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This is a postprint of a book chapter that originally appeared in *Biofouling and Biocorrosion in Industrial Water Systems* in 1990.

Geesey, G.G., "What is Biocorrosion?" in H.C. Flemming and G.G. Geesey (eds.), *Biofouling and Biocorrosion in Industrial Water Systems*, Springer, Heidelberg, NY, 1990, pp. 156-164.

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## WHAT IS BIOCORROSION?

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### ABSTRACT

Microorganisms growing on surfaces perform a variety of metabolic reactions, the products of which may promote the deterioration of the underlying substratum. These reactions refer to biocorrosion when the substratum consists of a metal or metal alloy. The effect of corrosive microbial products on an underlying metal surface is exacerbated when their concentrations are permitted to increase to high levels as may occur when the microorganisms grow on the surface in a biofilm. The biofilm contains exopolymers which impede the diffusion of solutes and gases between the surface and the bulk aqueous phase. The biofilm also permits the development of highly structured microbial communities on the surface. The various species are able to collectively carry out metabolic activities that are potentially more corrosive to the underlying surface than could be achieved by a single species acting alone. These features of sessile microbial growth represent important prerequisites of biocorrosion.

### INTRODUCTION

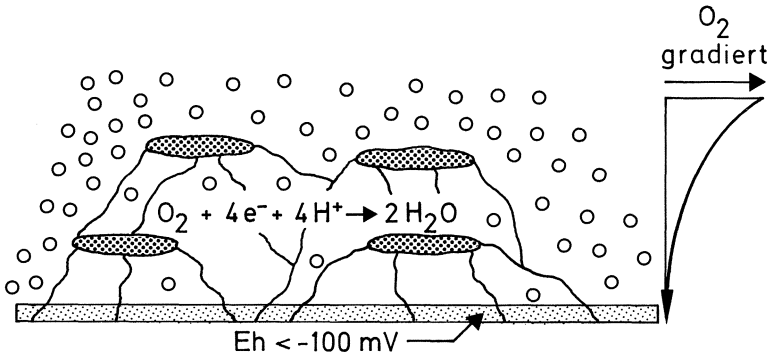
Corrosion is viewed primarily as a series of electrochemical reactions at a metal surface in contact with an electrolyte-containing aqueous phase. Until recently, biological processes were considered to contribute to relatively few forms of corrosion. Microbiologically-influenced corrosion (MIC) has been considered mainly in anaerobic environments where sulfide-producing bacteria are active. Von Wolzogen Kuhr and van der Vlugt (1) proposed an electrochemical process caused by sulfate-reducing bacteria (SRB). Since then other types of microorganisms, including aerobes, have been implicated in MIC. Whereas, it is generally agreed that MIC does not involve any new form of corrosion process, the number of different processes in which they participate appears to be greater than was originally believed. The following discussion highlights some of the more important microbiological processes that are believed to influence metal corrosion

## HETEROGENEITY CAUSED BY MICROBIAL COLONIZATION OF SURFACE

### Differential Aeration Cells

Corrosion may occur on a submerged metal surface as a result of uneven colonization of the surface by microorganisms. When a clean surface is submerged in an aqueous environment it is rapidly colonized by microorganisms present in the bulk

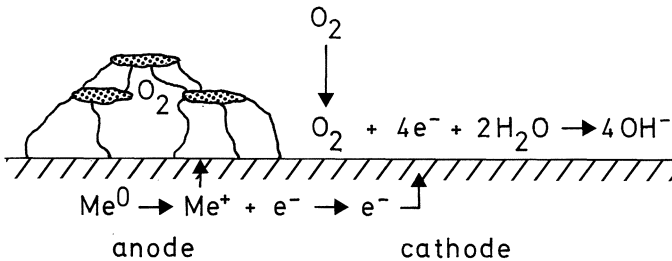
aqueous phase. As the surface-associated microbes replicate, microcolonies of each species are formed. The microcolonies are distributed in an uneven manner with some areas of the surface being less heavily colonized and exposed to the bulk aqueous phase than other areas. In environments where the bulk aqueous phase is aerated, the oxygen consuming activities of surface-associated bacteria can create an oxygen concentration gradient near the metal surface; the higher concentrations occurring in that area of the colony in contact with the bulk aqueous phase and the lowest concentrations developing at the bottom of the colony in contact with the metal surface (Fig. 1).



