodynamics).

Bacterial adhesion is a time-dependent process and can be divided into several phases:

First phase:

“The conditioning film”: adsorption of compounds from water on to the surface (bacterial adhesion).

Second phase:

Reversible adhesion: bacteria reach the surface by several transport mechanisms (convection, colloids [14, 15]. Depending on the distance between the particle and the surface the zeta potential allows two adhesion maxima to be predicted. Unfortunately, to do this, the properties of the particles must be idealised (e.g. they must be spherical, inert and with no interactions), so such calculations will permit no practical prediction [16].

Nutritional condition, growth phase, ionic strength, ionic species, charge conditions (on both the surface and the bacteria) and concentration of suspended cells all strongly influence the adhesion phase which can occupy minutes or hours. It is followed either by the third phase or ended by detachment of the bacteria from the solid surface.

Third phase:

“Irreversible adhesion”: the bacteria show no more Brownian molecular movement and they cannot be removed by rinsing. Adherence is due to chemical bonding (electrostatic, covalent, hydrogen), dipolar interactions and/or hydrophobic interactions. Extracellular polymeric compounds (EPS, glycocalyx) play a special role [17] by acting as the “adhesive”, i.e. “polymer bridging” between microorganisms and the surface). In some cases they are excreted as a response to adhesion (“active adhesion”), but they may be formed in the suspension thus making the cells “sticky” [18].

Fourth phase:

“Biofilm”: the irreversibly adhering bacteria multiply on the surface; additional cells settle on the biofilm and so a multilayer coating is built up; significant quantities of extracellular materials can be released (slimes). Bacteria from the inner side of the adhering biofilm will also multiply. These will be mainly anaerobic bacteria, as a result of the oxygen deficiency that will develop with time at the inner side of the biofilm.

Usually, the biofilm will contain several species, which will excrete different extracellular polymeric substances (EPS). These EPS are mostly acidic polysaccharides, but lipopolysaccharides, proteins, glycoproteins, lipids and glycolipids will also be present. Their different charge and complexing properties may cause local differences in the charge and solubility of the surface material. This may be the reason for the occurrence of bacterially influenced corrosion [19].

In the biofilm, i.e. as compared with the suspension, bacteria will be protected against biocides since these must penetrate into the film with correspondingly longer diffusion times. Biocides may also be consumed by reaction with the EPS (e.g. chlorine) [20]. Furthermore, biocide consumption by reaction with dead bacterial matter in the outer layer of the biofilm will protect the deeper layers against biocide action. All standardised activity tests for biocides refer to suspended and not to settled bacteria, and so these tests cannot say anything about the effectiveness of the biocides on microorganisms in biofilms. Some of the differences between laboratory studies and experience in practice can be accounted for by these considerations.

Fifth phase:

Removal of parts of the biofilm. After further growth, parts of the biofilm can be removed from the surface by the action of “streaming stresses” (shearing forces) or other features of the system. Cells which are lost in this way may settle at other sites and where a high local cell density develops this will favour adhesion. In this way the biofilm may eventually spread completely over a natural or artificial system.

Adhesion may be facilitated by polysaccharides (e.g. lipopolysaccharides, acidic polysaccharides), proteins (fimbriae, cell wall proteins), lipids (e.g. 1 mycobacteria on hydrophobic media [21]), or by a combination of these although the details of the interactions between these substances and the surfaces are not fully understood. Also, some species show different mechanisms of adhesion depending on whether the surfaces are hydrophobic or hydrophilic.

The parameters of surface charge, hydrophobicity, surface tension, etc. do not allow us to establish any general rules governing the colonisation of a surface and the prediction of the adhesion behaviour is possible only in a few cases with the present state of knowledge.

The phenomena are presented schematically in Fig. 2.8. (see over page).

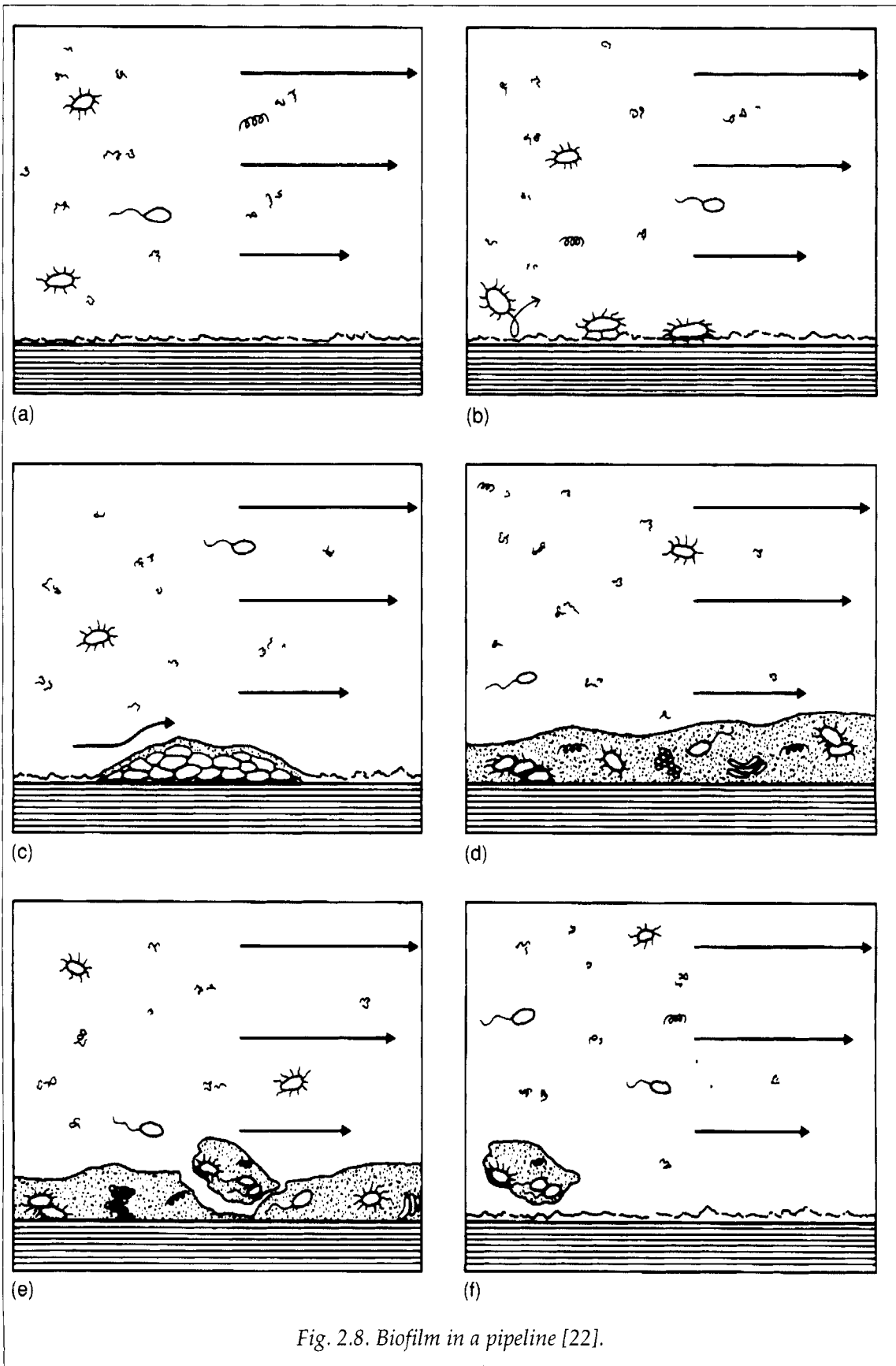


Fig. 2.8. Biofilm in a pipeline [22].

- (a) A “conditioning film” of macromolecules adheres to the metallic surface.
- (b) Primary adhesion; from the left: bacteria detach from the surface; reversible and irreversible adhesion.
- (c) Formation of microcolonies by cell division of adherent bacteria and self-protection by excretion of EPS.
- (d) A biofilm is formed, bacteria are embedded in EPS, the cross section of the pipeline is reduced by the thickness of the biofilm.
- (e) Parts of the biofilm are removed by the flow of the solution.
- (f) Bacteria coming from other parts of the biofilm settle on the free surface, the biofilm expands over the whole system.

Depending upon nutritional conditions many microbiological processes can take place in a biofilm — as described in 2.3. In most cases the oxygen content will have a great influence. The oxygen content essentially determines how well the microorganisms are provided with organic and inorganic compounds, since oxygen is consumed in the transformation of these compounds. Therefore, in a nutrient rich medium the biofilm will become more rapidly anaerobic as in a poor medium.

The microbiological reactions in the biofilm of a pipeline of a cooling system are shown in Fig. 2.9 (over page).

Biofilms are important in a wide range of situations. In medicine biofilms on implants, contact lenses, medical instruments, tubes etc, as well as on teeth (caries), bones, and tissues can cause severe problems.

Surface settlements in the form of biofilms (“biofouling”) occur in drinking water production (growth on ion exchangers, reverse osmosis membranes, activated carbon filters, pipelines, water reservoirs, etc.), as well as in cooling water systems. Biofilms are the source of contamination of treated water and can also lead to increase in the resistance to circulation of the water and sometimes even to clogging of valves.

Growth of legionellae in warm water systems is probably also due to biofilms, and it is, therefore, very difficult to treat these systems.

Biofilms may reduce heat transfer on heat exchangers, including solar systems. Biofilms are the first step in the development of microbial growth on the hulls of ships which in turn lead to speed reduction.

Biofilms can cause corrosion of high alloy steels [24], and many coatings do not provide protection. In such cases cathodic protection (see 4.3.4.), if practicable, may be the best method of protection.

Biofilms (on stones and sediments) are also very important in the degradation of compounds in the rivers [24] and, in fact, bacterial biofilms were used for a long time to purify waste waters.

Most soil biocoenosis may be recognised as a biofilm, since bacteria attach to very different materials.

One of the oldest and best known applications of biofilms is in the production of vinegar which involves the introduction of bacteria on a supporting substrate into wine.

The artificial fixation of bacteria on a surface (immobilisation of cells) is a technique that is being used increasingly in biotechnology — frequently to facilitate the separation of bacteria from products.

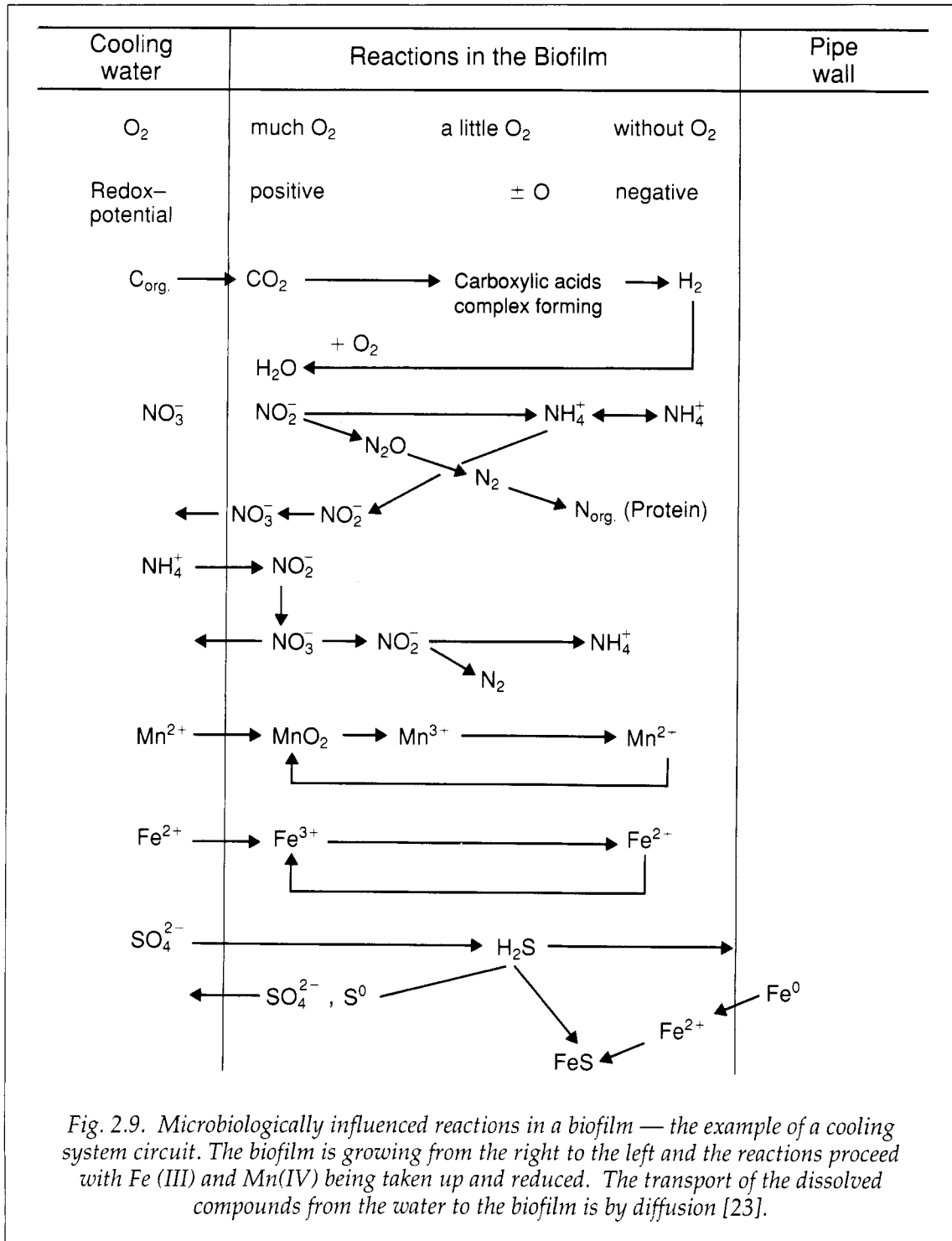


Fig. 2.9. Microbiologically influenced reactions in a biofilm — the example of a cooling system circuit. The biofilm is growing from the right to the left and the reactions proceed with Fe (III) and Mn(IV) being taken up and reduced. The transport of the dissolved compounds from the water to the biofilm is by diffusion [23].

It is well known, that the metabolic output may differ significantly between sessile and suspended bacteria [18] with much higher metabolic rates sometimes being measured for the former. The importance of the sessile state for the ecology of bacteria is however still not clear [26]. Measurements in this area need relatively high experimental input but nevertheless, a lot of essential knowledge can be expected to come forth in the future.

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Detection and Identification of Microorganisms

3.1. Introduction

To answer the questions, "Are microorganisms involved and how important are they in any particular case of damage?", is not easy for the non-microbiologist though some correlation has been established in practice between the behaviour of microorganisms and the damage caused by them. Sometimes this knowledge can be applied in developing an effective protection scheme but if complications arise the consequence may be a state of helplessness.

3.2. Microscopy

The first evidence of the presence of microorganisms on, or in, materials may be obtained by microscopy (light and scanning electron microscopy). Information may also be obtained about the predominant groups (bacteria, fungi, algae) and even the genera, if these can be distinguished by specific features when viewed under the microscope. The detection limit for quantitative counting of microorganisms is about $10^2 - 10^5$ /ml. Morphological details like fimbriae or slime formation can be observed especially by scanning electron microscopy although it is not possible to differentiate between active, resting or dead cells.

Microbiological studies in conjunction with microchemical methods can provide clear insights into the reactions which take place in biofilms.

3.3. Cultivation

Many physiological groups of bacteria can be detected qualitatively and quantitatively in, or on, materials. It is, without doubt, also possible to find genera of bacteria, which have not been previously described. One requirement for a successful detection of physiological groups of microorganisms via culturing is information about the chemistry of the biotope. In case of flow cultures (continuous cultures, see 2.2. & 2.3.) a comparison between the qualitative and quantitative input and output of the liquid will be useful.

Detection of microorganisms is made by usual microbiological methods, taking into account the fact that quantitative determinations will detect only a fraction of the bacteria actually present in the culture. Thus, the number of non growing bacteria may be 10–100 times higher than the number of the detected organisms.

3.4. Indirect detection

Indirect detection methods can be related to the bacteria themselves (determination of protein, DNS, EPS, ATP, chlorophyll, etc.) and also to chemical or physical changes like pH, CO₂-evolution, O₂-consumption, changes of the electric resistance, or in enthalpy, that occur in the medium as a result of the action of microorganisms.

The activity of microorganisms can be detected by the presence or absence of various

exoenzymes. Changes in the materials subject to bacterial action may become apparent and even measurable, for example, changes in weight or in some mechanical properties like tensile strength, or in the colour of organic materials.

3.5. Sampling

Sampling for analysis is as important as preparation and the actual analysis and should be correlated with the scope of the determination. Chemical analysis will use different sampling methods from those used for microbiological analysis but for both microbiological and chemical analysis deterioration of samples can be avoided only by "on site" analysis.

In most cases sampling of biofilms is difficult. Sampling and transportation can be facilitated by using replacement components (e.g. in cooling systems). Any biocides that may be present in the media as inhibitors must be inactivated immediately after sampling, e.g. by adding sodium thiosulphate to chlorinated samples.

3.6. Identification

The medium determines the composition of the microorganisms present. The identification of microorganisms sometimes leads to conclusions regarding possible damage and the extent of this and also to the selection of protective methods.

Cyanobacteria, algae, and lichens can be identified microscopically, while filiform fungi and yeasts must be cultured. Because of the relative uniformity of their shape, the majority of bacteria must be identified by culturing. Identification of heterotrophs starts by determination of their shape, size, flagellae, and staining ability, then the physiological parameters are determined (ability to degrade sugars, alcohols and other organic compounds; determination of enzymatic activities).

3.7. Evidence for Participation of Microorganisms in Deterioration of Materials

Often such evidence is not easy to acquire as bacteria, even if present in high numbers may not be the cause of the damage — although their massive presence might have been of influence.

Microbiologists like Henle and Koch gave the definition for pathogenic bacteria (the postulates of Henle-Koch*):

The bacterium has to be detected in the patient microscopically, it has to be multiplied in nutrient medium (with the same morphology), it has to cause in animals the same lesions as in humans, and it has to be detected microscopically in the animal and be capable of being cultured again in the original nutrient.

Materials deterioration by microorganisms is demonstrated in a similar manner: microorganisms are found at the site of corrosion, the microorganisms are isolated and identified, the cultivated microorganisms are used to inoculate (re-infect) the same materials in a laboratory experiment performed under the same conditions as at the site of the original corrosion damage, a similar form of corrosion occurs, and bacteria are isolated again from these sites. It may be useful to work in simulation chambers to accelerate the corrosion process and this is particularly the case for ceramic and metallic materials. No damage should appear in sterile control tests.

*H. J. Otte and H. Brandis (ed.), *Lehrbuch der medizinischen Mikrobiologie*, 4. Aufl. (Textbook on medical microbiology, 4th edn). 1978, G. Fischer Verlag, Stuttgart and New York.

3.8. Needs for Research and Development

3.8.1. General

The fact that results from the counting of living cells can be obtained only after one or more days is one of the basic problems of microbiological control. A more rapid and reliable method is needed for the counting of living cells.

Another complication lies in the uncertainty of the obtained figures (numbers). From experience the exponent is reliable, but all other figures are not certain. The variance is very high and more accurate methods must be developed.

The development of direct microscopic methods (e.g. epifluorescence) should be towards automation because counting is very time-consuming and tiring.

The methods for distinguishing between living and dead bacteria are unsatisfactory. In many cases it is very important to distinguish between the respective contribution of living and dead cells and relevant methods must be developed.

Another problem is that values for quantification of microorganisms obtained by different methods may show little agreement. A systematic comparison of methods is needed in this area.

The qualitative identification of some organisms (e.g. faecal indicators) is quite good but simple and effective methods should be found for other physiological groups. Further efforts are also necessary in this field.

3.8.2. Biofilms

Research on biofilms is a relatively new chapter of microbiology and basic questions still have to be considered. However, the importance of biofilms in materials deterioration means that intensive research in this field is unavoidable.

Practical problems make a recognition and detection of biofilms often difficult: simple methods need to be developed.

Quantification of biofilms is at present an unsolved problem. Cell numbers in suspension do not say anything about the number of bacteria in a biofilm.

The real adhesion process of the bacteria to the surface is almost unknown. The “adhesives” providing the adhesion have not been detected. Knowledge of the adhesion process is needed for avoiding or generating biofilms. The correlation between surface, medium, and bacteria is assumed, but quantitatively not known. The role of EPS seems to be of special importance.

The effectiveness of biofilm removal by reagents is unknown and is often subject to “trial and error methods”. The effectiveness of removal and killing techniques must be verified — simple methods must be developed for this purpose.

The understanding of the function and strength of biofilms makes assumptions about the constitution and coherence of these but the data available so far are insufficient. Which metabolic process is taking place and where in the biofilm?