**Fig. 1.** Oxygen concentration gradient in biofilm caused by respiratory activity of microorganisms

An oxygen concentration cell is likely to develop where an uncolonized area of the surface in contact with the oxygenated bulk aqueous phase meets an area covered by a colony of oxygenrespiring bacteria; the area under the microcolony being anodic to the area exposed to the bulk aqueous phase (Fig. 2).

## Differential Aeration Cell



**Fig. 2.** Differential aeration cell resulting from heterogeneous distribution of biofilm-forming microorganisms over the surface

Little et al. (2) presented evidence that growth of a thermophilic bacterium on a 201 nickel brazed joint resulted in the establishment of a differential aeration cell at 60 °C but not at 23 °C; the higher temperature supported the growth of the bacterium whereas the lower temperature did not. Microorganisms also facilitate the formation of differential aeration cells on metal surfaces that contain an uneven distribution of corrosion product formed through abiological reactions. The precipitated metal salts provide sites for microbial attachment and colonization. Respiration by these bacteria further reduces the concentrations of oxygen under the deposit, the diffusion of which is already hindered by the presence of the deposit. The reduced concentrations of oxygen under mineral deposits and microcolonies containing respiring microorganisms gives rise to localized areas that exhibit low redox potentials close to the metal surface. Such conditions permit the growth of facultative and obligate anaerobic bacteria even when the bulk aqueous phase is well-aerated. Thus, anaerobic sulfur-reducing and acid-producing bacteria, two groups of microbes that have been associated with corrosion, can grow in systems containing oxygenated water.

### **Microbial Consortia in Biofilms**

Within a short period of time of exposure to most sources of water, virtually all metal surfaces become colonized by a variety of physiologically-distinct microbial species, the composition of which is determined by the surrounding environmental conditions. Microcolonies of different species develop next to one another and eventually merge to form a biofilm. Biofilms are a common mode of microbial existence in aquatic environments. They reflect a complex community structure within which diverse microbial activities take place. The biofilm restricts the diffusion of products of microbial metabolism excreted from the cells in each microcolony. Thus, very high concentrations of metabolic by-products may accumulate at or near the underlying metal surface. In instances where the surface is not compatible with the metabolites, corrosion may result.

### **Sulfur-reducing bacteria**

Sulfur-reducing bacteria are highly dependent on the activities of other members of the microbial biofilm community (3). As obligate anaerobes, they depend on the oxygen respiring heterotrophs to reduce the oxygen concentration in the biofilm to low levels. They also depend on fermentative facultative anaerobes to supply organic electron donors for energy production. It is now known that sulfur reducing bacteria, as a group, can utilize a wide range of organic electron donors which include fumarate, acetate, propionate and fatty acids. The ability to utilize these organic compounds as well as hydrogen as electron donors contributes to the ubiquitous nature of this diverse physiological group of bacteria. Sulfur-reducing bacteria may promote metal corrosion in several ways. Through the action of an active hydrogenase enzyme, these bacteria can prevent the accumulation of atomic or molecular hydrogen at the cathode, thus impeding cathodic polarization (1) (Fig.3). This enzyme activity alone, however, does not appear to be sufficient to account for the high rates of corrosion experienced in the field. Another theory considers the influence of the hydrogen sulfide produced during respiration of sulfate and other oxidized forms of sulfur by this group of bacteria. The sulfides of iron and hydrogen are effective cathodic depolarizing agents (4) (Fig.4). Sulfide also

### Cathodic Depolarization

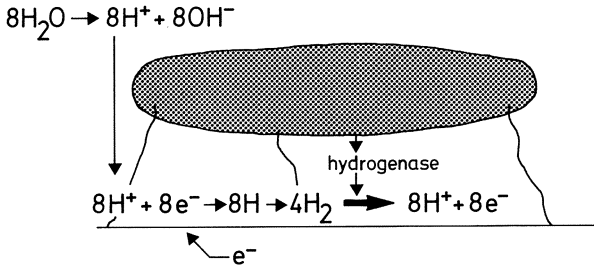


Fig. 3. Cathodic depolarization of surface due to utilization of hydrogen by hydrogenase-producing microorganisms