The action of different biocides towards microorganisms in a biofilm must be studied. Data obtained for suspended bacteria have no qualitative value for the effectiveness of biocides in the case of biofilms.

Which possibilities exist to standardise a biofilm reliably?

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Microbiologically Influenced Deterioration of Materials

4.1. Introduction

In the following sections a detailed description of deterioration processes of materials is given. Auxiliary materials and raw materials are included if they are of relevance to practical applications as is the case, for example, with paints, lacquers, and varnishes when used for surface protection of materials. Similarly, adhesives are used in joining techniques and lubricants in the tribological requirements of materials.

Materials are, by definition, solids with mechanical, physical, and chemical properties, which fulfill certain technical demands. They are classified into three main groups: ceramic materials (mineral materials), metallic materials, and organic materials (polymers), as will be discussed below [1]. A fourth group — composite materials — are obtained by combinations of the above. Typical examples are fibre-reinforced materials, such as glass fibre reinforced plastics (ceramic + plastics) or carbon fibre reinforced aluminium (ceramic + metal). The group of composite materials will not be treated separately, i.e. the corrosion damage will be described in relation to the main component (ceramic, metallic or organic material).

Corrosion plays an important role in materials damage. In the case of metals, corrosion is the reaction of the material with the environment resulting in a measurable deterioration which can amount to damage. In most cases the reaction is of an electrochemical nature although it might sometimes be a chemical or metal–physical process (DIN 50900) [2]. Damage by corrosion may include impairment of the function of a metallic part or of a whole system (metal/medium). At present, existing definitions of corrosion do not include microbiologically influenced processes.

The DIN-definition may be used for all materials although the mechanisms and symptoms of the deterioration processes may be very different.

4.2. Ceramic Materials

The most important ceramic materials are natural rocks (magmatic like granite and basalt, sediment rocks like marble, quartzite, schist), synthetic stones (concrete materials), concrete (including resin-modified concrete), ceramics (including oxide ceramics and special materials) and also glass.

The economic importance of ceramic materials may be judged from the following data. Building materials in the Federal Republic of Germany represented in 1988 a value of about $5 \cdot 10^{15}$ DM. Each year between 40 and $60 \cdot 10^9$ DM are spent on repair work. Such expenses could be reduced substantially if it were possible to reduce the microbiological influences on this corrosion by research on the causes.

4.2.1. Description of materials

Definitions of the different materials are given below. These are extracts of the definitions

given in *Meyers Encyclopadisches Lexikon 1977* (Reprint 1977, Bibliographisches Institut, Mannheim).

4.2.1.1. NATURAL STONES

“Rocks obtained in quarries of natural deposits and used for construction or as materials are defined as natural stones”.

“Rocks” are defined as natural, solid formations of the earth’s crust. They consist of a mixture of minerals, a single mineral or organic residues. A rock is characterised by its main, secondary, and auxiliary minerals, by its structure, and by the stratification. Rocks may be distinguished by origin as follows:

- (a) Magmatic rocks (basalt, granite, porphyrite, trachyte, andesite, feldspar-basalt, and others)

Basalts are represented by a group of dark effusive rocks; plagioclase, augite, and olivine, iron ores, feldspars, hornblende, biotite, native iron and even glass will be either the main components of, or disseminated in, the basic mass. Two types of basalts can be distinguished: alkaline and alkaline–earth basalts. They are used for road-making, millstones, casings, etc.

Granites are grained rocks and quantitatively the most prevalent of the plutonic rocks of the earths crust. They are formed by slow cooling of plutonic silicate melts with high silica contents (up to 70% SiO₂). Granite contains approximately 30% potassium feldspar, albite-containing plagioclase, quartz, and approximately 10% mica and other dark coloured minerals; its density is 2.7 g/cm³. The secondary components of this mixture are distributed non-uniformly, i.e. concentrated in the body of the rock. Jointing is mainly at layers parallel to the surface, and hence granite is used technically as a hard rock.

- (b) Sediment rocks (gypsum, limestone, dolomite, pumice, sandstone, clayschist, and others)

Sandstone is a sediment rock containing mainly quartz grains (also feldspar, mica, and glauconite grains also) held together by a binding material. Sandstones can be distinguished by the nature of the binding material thus, clay-, calcareous-, quartz- and iron-sandstones exist. Sandstone is the storage rock for mineral oil and natural gas and is used in construction work, millstones and grinding stones.

- (c) Metamorphic rocks (formed by transformation of magmatic or sediment rocks by mineralogical and structural changes as a result of pressure and temperature changes; quartzite, marble, crystalline schist, and others)

Schist is a rock formed under the influence of pressure. It often breaks in thin, even plates. Clay schist and metamorphic crystalline schist have a characteristic structure of parallel planes, which is independent of stratification.

4.2.1.2. ARTIFICIAL STONES

This is an earlier designation used in the construction industry for concrete materials, hollow block materials, and other structural components that are obtained artificially from concrete, binding materials and natural stones (artificial basalt, now — concrete basalt; artificial sandstone, and more recently — concrete sandstone, etc.).

4.2.1.3. CONCRETE

Concrete is a mixture of coarse-grained aggregate, hydraulic binding agents (e.g. cement — to give cement concrete; gypsum, lime — to give lime concrete; asphalt) and water. For a limited

period after preparation the mixture can be given different shapes that is, until hardening occurs as a result of the chemical reactions between its components. The hydraulic binding agent, the water, and the finest grains (below 2mm) form the so-called cement stone.

Concretes may be classified as:

Heaviest concrete (with heavy spar, magnetite, or steelscrap)

Heavy concrete (with sand, shingle, chippings, rubble)

Light concrete (with pumice, metallurgical pumic clay, swellsclay, slags).

4.2.1.4. CERAMICS

Ceramics are products made from burned clay-containing masses such as kaoline and so-called special ceramic materials.

The following may be distinguished:

Coarse stoneware: glazed and unglazed, dense coloured ceramics (e.g. used in pipework).

Construction ceramics: produced from loam, brick clay, or clayey raw materials together with brick powder, cinders, and sand (used e.g. for bricks and tiles).

Fire-resistant products: materials suitable for temperatures above 1000°C (used for fireclay and the like).

Fine ceramics: pottery (made from ordinary clays), stoneware (made from clays like kaoline, quartz, feldspar, alkaline earth carbonates, magnesium silicates), porcelain.

Oxide ceramics: SiO₂-free materials containing aluminium, magnesium and beryllium oxides.

Special ceramics: steatite, rutile, lithium materials, semiconductors, cermets.

4.2.1.5. GLASS

Glass is a transparent, colourless or coloured inorganic material which is fragile and predominantly non-crystalline. It has no well-defined melting point, but by continuous heating it changes from a viscous to a soft and finally thin fluid state (i.e. an undercooled melt without crystallisation).

Components are the glass-forming agents: SiO₂, B₂O₃, P₂O₅, BeF₂; fluxing agents: alkali-carbonates, -nitrates, -sulphates; stabilising agents: alkaline-earth, lead, and zinc carbonates or oxides.

Products include: broad glass (thin-, construction-, thick-, mirror-, fibre-, ornament-, mono or multilayer security-, colour-, opaque glass), bottle glass, hollow glass, pressed glass, illumination glass, chemo-technical glass, special glass (optical glass, instrument glass such as borosilicate glass).

4.2.2. Processes involved in the microbial damaging of ceramics

Metabolic intermediate or end products excreted by organisms may react with ceramic materials and change their structure. These changes can go so far as complete destruction [3]. In principle, the involvement of organisms in such processes can be recognised by employing Koch's postulates, i.e. the damage-causing organisms must be identified and isolated and on materials reinfected by the isolated organisms should show the same type of damage and the organisms then again isolated.

4.2.2.1. DIRECT PROCESSES

Microorganisms excrete aggressive metabolites which cause deterioration of materials, i.e. inorganic and organic acids, complexing agents (often organic acids), hydrogen sulphide and nitrogen oxides ($\text{NO} + \text{NO}_2$) [3–5].

Inorganic acids are notably sulphuric, nitric, nitrous and carbonic acids. They attack materials by a solubilising process.

Organic acids are mainly those that appear in the citric acid cycle (i.e. citric acid, succinic acid, malic acid), acetic acid, gluconic acid, oxalic acid and others. Like inorganic acids, they dissolve acid-soluble components of materials.

Complexing agents include organic acids-like citric acid (which thus has a double function), amino-acids, etc. Complexing agents damage materials by binding cations dissolved specifically and/or non-specifically, or by disturbing their equilibrium with the material as a consequence of mass action or solubility product effects.

Hydrogen sulphide reacts with heavy metal cations forming sulphides which are usually insoluble so that reactive components are lost from the material.

Little is known about the mechanism of action of nitrogen oxides. Two mechanisms are possible: by an oxidising action, since NO_2 is a strong oxidising agent, or by reaction with water to form nitrous and nitric acids. Both will act as oxidising agents and nitric acid also as a solubilising agent.

4.2.2.2. INDIRECT PROCESSES

Besides the direct processes there are other processes resulting in materials damage that are caused by the presence of reaction products from a compound or compounds acting directly. Such compounds may be harmless by themselves, like heteropolysaccharides [3–5]. Other indirect processes include salt formation (for example by reaction with acids); recrystallisation (for example uptake of crystal water, e.g. hydration of CaSO_4 resulting in ettringite) which cause disruptions in the structure (swelling attack); biofilm formation (growth of organisms on a material with the consequence that capillaries are clogged) and others including changes in humidity, porosity, permeability, redox-potential, pH, etc.

4.2.3. Microorganisms involved

All groups of microorganisms may be involved in the processes described above. However, for some processes “specialists” are needed.

4.2.3.1. BACTERIA AND CYANOBACTERIA

Bacteria act by excretion of mineral acids and hydrogen sulphide. Sulphuric acid is produced by *Thiobacillus* and *Sulfolobus*. Nitrous and nitric acid are produced by ammonia- and by nitrite-oxidisers. Carbonic acid is produced by aerobic bacteria from oxidation of organic substrates. Hydrogen sulphide is produced anaerobically by sulphate-reducing bacteria [4]. Organic acids (also amino-acids) are excreted by main heterotrophic bacteria with unbalanced growth. As well as acid dissolution *per se* of the materials many of the acids promote attack by chelating cations [4].

The production and excretion of bacterial slimes — heteropolysaccharides and proteins — is another factor which may cause deterioration of ceramic materials. As a rule bacteria excrete these compounds in order to attach themselves to the surface or to protect themselves against environmental influences (pH, salts, drying etc.).

4.2.3.2. FUNGI

Carbonic acid, resulting from respirational oxidation of organic substrates, is the only mineral acid excreted by fungi. On the other hand, fungi are of great importance in the excretion of organic acids (including amino-acids) by unbalanced growth. In addition to acid attack, the

attack by chelation of cations must also be considered as most of the organic acids are able to chelate cations.

The excretion of slimes — heteropolysaccharides and proteins — is also a factor that may lead to deterioration of ceramic materials.

4.2.3.3. ALGAE

It is known that algae excrete organic acids and slimes and it is assumed that they are not involved in other mechanisms of damage.

4.2.3.4. LICHENS

Lichens are of importance in the production of organic acids and lichenic acids should be specially mentioned. They can participate in acid attack as well as in chelation. The excretion of slimes by lichens is also assumed to take place.

4.2.4. Examples

Two case histories will be described to provide a better understanding of the processes that have been discussed.

(i) In a case of “Biogenic Sulphuric Acid Corrosion of Concrete Surfaces of Partially Filled Sewage Transport Pipelines” investigations showed that corrosion had been caused by sulphuric acid producing bacteria of the genus *Thiobacillus* [6]. The number of *Thiobacillus thiooxidans* on the concrete surface was directly correlated with the extent of the biological attack. The situation existing in sewage pipelines was reproduced in a simulation system and the conditions optimised for the bacteria. In this system concrete test blocks were inoculated with pure cultures of bacteria (isolated from the surface of sewage pipelines) and maintained for 9 months in an H₂S-containing atmosphere. This experiment showed that by exact reproduction of the environmental conditions thiobacilli were able to destroy the concrete test blocks. Again, cell numbers of *Thiobacillus thiooxidans* were in direct correlation with the extent of the attack. The simulation system produced a time acceleration factor of at least 8 [7]. The simulation experiment fulfilled Koch’s postulates as applied to stone deterioration. Because of the acceleration factor the simulation chamber is still in use for the testing of materials [15]. The results obtained were published in the international literature and resulted in the term “biogenic sulphuric acid corrosion” [14].

(ii) The second example is concerned with concrete and natural stone. Studies on cooling towers made of concrete showed that nitrifying bacteria (ammonia- and nitrite-oxidising bacteria) were growing on the inner wall and producing nitric acid, which was attacking the concrete [8, 9]. Nitrifiers were also detected on the outer wall of the cooling towers, on other concrete buildings, and on buildings made of natural stone which were subject to weathering processes. In weathering, chemical, physical, and biological influences are involved. Weathering of natural stone used for construction causes deterioration of buildings. Natural stone subjected to natural weathering can lead to formation of soils [12,13]. Due to the anthropogenic burden on the environment these damages have been intensified in recent years and have now become more obvious. There is little knowledge about the involvement of microorganisms in weathering and architectural experts attribute the deterioration of buildings only to physical and chemical effects. Research on accelerated weathering and its influence on deterioration of buildings is now being conducted for the first time in joint work involving microbiologists, chemists, building physicists, experts in materials sciences, monument conservationists, restorers, and others in the BMFT-project “Research on Monument Care”.

Natural stones used as material for buildings like the domes of Köln and Regensburg or the Alte Pinakothek (München) have been found to be populated not only by heterotrophic

bacteria, algae, fungi and lichens but also by nitrifiers [10,16,17]. By their metabolism these bacteria produce nitric acid, which will react with the calcite binding material of the natural stone to form soluble alkaline and alkaline earth nitrates. Loss of the binding material reduces the coherence of the stone which in places may be lost completely. This degradation can be seen as a superficial bursting or flaking-off of the stone. Nitrifiers on natural stones (and presumably also other microorganisms) excrete slimes (heteropolysaccharides and proteins) and by this mechanism adhere to the surface and enter the pores of a stone where they are protected from physical influences such as variations of humidity or of temperature and from chemical influences such as heavy metals or concentrations of salt. These slimes modify the physical and chemical influences on natural stone and probably will significantly enhance them. Nitrifiers are supplied with nutrients (gaseous ammonia, and components of solid dusts like ammonium chloride, ammonium sulphate and ammonium nitrate) by the anthropogenically polluted air. The origin of these pollutants is not fully known. Ammonia emission is primarily the result of intensive live stock breeding and agricultural fertilising but industrial processes (transport and power plants) are of little influence.

NO_x -emission is, however, due to transport and industry although N_2O is also produced by biological processes. More than 50% of nitric acid is presumed to be formed by biological nitrification.

According to Koch's postulates the importance of nitrifiers for corrosion of natural stone must be assessed by reproduction of the damage. Materials damage has to be caused by reinfection with pure cultures of nitrifiers isolated from deteriorated stones and such evidence was obtained by a simulation experiment in which biogenic nitric acid corrosion of concrete and natural stone by nitrifiers was confirmed. In the simulation experiment samples of concrete and natural stones inoculated with nitrifiers were exposed in a simulation chamber under optimal conditions (28°C, relative humidity higher than 95%, ammonium chloride aerosol as nutrient). After approximately one year all samples were overgrown with nitrifiers. A high loss of calcium and an average loss of weight of about 3% was measured [11]. In a further step the importance of the biological nature of the attack will be distinguished quantitatively from the purely chemical attack by gases like SO_2 and NO_x and also quantified. However, the planning and construction of a suitable simulation chamber has been very complicated and preliminary results indicate that microorganisms contribute substantially to the deterioration of sandstone.

4.2.5. Special protection of materials

Measures for the protection of materials against microbial deterioration and corrosion should be chosen in relation to the material and the microorganisms involved. Protection can often be achieved by simply preventing microbial growth. If exact knowledge of the microorganisms involved is available, it is possible to minimise at least one of the factors mentioned in section 2.4. If this is not possible, then, in general, the chemical and physical measures listed in section 5 should be applied. However, it should be kept in mind that the protection methods should not change or destroy the material.

4.2.5.1. NATURAL STONES

For protection of natural stones a lot of measures are used although their efficacy is controversial even among experts. Because of this only the most important possibilities are listed and these are without evaluation. The possibilities include strengthening of the stone, hydrophobic treatment, impregnation with resins, coating with plastics, lining and treatment with biocides.

4.2.5.2. SYNTHETIC STONES AND CONCRETE

Measures for protection are principally the same as for natural stone. By preparing special

concrete of high density, optimal water–cement ratio, and high reserve alkalinity it may be possible to obtain fairly acid resistant materials (sacrificial concrete).

4.2.5.3. CERAMICS

Ceramics can also be protected against microbial attack in the same way as for natural stone. Additionally, in some cases physical methods may be applied, e.g. steam cleaning, but this will depend on the size of the object.

4.2.5.4. GLASS

Glass may be protected in the same way as natural stone. Physical methods are also applicable.

4.2.6. Environment, deterioration and protection of materials

It seems that attack on ceramic materials has been increased by anthropogenic pollution of the environment. SO_2 and NO_x need to be considered first. However, reports exist that in the last nine decades the extent of emission of these two pollutants has not changed. Furthermore, emissions of ammonia (agriculture, desulphurisation of flue gases) and of organic compounds (natural gas, oil) are supposed to occur but they have not been demonstrated by figures.

As a general rule, the best way for protection of materials would be to minimise emissions. At present effective protection can be achieved for single objects only by considering carefully all parameters involved.

4.2.7. R & D

For all ceramic materials there exists an important need for research, because it is suggested that microorganisms interfere with both the primary and secondary processes that lead to deterioration of materials and thus also influence physical and chemical processes. Little is known about the basic mechanisms which result in biocorrosion of ceramic materials. There has been some limited research but not a lot of problems have been studied. It is necessary to demonstrate the cause of damage by applying Koch's postulates but this evidence is often hard to obtain. The environment of the material has to be reproduced and simulation experiments need to be applied but the development of appropriate apparatus requires a lot of R & D effort. Often those who criticise ("all processes are chemical and/or physical") can be convinced of the importance of microbiologically induced deterioration of materials only by these simulation tests.

4.2.7.1. NATURAL STONE

Studies regarding natural stone are supported by the BMFT within the research program for "monument care". However, there is need for research on the attack by carbonic acid and hydrogen sulphide, and on questions concerning attack by heterotrophic bacteria, cyanobacteria, fungi, lichens and algae. Studies regarding the content and distribution of slimes in pores of stones as well as the spectrum and quantity of organic acids are also needed and are missing at present.

4.2.7.2. ARTIFICIAL STONE

Studies on these problems are treated only peripherally within the "monuments care" research. Studies of carbonic acid and hydrogen sulphide attack as well as of the importance of microbial slimes, the attack by organic acids, and the indirect effects are missing.

4.2.7.3. CERAMICS

At the present time there is little knowledge concerning the importance of microorganisms in the deterioration of ceramics. Research is needed in all areas, e.g. attack by mineral acids, hydrogen sulphide, microbial slimes, as well as indirect effects.

4.2.7.4. GLASS

Glass will be studied within a BMFT project since so far only a few studies exist on the importance of microbial attack. Research work is thus needed on attack by mineral acids, hydrogen sulphide, organic acids, microbial slimes and indirect effects.

4.3. Metallic Materials

4.3.1. Description of materials

Metals are an important group of construction materials and are divided by special properties into light and heavy metals (density below or above 4.5 g/cm^3), noble metals, ferrous and nonferrous metals (according to the main component in the case of alloys). The systematic classification of metals is based on their structure [18]. Examples include pure metals, solid solution alloys (e.g. brass), precipitation hardenable alloys (copper–beryllium alloys, aluminium–copper–magnesium alloys), phase transformable alloys (steel), casting alloys (grey cast iron, aluminum casting).

An evaluation of the resistance to corrosion can be based on the electrochemical series of metals [19]. The electrochemical series of metals was established for metals in equilibrium with their ions in solutions at standard conditions. The series starts with lithium, the most electronegative, aluminium, zinc, iron, copper, silver and finally gold, the most electropositive. In practice, a more useful series may be the galvanic series which arranges metals in order of their actual corrosion potentials as measured in sea water.

Another criterion for resistance against corrosion is based on the property of some metals to form passive layers on their surface. Typical examples are aluminium, titanium, tantalum and the high alloy steels. Passive layers are usually very thin oxide layers. In such cases the metals behave in a more noble manner than their position in the electrochemical series would allow. On the other hand, these groups of metals show a particular sensitivity towards local corrosion effects like pitting, crevice corrosion and stress corrosion cracking.

4.3.2. Practical examples and damage processes

Several studies have shown that the cost of metal corrosion in the industrialised countries is about 4% of the gross national product. An important part of these costs is due to corrosion in soil, e.g. on pipelines and reservoirs and half of this is probably caused by microbial corrosion [20].

Systematic studies which consider the joint action of microbiological activity and corrosion are rare because of the interdisciplinary commitment required [20, 21] although one survey has been published [22].

Microbial corrosion is probably based not on direct interaction of bacteria with the metal, but on the interaction of certain metabolic products of the bacteria with certain steps of the corrosion process. In the conditions in which bacteria exist, these steps are of an electrochemical nature so the process will be one of stimulation of the anodic and cathodic steps in the total reaction [23].

Corrosion of metals by moulds is based on the same principles. Metabolic products excreted (organic or inorganic acids or other compounds) set up a secondary corrosion process.

Most processes of corrosion of metals depend on the presence of free oxygen as an oxidant (corrosion by oxygen, oxidative metabolism). In the case of bacterial corrosion the opposite situation can also be of importance. Thus, anaerobic microorganisms, e.g. *Desulphovibrio desulphuricans*, can initiate corrosion, even if oxygen is absent. In Fig. 4.1. the most important connections are presented schematically:

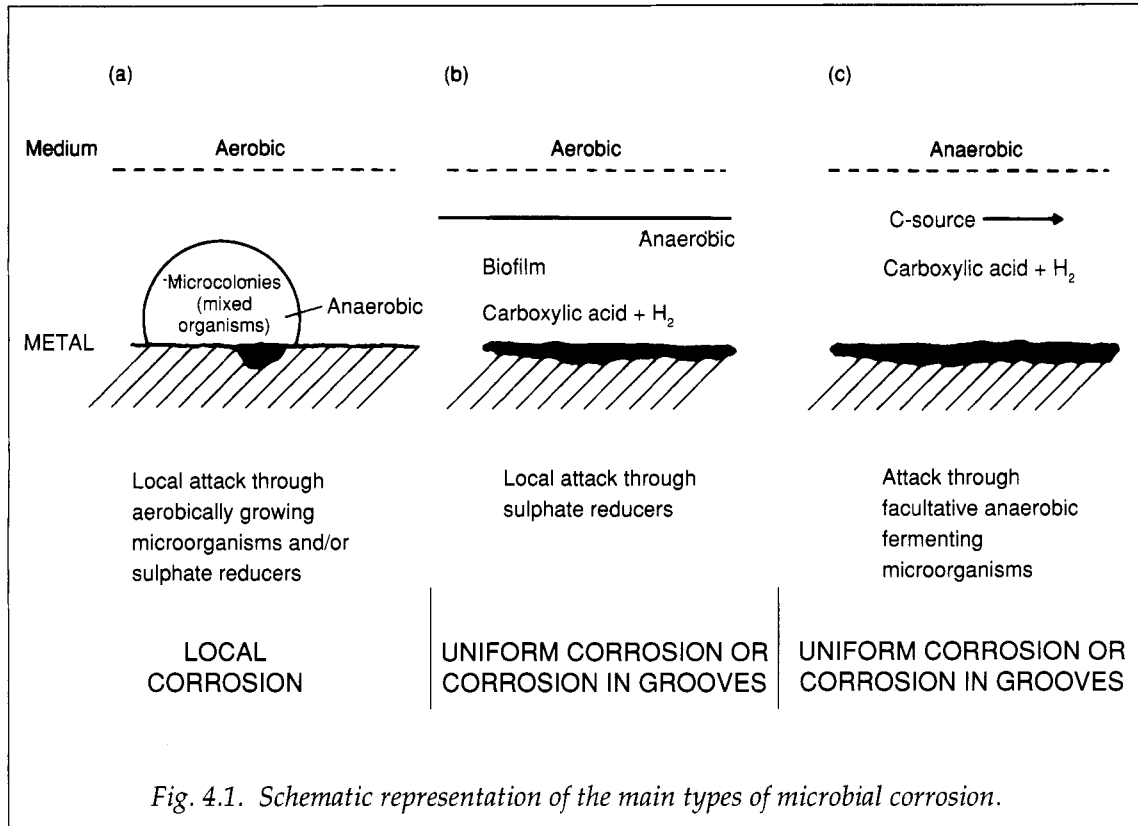


Fig. 4.1. Schematic representation of the main types of microbial corrosion.

(a) Local corrosion arising from the operation of differential aeration — and other concentration cells due to the presence of sessile bacteria (e.g. *Pseudomonas*).

Pitting under $Fe(OH)_3$ deposits — tubercles formed by sulphate reducing and iron-oxidising species (*Gallionella*).

Pitting by sulphate reducers under biofilms.

(b) Stimulation of acid corrosion (hydrogen from H_2S ; see 4.3.3.) by sulphate-reducers. Formation of iron sulphide layers, which accelerate oxygen corrosion.

(c) Attack by organic acids and complexants in anaerobic media in the presence of a carbon source and/or hydrogen.

Bacteria causing transformations of sulphur and sulphur compounds are of special importance (see Fig. 2.4. in section 2.3.3.).

Compounds with different valencies of sulphur can be formed and these will have different corrosion aggressivity. The most important are shown in Table 4.1.

An important step is, for example, the oxidation of S^{2-} and elemental sulphur by *Thiobacillus thiooxidans*, to form sulphate and then sulphuric acid. These bacteria grow aerobically and tolerate sulphuric acid concentrations up to 10%. Almost all metallic materials are corroded under such conditions. Acidification of mine waters and of sewage are known examples [24–26]. *Thiobacillus denitrificans* can form sulphate under anaerobic conditions when NO_3^- is present.

Table 4.1. Examples of products of the sulphur cycle that affect corrosion

Reaction (schematic)	Microorganism (selection)	Product	Aggressivity
$S^{\circ} \rightarrow SO_4^{2-}$	<i>Thiobacillus</i>	H_2SO_4	strong
$S^{2-} \rightarrow S^{\circ}$	<i>Thiobacillus</i>	S° (finely dispersed)	weak
$SO_4^{2-} \rightarrow S^{2-}$	<i>Desulphovibrio</i>	S^{2-}	moderate
$SO_3^{2-} \rightarrow S^{2-}$	<i>Clostridium</i>	S^{2-}	moderate
$RSH \rightarrow CH_3SH$	<i>Vibrio</i>	CH_3SH	weak

Sulphate-reducing bacteria (e.g. *Desulphovibrio*) are very important. By a complicated mechanism they use the oxygen of the sulphate ion and reduce the sulphur to sulphide and then to hydrogen sulphide. Sulphate reduction is a wide spread microbiological process with extensive economic, ecologic and aesthetic implications. A typical example is the acidification of oil- or gasfields. Initially "sweet" (i.e. hydrogen sulphide-free) oil sources turn acid by H_2S -formation after contamination with sulphate-reducing bacteria by water-injection (secondary oil-extraction). The final result is intensive corrosion of the equipment and pipelines made from unalloyed steel. The very dangerous hydrogen sulphide induced stress corrosion cracking of high strength steel resulting from hydrogen uptake must be particularly mentioned [27] (see section 4.7).

In principle, all equipments made of sulphide sensitive materials are endangered if they contact sulphate-containing waters contaminated with sulphate-reducing bacteria especially when sufficient organic matter is present. In this context, pipelines, cooling circuits, cooling towers, water- and oil tanks, as well as installations for off-shore oil- and gas-winning should be mentioned.

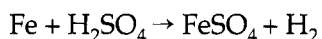
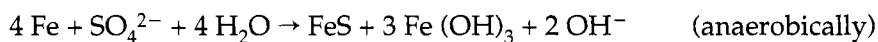
The pitting of fuel tanks in jet planes as a result of the action of sulphate-reducing bacteria and fungi has been thoroughly studied. Water, present as impurity, sulphates and organic compounds are the substrates for bacterial sulphide formation. Zinc- and magnesium-containing aluminium alloys can be extremely sensitive to sulphide induced pitting.

The so called iron bacteria are of some importance. They promote deposition of rust from iron-containing water (rust corrosion), but the mechanisms are still not well understood. Iron rust can lead to pitting of unalloyed steel as well as high alloy steel if chlorides are present. *Gallionella* and *Leptothrix* belong to this group of iron bacteria.

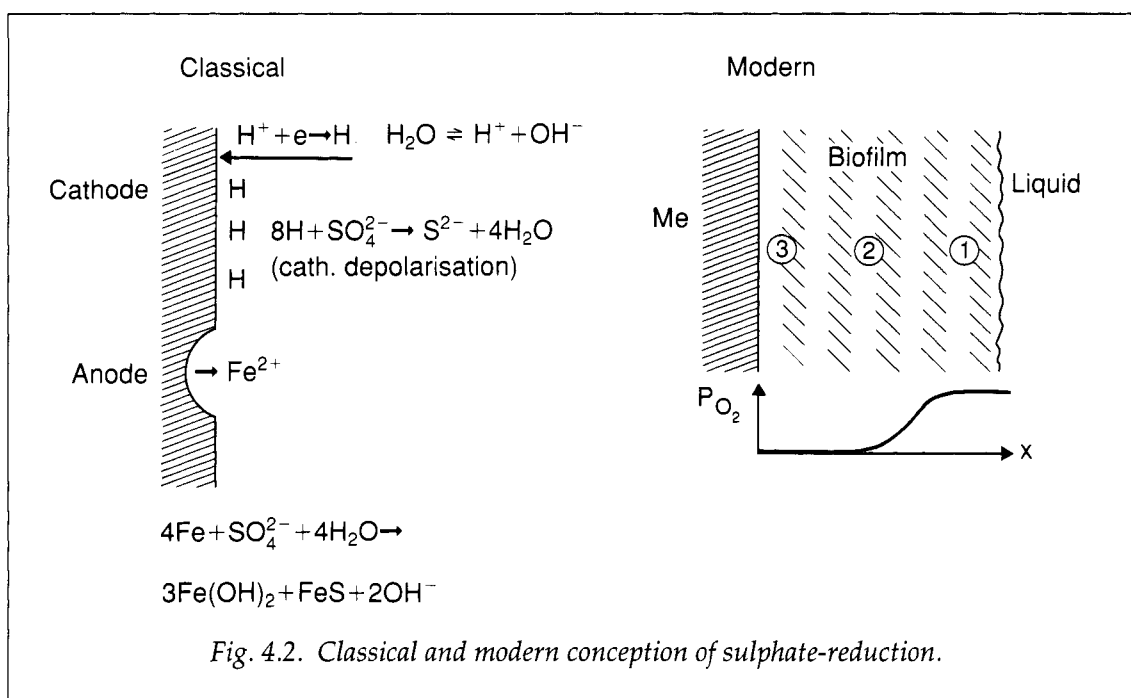
Other microorganisms of relevance to corrosion include *Pseudomonas* strains which form hydrogen sulphide and mercaptans by protein degradation; cellulose-decomposing bacteria which excrete acetic acid or butyric acid; and also ammonia-forming species [20]. The reactivity of iron materials in organic acids is well known, copper and copper alloys are attacked by ammonia with these alloys being particularly susceptible to stress corrosion cracking.

4.3.3. State of knowledge on the mechanisms

The overall reactions of sulphate-reduction and sulphur oxidation can be described by the equations:



but the partial steps are more complicated. It seems that the hydrogen layer at the metal surface that is postulated by the classical depolarisation theory of sulphate-reduction does not correspond to reality. A complex interaction of several microbial steps occurring in a biofilm should be accepted as in Fig. 4.2. in which the biofilm is a system, where the oxygen partial pressure is higher on the outer side and becomes lower in the inside.



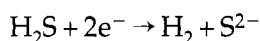
1. Aerobic bacteria: oxidation of organic compounds by oxygen to degradation products.
2. Anaerobic bacteria: oxidation products form hydrogen and organic acids (fatty acids) by fermentation.
3. Anaerobic, sulphate-reducing bacteria: hydrogen + organic acids + sulphate are transformed into sulphides and water.

Thus, under anaerobic conditions hydrogen can be formed, and transferred by microorganisms to sulphate ions. Some new studies have shown that there is no quantitative correlation between bacterial activity and corrosion-rate [28].

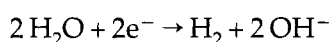
In these three steps adenosinetriphosphate (ATP) is involved. The sulphate is activated

by adenosine-phosphosulphate (APS). The other steps of H₂S formation are not yet understood.

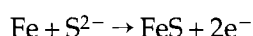
Cathodic hydrogen evolution from hydrogen sulphide



has a corrosion stimulating effect on metals, for example, on ferrous materials. This reaction is favoured kinetically compared to the reaction:



The anodic step is accelerated also by formation of iron sulphide:



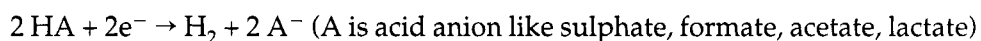
Where the hydrogen formed goes to during the corrosion process is a question not completely answered [29].

An important finding of some recent corrosion studies is that a sulphide covered iron surface is very sensitive to increases of oxygen partial pressure. The FeS-layer apparently catalyses the reduction of oxygen and the corrosion rate is thus enhanced [28].

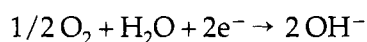
Microbially induced pitting on high alloy steels has been reported in natural seawater. In these cases a biofilm accelerating the cathodic oxygen reduction process was found on the surface. Such "catalytic" activity of biofilms has been demonstrated by long term electrochemical measurements with cathodic polarisation as well as by model experiments simulating crevice corrosion. Differences in corrosivity between natural and artificial seawater, which until now have not been understood, can now be explained [30].

In summary, many cases of microbial damage to metals can be attributed to known corrosion mechanisms, as follows:

- Formation of aggressive metabolites reacting electrochemically with metals (e.g. uniform corrosion by microbiologically produced acids):



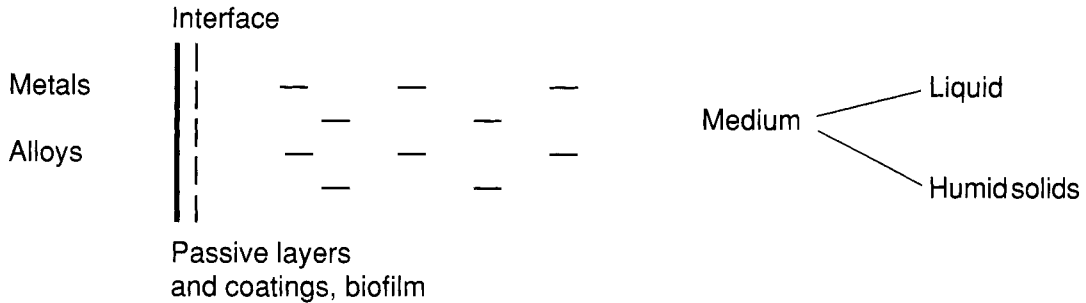
- Formation of differential aeration- and concentration cells on biofilm- and slime-coated metal surfaces, pitting and crevice corrosion being the consequences:



- Local destruction of passive layers and coatings results in pitting
- Stimulation of cathodic reactions by microbially formed hydrogen sulphide as already described
- Stimulation of oxygen corrosion by iron sulphide layers.

4.3.4. Corrosion protection with special consideration given to microbial corrosion

The choice of suitable methods of protection will depend on the nature of the corrosion system [23, 31]. The corrosion system includes the material, the medium and the conditions as shown in the scheme below:



Several possibilities for protection have thus to be considered:

The metal:

- selection of more noble materials, to increase thermodynamic stability; improvement of passivity by suitable alloying elements, e.g. chromium addition to iron; selection of metals with bactericidal properties (silver, and with some restrictions, copper).

The medium:

- addition of microbiocides (see section 5)
- neutralisation of acids
- avoiding oxidants like oxygen, metal ions with high valence halogens
- avoiding chemically bound oxygen, which is microbially accessible (nitrate, sulphate)
- avoiding organic and inorganic compounds oxidisable by microorganisms (e.g. alcohols, hydrocarbons, ammonia).

At the interface:

- avoidance or removal of biofilms
- use of organic coatings
- use of microbiostatic paints
- use of metallic and inorganic coatings
- cathodic and anodic electrochemical protection.

Detailed information for general protection methods is available in the literature [23, 31].

4.3.5. Environmental aspects and corrosion protection

Intensive pollution of the environment with phosphates and nitrates (e.g. overfertilising) has led to an increase of microbial growth in waters and this has caused increased microbially influenced deterioration of materials. Emissions and subsequent absorption of sulphur dioxide and nitrogen oxides also provide starting compounds for microbial attack. An improvement of the situation can be expected only in the long term and, therefore, a controlled application of microbiocides with careful consideration given to environmental aspects is unavoidable.

4.3.6. R & D

First of all it is necessary to carry out interdisciplinary research with joint participation of corrosion experts and microbiologists. Within the national R&D program supported by BMFT "Corrosion and Protection against Corrosion" some questions are studied, but intensive work on these problems is still missing.

The following questions are to be studied:

- mechanism of iron corrosion by sulphate-reducing bacteria with special regard to electrochemical processes; elucidation of the cathodic steps and of their influence on corrosion rates;
- influence of cathodic protection on microbial corrosion; effect of microbially formed hydrogen in the embrittlement of metals caused by hydrogen uptake;
- mechanism of action of iron-bacteria on corrosion of iron;
- elucidation of similarities and differences in microbial corrosion of copper, aluminium, high alloy steel, titanium;
- action of biofilms on the electrochemical behaviour of metals, elucidation of the cause of acceleration of the cathodic step;
- formation of biofilms on metals in water containing systems.

4.4. Organic Materials of Natural Origin

4.4.1. Introduction

Although green plants have been synthesising organic compounds from carbon dioxide for millions of years, none of these compounds has been significantly enriched in the Earth's crust. In fact, only a small fraction has been preserved under the anaerobic conditions in the form of a mixture of strongly reduced carbon compounds like natural gas, oil and coal. Under aerobic conditions all biosynthetically produced compounds are degradable. Each and every compound, even the most complex, may be partially or completely degraded by microorganisms and the resulting products consumed by other species. Microorganisms as a whole, therefore, seem to be biochemically omnipotent, so a "principle of microbial omnipotence" has been established.

However, a limitation of this principle is now necessary since some of the man-made low molecular-weight compounds (some plant protecting agents, detergents etc.) and highly polymerised plastics are biologically not degradable, at least in so far as such statements can be made after some years of observations and experiments.

4.4.2. Wood and wood-based materials

4.4.2.1. WOOD

Wood is the most important organic natural product because of its versatility (for example, as an energy source, raw material or construction material).

In developing countries wood is for most people the only energy source (firewood). In industrial countries it is an important raw material for various products such as cellulose, paper, wood-based materials, building timber, furniture etc.

Description of material

The main components of wood are cellulose, polyoses (hemicelluloses), and lignin. In general, wood growing in the temperate zone consists of 97–99 % of these compounds of which 40–50 % is accounted for by cellulose, 15–35 % by polyoses, and 25–35 % by lignin. Generally the lignin content of softwoods is higher than that of hardwoods. The content of extractable compounds like terpenes, waxes, tannins (1–3%), and inorganic compounds (0.1–0.5%) is considerably lower although for tropical woods the content of extractable compounds can reach up to 15 %. The economically most important component is the cellulose which is used as a raw material for the production of paper, cardboard, foils, films, and fibres. The tensile strength of wood is determined by the cellulose cell structure. The cellulose molecule is made up of β -(1-4) glycosidically bonded glucose units. In wood, one cellulose molecule is formed by 10 000 to 14 000 units. Polyoses are polysaccharides differing from cellulose by the presence of lateral chains and ramifications. The degree of polymerisation of polyoses is much lower than that of cellulose (50 to 200). The main component of softwood polyoses is galactoglucomannan, hardwood polyoses contain 4-O-methyl-glucuronoxylane. The polyoses connect the polysaccharides with the lignin of the cell wall. They determine the swelling and shrinkage of wood. Lignin is a complex macromolecule. In softwoods the units are guaiacyl-propane, whereas in hardwoods there are units of guaiacylpropane and syringylpropane. Lignin makes the wood resistant to pressure. Some components may be extracted with solvents. Softwoods primarily contain terpenes. These extractives are also responsible for the natural durability of wood. Starch, sugar, pectins and proteins are also present in small amounts. Cell wall components include important nutrients for plant and animal parasites that can damage wood [32, 33].

Damage

Under certain circumstances wood can be colonised and/or attacked by moulds, bluestain fungi, soft rot as well as by white and brown rot fungi (basidiomycetes) although the heartwood of most wood species is naturally more durable than the sapwood. Under conditions of extreme humidity bacteria can be involved but they are of minor importance in the destruction of wood.

Moulds grow only on the surface of wood and penetrate to a depth of 1 mm. They feed principally on the wood extracts, the cell walls not being attacked, so that the strength of the wood is not influenced by their growth. Moulds can cause discolourations.