### Cathodic Depolarization (by production of sulfide)

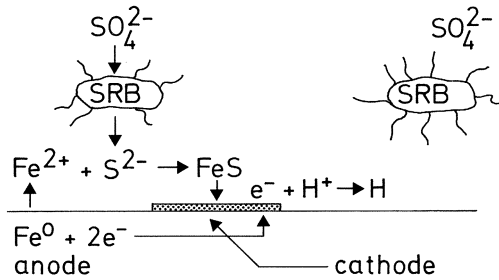


Fig. 4. Cathodic depolarization of surface by iron sulfide as a result of respiration of sulfate by SRB's

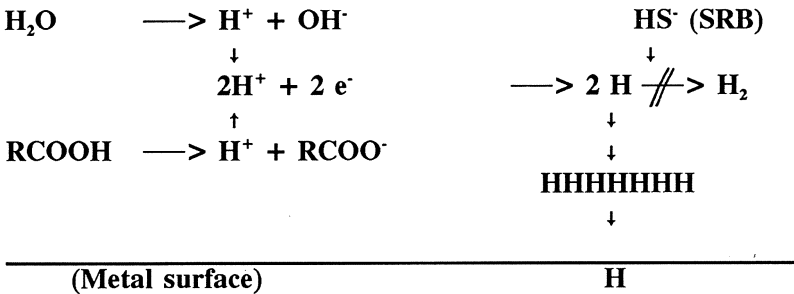


Fig. 5a. Hydrogen embrittlement caused by sulfide generation by SRBs

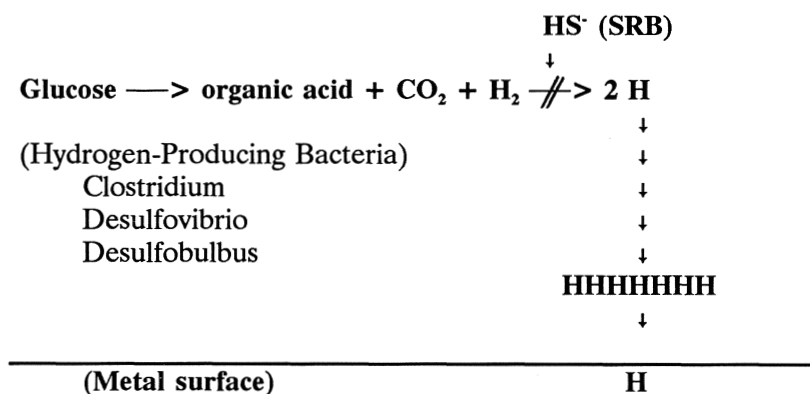


Fig. 5b. Hydrogen embrittlement caused by hydrogen-producing bacteria

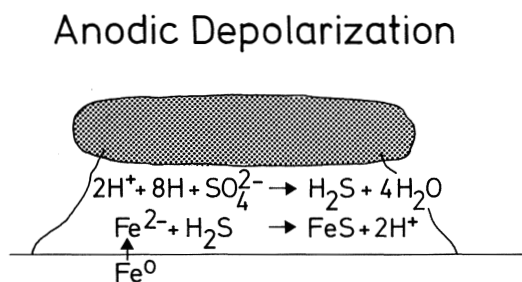


Fig. 6. Anodic depolarization of metal surface caused by reaction of hydrogen sulfide produced by SRBs

In the presence of sulfide, atomic hydrogen produced at the cathode as a result of the reduction of protons derived from the dissociation of water or acids may accumulate at the metal surface. This accumulation may facilitate adsorption of hydrogen into the metal, which in turn, may cause hydrogen embrittlement in sensitive metals. Sulfide also promotes ionization of many metals and therefore accelerates the anodic reaction (Fig. 6). The relative contribution of sulfide formation and hydrogenase activity to a particular corrosion event likely depends on the nature of the metal surface and the conditions in the system.