Bluestain fungi also do not decompose the cell walls of wood and do not reduce its strength. These fungi are called bluestain as the wood is stained blue or grey by their dark-coloured hyphae which spread particularly in the radial nutrient-rich wood rays.

Damage caused by bluestain fungi may be classified into three groups:

1. Bluestain of stemwood (forest bluestain), appears mostly on freshly cut wood stored at the felling site;
2. Bluestain of felled timber in storage yards during the period while the logs are not dry enough for cutting, i.e. before the warmer season in spring;
3. Bluestain on processed or painted wood which has become wet. This form of bluestain is often encountered on wooden windows, doors, garden furniture etc. The fungi may grow through, or raise the paint. Damp may enter, and decay may spread below the paint.

Soft rot fungi: Contrary to the situation with mould and bluestain fungi soft rot may lead to important weight and strength losses. It is mainly cellulose that is degraded. The attacked wood turns a dark colour and its surface — if wet — becomes mouldy. Hardwoods are more susceptible to softrot than softwoods.

Wood-destroying basidiomycetes cause decay of wood (brown rot or white rot) by degrading the cell walls. The term "brown rot" (destruction rot) refers to the dark discolouration caused by the proliferation of these fungi. They degrade mainly cellulose and polyoses so that only lignin — responsible for the brown colour — is left. In the final phase of destruction the wood can simply be crushed between the fingers. The "white rot" fungi (corrosion rot) generally produce a whitish residue on the wood. They degrade the cellulose and either simultaneously or successively the lignin. The colour of the wood lightens but — depending on the fungal species — it may become streaky. In an advanced stage of attack the wood is light, soft, and fibrous or "spongy", and its mechanical properties are reduced.

Microorganisms involved

Moulds: The term "moulds" is not a systematic one and covers Zygomycetes, Ascomycetes, and Fungi Imperfecti (fungi with unknown sexual stages). They produce coloured surface coatings of woolly, floury, velvety, or powdery appearance. They comprise about 100 000 species.

Bluestain fungi: About 100 different bluestain fungi have so far been identified, belonging to the Ascomycetes and Deuteromycetes. They occur particularly on softwoods and on bright, nutrient rich tropical wood species without coloured heart. Of the softwoods pine is preferred, but growth is limited to its sapwood. The optimum growth temperature for bluestaining fungi — depending on the species — is between 18 and 25 and even up to 28°C. Optimum wood moisture for many species is between 30 and 40%, for certain bluestain fungi infesting living trees it is distinctly higher, i.e. between 50 and 100%.

Soft rot: In this form of damage different Ascomycetes and Deuteromycetes requiring high moisture levels are involved. They occur on wood which is exposed to permanent ground contact, such as poles, posts, sleepers and marine timbers or cooling tower timbers.

Systematically, Basidiomycetes (mushrooms) rank higher than the fungi mentioned thus far.

All fungi of economic significance, which in these latitudes means those wood-destroying fungi occurring on wood *in situ* are brown rot fungi. Both types of this fungi groups occur on the living tree as well as on stored moist wood, with white rot occurring more frequently on hardwoods than on softwoods.

Brown rot fungi: The most dangerous destroyers of wood in service belong to this group, e.g. the Dry Rot Fungus *Serpula lacrimans*, the Cellar Fungus *Coniophora puteana*, the White Cellar Fungus *Poria vaillantii*, and *Gloeophyllum* species. The first fungus mentioned is the most dangerous wood destroyer and therefore in some of the "Länder" of the Federal Republic of Germany its occurrence must be registered. It is so dangerous because its highly developed surface and strand mycelium enable it to survive and develop at lower moisture contents than other fungi occurring in buildings. It may even grow through walls and may also attack dry wood due to its ability to transport water and supplementary nutrients over great distances through its mycelium and its mycelial strands. The Dry Rot Fungus as well as other decay fungi occurring in buildings may survive for quite some time under dry conditions. The fungus may develop between 3 and 26°C. Optimum conditions are between 18 and 22°C with a wood moisture content of between 30 and 40%.

White rot fungi especially attack trees and seasoning wood. Typical representatives are *Coriolus versicolor*, *Fomes fomentarius*, and *Armillaria mellea*. *C. versicolor* is a well known destroyer of hardwood and particularly attacks beech wood. It grows on stubs, on sick or damaged trees, in timber yards as well as on exterior timber (poles, stakes, sleepers and timber used for horticultural purposes) [32].

Special protection of materials

The protection of wood against biodeterioration involves constructional and chemical methods. Constructional protection includes all methods that can prevent timber from getting too wet. Chemical methods use preservatives which are effective against the respective organisms. The efficacy of these products is based on the biocidal properties of some of the constituents.

We distinguish between salt-type and solvent-type (so-called oil-borne) preservatives, and these are described in detail in section 5. There are several European standards for testing the effectiveness of wood preservatives. The threshold values of wood preservatives for use against wood-destroying basidiomycetes are determined by DIN 113 [34], with their effectiveness against bluestain given by EN 152 Part 1 [35].

Building regulations specify that building elements made of wood or wood-based materials designed to support or strengthen structures must be preserved. For this purpose only those wood preservatives may be used that are tested for their effectiveness and that are considered to be non-hazardous to health. These products are approved by the Institut für Bautechnik (IfBt) (Institute for Construction Techniques) in Berlin. The "Catalogue of Approvals for Wood Preservatives" [36] lists all wood preservatives which have been approved by the IfBt. A new edition is issued every year.

Environment and protection of materials

The Bundesgesundheitsamt (BGA) (Federal Bureau of Health) is in charge of evaluating the health hazards of wood preservatives and granting approvals. They test whether the wood preservatives when used correctly are harmless to the environment and to man. In 1986 for instance the BGA announced [37] that the active ingredient pentachlorophenol (PCP) may no longer be added to approved products. This decision was made following controversies regarding the harmfulness of PCP as well as the fact that technically produced PCP was contaminated by small amounts of dioxins.

R & D requirements

The following items are considered important for future research:

1. *Material*: Further elucidation of the degrading mechanisms of wood as well as questions regarding the natural durability of several wood species.
2. *Wood preservatives*: Formulation of anti-bluestain preservatives with no secondary effects to replace PCP, especially for cut wood in the forest or wood stored for seasoning. Protection of wood with natural compounds (naturally occurring compounds imparting resistance). Examinations of questions regarding the detoxification of active compounds.
3. *New principles for protection*: Modification of wood to make it resistant to microbial attack; e.g. devitaminisation, modification of the lignin and/or of the cellulose.
4. *Growth of fungi in preserved timber*: Preserved wood exposed in field trials can be penetrated by fungi if the surface becomes altered as a result of ageing processes. How the fungi are able to penetrate preserved wood should be studied. A first step would be the microscopical examination of such wood samples. The next step would be a study of the mechanism of how various preservatives act on the fungus.
5. *Test procedures for wood preservatives*: (a) Development of an accelerated test method to replace the time- and material-consuming method described in EN 113; (b) Development of a non-destructive test method for wooden constructions based on ultrasonic testing; (c) Development of an accelerated ageing method (artificial weathering) to replace field trials to determine the permanence of wood preservatives.

6. *Effect of wood preservatives on plants:* An increasing number of complaints have arisen concerning the damage of garden plants by the application of wood preservatives used in the do-it-yourself area for fences, plant-supporting poles etc. The effects of various types of wood preservative (water-soluble, solvent-containing, carbolineum) should be examined in preliminary laboratory tests, and in the case of solvent-containing formulations the effect of pure solvent on germinating water cress, beans or lupins in relation to the storage period of treated wood specimens should also be examined. Field trial experiments will then be necessary using sensitive plants to study the air- and soil-borne effects of the substances that may be transported to the plants.

4.4.2.2. WOOD-BASED MATERIALS

Description of materials

In contrast to solid wood, wood-based materials are defined as materials obtained from wooden lamellae or chips glued together with binding agents. Wood-based materials include: glued laminated timber, blockboard, plywood, chipboard and fibreboard. Plywood and chipboard will be briefly discussed here. The binders used for these panels are synthetic glues or adhesives, such as urea-formaldehyde resin, phenol-formaldehyde resin, cresol-formaldehyde resin, isocyanate etc.

For plywood production the veneers are cut from logs. Depending on the slicing method the thickness of the veneers may vary from 0.05 to 3.0 mm or more. The lamellae are always glued together crosswise by pressing at high temperatures, the panels then being sanded and edged. A wood preservative may be incorporated in the glue to protect the panels from fungal attack.

Chipboards are produced by glueing wood chips together, in general with resins of the urea-formaldehyde, phenol-formaldehyde or isocyanate types. At the present time urea-formaldehyde resins are preferred. Glueing is conducted by pressing (at 15–40 kp/cm²) at higher temperatures (140–200°C). Different types of board, depending on type, position and arrangement of the chips, are obtained [38].

Deterioration processes

In the Federal Republic of Germany the use of wood-based materials is subject to building regulations which are based on DIN standards, laws, regulations and administrative provisions. The preservation of the strength of constructional materials is given the highest importance by building control authorities.

Wood-based materials — like solid timber — are susceptible to fungal attack if the conditions — particularly the moisture content — are favourable. Damage may range from surface growth to complete destruction. The organisms involved are moulds, soft rot and wood destroying basidiomycetes. When the surface of wood-based materials is attacked by mould (fungi) the strength of these materials is not usually reduced, unless the mould in question belongs both to the mould and the soft rot fungi, such as *Chaetomium globosum*. Interest has been focussed on hygiene problems since mould attack has been increasingly found on chipboard used in private houses and storage rooms.

Attack by wood destroying basidiomycetes may quickly reduce the strength of wood. In the case of chipboards the glue can have a distinct influence on the wood destroying agents. Thus, phenolic-resin-bonded boards inhibit basidiomycetes, while urea-resin-bonded boards and isocyanate may encourage the growth of wood destroying fungi.

Special protection of materials

Protective agents against fungi can be added to the glue but may only be added at the manufacturing plant. Compatibility with the glue must be guaranteed.

R & D requirements

At present there are no standards for testing the efficacy of wood preservatives except a draft standard for plywood and chipboard. A Working Group of the CEN (Comité Européen de Normalisation) is drafting a mycological test for plywood panels. The Bundesanstalt für Materialforschung und -prüfung (Federal Institute for Materials Research and Testing) coordinates international cooperative tests to compare the results of three national test procedures [39].

The development of a standard method to test the efficacy of wood preservatives for chipboard is very urgent. It is well known from the literature that many wood-destroying fungi only very rarely attack phenol-resin-glued chipboards. Those fungi, however, that colonise such panels have different effects on the chipboards. Some of them have caused high weight losses after a test period of 16 weeks, while the strength perpendicular to the surface of the samples has been hardly affected; other fungi cause only small weight losses but important reductions of the strength perpendicular to the surface. For the interpretation of the experiments both weight and strength losses should be taken into account; further investigations are still necessary to solve this problem.

4.4.3. Leather

4.4.3.1. GENERAL

Due to its composition (about 33% protein, 1.5% lipids, 65% water) freshly obtained hide is attacked very rapidly by microorganisms and must be preserved by salting, drying, or by processing immediately into leather. From the many layers of the raw hide only the leather skin (corium), consisting of collagen fibres, is used. After cleaning of the raw material, removal of the hair, etc. it is finally tanned, dried and often greased.

Apart from special tanning procedures chromium tanning is the process mainly used today and accounts for approximately 80% of the total leather processed. Tanning with plant extractives is rarely used. After chromium tanning the leather contains 4–7% chromium. Leather tanned with plant extracts contains 20–35% bound tanning agents. The fat content of finished leather is 5–15%, the water content 10–14%, the natural pH is about 4.0–4.5.

4.4.3.2. DAMAGE

Leather is in danger of attack by microorganisms throughout the whole processing stage, i.e. from the hide to the finished product. Under moist storage conditions all kinds of leather may be attacked by moulds (Ascomycetes and Deuteromycetes), bacteria, and even yeasts. The damage may consist of spots of mould, parts of the surface may turn dull or be stained during the decomposition or may deteriorate completely, as for example bookcovers made of leather [40].

The past few years have seen increasing complaints about the appearance of mould on leather used for shoe manufacture [41].

A notable and increasing number of these complaints pertain to leather from the Indian sub-continent. The inadequate production processes in leather manufacture and the particular climatic conditions are obviously responsible for this, but so is the failure to treat the leather with agents protecting it against microbial attack. This is crucially important, particularly under such conditions.

The development of moulds on leather is influenced by the tanning procedure and by the substances used. Chromium leather is usually more resistant than leather tanned with plant extracts. However, fungi can also grow on chromium leather. If leather contains hydrophilic compounds (sugar, glycerine etc.) or fats, dyes, and glazing substances, fungal growth will be encouraged.

4.4.3.3. MICROORGANISMS INVOLVED

Raw hide

On raw hide an abundant microbial flora can develop with up to 5×10^6 bacteria per gram of dry weight and containing particularly proteolytic bacteria. Most of them use only interfibrillar, non-collagenous proteins, modifying only the collagen fibres (Bacillus species). However, some collagen-degrading species exist as well, such as *Clostridium histolyticum* [42]. On salted raw hides halotolerant and halophilic bacteria such as *Micrococcus luteus*, *M. roseus* and *Halococcus morrhuae* produce a range of yellow to red spots.

Severe deterioration of raw hides may render them brittle or spongy and “self-splitting” of leather sometimes occurs. Moulds on raw hides may also influence the quality of leather, for example, some species degrade the fat to fatty acids causing a fine white efflorescence on the surface of the leather.

Finished leather

On finished leather as well as on leather products mould damage — caused by the genera *Aspergillus* and *Penicillium* [43] — and by bacteria and yeasts may occur under unfavourable storage conditions. Some fungi isolated from leather and the different types of damage that occur are described in Table 4.2.

4.4.3.4. MEASURES OF PROTECTION

As leather manufacturing is increasingly being transferred to the agrarian and tropical countries which produce raw hides, a chemical protection against fungi and bacteria is often essential although, depending on the end use, consideration will have to be given to economic and toxicological factors (see section 5).

4.4.4. Textiles

4.4.4.1. GENERAL

Textiles are produced from natural or synthetic fibres. In this section only natural fibres are considered and divided into plant and animal fibres:

Origin of fibres	Kind of fibres	Main component	Examples
Plants	Plant hair	Cellulose	Cotton, kapok flax, hemp, jute, manila hemp, coconut fibres, sisal
	Bast fibres	Cellulose	
	Hard fibres	Cellulose	
Animals	Wool and hair	Keratin	Sheep’s wool, llama, mohair, true silk, raw silk
	Silk	Fibroin Sericin	

Despite the increasing production of synthetic fibres about 50% of global demand is still met by cotton, with the share from wool less than 10%.

Plant fibres: Due to their high cellulose content (cotton more than 80%, jute more than 60%) plant fibres and textiles made of these fibres may be attacked by microorganisms when used under humid-warm conditions or in permanent contact with water or soil.

Animal fibres: Wool and related materials consist mainly of keratin which is a complex of sulphur-containing proteins. Keratin is relatively resistant against proteolytic enzymes, i.e. damage of animal fibres caused by microorganisms is less severe than that of plant fibres.

Table 4.2. Fungi isolated from leather and damage caused by them [40, 43, 44–46]

Fungus species	Occurrence	Damage produced
<i>Aspergillus flavus</i>	generally on leather	saponification of fats
<i>Alternaria</i> spp. <i>Aspergillus niveo-glaucus</i> <i>A. parasiticus</i> <i>A. repens</i> <i>A. unguis</i> <i>A. versicolor</i> <i>Ap. ventii</i> <i>Cladosporium</i> spp. <i>Fusarium</i> spp. <i>Mucor</i> spp. <i>Penicillium crysogenum</i> <i>P. cyaneum</i> <i>P. expansum</i> <i>P. frequentas</i> <i>Rhizopus</i> spp.	generally on leather	formation of spots and little loss of strength
<i>Aspergillus flavus</i> <i>A. fumigatus</i> <i>A. nidulans</i> <i>A. niger</i> <i>A. unguis</i> <i>Mucor circenelloides</i> <i>M. hiemalis</i> <i>Paecilomyces varioti</i> <i>Rhizopus orizae</i>	on museum exhibits/ exhibition pieces of leather tanned with plant extracts	growth and damage
<i>Chaetomium globosum</i> <i>Fusarium oxysporum</i> <i>Scopulariopsis brevicaulis</i> <i>Verticillium lateritium</i>	on shoes	growth and damage
<i>Mucor racemosus</i> <i>Paecilomyces varioti</i> <i>Penicillium claviforme</i> <i>Rhizopus stolonifer</i>	on book covers	growth
<i>Penicillium rubrum</i> <i>P. verruculosum</i>	on chrome leather	colour changes to red
<i>Penicillium verrucosum</i>	on dye layers	brightening
<i>Torula mucilaginosa</i>	on bright chrome leather	pink spots

4.4.4.2. DAMAGE AND MICROORGANISMS INVOLVED

Damage of textiles by microorganisms is not so important as it was before the middle of this century. The reason is that natural fibres can often be replaced by much more resistant synthetic fibres (as in the case of fishing nets, cordage, sandbags, tent-cloth, canvas blinds, etc.). In the meantime growth conditions for microorganisms have been studied more intensively and it is now known how to avoid damage by respecting certain conditions, e.g. by limiting the moisture content. However, this type of damage cannot always be prevented. Significant economic losses of natural and synthetic fibres due to microbial deterioration may occur at all stages of textile processing and in end-use situations. Recent estimates have suggested that the overall effects of biodeterioration could be costing the UK wool textile industry £8–10 million a year [47].

Eckhardt [48] identified microbial damage of oil paintings on canvas. When the canvas was improperly stored and became wet the fibres were attacked by *Chaetomium* sp. and *Penicilliae* and caused the paint to peel away from the canvas. Some penetration of the mycelium through fissures of the paint occurred with the development of fructification on the painted side. Such damage may also occur on paintings hung on damp walls — e.g. in churches — which are insufficiently aerated on the reverse side.

Plant fibres: Damage appearing on textiles made of vegetable fibres ranges from harmless discolourations to complete destruction. While textiles with permanent water contact are attacked principally by cellulolytic bacteria, those wetted only temporarily or stored in wet conditions are attacked mainly by moulds through the production of cellulases. They are able to destroy the fibres to a greater or lesser extent. Other fungi — without cellulolytic enzymes — are able to utilise lignin and pectin particles bound to the cellulose fibres as well as to sizing and finishing materials. This type of damage does not reduce the strength properties of the fabrics but can lead to the development of disagreeable smells and spots [49].

Animal fibres: Wool and related materials are attacked in warm and humid conditions especially by bacteria (*Bacillus mesentericus*, *B. subtilis*, *B. cereus* var. *mycoides*, *B. megaterium*, *B. putrificus* etc). Only a few moulds are able to attack animal fibres. Impurities like fat, residual soap, etc. encourage fungal growth. Initially discolourations may appear but excreted proteolytic enzymes may even destroy the fibres. Discolourations of sheep wool are caused by *Peyronellaea glomerata*. *Chaetomium globosum*, *Cladosporium herbarum*, and *Penicillium lilacinum* have been isolated from wool.

4.4.4.3. PROTECTIVE MEASURES

Graf and Segmueller [50] described the possibilities and the limitations of protection of cellulose fibre textiles against rotting. They distinguish two kinds of protective measures.

1. *Passive protection:* Choice of rot-resistant fibres (e.g. manila is more resistant than hemp), suitable storage conditions (relative humidity below 70%), use of products making the cellulose fibres resistant to microbial attack (e.g. synthetic resins) and finally modification of the submicroscopic or molecular structure of the fibres.

2. *Active protection:* Treatment with antimicrobial compounds inhibiting or killing microorganisms (see section 5).

A good survey on test methods for antimicrobial textile additives is given by Raschle [51].

4.4.4.4. NEED FOR R & D

Tests on the resistance of technical textiles to soil-burial conditions are required to predict changes of important properties (such as tensile strength) within the envisaged service life. Certain geotextiles made of flax or coconut fibres are degraded within 3–5 years. Some waterproofed textiles (e.g. for storage tanks, folding tanks, damp proof membranes) should have a service life of between 50 and 100 years.

Field trials and simultaneously accelerated tests in climatic chambers with controlled temperature and moisture conditions should be carried out.

4.4.5. Paper and cardboard (general literature [52–56])

4.4.5.1. DESCRIPTION OF MATERIALS

Paper and board vary in thickness and density (weight per unit area). Cardboard is thicker than 1 mm and weighs more than 225 g/m². It is produced by compact matting, pressing, and glueing of usually fine vegetable fibres. Cellulose, waste paper, or wood pulp are mainly used. For high quality paper rag is also sometimes used. In the Federal Republic of Germany recycling of waste paper plays an important role as 40% of demand is covered by waste paper.

Depending on the end use (newsprint, printing or writing paper, packaging material) the paper and board industry uses filling materials (e.g. retention agents, antifoaming agents).

In the paper mills the raw materials are disintegrated and transformed into a pulp by mixing them with water. The pulp is dehydrated on travelling metal screens and passes through couch presses. Finally the mat is dried on steam-heated cylinders. For environmental reasons and with a view to reducing production costs the water which is squeezed off is reused for the preparation of fresh pulp. As a result of the recirculation the water organic materials accumulate in the water and the growth of microorganisms is encouraged.

4.4.5.2. DESCRIPTION OF DAMAGE

Damage due to microorganisms may occur during the manufacturing process of paper or board as well as on the finished products. Damage occurs during the manufacturing process when the conditions are favourable for microbial growth in the pulp. When these microorganisms (especially bacteria) produce slimes (sugar polysaccharides, such as dextrans, levans and the like) the pulp cannot be dehydrated uniformly. The slime lumps cause pull-offs on the paper machine and thus they cause important economic losses.

The finished products (paper and board) can also deteriorate under the actions of bacteria and moulds when these are present in humid conditions. Microbial damage, caused particularly by moulds, renders paper and board unsuitable for their intended purpose.

4.4.5.3. MICROORGANISMS INVOLVED: MECHANISMS OF DAMAGE

Failures in the manufacturing process due to microorganisms are caused mainly by slime forming bacteria of different genera (*Leuconostoc* sp., *Bacillus* sp.). On account of slimes (mainly polymers of sugars) tears may occur in the web of paper on the paper machine since uniform fibre formation is impeded.

Paper may be attacked by several fungi (*Penicilliae*, *Aspergillae*, *Acremonium*) as well as fungi with cellulolytic activity (*Trichoderma viride*, *Humicola fuscoatra*, *Gloeophyllum sepiarium*). Damage occurs mainly at high humidities (rel. humidity of 60%).

Moulds make paper and board unsuitable for packaging, for example, hygiene risks with foodstuffs or deterioration of optical and electronic instruments. Paper used for writing and printing that is stained by moulds can no longer be marketed. Sometimes it cannot be avoided that paper and board will get wet, e.g. during transportation by ship, or where there is condensation in sealed pallets. Therefore, special protection is required by adding biocides to prevent, or at least to retard, slime formation.

4.4.5.4. SPECIAL PROTECTION OF MATERIALS

Anti-slime preservatives should be applied in such a way that smooth operation of the paper mill is ensured. The use and approval of such preservatives, e.g. methylene-bis-iso-thiocyanate, tetramethyl-thiuram-disulphide, are subject to severe regulations (xxxvith recommendation of the law for food and commodities).

To prevent mould from developing on paper and board, biocides (usually fungicides)

are used, being either added to the pulp or sprayed on to the surface. Their effectiveness is evaluated according to standard methods of test (e.g. DIN 54 380).

It is difficult to obtain long-term protection as many fungicides are lost by leaching, by deterioration or through inactivation by ultraviolet radiation.

4.4.5.5. NEED FOR R & D

A lot of research work is still needed to recommend the optimal fungicidal treatment of paper and board, and particularly the development of relevant test methods.

The producers of antimicrobial compounds (anti-slime agents) for the paper and board industry are carrying out important research work in this area.

As the conditions differ slightly from one paper mill to another the available substances cannot universally be recommended, i.e. the effectiveness must be tested in the specific mill. Moreover, a long-term application of these microbiocides may make certain species of the microflora resistant. For this reason different compounds will be needed after various periods.

4.4.6. Parchment

Apart from paper and papyrus, parchment was used in earlier times as an important writing material. It was used for the first time in the 4th–5th century instead of papyrus and it was the only writing material till the introduction of paper (12–14th century).

4.4.6.1. DESCRIPTION OF MATERIALS

In contrast to 'parchment substitutes' (greaseproof paper) or "true parchment" (packaging material impermeable to grease) — parchment is of animal origin. It is made from hides of calf, goat, or sheep, and at one time from hides of donkeys. It differs from leather in that it is not tanned and is therefore not subject to such chemical modifications as that material. The protein fibres maintain a higher tensile strength and durability. It has a basic chemical reaction and is hygroscopic, so that it must be protected from high relative humidities. It is more resistant than paper, but it degrades at temperatures above 22°C and 65% relative humidity because the collagen of hides is transformed enzymatically to gelatine [57]. Although parchment is rarely found nowadays, it is occasionally used for special bookcovers (cover material for luxury editions), drums and lampshades.

4.4.6.2. DAMAGE

Damage of parchment [61] is caused by a microbial flora consisting almost exclusively of bacteria, which produce clearly delimited, round to oval, 1–10 mm, brown to violet spots. Within those colonies the parchment substance is first weakened and then it is progressively degraded until the collagenous fibre network is liquefied. Perforations are visible after drying. Damage can advance to complete destruction: a parchment book, for example, will be transformed to a formless mass which cannot be saved [58].

4.4.6.3. MICROORGANISMS INVOLVED

Kowalik [59] attributes damage of parchment to Actinomycetales, because they prefer a slightly alkaline medium with a pH between 7 and 8. Krempf-Lamprecht [60] reports that bacteria may develop abundantly on parchment and that many of them are capable of producing discolourations as is known for raw hides, for example *Serratia marcescens*, *Micrococcus aurantiacus*, *Pseudomonas fluorescens*, *Chromobacterium violaceum* etc. Fungi colonising parchment belong to the keratinophilic moulds: *Scopulariopsis*, *Chrysosporium*, *Aspergillus*, *Penicillium* and *Cladosporium* spp.

Other authors have isolated *Bacillus subtilis*, *B. licheniformis*, *B. megaterium* and *B. pumilus* as well as proteolytic fungi like *Aspergillus flavipes*, *A. flavus*, *A. versicolor*, species of *Penicillium*, *Paecilomyces* and *Botryotrichum* from parchment.

4.5. Organic Materials — Plastics (general literature [63–65, 67, 70–85])

4.5.1. Introduction

In the last decades plastics have substituted classical natural materials in many fields. One reason is their better stability towards deterioration compared to natural materials. As the use of plastics is expanding different types of damage are being found on these materials. On the other hand, attempts are also being made to combine partial or total degradation of plastics materials with their controlled recycling and waste management.

Several physico-chemical treatments of polymers are used, e.g. pyrolysis and oxidation. However, in sterile environments, microorganisms can also effectively alter, damage, or even degrade plastics and rubber. This fact can be related to the elemental composition and structure of the polymers, their surface-properties and the specific environmental conditions.

4.5.2. Plastics and rubber

4.5.2.1. DESCRIPTION OF MATERIALS

A DIN committee has defined plastics as materials consisting mainly of macromolecular organic compounds obtained synthetically or by modification of natural products. Under certain circumstances, e.g. by heating and pressure, synthetics will melt and become formable. A survey of the most important synthetics is given in Table 4.3.

In Table 4.4. the main components of some economically important synthetics are listed in relation to both their degradability and stability.

Technological properties of synthetics can be influenced by mixing with different additives (Table 4.5. and 4.6.). Many of these additives, especially softeners, can be utilized by microorganisms and initiate microbial attack.

Rubber is a vulcanisation product of natural and synthetic caoutchouc. Contrary to the case with the raw material it maintains its elasticity for a long time. Natural caoutchouc — a macromolecular hydrocarbon — consists of 2-methyl 1,3-butadiene (isoprene) in a 1,4 - cis linkage. Its general formula is $(C_5H_8)_n$, the molecular weight is higher than 100 000. The most important raw materials for synthetic rubber production are butadiene and its copolymer (polybutadiene). During the processing of rubber the raw materials are mixed with many other compounds like accelerators (xanthates, dithioacids, thiophenes, dithio-carbo-nitrates, tetrabutyl-thiuram-disulphide, mercaptobenzthiazole and others), activators, e.g. zinc oxide, softeners (mineral oils, paraffin, stearic acid etc.), filling materials, e.g. soot, zinc oxide, kaoline, talcum, etc., anti-ageing-agents, e.g. phenyl- β -naphthylamine and colouring pigments (iron oxide, zinc oxide, antimonium pentasulphide, cadmium compounds, ultramarine, etc.). As in case of the synthetics the stability of rubber is very much influenced by the additives.

4.5.2.2. DESCRIPTION OF TYPES OF DAMAGE

Microbial damage of synthetic materials as well as detrimental effects on the properties and functions of products made of plastics has been recognised for some decades. The first significant cases of damage were reported during World War II especially from hot-humid climatic areas. These were concerned with the damage of insulating materials, plastics parts of electrical and optical instruments as well as of plastics coated clothes.

Table 4.3. List of some important polymers

Processed natural materials	Synthetics			
	Polycondensates		Polymerisates	Polyadducts
Duroplasts	Duroplasts	Thermoplasts	Thermoplasts	Duroplasts
caseine-products	phenolic resins	polyamides	polyethylene	epoxidic resins
	urea resins	poly-carbonates	polypropylene	crosslinked polyurethanes
	thiourea resins	polyesters	poly-1-butene	
				Thermoplasts
	melamine resins	polyphenylene oxide	poly 4-methyl-1-pentene ionomers	linear poly-urethanes
	unsaturated polyester resins	poly-sulphones		chlorinated poly-ethers
	alkydic resins	polyvinyl acetal	polyvinyl chloride	
	allyl resins		polyvinylidene-chloride	
	silicones		poly methyl-methacrylate	
	polyimide		polyacrylonitrile	
	poly-benzimidazole		polystyrene	
			polyacetal fluor-synthetics polyvinyl-alcohol polyvinyl-acetate poly-p-xylylene	

Table 4.4. Basic groups of some easily degradable(*) and not easily degradable(**) synthetics [62]

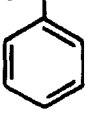
Material	Basic group	Molecular weight
polyurethane (*) DIS = di isocyanate PES = polyester PET = polyether	$-\text{OCN}-(\text{DIS}^+)-\text{N}-\underset{\text{H}}{\underset{\text{O}}{\text{C}}}-\text{O}-\begin{matrix} (\text{PES}^+) \\ (\text{PET}^+) \end{matrix}-$	10 000 and higher
polyethylene (*)-(**)	$(-\text{CH}_2-\text{CH}_2-)_n$	1500 – 7000
polypropylene (*)-(**)	$-\text{CH}_2-\underset{\text{CH}_3}{\text{CH}}-$	25 000 – 500 000
polymethylmethacrylate (*)-(**)	$-\text{CH}_2-\underset{\text{COOCH}_3}{\text{C}(\text{CH}_3)}-$	500 000 – 1 000 000
polyamide (*)-(**)	$-\text{NH}(\text{CH}_2)_5 \text{CO}-$ (Nylon 6) $-\text{NH}(\text{CH}_2)_{10} \text{CO}-$ (Nylon 11) $-\text{NH}(\text{CH}_2)_6 \text{NH}-\text{CO}(\text{CH}_2)_4 \text{CO}-$ (Nylon 6,6) $-\text{NH}(\text{CH}_2)_6 \text{NH}-\text{CO}(\text{CH}_2)_8 \text{CO}-$ (Nylon 6,10)	10 000 – 100 000
polystyrene (**)	$-\text{CH}_2-\underset{\text{C}_6\text{H}_5}{\text{CH}}-$ 	200 000 – 300 000
polyvinylchloride (**)	$-\text{CH}_2-\underset{\text{Cl}}{\text{CH}}-$	30 000 – 520 000
polytetrafluorethylene (**)	$-\text{CF}_2-\text{CF}_2-$	500 000 – 5 000 000

Table 4.5. The most important additives to synthetics

<p><i>Softeners</i></p> <ul style="list-style-type: none"> — phthalic acid esters — dicarboxylic acid esters — polyesters of adipic, sebacic, azelaic or phthalic acid with diolene — phosphates — fatty acid esters — citric acid esters — epoxidic softeners 	<p><i>Light protecting agents</i></p> <ul style="list-style-type: none"> — benzophenones — benzotriazoles — nickel-organic compounds — cyan-cinnamic acid esters — benzylidene malonate — sterically hindered amines — polymeric sterically hindered amines
<p><i>Stabilisers</i></p> <ul style="list-style-type: none"> — benzophenones — lead-, tin-, barium/cadmium-stabilisers — alkyl- and dialkyl tin-compounds 	<p><i>Optical brighteners</i></p> <ul style="list-style-type: none"> — benzotriazole phenyl cumarines — triazine phenyl cumarine
<p><i>Antioxidants</i></p> <ul style="list-style-type: none"> — thio bisphenols — alkylidene bisphenols — alkyl phenols — hydroxybenzyl-compounds — hydroxybenzyl propionate — amines — thio ethers — phosphites and phosphonites — zinc dibutyl dithio carbamate 	<p><i>Anti-ignition agents</i></p> <ul style="list-style-type: none"> — organic bromine compounds — chlorinated paraffins — organic phosphates — phosphoric acid esters — antimony trioxide
<p><i>Antistatics</i></p> <ul style="list-style-type: none"> — poly ethyleneglycol-alkyl ethers — alkyl phosphates 	<p><i>Microbiocides</i></p> <ul style="list-style-type: none"> — 10,10' oxy-bis-phenoxy arsine — N-(trichlormethylthio) phthalimide — N-(trifluormethylthio) phthalimide — tributyl tin oxide and derivatives — copper 8-hydroxyquinoline — zinc dimethyl dithio carbamate — diphenyl antimony 2-ethylhexanoate

Table 4.5. Continued

<i>Lubricating agents</i>	<i>Filling agents</i>
— metal stearates	— aluminium hydroxide
— waxes	— barium sulphate
— amides of fatty acids	— calcium carbonate
— fatty acids and their esters	— dolomite
	— glass fibres
	— kaoline
	— magnesium oxide
	— zinc oxide
	— silica, natural and synthetic
	— talcum
<i>Accelerators</i>	
— cobalt naphtenate	
— 2-mercapto benzthiazole	
— tetramethyl thiuram disulphide	
— tetramethyl ammonium sulphide	
— diphenylguanidine	
<i>Pigments</i>	
— titanium dioxide	
— iron oxide pigments	
— carbon black	
— chrome yellow pigments	
— azo-pigments	
— polycyclic pigments	

Table 4.6. Additives for polymers and their usual concentrations

Additive	Concentration (%)
Antioxidants	0.01–2
Light protecting agents	0.1–1
Microbicides	0.3–5
Processing aids	0.5–5
Pigments (Dyes)	0.02–5
Anti-ignition agents	up to 30
Softeners	up to 60
Filling agents	up to 30

Based on theoretical considerations as well as on practical experience synthetic materials can be:

- (a) degraded directly by microorganisms (in which these, or their components, act as C- and/or N-sources);
- (b) damaged indirectly by microbial metabolites (degradation of synthetics by acids, bases or enzymes; colour changes due to microbial pigments);
- (c) influenced by a simple contamination (microchips, contact lenses, medical implants and instruments).

Microbiologically caused damage of synthetic materials may occur also by combination of direct and indirect mechanisms. Microbial growth on instruments made of synthetic materials may have several technological consequences as well as causing damage of the products — even if direct or indirect degradation does not occur.

Some examples are short circuits in electrical instruments by mycelium of fungi growing on plastics parts, effects on the quality of foodstuffs (drinking water, milk, juices etc.) from biofilms on the wall of plastics tubings and tanks and epidemiological risks by proliferation of facultatively pathogenic bacteria (e.g. *Pseudomonas aeruginosa*) in plastics tubings of medical instruments. Often this type of effect is the result of microbial utilization of the additives listed in Table 4.5.

Some plasticisers are very sensitive to microbial attack, e.g. esters of phthalic, sebacic, and fatty acids as well as complex compounds. Microbial degradation of ester-based plasticisers can take place by the action of exo-enzymes (esterases).

The compounds formed by the splitting of esters, i.e. acids and alcohols can be utilized as carbon sources. However, plasticisers resistant to microbial attack are known and include glycol derivatives, epoxy-tetrahydrophthalates, and others. Microbial attack on additives may also cause changes in the physical properties of materials (embrittlement and change in bonding, tensile and tearing strengths).

4.5.2.3. MICROORGANISMS INVOLVED AND THEIR EFFECTS ON SOME PLASTICS AND RUBBER

Many types of microorganisms are involved in degradation of plastics. So far more than 250 species have been isolated from damaged plastics or used as test organisms. Fungi are the most important organisms settling on plastics. They include the genera *Aspergillus*, *Penicillium*, *Fusarium* and *Trichoderma*. Also species like *Alternaria tenuis*, *Chaetomium globosum*, *Cladosporium resinae*, *Memoniella echinata*, *Myrothecium verrucaria*, *Paecilomyces variotii*, *Stachybotrys atra* and others are often mentioned in this respect. Yeasts of the genera *Candida* and *Rhodotorula* seem to play a minor role.

Plastics are often attacked by *Pseudomonas aeruginosa*, *Serratia marcescens* as well as *Micrococcus*, *Bacillus* and *Streptomyces* species. Bacterial attack occurs mainly in soil and water.

A listing of relative stabilities of plastics and other polymers to attack by microorganisms is presented in Table 4.7. Each case has to be decided individually. Whether stability is defined by the technological applicability of a plastics, e.g. decay of mechanical properties, or by its structural integrity has to be decided for the particular case under consideration.

Details regarding damage of some specific plastics by microorganisms are given below.

Polyethylene

Polyethylene (PE) has a good to very good stability towards microbial degradation depending on its molecular weight: above 10 000 it is especially stable against moulds. The surface of PE undergoes colour changes under the action of some fungi (e.g. *Aspergillus oryzae*).

Table 4.7. Relative stability of polymeric materials to microbial attack [66]

Material	Stability
polyethylene	1 – 2
polypropylene	1 – 2
PVC-softeners	2 – 3
vinylchloride–vinylacetate copolymers	1 – 3
polyvinylfluoride	1
polytrifluorochlorethylene	1
polytetrafluorethylene	1
polyvinylalcohol	3
polystyrene	1
polymethylmethacrylate	1 – 2
polyamides	1 – 2
polyurethanes	3
epoxy resins	1
polyesters (glass fibre reinforced)	1 – 2
phenol–formaldehyde resins	1 – 3
urea–formaldehyde resins	1 – 3
melamine–formaldehyde resins	2 – 3
cellulose derivatives	2 – 3
natural rubber	2 – 3
butadiene–styrene rubber	2 – 3
butadiene–acrylonitrile rubber	2 – 3
butyl rubber	1
polychloroprene rubber	1 – 2
polysulphide rubber	2 – 3

1 = very stable

2 = medium stable

3 = less stable

Polypropylene

The sensitivity towards microbial degradation is similar to that of PE. Growth of fungi has been observed but no changes in mechanical properties reported.

Polystyrene

This plastics is known to be very stable towards microbial attack. Growth of fungi can be encouraged by a fissured surface.

Polyvinylchloride

Bacteria and fungi attack hard-PVC only very slightly. In cooling towers biofilms are formed

on PVC-surfaces following the deposition of organic sediments but little damage has been observed [70]. Some PVC-powders show fungicidal properties. Stability of soft-PVC is determined very much by the character of the additives (plasticisers) used. Colour changes caused by microbial effects are often observed on PVC.

Polyesters

The stability of polyesters towards microbial attack depends mainly on the acids used, i.e. di- or polycarboxylics. Adipic, sebacic, succinic and azelaic acid esters are biodegradable. Phthalic acid esters — economically the most important group — are resistant to microbial degradation. Similarly, polycarbonates are also resistant. The molecular weight of the polyester seems to have no influence on microbial degradability attributable to the activity of extracellular hydroxylases.

Polyurethanes

The resistance of polyurethanes (PU) towards microbial degradation depends on the chemical structure which can vary considerably. PU based on polyethers are generally more resistant than those based on polyesters. One sample of polyether-PU made of diphenylmethane diisocyanate and polytetrahydrofuran with butanediol as chain stabiliser proved to be microbiologically stable after two years burial in the soil.

Under the same conditions a sample of a polyester-PU (where ethylene glycol adipate instead of polytetrahydrofuran was used) was attacked by fungi within four to eight weeks and showed colour changes as well as formation of fissures. The microbial attack occurs mainly by the action of esterases. In the case of fungi (e.g. *Aspergillus niger*, *Cladosporium herbarum*) phenolic metabolites contribute to the PU-degradation as well. It was shown [68, 69] that microbial degradation of PU-structures occurs successively in the following order: free isocyanates, urea, amide groups, urethane groups, isocyanic acid.

Polyamides

These thermoplastic polycondensates contain linear polymer chains spiked at regular distances with carbonamide groups. Information concerning microbial degradation of polyamides tends to be contradictory. Thus, nylon textiles are subjected to colour changes by fungi growing on their surface. Signs of corrosion due to fungal mycelium were observed on a pure polyamide sample exposed to forest soil for two years. Yet the rest of the monomeric caprolactam present in polymers shows fungistatic properties.