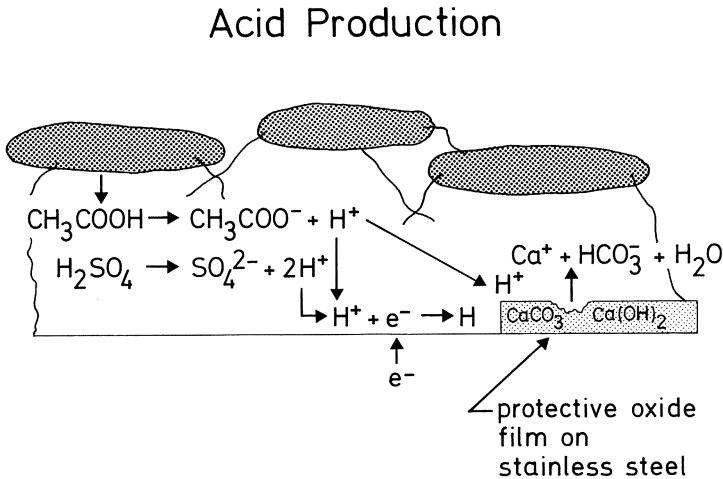
#### Hydrogen-producing bacteria

Many microorganisms produce hydrogen gas as a product of carbohydrate fermentation (Fig. 5). Walch et al (5) showed that pure cultures of *Rumenococcus albus* produced small amounts of hydrogen that diffused into steel. It now seems that sulfide

may reduce hydrogen adsorption by preventing the conversion of molecular hydrogen to atomic hydrogen. Whether the reactions resulting from such a microbial consortium are responsible for hydrogen embrittlement observed in the field remains to be verified.

### Acid-producing bacteria

Some bacteria produce and excrete copious amounts of acid as by-products of metabolism. When the rate of production is greater than the rate of utilization by other microbial populations in the biofilm the acids may accumulate and create localized gradients in pH at the metal surface. Acid products of microbial metabolism cause thermodynamic "depolarization" of the cathode under deaerated conditions because the reversible potential for the hydrogen reaction shifts in a more noble direction with decreasing pH (Fig. 7).



**Fig. 7.** Acid production (organic and inorganic) by adherent film-forming bacteria with consequent promotion of electron removal from cathode by hydrogen or dissolution of protective calcarious film on stainless steel surface

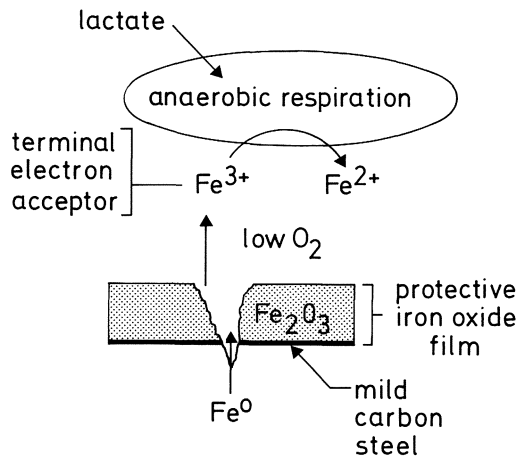
Acid production by the fungus *Cladosporium resinae* is believed to be the cause of corrosion of aluminum fuel tanks of jets. Little et al (2) suggested that the production of isobutyric and isovaleric acids by a thermophilic bacterium contributed to the corrosion of a 201 nickel brazed joint at elevated temperatures. In another study, Little et al (6) demonstrated that an aerobic acetic acid-producing bacterium (*Acetobacter aceti*) depolarized an Allegheny-Ludlum 6X stainless steel electrode cathodically polarized to -900 mV vs. a standard calomel electrode. The acetic acid produced by the bacteria destabilized or dissolved the protective calcarious film that was formed during cathodic polarization. Sterile solutions of similar composition to those which supported the growth of the bacteria promoted corrosion rates that were significantly less than those observed in

solutions containing the bacteria. Acid-induced corrosion of concrete and iron reinforcing bar used in the construction of sewage pipes can occur through the activities of autotrophic bacteria. *Thiobacillus thiooxidans* and *Thiobacillus ferrooxidans* produce sulfuric acid during metabolism of reduced sulfur compounds present in the sewage effluent. In some instances, the reduced sulfur is generated by sulfur reducing bacteria in the system.