Polymethyl methacrylate

This polymer is known to be very stable if it contains no plasticisers. Growth of fungi may cause a reduction of mechanical properties.

Natural rubber and rubber products

These materials are attacked by many bacteria and fungi. Genera involved include *Micrococcus*, *Bacillus*, *Pseudomonas* and *Actinomycetes*, *Torula*, *Aspergillus*, *Penicillium* and others. Microbial attack starts at the surface and causes pitting. Elasticity and tensile strength of rubber can be very much reduced as a result of bacterial attack.

Synthetic rubbers

These as compared with natural products are much more stable towards microbial attack. Polychloroprene, butadiene-styrene, and butyl rubber are very stable.

The behaviour of rubber products against microbial attack is very much influenced by additives. Some vulcanisation accelerators and antioxidants show bactericidal and fungicidal properties. By contrast, other additives such as plasticisers based on fatty acids may be susceptible to microbial attack.

4.5.2.4. PROTECTION AGAINST MICROORGANISMS

Plastics and rubbers may be protected against microbial attack by:

- (a) technological measures
 - choice of proper monomers and additives
 - optimisation of technology, e.g. by reduction of the amount of biogenic elements like C, N, P etc. by complete chaining).
- (b) prophylactic measures
 - addition of microbiocidal additives.
- (c) environmental measures
 - prevention of organic deposit
 - control of aeration, humidity, temperature, and pH
 - proper decontamination methods (sterilisation, disinfection, air sterilisation etc.).

4.5.2.5. NEED OF R & D

Problems are numerous and comprise:

- Investigation of the biological affinity of polymeric materials.
- Investigation of microbial stability *per se* (including superficial properties of materials) to elucidate the degradation mechanisms.
- Research into the microorganisms or successions of microorganisms involved, and (into) the genetic coding of the potential for degradation of the microbial cells.
- Evaluation of the specific influence of environmental conditions on microbial degradation activity (humidity, temperature, aeration, pH, salinity, enzyme immobilising agents).
- Formation and effects of biofilms.
- Development and verifying of test methods and their national and international standardisation.

4.5.3. Packing and gasket materials

4.5.3.1. INTRODUCTION

In many fields of construction techniques one has to deal with joints. These may be technically necessary in the initial construction or they may be introduced at a later stage. Expansion joints made to allow for different movements of parts are one important example. Elastomeric gaskets used in sewage pipelines are discussed below. Joints are frequently filled with packings and gaskets. These materials must be elastically durable and show good adherence to ensure effective sealing. Proven materials include various products made from silicones, polysulphides, epoxy resins, and polyurethanes. Depending on the application they will be used with other, mainly organic, additives. Although some basic compounds such as polyorganosiloxanes (silicones) are, as far as is known, hardly attacked microbially, some auxiliary and filler materials can be potential nutrient sources for microorganisms. Studies of tapwater systems have shown that different packing materials can sustain different microbial growths. In the case of silicones and especially polysulphide materials colour changes and slime formations can be observed. Polysulphidic packing materials have proved to be

unsuitable for sewage systems because of anaerobic microbial degradation [86]. Settling of microorganisms on packings and gaskets may have an adverse effect on their mechanical properties, i.e. on their functioning. In addition, it can cause deterioration of the microbiological composition of some products, particularly in the field of foodstuffs (drinking water). Problems concerning microbiological damage and protection of packing materials should generally follow the same principles as used for other synthetic materials.

Packing materials for sewage systems

The following data refer to packing materials made of elastomers used for sewage channels and pipelines. The reliability of pipeline connections depends on the specific properties of the packing materials as well as on the geometry and construction of the system.

As well as polyurethane materials other systems are used, for example, ethylene-propylene–diene–methylene rubber (EPDM), styrene–butadiene rubber (SBR), nitrile rubber (NBR), polychloroprene rubber (CR) and natural rubber (NR).

Damage processes

It has been determined that damage to the packing materials of sewage systems has led to total loss of material in some sections [87–93].

Microorganisms involved

In principal, damage may be caused by widely differing types of microorganisms. On the basis of the few cases studied, which are those that will probably have important consequences on the environment and ground waters, it is concluded that the bacteria involved are anerobes.

Damage

Isolated cases have been reported from service. In these, packing materials were so damaged by microorganisms that they could not fulfill their function. Packing materials have been in use now for approximately 30 years only, and therefore very little or no information is available concerning the long term behaviour.

Special protection of materials

Stability against microbiological influences can be obtained only by the choice of suitable elastomers, since microbiocides are active only for a relatively short time because of loss by leaching processes.

Environment, destruction and protection of materials

The chemical composition of domestic waste waters has changed significantly in the last 10–20 years as a result of increased use of various domestic cleaning agents. (Germany has a very high *per capita* consumption of detergents and softeners.) Moreover, the waste water temperatures are higher because of an increase in the use of domestic washing machines — for clothes and dishes.

The leak-tightness of sewage pipelines and systems plays a special role in the protection of the environment and waterways.

The requirements relating to the specific properties of elastomers are well known and are described in a 1988 revised norm (DIN 4060)[93].

R & D requirements

Methods for physical testing as well as for chemical stability have been developed on the basis of the experiences of many years. Testing methods for microbiological stability, however, still do not exist. Test methods of this kind, for example for plastics, are unsuitable (e.g. digging tests as well as testing with certain moulding fungi). The development of long term microbiocides would be desirable.

4.6. Auxiliary Materials

4.6.1. Introduction

The durability of materials discussed in section 4.2.–4.5. can be increased by coating their surfaces with more stable materials, although an acceptable aesthetical impression must usually be preserved.

In addition to this, the application of materials requires that a suitable joining technology be used, and this is becoming increasingly important on account of the use of organic adhesives.

All these auxiliary materials are susceptible to attack by microorganisms with the result that not only their particular functions but the whole system of material and auxiliaries can be altered.

4.6.2. Paints, varnishes and plasters

4.6.2.1. DESCRIPTION OF MATERIALS

The various types of water-containing wallpaints can be subject to microbial damage. Wallpaints may be divided into three main groups, viz. paints, plasters and varnishes.

Dispersion paints for façades as well as paints for humid regions of buildings often contain some synthetic materials, e.g. acrylates. Natural products like chalk or cellulose are also used in some complex formulations.

Paints will also contain thickeners as well as binding and wetting agents. These compounds are microbiologically degradable and, therefore, will be used by microorganisms as substrates [94, 95].

The same applies to the different exterior and interior plasters, e.g. plaster undercoats, trowelled plasters, spatula and scratched plasters. Often these are quite coarse dispersions containing some gritsand, and are correspondingly grained. Such plasters can be subjected to microbial decay, either in the can or when used as a finishing coat.

Water based varnishes, e.g. acrylic dispersion varnishes, are not protected against destruction by microorganisms when manufactured. But they are often not as susceptible as paints and plasters, since they contain non-degradable compounds. Solvent based lacquers may also be destroyed by corrosion after application.

4.6.2.2. DESCRIPTION OF TYPES OF DAMAGES

During the production of wall coatings there are many ways in which harmful microorganisms can get into the product [94, 95]. Similarly paints, plasters or varnishes can be contaminated after application so that microorganisms can grow and degrade them.

Sources of contamination are mainly the raw materials that are used, e.g. pigments, filling materials (chalk), thickeners (carboxymethyl–cellulose) — as well as packing materials and especially water of lower quality. Often microorganisms can come from air or dust as well as from residues of other materials [94, 95].

The consequences of microbial growth include changes on the coating surface of rheological properties, e.g. coagulation, break up of the dispersion etc. and of pH. Gases can be produced and foul smells can develop [96].

4.6.2.3. MICROORGANISMS INVOLVED AND THEIR EFFECTS

The described types of damage as described are caused by bacteria, yeasts and moulds, as well as by green algae [95]. Some microorganisms that are able to cause such damage are described below [96–98].

Colour changes of surfaces towards grey and black are mainly caused by moulds of the genera *Alternaria*, *Cladosporium* and *Aspergillus*.

Very often, green or similarly coloured growths can occur on plasters. These are caused by green algae and moulds of the genus *Penicillium*. Also yeasts of the genus *Rhodotorula* have been isolated from plasters. Colour changes are due to microbial proliferation on the surface or to degradation of components of the coating.

Colour changes in the can are caused mainly by bacteria. Some examples are yellow-orange (*Micrococcus*), yellow-brown (*Corynebacterium*), bluish-green and yellowish green (*Pseudomonas*).

Moulds also grow on the surface of products in cans. The genera *Alternaria*, *Aspergillus*, *Penicillium* and *Cladosporium* are involved in such situations.

Gas evolution and foul smells are produced mainly by bacterial degradation of components either during manufacture or later in the finished product.

Foul smells are caused by enterobacteria (H_2S , amines, carboxylic acids), clostridia (NH_3 , butyric acid, acetic acid, amines), sulphate reducing bacteria (H_2S , carboxylic acids), and pseudomonads (H_2S , amines).

Besides the strong gases already mentioned (NH_3 and H_2S), CO_2 and H_2 can also be produced by these or other bacteria as well as by yeasts.

pH-changes of the product are quite often observed. Acids are produced by moulds and by bacteria as a result of incomplete oxidation (acetic, formic, succinic and citric acid). Species of *Acetobacter*, *Corynebacterium*, *Staphylococcus* as well as several enterobacteria produce different quantities of acetic acid, ketonic acids, lactic acid, fumaric acid and oxoacids. Degradation of acids (propionic, butyric and acetic acid) by pseudomonads may be responsible for a pH-increase in the products.

Changes in the rheologic properties have often been observed in the past. This is due to the activity of bacteria and fungi which together, as they often are, degrade thickeners, stabilisers and surfactants.

Breaking of the dispersion, phase-separation, or demixing of components may be the consequence of such degradation. Raising or lowering of the viscosity may cause problems during the production and application of paints or coatings.

The flow-behaviour of products can also be changed by the so-called "nest formation". These coagulation-phenomena are caused by the joint action of slime forming bacteria and fungi. They produce high amounts of encapsulating substances, which are polysaccharides (*Streptococcus*) and polypeptides (*Bacillus*). These metabolic activities of microorganisms often lead to the clogging of pipelines and nozzles in anaerobic processes.

4.6.2.4. SPECIAL PROTECTION OF MATERIALS

Physical preservation methods can be applied to water-containing paints only as far as empty tanks and pipelines are concerned. Chemical preservation is at the moment the most usual procedure to protect dispersions [95, 99, 100].

In the manufacture of paints, varnishes, and plasters special hygienic measures are essential. Improvements can be achieved by measures taken during the construction of equipment. Deleterious contaminants and the damage which they cause can be minimized by careful cleaning and proper disinfection of all equipment in contact with the paint.

4.6.2.5. TESTING OF EFFECTIVENESS

Application of conservation agents must be considered from the beginning of the development of paint, varnishes, and plasters. Many testing methods for the effectiveness of such agents are known [99, 101–105]. Microbiological efficacy can be evaluated by agar-diffusion tests, serial dilution tests, qualitative and quantitative suspension tests. These methods are not relevant to service conditions, but they do provide a screening procedure and a good appreciation of the concentrations important for use in practice.

To obtain reliable recommendations for use in practice germ reduction tests, inoculation

tests and tests to determine fungistatic and algistatic properties are carried out [108]. The reliability of these methods must be known for predictions of microbiostatic, microbiocidal and long term effectiveness of products.

4.6.2.6. NEEDS FOR R & D

The aims of research are established mainly by the producing industry. For the most part this involves the development of both environment-protection paints (e.g. without solvents) and formulations of preservatives or products which require only very small or no quantities of biocides.

Another aim of development is the establishment of standardised test-methods to assure comparability of different products [99, 101, 103, 106–108]. These are not so far available. Existing test methods often suffer from low efficiency. New test procedures must be adapted to the practical requirements. A further requirement is that screening tests and practice related test methods for microbiological effectiveness have to be easy to conduct, relevant to practice and have good reproducibility.

Research regarding the causes of the degradation of paints, varnishes, and plasters must also be continued. This entails explaining the various routes to infection so as to confirm the knowledge gained to date, diagnosing the harmful contaminants and examining the multi-faceted effect which the microorganisms have in the degradation of materials.

4.6.3. Adhesives

4.6.3.1. GENERAL

In DIN 16920 (adhesives, processing of adhesives, terms) an adhesive is defined as “a non-metallic material able to bind parts by adhesion and cohesion” [109].

Adhesive is a general term which includes similar terms in use for this category. Thus the terminology is guided by the physical, chemical or processing aspects as follows:

GLUE is made of animal, plant or synthetic compounds with water as solvent. The term “synthetic compound” is used instead of “film forming and binding agent”.

PASTE is a water-containing swelling product. It differs from glue in its ability to produce a non-stringy highly viscous mass even at low concentrations of the material.

DISPERSION ADHESIVES consist of organic materials and a liquid dispersion medium in which the material is not soluble.

ADHESIVE SOLVENTS consist of organic materials dissolved in organic solvents.

MELT-ADHESIVES are solid and without solvents. They are used in the molten state.

REACTING ADHESIVES bind by chemical reaction.

GLUEING MORTAR is bound by cement and consists of cement, organic material(s) and water.

CONTACT ADHESIVES are used as two relatively dry adhesive films which are pressed together.

ADHERENT ADHESIVES are used as a film which adheres even at low pressure.

The names of adhesives sometimes contain indications of the principal component used, e.g. polyvinylacetate dispersion adhesive.

Other names contain indicators describing their method of application (e.g. melt-, activating, contact-, adherent-). In addition, there are names which are indicators of temperature (e.g. cold glue), colour (e.g. white glue), form of delivery (e.g. powder, droplet, tablets, stick), use (e.g. for paper, wood, assembly, wallpaper paste, rubber gum, floorstone adhesive, etc.). Besides the basic material — which is the film forming component and which determines the essential properties of the adhesive — the following components may also be present:

- solvents
- dispersion agents
- diluting agents (reactive diluents can react with other components)
- thickeners
- resins (resins may be basic material as well), non-crystalline organic compounds with a melting- or softening temperature
- filling material
- softeners
- hardeners, wetting agents
- accelerators.

Methods of glueing are divided into wet glueing, contact glueing, heat-activated glueing, solvent activated glueing and adhesive glueing.

4.6.3.2. MICROBIAL DETERIORATION OF MATERIALS

Several of the adhesives mentioned may be attacked and degraded by microorganisms. Products particularly susceptible to microbial attack are those which are put to use together with water and whose water base must be stable for a longer processing period. This refers especially to wallpaper pastes containing starch or methylcellulose. Glues based on polyurethanes, caseine and dextrine as used for labelling or for packing are suitable substrates for bacteria and moulds.

The microorganisms involved in contamination include various gram-negative bacteria, e.g. *Aerobacter aerogenes*, *Escherichia coli*, *Proteus mirabilis*, *Pseudomonas aeruginosa* and *Bacillus mycoides*, yeasts, especially species of *Saccharomyces* and *Rhodotorula* as well as moulds of the genera *Aspergillus*, *Chaetomium*, *Geotrichum*, *Penicillium*, *Scopulariopsis*, *Stachybotrys*, *Trichoderma*, *Mucor* and *Aureobasidium pullulans* [110].

Water-containing dispersion-adhesive-formulations on the basis of polyvinylacetate or styrene-acrylic acid esters (e.g. floorstone adhesives) are often susceptible to microorganisms. Joints may be attacked by moulds [111].

As a result of the activities of microbial enzymes in pastes viscosity changes may occur; thus, liquefaction of the substrate may reduce its processing capabilities. Quality of water, brushes, rollers as well as hygiene play an important role regarding contamination with germs.

Adhesive sticks based on synthetic resins may be attacked by moulds, especially where condensed surface water films are present if climatic conditions are favourable (high temperature and relative humidity), even if they have antibacterial properties.

Thermoplastic melt-adhesives containing polyamides or stranded polyethylene must be resistant to rotting, especially when used in the cable industry, where they are exposed to soil at high air-humidity or dew-water. Microorganisms — especially moulds — are able to degrade rapidly such chemicals and cause operational upsets.

The possibility of the integrity of glued joints in wood products, particularly in chip board, being adversely affected by mould, cannot be ruled out [112–115] (see 4.4.2). It has been shown experimentally that moulds are able to use different resins (phenol-formaldehyde, urea-formaldehyde, isocyanate) as a carbon source [116, 117].

Table 4.8. Classification of adhesives and their components by DIN 16920 [109]

Product class	Basic component	Number of components*	Temperature of binding*	
<i>(a) physical adherence:</i>				
GLUES	starch, dextrine	1	c	
	cellulose ethers caseine polyacrylic acid derivatives polyvinyl alcohol polyvinyl pyrrolidone			volatile solvent is evaporating during application (usually water)
	glutine (animal glues)	1	h	
PASTES	starch cellulose ethers	1	c	
SOLVENT- AND DISPERSION ADHESIVES	natural rubber, synthetic rubber of low polarity, e.g. styrene-butadiene-copolymers acrylonitrile-butadiene-copolymers polychlorbutadiene polyurethanes polyvinyl acetate vinyl acetate copolymers, e.g. ethylene-vinyl acetate copolymers polyvinyl propionate polyacrylic acid esters polyvinyl ethers polyvinyl chloride vinyl chloride copolymers vinylidene chloride copolymers polyesters polystyrene styrene-acrylic acid esters	1 (2)	c, h	volatile solvent or dispersion agent evaporates mainly before or during application
	vinyl chloride polymers (plastisol adhesives)	1	h	without any solvent or dispersion agent
MELT ADHESIVES	styrene-butadiene and styrene-isoprene block copolymers ethylene-vinyl-acetate-copolymers vinylacetate-vinyl-ester-copolymers polyamides and polyamidoamines polyesters	1	h	
<i>(b) chemical adherence:</i>				
REACTING ADHESIVES	waterglass	1, (2)	c, (h)	volatile solvents or water are evaporating (together) with volatile reaction products during application
	cement and organic basic compounds	1, (2)	c	
	water soluble condensation resins (phenol-, melamine-, -urea-, formaldehyde resins)	2, (1)	h, c	
	phenol formaldehyde resins in combination with polyvinylacetals or nitrile-rubber	1, 2	h	volatile reaction products escape during application
	polyimides, polybenzimidazoles	2	h	
	special silicone-resins, binding with moistening	1	c	volatile but reactive reaction products are involved in formation of adhesive layer
	unsaturated polyester resins vinyl- and acryl-compounds	2	c	
	dimethyl acrylic acid ester of diolene, binding anaerobically	1	c	
	cyan acrylic acid ester	1	c	
	polyisocyanates, binding with moistening	1	c	
	polyisocyanates + polyol compounds	2	c, (h)	
	epoxy resins + polyamines or polyamidoamines	2	c, (h)	without volatile components
epoxy resins + acid anhydrides	2	h		
epoxy resins, special formulations	1	h		

* symbols in brackets represent possible alternatives

c = cold

h = hot.

4.6.3.3. PROTECTION OF MATERIALS

Protection of water-containing adhesive mixtures against microorganisms is usually achieved by using chemical preservatives. Hygiene of the product is very important and so Good Manufacturing Practice (GMP) — must be adopted. Clean receptacles or containers should be used. So as to guarantee a good level of the processing stage bactericide and fungicide additives are used to try to ensure adequate preservation of glues and pastes, for example. This curbs the contaminations brought about by the use of handtools.

Macromolecular melting adhesives in contact with soil cannot be easily protected. In some cases stability against microorganisms is provided only by the quality of the raw materials used.

4.6.3.4. TESTING OF EFFECTIVENESS

During development of microbially sensitive adhesives it is necessary to check the effectiveness of antimicrobial agents. Estimation of effectiveness against microorganisms and determination of suitable concentrations can use methods like the agar diffusion or serial dilution tests. In this way it is possible to distinguish between microbiologically active and inactive systems.

Reliable recommendations for practical use regarding the long term germ reduction properties of a product may be obtained using the cyclic inoculation test.

Polymeric melting adhesives can be tested using the international standard method ISO 846-1978 which covers the stability of raw materials against microbial attack. DIN 53739 [118] corresponds to the ISO standard 846-1978 [120].

Testing of the resistance of floorstone and mosaic adhesives against moulds is described in British Standard BS 5980, Section 7 [119].

In British Standard BS 3046 specifications are established for adhesives used for suspended mobile wall coverings. In appendix No. 6 of this standard the behaviour against moulds is described [120].

4.6.3.5. R & D REQUIREMENTS

- Increase of the stability of adhesives, as well as improvement of working with adhesives, and of their binding strength. Consideration of production hygiene, toxicological and ecological factors.
- Development of melting adhesives having better biostability without addition of biocides.
- Long term studies regarding behaviour of adhesives at the interface of two materials against microorganisms in different climatic conditions.
- Development of test conditions with special regard to practice.
- Standardisation of test methods.

4.7. Mineral Oil and Other Hydrocarbons

4.7.1. Introduction

Oil and the products of its distillation and cracking products as well as all the various auxiliary products containing these are attacked by bacteria and fungi, i.e. they are used as carbon- and energy sources. All gaseous (C_1 - C_4) and volatile hydrocarbons are also used.

The number of microorganisms in soil degrading hydrocarbons is 100–1000 times below that for other usual heterotrophic bacteria.

Degradation starts under aerobic conditions. Many species of bacteria are able to degrade hydrocarbons anaerobically, i.e. in conditions with less than 1.5 mg/l oxygen using nitrate as the hydrogen acceptor, and this property has been used for *in situ* cleaning of polluted environments. The production of bacterial and yeast-proteins from hydrocarbons is, for the time being, the focal point of biotechnological concern.

Depletion of oxygen, metabolic products, and hydrogen sulphide produced by desulphurisation may cause corrosion to occur at all stages beginning with the extraction and storage of oil.

4.7.2. Description of materials

Oil contains hydrocarbons and other organic compounds as well as carbon, oxygen, sulphur, nitrogen and trace elements. The hydrocarbons are alkanes (straight chain carbon compounds) or isoalkanes (branched carbon chains), cycloalkanes (cyclic compounds), or aromatics (cyclic, unsaturated compounds). The ratio between these compounds varies depending on the origin of the oil. Like oil, the gaseous hydrocarbons methane, ethane, propane and butane were and are still being produced biologically with or without physical influences.

Refined products are obtained by distillation or by cracking. Final products are often mixtures with other organic or inorganic additives. Some end products additionally contain emulsifying agents.

4.7.3. Processes causing damage

Most of the compounds and mixtures mentioned are degraded by bacteria and fungi either partially or completely. Attack by microorganisms leads to a reduction of concentration or to the disappearance of some compounds. Metabolites resulting from such degradation consist of organic acids and esters. These can cause deterioration of materials and promote growth of other microorganisms.

At the present time discussions are taking place on the anaerobic degradation of pure hydrocarbons. Oil and its refinery- and end-products can be attacked anaerobically especially if supplementary hydrogen acceptors like nitrate and sulphate are present in the biotope. Hydrogen sulphide is produced by microbial sulphate reduction, and this will promote the corrosion of metals.

Many hydrocarbons are insoluble in water. During the degradation of hydrocarbons bacteria may produce emulsifying agents, which may promote further degradation.

4.7.4. Microorganisms involved

Numerous species of bacteria and fungi are known which can degrade hydrocarbons and at least one green alga (*Chlorella vulgaris*) may also be involved. Several other genera and species may attack compounds present in oil. In an overview, it is necessary to mention many species and genera which use intermediates from the degradation processes.

Among methane-degrading bacteria and yeasts there is a group of bacteria which specialise in using chlorine-containing compounds. There are also other methane-using bacteria that are able to degrade longer carbon chains.

4.7.5. Typical examples of cases of damage

Already during extraction of oil — especially during flooding and other subterranean treatment of oil fields as well as during treatment of water—containing oil — corrosion occurs which is not only brought about by microbial sulphate reduction. Extraction of oil can be reduced by clogging of initially open pores of the rock by biomass.

Oil and gas are stored in geological formations. Aerobic bacteria and sulphate reducers

(either indigenous or present from drilling processes or water flooding) enrich hydrogen sulphide in the product. Water flooding installations are exposed to microbiological corrosion independently of the salt content of the water which was originally present or introduced later.

In the case of the overhead storage of hydrocarbon-containing products the accumulation of condensed water is unavoidable. Domestic oil tanks are also corroded as a result of aerobic and anaerobic bacterial activity if water from condensation is present.

Cooling systems (cooling circuits) of refineries and similar installations suffer from proliferation of bacteria with biofilm formation, especially if products (hydrocarbons) enter by leakage. The biofilms growing on the inner surface reduce heat exchange to a greater extent than chemical depositions. They also cause accelerated corrosion. In the biofilms microbiological processes take place as described in section 2.4.4.

Lubricating oils can lead to corrosion of metals if sea water or sweet water is present. The driving shafts of ships are corroded in such situations. In engine oils of cars which are out of operation bacteria grow and cause corrosion of the sump. Fuel (gasoline, Diesel-fuel, kerosine) is also attacked by microbes. Clogging of carburetors by bacteria in tropical countries as well as the growth of the fungus *Cladosporium resinae* in fuel tanks and pipelines of aeroplanes are known to be cases of biodeterioration.

Cooling lubricants are used for metal cutting in quantities of about 100 000t annually. They are mainly oil-water emulsions containing up to 10 components. Both the oil and the additives are attacked by bacteria and fungi. The effects are pH-reduction, desulphurisation with evolution of hydrogen sulphide, consumption of components and finally breaking of the emulsion.

Oil-containing hydraulic liquids also need to provide protection against corrosion. The "Luxemburg Reports" contain the results of tests but these did not consider the effects of microorganisms. If parallel tests had been conducted with and without microorganisms significant differences of weight loss would be observed for different metals.

4.7.6. Special protection of materials

Biocides can become effective if the substrate is not consumed or changed and neither acid nor hydrogen sulphide produced. In such cases metals can be protected against corrosion and protective coatings are effective. In other cases aeration is useful, for example, in inhibiting the growth of sulphate reducing bacteria.

4.7.7. Environment, materials degradation and protection

Any protection of materials is environmentally relevant in the sense that it will reduce the need for new, i.e. replacement, products. Corrosion occurring during oil production cannot be prevented. But biocides can be added to the wash and rinse liquid used during drilling. The same method can be used for extraction of remnant oil from its deposits when pore clogging has occurred. In case of overhead storage of hydrocarbons protective coating of the metal tanks is required. Addition of biocides to products can partially inhibit corrosion and degradation of products. Corrosion of cooling circuits by biofilms causes leakages, which may become significant for the environment. Cooling lubricants as well as hydraulic liquids can be protected against degradation by addition of biocides (environmental problems), but maintenance procedures of the pipeline (i.e. proper cleaning) may also be useful in preventing early destruction. Stable emulsifiers prevent the breaking of emulsions, but they can promote proliferation of fungi.

4.7.8. R & D requirements

In Germany the cooperation between research on corrosion and microbiology has recently been organised more intensively by DECHEMA. In the UK and the USA studies are being

made in the Universities and in the relevant industries. Research on biocides is conducted in Germany almost exclusively in a few industrial laboratories. There are only a few exceptions. Practically no basic research is being carried out and much R & D work is needed, for example in the following areas:

- origin, effects and prevention of bacterial contamination during oil extraction.
- development of biocide-free extraction methods.
- inhibition of the growth of bacteria during storage of gas and mineral oil (storing in tanks or caverns).
- inhibition of the growth of bacteria and fungi during application (use) of fuel and lubricants.
- fundamental research into the triggering of microbial corrosion by microorganisms in suspension and in biofilms.
- prevention of biofilm formation and removal of biofilm using environmentally-friendly measures.
- prevention or control of the growth of microorganisms in cooling lubricants and hydraulic fluids.
- development of suitable test methods for national and international use.

4.8. Processing and Refining of Raw Materials and Working Materials

4.8.1. Introduction

Raw materials and working materials, as defined in this study, are processed by physical or chemical treatments and microbial processes have hitherto been used only rarely.

In historical China high quality kaoline for manufacturing of high quality thin porcelain used to be treated with liquid manure and then matured for decades. Bacterial slimes increased the plasticity while the organic acids shifted the grainsize distribution towards lower values. High quality kaolines are clean white. Natural impurities e.g. Fe (III), cause undesirable colour changes during firing. The addition of organic matter removes iron by complexation and/or reduction by microbial metabolites (see 4.8.2.).

Extraction of valuable metals (Cu, U, Zn) from lowgrade ores by microorganisms is successfully carried out at several places. At the moment, newly described organisms are used to optimise different processes in Germany. In the context of environmental protection, more importance should be given to microbial leaching of slag and dust, even, where necessary, prior to recycling (building materials!) (see 4.8.3.). Inorganic sulphur from certain coals can be removed economically to an extent of more than 90% using bacteria. In this way SO₂ emissions during burning are reduced. Hardcoals are solid materials, their handling is often inconvenient, uneconomic, or even impossible especially when compared to handling of oil. Some fungi are able to liquefy completely certain brown coals. Hard coal is also attacked by microorganisms. Therefore, the liquefaction of coal or the production of coal slurries by microbial routes is being studied (see 4.8.4.).

4.8.2. Ceramic materials

4.8.2.1. DESCRIPTION OF MATERIALS

Today the oldest and most important ceramic raw materials are clays and kaolins. They were produced by weathering and other natural transformation processes from primary rocks. Their grain sizes are extremely low typically between 0.1 and 10 μm . At 1 μm grain size 1 ml contains approximately 1 billion grains with a total surface of about 600 m^2 . This grain size allows a very high number of particles to be in contact and react with each other. The surface forces that are present in all solids are in this case very strong, so there is considerable coherence. Dried clay lumps are very hard. Clays and kaolins are natural sedimentary rocks and consist of a mixture of different very fine mineral particles, mainly of clay minerals (layer silicates). Untransformed particles of the original rocks, especially very fine quartz particles and feldspar grains as well as tourmaline crystals, small rutile and zircon crystals, and iron-containing minerals are also present. Furthermore, a whole series of other minerals newly formed in the sediment can occur, the most significant being sulphides (pyrite), sulphates (gypsum), carbonates, and bicarbonates as well as hydroxides.

4.8.2.2. DISTURBING PROPERTIES

Colouring minerals e.g. iron containing minerals, titanium, copper minerals etc. are of particular importance for ceramics. During firing a coloured product is obtained with iron and titanium impurities giving a yellow to red colour which will depend on their concentration. Materials giving pure white products are very valuable but are seldom encountered naturally.

The intention in refining raw materials is to remove the colouring components without changing the basic properties.

Furthermore, by treating kaolin with bacteria to refine the composition of its grains, it can be rendered more readily processible.

4.8.2.3. MICROBIOLOGICAL EFFECTS DURING AGEING

The idea of improving ceramic raw materials by microbial treatment is very old. The ability of the Chinese to produce extremely thin porcelain is attributed to the fact that they use kaolins that had been organically exposed to bacteria for decades. Scientific papers regarding microbial treatment of clays can be found in the literature of the fifties and sixties [121–124].

Plasticity has been positively influenced, bending strength was improved, and tensile strength of the fired product enhanced by treatment with liquid manure for 12 years and by *Azotobacter* B25 for 85 days.

More recently, papers from Russian authors [125–129] discussed bacterial treatment although the precise species of the bacterium used has not been described. Four varieties of silicate bacteria which were discovered in the fifties are mentioned, and some details are given of optimal conditions for treatment of clay suspensions with these bacteria. The results agree with the statements made by Oberlies *et al.* [121–124], i.e. improvements in plasticity, bending strength of the dried product and tensile strength of the fired products. In both cases results were attributed to the action of slimes produced by bacteria as well as to the improvement of the plasticity and increase in the coherence of the particles. Attack by organic acids resulted in the grain size becoming smaller. However, in none of these examples was any analytical evidence given concerning the compounds involved. A recent Russian paper has provided information about the construction of a pilot plant for production of ceramic floor tiles using microbially aged clays [129].

4.8.2.4. MICROBIOLOGICAL IRON REMOVAL

An increase in the concentration of iron ions was observed in some cases in the supernatant liquid during treatment of kaolinitic and illitic clays with heterotrophic fungi and bacteria [133] after treatment times of 30 to 150 days. The maximum quantity of dissolved iron was 5000 times

higher than in sterile controls. This corresponds to 10% of the total iron content in a single treatment. Organic acids as well as slimes were detected, especially gluconic and citric acids. Therefore, chelation must be very important. Reduction of Fe^{3+} is possible due to the slightly reducing conditions which are accelerated by the fact that iron oxides have a relatively high solubility product. The reduction rate of Fe^{3+} by bacteria in soil is dependent on the activity of the bacteria involved; the concentration of easily degradable organic matter; the oxygen concentration; the reactivity of the species and the concentration of iron minerals present [131]. A survey of the processes is shown in Fig 4.3.

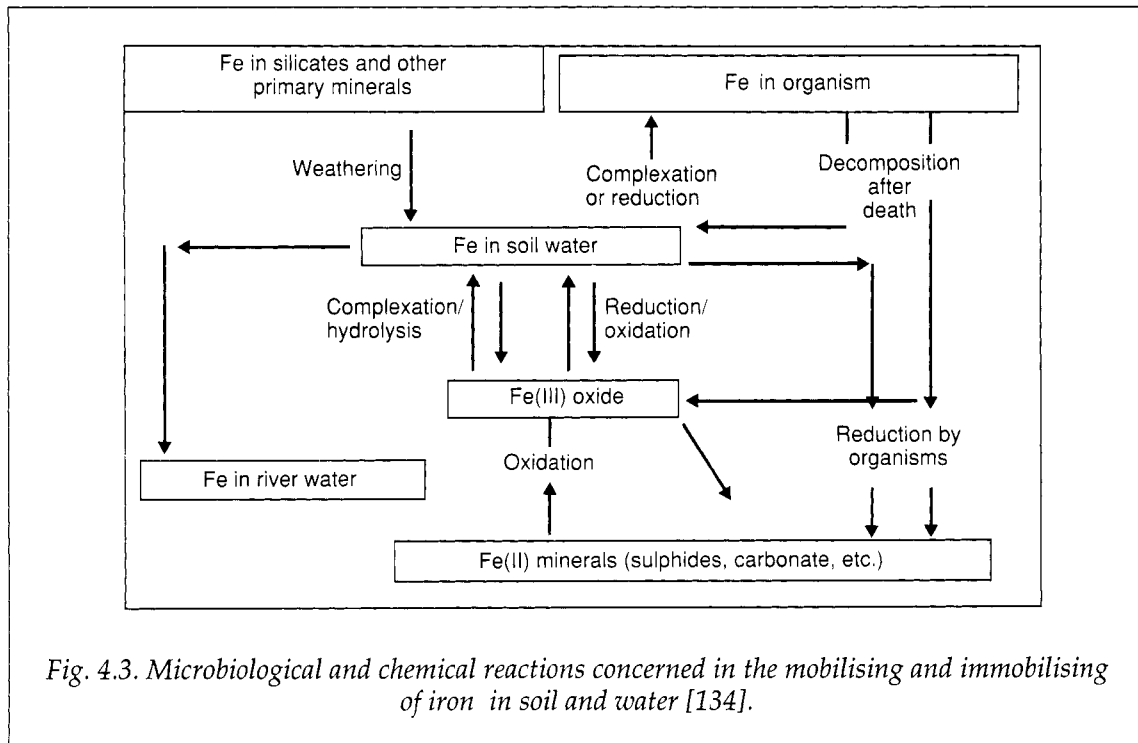


Fig. 4.3. Microbiological and chemical reactions concerned in the mobilising and immobilising of iron in soil and water [134].

4.8.2.5. R & D REQUIREMENTS

High quality raw materials will not be at our disposal for an unlimited time or in unlimited quantities. It is therefore necessary to develop microbial technologies for upgrading low quality clays as well as for purifying synthetic raw materials. One possible way for the extraction of iron is by the use of fungi and bacteria as is generally applied in ore leaching [130]. Soil science studies have shown, for example, that bacteria and fungi are able to solubilise iron after reduction [131]. And, in the same way, iron has been successfully extracted from sand by use of a fungus [132].

Current work on different clays using fungi (*Aspergillus niger*, *Penicillium citrinum*) as well as bacteria (*Arthrobacter uratoxidans*, *Pseudomonas acidovorans*, *Bacillus subtilis*, *B. megaterium* and *Thiobacillus ferrooxidans*) is promising.

The aim of such work should be towards a qualitative improvement of indigenous ceramic raw materials by applying biotechnological processes.

Optimised biosystems should be used in laboratory experiments which must then be scaled up to the technical level that deals with raw material in the pilot plant. For this purpose adequate instruments including those for measurement and control must be developed and optimised. The scale up to an industrial level must be proved by pilot plant production. The

treated products, e.g. upgraded ceramic raw materials, should be used to reproduce all usual manufacturing steps until the final product is obtained. The results must be confirmed by comparison with those obtained using the untreated raw materials.

4.8.3. Leaching of valuable metals

4.8.3.1. FUNDAMENTALS

Microbiological leaching methods are being increasingly applied to low-grade ores and concentrates as well as to metal-bearing industrial wastes that cannot be processed by conventional methods.

As is the case with many biotechnical processes, such methods have been used since prehistoric times; it is probable that the Greeks and Romans extracted copper from mine water more than 2000 years ago. However, it has been known only for about forty years that bacteria are mainly responsible for the enrichment of metals in water from ore deposits and mines [135].

These bacteria belong to the genus *Thiobacillus* and grow under aerobic conditions. They are chemolithoautotrophic, i.e. to grow they require only inorganic salts and carbon dioxide from the air. The most important of the *Thiobacilli* for the leaching of metals are *T. ferrooxidans* and *T. thiooxidans*. They are capable of transforming insoluble metal sulphides and elemental sulphur into water-soluble metal sulphates and sulphuric acid via biochemical reactions.

Since the discovery of the *Thiobacillus* species, a number of bacteria have been found that are capable of leaching metals. Some of them are extremely thermophilic, growing at temperatures up to 80°C and, moreover, showing specificity to certain metals [136].

Research on the leaching processes occurring in fissured ore deposits and abandoned mines have led to the development of the new technology of microbial leaching. Bacteria isolated from acidic mine water are used for economical leaching of valuable metals, especially copper and uranium, from low-grade ores and mining wastes.

The simplest way to conduct microbial leaching is to pile the material in heaps, allow water to flow through the heap, and collect the seepage water (leachate). Because bacterial oxidation of sulphides is much slower than other biotechnical processes, the leachate is recirculated through the ore. There are three main procedures in use: underground leaching, heap leaching and dump leaching.

4.8.3.2. UNDERGROUND LEACHING

Underground microbial leaching is usually carried out in abandoned mines. Drifts are flooded or the unmined ore or mine wastes in a drift are sprinkled or washed under pressure. The water collects in deeper drifts and shafts and is then pumped to a processing plant at the surface. The best known application of this procedure is at the Stanrock uranium mine at Elliott Lake in Ontario, Canada [137, 138].

Ore deposits that cannot be mined by conventional methods because they are too low-grade or because they are too small can be leached *in situ*. Solutions containing the appropriate bacteria are injected into boreholes in the fractured orebody. After a sufficient time for reaction, the leachate is pumped from neighbouring wells or collected in drifts. Prerequisites for this are a sufficiently high level of permeability in the ore body and impermeability of the country rock so that seepage of the leachate is avoided.

4.8.3.3. DUMP LEACHING

Low grade ore or mining waste is piled in a dump. The top of the dump is sprinkled or flooded. The leachate is collected at the bottom of the dump and recirculated through the dump after the metal content has been extracted. Before recirculation, the leachate is passed through a so-called "oxidation basin", in which the bacteria and iron(III) are regenerated.

4.8.3.4. HEAP LEACHING AND LEACHING OF SUSPENSIONS

This procedure is used mainly for fine-grained ores that cannot be concentrated by flotation.

The leaching is done in large basins containing up to 12 000 t of ore. The procedure is similar to that of dump leaching. Metals are precipitated or extracted from the leachate. Considerably higher yields can be obtained by leaching of the fine-grained material in stirred tanks (bioreactors) [139].

4.8.3.5. OPTIMIZATION OF THE PROCESS AND ECONOMIC ASPECTS

The effectiveness and economics of microbiological leaching are highly dependent on the activity of the bacteria and the chemical and mineralogical composition of the ore. Maximum yields can be obtained only if leaching conditions correspond to the optimum conditions for bacterial growth. Therefore, the results obtained for one ore cannot be expected to be unconditionally valid for another. It is necessary to determine optimum conditions on a laboratory scale before pilot plant tests can be made.

Important parameters influencing bacterial activity are grain size, temperature, pH, essential nutrients, oxygen supply, and sensitivity to heavy metals. Within certain genetic limits microorganisms can adapt to special types of ores and leaching conditions.

At present, microbiological leaching processes are being used essentially only for copper and uranium. In the future, however, these processes will become important for zinc, nickel, cobalt and molybdenum. Investment and operating costs are much lower than for conventional pyrometallurgical and hydrometallurgical processes. The processing plant can be built in the immediate vicinity of the ore-deposit, saving transport costs. The procedures are not complicated and are easy to control since extensive technical knowledge is not required. This technology should be of great interest for developing countries.

Besides the metals recovered in the leachate, there is increasing interest in the insoluble metals left in the residues, e.g. gold, silver and lead. Inferior lead sulphide concentrates can be transformed into high-value concentrates by leaching of metals (e.g. zinc, cadmium and copper) that interfere with conventional processes for the recovery of the lead [140]. Similar procedures are being researched for the extraction of gold and silver that are disseminated in iron, arsenic, copper and zinc sulphides. The metal sulphides are first removed by microbial leaching and the noble metals are then recovered by cyanide leaching. Combination of these two processes proved to be much more efficient than cyanide leaching alone [141–143].