### Iron bacteria

Iron reducing bacteria can modify the protective oxide film that forms over a mild steel surface causing the surface to depolarize (7) (Fig. 8). Facultative anaerobes of *Pseudomonas* capable of using ferric ions and sulfite as terminal electron acceptors for anaerobic respiration use low molecular weight compounds such as lactate as carbon source. Some of these bacteria attach to mild steel coupons and remove a passive gamma  $\text{Fe}_2\text{O}_3$ -film and replace it with a biofilm under which pits developed. One isolate depolarized the anode (7). The reaction at the cathode was unaffected by the bacterium. The bacteria used the ferric oxide as an alternate terminal electron acceptor. Uninoculated controls remained passive with the anodic current decreasing steadily with exposure. The cathodic reaction was polarized during these experiments under both inoculated and uninoculated conditions (8). Iron oxidizing bacteria which oxidize ferrous iron to ferric iron sometimes promote the corrosion of iron and stainless steel pipes in aerobic environments. Corrosion products composed of ferric hydroxides and other metal salts form tubercles which accumulate on the inner surface of the pipes. The area beneath the deposit becomes anaerobic due to the oxygen diffusion barrier created by the precipitate and the respiratory activities of the bacteria. Bacteria that have been commonly found in tubercles over pits in stainless steel include *Sphaerotilus natans*, *Gallionella* and *Siderocapsa* spp..

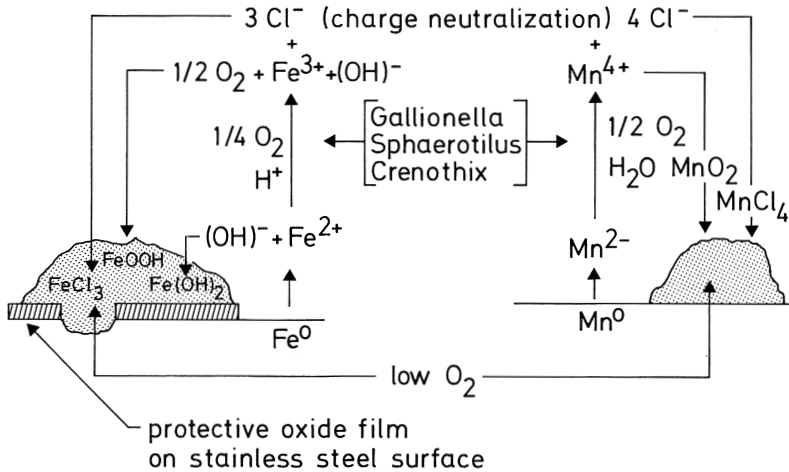
### Metal Reduction



**Fig. 8.** Iron production by anaerobic respiration of ferric iron associated with protective gamma ferric oxide film on mild carbon steel

Bacteria such as *Gallionella* and *Sphaerotilus* act to produce or concentrate oxidizing species such as  $\text{Fe}^{3+}$  or  $\text{Mn}^{4+}$  at the metal surface (Fig. 9). On stainless steels in the presence of chloride ions this increases the potential to a value more noble than the pitting potential and leads to breakdown of a passive oxide film and promotes pit formation (Fig. 9).

## Metal Oxidation + Precipitation



**Fig. 9.** Iron and manganese oxidation and precipitation in presence of filamentous bacteria. Stainless steel pitting in presence of chloride ions concentrated at surface in response to charge neutralization of ferric and manganic cations

### Role of Biofilm Bacteria in the Establishment of Metal Concentration Cells

Anodic "depolarization" may occur as a result of the formation of metal ion diffusion gradients in biofilms. Reduced metal ion activity within localized regions of a biofilm can be mediated by bacterial processes that result in metal ion uptake or binding at the metal surface. Many species of bacteria, algae and fungi are known to bind various metal ions through both metabolically-energized and non-metabolic processes (9).