At present, microbial leaching at the plant scale is done only with *Thiobacillus ferrooxidans*. However, these bacteria cannot be used for many industrial metal-bearing wastes because, for example, the metals in fly ash and slag are present mainly as oxides rather than as sulphides. Experiments have shown that the metal oxides in such residues can be leached by acids produced by *T. thiooxidans*. Depending on the substances in the residue, vanadium, chromium, copper and zinc can be almost completely recovered [144]. In some cases, chemical leaching is easier. Microbial leaching using *T. thiooxidans* is advantageous if inexpensive sulphur is available so that transportation costs for shipping of the acid needed for chemical leaching can be avoided.

Thiobacilli are also usually unsuitable for oxide, carbonate and silicate ores although research is in progress on the use of heterotrophic bacteria and fungi for such ores. The metals in this case are dissolved by organic acids or complexing or chelating agents produced by the bacteria or fungi [145].

Studies on lateritic nickel ores show that nickel is dissolved by organic acids produced by microorganisms, the most effective being citric acid. With nickel-tolerant strains of penicillium, up to 80% of the nickel is extracted, depending on the mineralisation. Various other valuable metals (e.g. gold, titanium, aluminium, chromium, copper and uranium) can also be leached using heterotrophic microorganisms, although much development work remains to be done. Commercial application will ultimately depend on supply and demand of raw materials.

4.8.3.6. R & D REQUIREMENTS

Microbial leaching is being taken into consideration today not only because of its use in recovering valuable metals but also because there is a demand for less expensive and environmentally friendly processes. Further development is necessary with respect to both the technical and biological aspects. The latter include increasing the rate of leaching and increasing the tolerance of the microorganisms to heavy metals. Gene technology may bring results more quickly than conventional procedures like screening or adaptation.

4.8.4. Microbial beneficiation of coal

Studies concerned with the microbial processing of coal have had varying degrees of success. Several topics can be mentioned:

- liquefaction or gasification of coal
- sulphur removal from coal
- demineralisation of coal
- preparation of coal slurries
- transformation of coal products.

4.8.4.1. LIQUEFACTION OR GASIFICATION OF COAL

The aim of this process is to obtain material which is easy to handle, for example, as a pumpable liquid or an ash- or pollution-free gas, by breaking up the organic polymeric structure of the coal. Work is done using naturally or chemically/thermally pretreated coal. Certain brown coals can be liquefied to extents of more than 90% by fungi and bacteria with only a small decrease in the content of combustibles. The disadvantage is the hydrophilicity of the brown coal compounds with molecular weights between 50 000 and 100 000. Bioconversion of hard coal is much more difficult, but it has been shown that bacteria as well as fungi are able to attack hard coal, dissolving about 10% of the coal. Investigations are currently being carried out to determine how the products of these microbial processes can be exploited.

4.8.4.2. SULPHUR REMOVAL FROM COAL

Coal contains two types of bound sulphur: inorganic sulphur as pyrite (FeS_2) as well as organic sulphur present in thiol groups, thio-ethers and heterocyclic (e.g. thiophene).

Sulphur dioxide formed during burning of coal is disadvantageous for several reasons. However, inorganic sulphur in coal can be removed by thiobacilli and other sulphur oxidising bacteria. Thus, pyrite clusters can be transformed into soluble sulphate ions. Pilot plants are already working in this field. The economics of the process *vis a vis* chemical/technical processes are however still not definitively known.

Removal of organic sulphur has not been so successful, and research is still at a rather basic level. Trials have been made using model compounds and in the USA a pilot plant has already been built.

4.8.4.3. EXPERIMENTS TO DE-ASH COAL

After burning, non-flammable components of coal are left as ashes or slags. They make handling of coal more difficult and lower its value. Thiobacilli, in particular, are being used for solving this problem.

4.8.4.4. PREPARING OF COAL-SLURRIES

The preparation of coal slurries provides another possibility for transforming coal into a liquid-transportable form. Coal slurries are pumpable coal powder suspensions in oily or aqueous medium which can be transported through pipelines or tanks. Whereas in oily suspensions there is no alternative to the use of microorganisms, aqueous coal suspensions can be prepared by adding chemicals like surfactants for stabilisation and polymers for increasing viscosity.

Such compounds can also be produced by microorganisms and probably offer a cheap alternative to chemical additives.

4.8.4.5. TRANSFORMATION OF COAL PRODUCTS

In the field of the so-called “white coal chemistry” it is intended to transform certain coal derivatives (e.g. coal tar) by microbial treatment (e.g. oxidation) into valuable products. An example is the transformation of tetralin to raw materials for the synthesis of insecticides and pharmaceuticals.

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Protection of Materials

5.1. Introduction

The aim of the protection of materials is to maintain unchanged a certain material for a sufficiently long time under given conditions. Therefore, as many as possible of the damaging and destructive influences must be eliminated.

Degradation caused by microorganisms is of worldwide importance. Annually about 10–20% of crops and their derivatives are destroyed. The danger is based on the rapid proliferation of microorganisms, on their high capacity to degrade, as well as on their metabolic activities. The term “omnipotent degradability” is known.

5.2. Deterioration of Materials

The stability in storage, “survival”, of a material can be adversely influenced by many factors. The damaging influences can be physical, chemical and biological.

Physico-chemical damages are caused by air and gases (SO_2 , NO_x , O_3 , UV-light), humidity, heat, complexation, hydrolysis and by foreign substances from packing materials.

Microorganisms can cause changes in materials properties like odour changes, colour changes, gas formation, pH-changes, changes of consistency, corrosion and surface growth. Enzymatic damage is also due to microorganisms even if they (mainly bacteria and fungi) can no longer be detected in the product. The enzymes excreted by microorganisms are able to degrade natural products because enzymes are often not rendered inactive by preservatives.

5.3. General Measures of Protection

Many materials are exposed to microbial deterioration and important economic losses can occur. A few examples include textiles, wood, cooling-lubricants, soft PVC, metals, natural stones and concrete. Cosmetics and pharmaceuticals as well as foodstuffs are also subject to microbial degradation, but destruction of these has not been within the objectives of the “Microbial Deterioration and Protection of Materials” working group; and therefore, they are not discussed here.

Protection of materials from microbial effects can be achieved in various ways: physical, chemical and the use of coatings and platings. Combinations of these methods are used.

Physical measures involve controlling the humidity, the use of temperature effects (coldness, heat), irradiation as well as design measures (drainage of water).

Chemical measures include the application of preservatives (microbiocides), fungistatics, bacteriostatics and algistatics as well as pH-changes. Impregnations are also often used.

Protection by surface treatment can be achieved according to the DIN Standard 8580 (Coatings) by coating or hydrophobising. Solidification, e.g. the use of silicon organic compounds is also a common protection method.

In combating the microbial deterioration of materials it is often not necessary to kill all microorganisms present. It is usually sufficient to suppress their growth by a change of conditions, e.g. by reducing the water content. Drying processes lead to a very labile

microbiological condition in which the surviving germs may grow again, if the minimal water content is exceeded. The product is then ruined. Similar conditions are fulfilled in cases of storage by cooling since most microorganisms survive and as soon as the temperature is increased proliferation of the germs will start again. Pasteurisation and boiling are heat treatments with a temporarily preserving and disinfecting effect. Thus, vegetative germs are killed, but bacterial spores are able to survive and germinate after a short time interval.

Raw materials, which have to be biologically degradable (e.g. detergents, surface active compounds), must be preserved, otherwise they can be degraded during transport before use. Fluids and half-solid products containing water are obligately sensitive towards microorganisms. Such products should be marketed in a stable form in containers suitable for multiple dispensing. It must be accepted that there is a potential for infection at each opening of the container with the consequence that the product may soon be altered. The risk exists that such articles will become unsuitable for use and even present health risks. These risks concern the product, as well as the users, and can be avoided by addition of a suitable preservative. This kind of preservation is generally called "in can preservation": and means that growth of bacteria, yeasts and moulds in the container must be suppressed during storage and use.

It must be pointed out that preservative agents do not replace the need for hygiene. If manufacturing hygiene is not good, i.e. manufacturing is not based on GMP-regulations (GMP = Good Manufacturing Practice), the product will contain high numbers of germs. In such cases addition of preservatives will only seldom provide the required sanitation. But even where disinfection is successful, it is still possible that enzymes liberated from dead microorganisms can lead to degradation of some other compounds and so cause degradation of the product.

A special case of chemical preservation is the microbiostatic finishing (biocidal finishing) of products in which the preservative becomes active only after treatment of the surface. This inhibiting treatment protects the surfaces against growth of moulds and green algae for a certain period.

From these considerations a definition of preservatives was deduced by Wallhauser in 1988:

Preservatives are well defined chemical compounds or mixtures able to kill microorganisms at low concentrations or to inhibit their growth, showing at the same time good compatibility towards the product to be protected.

This definition can be extended to all materials but interactions with human beings and the environment must still be considered. It can be concluded that for a new product questions regarding proper preservation should be met during the product development stage.

5.3.1. Claims for preservatives

Preservatives for different fields differ very much regarding the conditions they must fulfill. The number of compounds are in use illustrates this situation. For food only five preservatives are allowed whereas for chemical-technical products about 80 compounds are used.

5.3.2. Selection of a preservative

Because there is no "universal" preservative suiting all demands it is very important to consider all criteria for a selection. The well known and proven preservatives differ very much from each other across their spectrum of activity, optimum pH, solubility, distribution coefficient, compatibility with other components and temperature dependence, as well as by their price effectiveness ratio. In the following table below some common preservatives are shown.

Table 5.1. Common preservatives (From Wallhaeußer, IVth Edition, 1988, Georg Thieme Verlag, Stuttgart)

Preservatives	Application
sorbic acid	food, cosmetics
benzoic acid	"
PHB - ester	"
formic acid	"
carbendazime	wood
copper pentachlorophenolate	textiles
copper 8-hydroquinoline	textiles, paints
hexahydrotriazine	cooling lubricants
oxazolidine	drilling and cutting oils
methylene-bis-thiocyanate	paper
chloracetamide	leather
p-chlor-m-xylene	leather, dyes
1,2-benzisothiazole -3-on	adhesives
iso-thiazolinone	dispersion paints

5.3.3. Testing of microbiological efficacy

As in the cases of sterilisation and disinfection the methods of testing the effectiveness of preservatives in preventing microbial degradation cannot be conducted without microbiological validation. This can be carried out by various methods, which are not standardised. These various types of tests are concerned with microbistasis and microbicity, like cyclic inoculation tests, germ reduction tests and other methods. In these studies representatives of different damaging microorganisms must be used with the selection based on the aim of the test and the field of application of the particular preservative. Organisms for testing are mainly defined strains of gram positive and gram negative bacteria, yeasts, and moulds, as well as green algae. To render test conditions more difficult and to avoid possible mistakes during estimation of a preservative test germs adapted to the studied medium are often used. Validation can be performed at different temperatures and relative humidities, so it is possible to adapt testing methods to different climatic conditions.

5.3.4. Environmental and human toxic aspects

Demands regarding toxicity of antimicrobial compounds depend mainly on the field of application but freedom to objections in respect of human health is the most important demand. It is required both in the field of application as well as in processing.

For estimation of the health risks the toxic profile is determined. A series of toxicological examinations is used. The most usual are acute toxicity (L_{D50}), subacute toxicity, chronic toxicity, and toxicological studies concerned with resorption, metabolism and excretion as well as influences on proliferation. Examples for these studies are determination of teratogenicity, fertility, mutagenicity and carcinogenicity. In this context the demands of the laws for chemicals must be mentioned, i.e. verification of compatibility with skin and mucous

membranes. If relevant data are available an advantage/risk analysis is considered for a decision to approve, restrict, or interdict application.

Besides human toxicological studies ecotoxicological aspects must also be considered. It is quite possible that chemical preservatives will enter the environment. This can happen as a result of rainwater washing out, for example, the dispersion paints used on exterior walls with high levels of dilute solutions being produced. Measures used in the cleaning of containers can also result in preservative residues entering the waste water and thus endangering the biological stage of the wastewater treatment system of the drainage system (rivers). It is therefore necessary to obtain relevant data on the environment. This could be achieved by determining sewage mud toxicity and biodegradability. Various methods are available for the determination of these parameters. The choice is made depending on the field of application or on the type of products.

5.3.5. R & D requirements

The aim of research on the protection of materials is to improve physical and chemical methods and to develop new methods or techniques with advantages in effectiveness, compatibility or toxicity. Other improvements are possible, e.g. in the economic aspects. Another aim of research may be the estimation of the resistance of already known or new compounds. Mention must be made of the great need for development of standardisation of test methods for comparison of different preservative products. In addition to this, the search and selection of practice-relevant germs are important areas for future research.

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S. Block, *Disinfection, Sterilisation and Preservation*, 1983, Lea + Febiger, Philadelphia

DEV Deutsche Einheitsverfahren zur Wasser-, Abwasser- und Schlammuntersuchung (Standard German procedure for examination of water, sewage and slurries), 1984, Verlag Chemie, Weinheim

OECD-Methoden (Proposed Method for the Determination of the Biodegradability of Surfactants Used in Synthetic Detergents), 1976, OECD, Paris

H. G. Schlegel, *Allgemeine Mikrobiologie*, 6 Aufl. (General Microbiology, 6th edn), 1985, Georg Thieme-Verlag, Stuttgart and New York

K.-H. Wallhäußer, *Praxis der Sterilisation - Desinfektion - Konservierung* (The Practice of Sterilisation - Disinfection - Preservation), 1988, Georg Thieme-Verlag, Stuttgart and New York

Education — An Interdisciplinary Problem

6.1. Education Until Now

In Germany there is no special plan for studying “Microbiological deterioration and protection of materials” either as a principal or as a secondary teaching subject. The question should be answered if such special education would be useful since there are few opportunities for full time employment in this area.

Microbiologists working in this field acquire their skills through studying microbiology, i.e. during working for a diploma, or on a dissertation. This specialisation is the result of individual education or by working in groups experienced in the field of microbial destruction and protection of materials.

For this kind of activity a solid microbiological education is, and will continue to be, needed — a knowledge of chemistry and physical chemistry is especially important. In future graduates of biotechnology will certainly be able to work in this field but, naturally, engineering sciences do not cover this field. Although within the materials sciences physical chemistry forms part of modern teaching, the teaching of microbiology is probably not normally included.

6.2. Desirable Education (Training)

At the universities in which microbiology and/or biotechnology are part of the curriculum (lectures and experimental courses) it would be desirable to treat problems of microbiological degradation of materials as well as the protection of materials in lectures and possibly in experiments.

This approach should also be applied within those universities with faculties of materials sciences and biology, although interdisciplinary treatment of these problems may be difficult.

6.3. Recommendations

It should be the aim to engage teachers to lecture for 1–2 hours per week and to organise integrated experimental courses at suitable universities and polytechnics. Lectures should be offered at the faculties of microbiology, biotechnology or materials sciences, especially if in the engineering sciences there is a focus on corrosion and corrosion protection.

The attention of students should be drawn to centers of research in this field. Some of the institutes are listed in section 7.

Besides teaching at the universities education should be carried out in a similar manner at polytechnics. Later on, organised teaching in courses should be considered in Germany. Such courses should be organised and offered by DECHEMA. They should be 1–2 weeks long to cover the whole field by lectures and experiments. Such courses could be organised as well

at technical academies, e.g. in Germany at Essen and Esslingen with the organisation linked to the corresponding working party of DECHEMA.

6.4. Target Groups

Target groups for education are mainly biologists. Chemists and engineers having an interest in this field have to be considered. Because of the close relationship of the different specialities like microbiology, biochemistry/chemistry, physical chemistry, materials science and engineering an interdisciplinary education is of special importance.

Research Institutes and their Interests (in Germany)

The listing presented below is a selection considering especially the fields of preoccupation of the experts involved in this study.

Dr. M. Beyer	- Destruction of materials in mining
Prof. Dr. E. Bock	- Biocorrosion of natural and artificial stones, leaching of metals
Dr. K. Bosecker	- Leaching of metals, degradation of hydrocarbons
Dr. H. Brill	- Protection of materials
Dr. G. Czerny	- Destruction of paper and pasteboards
Priv. -Doz. Dr. habil. F. E. W. Eckhardt	- Biocorrosion of natural stones, plasters, frescos
Dr. R. M. Fakoussa	- Benefication of coal
Prof. Dr. Z. Filip	- Destruction of plastics
Dr. H.-C. Flemming	- Biofilms and biofouling
Prof Dr. E. Heitz	- Corrosion and protection against corrosion of metals and plastics
Prof. Dr. P. Hirsch	- Destruction of natural stones
Dr. Waltraut Kerner	- Destruction of wood, protection of wood
Prof. Dr. Krumbein	- Geomicrobiology
Prof. Dr. W. Liese	- Protection of wood
Dr. W. Metzner	- Protection of wood
Dr. H. Mörtel	- Benefication of raw materials
Dr. R. Orth	- Adhesives
Dr. W. Paulus	- Protection of materials
Dr. E. Pommer	- Destruction of materials
Prof. Dr. H.-J.Rehm	- Biotechnology
Dr. W. Sand	- Biocorrosion of natural and artificial stones, leaching of valuable metals
H. Schremmer	- Materials for gaskets underground
Prof. Dr. Schweisfurth	- Deterioration of metals, cooling-lubricating agents, hydraulic liquids

Summary of R & D Requirements

This summary covers the most important points regarding the needs for R & D mentioned in the different sections of this study. It follows the structure of the study and is divided into the main problems concerning microbiological fundamentals and methods of detection, materials problems, studies on auxiliary and raw materials, as well as protection of materials.

An important basic problem is the correlation between composition and structure of materials and microbiological changes. Surface properties play a special role, because they are of great importance in the build up of biofilms. Little knowledge exists about biofilms and biogenic polymers on the surface of materials, although it is known that they are in causal relation to the destruction of materials. Of equal importance is the evaluation of the succession of microorganisms in relation to the interaction between material and microorganisms as well as destruction of materials.

The general knowledge regarding ceramic materials is comparatively small, so elucidation of the microbial processes of destruction is only at the beginning. In part, the problem of care of monuments, the project supported by the Ministry of Research and Technology (BMFT), has been the subject of other projects, but there is still great need for research in the field of microbiologically induced corrosion by CO_2 , H_2S , mineral, and organic acids. A very important question in this context is the influence of anthropogenic pollution of the environment on degradation processes of materials.

Corrosion of metallic materials as a traditional object of research for materials sciences in physical chemistry has reached a high level of knowledge. Interdisciplinary R & D projects involving both microbiologists and corrosion experts are still absent. The R & D program promoted by BMFT "Corrosion and corrosion protection" is of high international level, but problems of microbiological corrosion often receive little attention.

Priority should be given to research on the mechanisms of corrosion by sulphate reducing bacteria with special regard to electrochemical aspects, the study of the action of biofilms on electrochemical processes, other corrosion related questions like comparative studies on aluminium, copper, high alloy steels and titanium.

Problems concerning microbial destruction of natural organic materials have been studied for a long time. In contrast to metallic and ceramic materials the material itself is here the substrate and must be the aim of protection. The methods of protection have reached a high level, but consideration of toxicological and ecological aspects raised new questions. A need for R & D exists especially for test methods.

Corrosion of plastics has been the focus of interest in the last few years, after it was recognised that ageing can be interpreted mechanistically as a corrosion process. In connection to the microbial degradation (desired as well as undesired) the biological affinity, and the degradation mechanism of polymeric materials is of special interest. The genetic code of the microbial degradation potential is of great importance. Analogous questions arise in case of gasket materials, adhesives, and auxiliaries like paints, lacquers and plasters.

Microbial degradation of mineral oil and other hydrocarbons is of great importance for oil winning and storage as well as for fuel and lubricating agents. It is mainly the basic processes that have to be cleared up, for example, inhibition of growth of microorganisms and establishing suitable test methods. An association with the questions of microbial corrosion of metals is evident.

Finally, a series of process developments should be mentioned, where the interest lies in improved materials. In the case of leaching of ores, process and microbial optimisation eventually by modern genetic methods are the main problems.

In the case of biotechnological improvement of the quality of clays and microbial refinement of coals new approaches have been discovered, which need continuous support of R & D. Thus interesting processes can be expected.

General problems that have been mentioned in all sections of this study are of highest importance, viz.

— development of standardised test methods for microbial degradation processes for national and international use

— improvement in protection of materials using physical and physico-chemical, as well as chemical, measures.

By means of specific R & D programmes related to the themes that have been discussed, deterioration can be minimised or prevented, safety of installations and of their components can be improved, and duration of materials and products can be prolonged.