### Role of exopolymers in the establishment of surface heterogeneity

Chemical variations among microcolonies of physiologically distinct microorganisms may occur as a result of differences in the chemical properties of the exopolymers excreted by the cells. Exopolymers are elaborated by most aquatic bacteria, cyanobacteria and algae. They form a matrix between the cells in a microcolony and in many instances anchor the cells to solid surfaces. The chemical properties of the exopolymers vary depending on the type of microorganism. Most water bacteria produce acidic

exopolysaccharides which vary in their tendency to ionize and interact with metal ions (10). When one species of bacteria which excretes exopolymer with a high affinity for ions of the underlying metal forms a microcolony next to another bacterial species which produces exopolymer with low affinity for the metal ion, a metal concentration cell may develop; the area under the exopolymer with high affinity being anodic to that under the exopolymer with low affinity (11). Different interactions between exopolymers and copper ions have been proposed to lead to the formation of a copper concentration cell on a copper metal surface containing a mixed species microbial biofilm (12). The exopolymers also hinder diffusion of excreted products of microbial metabolism out of the biofilm. The concentrations of some particularly corrosive products such as those described above may increase to sufficiently high levels to promote deterioration of the underlying metal surface. Some types of pitting corrosion are believed to occur as a result of excretion and accumulation of microbial metabolites in localized regions of biofilms that have developed on copper surfaces (13).

## CONCLUSIONS

At present, the importance of microorganisms in the corrosion of metals is not known. Circumstantial evidence provides the bulk of evidence for a role for microbes in corrosion reactions. As our understanding of biofilm processes improves, it should become easier to relate specific biochemical activities on surfaces to electrochemical reactions that cause metal corrosion. This understanding will likely develop through a combination of highly-controlled studies in the laboratory and examination and characterization of corrosion events in the field.

## REFERENCES

- 1 von Wolzogen Kuhr CAH, van der Vlugt IS (1934) The graphitization of cast iron as an electrochemical process in anaerobic soils. *Water* 18, 147-165
- 2 Little B, Wagner P, Gerchakov SM, Walch M, Mitchell R (1986) The involvement of a thermophilic bacterium in corrosion processes. *Corrosion* 42, 533-536
- 3 Costerton JW, Geesey GG (1986) The microbial ecology of surface colonization and of consequent corrosion. In: Dexter SC (ed) *Biologically Induced Corrosion*, NACE, Houston, TX; 223-232.
- 4 Wanklyn JN, Spruit CJP (1952) Influence of sulfate-reducing bacteria on the corrosion potential of iron. *Nature* 169, 928-929.
- 5 Walch M, Ford TE, Mitchell R (1989) Influence of hydrogen-producing bacteria on hydrogen uptake by steel. *Corrosion* 45, 705-709

- 6 Little B, Wagner P, Duquette D (1988) Microbially-induced increase in corrosion current-density of stainless steel under cathodic protection. *Corrosion* 44, 270-274
- 7 Obuekwe CO, Westlake DWS, Cook FD, Costerton JW (1981) Surface changes in mild steel coupons from the action of corrosion-causing bacteria. *Appl. Environ. Microbiol.* 41, 766-774
- 8 Westlake DWS, Semple KM, Obuekwe CO (1986) Corrosion by ferric iron-reducing bacteria isolated from oil production systems. In: Dexter SC (ed) *Biologically Induced Corrosion*, NACE, Houston TX; 193-200
- 9 Geesey GG, Jang L (1989) Interactions between metal ions and capsular polymers. In: Beveridge TJ, Doyle RJ (eds) *Metal Ions and Bacteria*, Wiley, NY; 325-257
- 10 Ford, TE, Maki JS, Mitchell R (1988) Involvement of bacterial exopolymers in biodeterioration of metals. In: Houghton DR, Smith RN, Eggins HOW (eds) *Biodeterioration* 7, Elsevier, New York; 378-384
- 11 Geesey GG, Jang L, Jolley JG, Hankins MR, Iwaoka T, Griffiths PR (1988) Binding of metal ions by extracellular polymers of biofilm bacteria. *Wat. Sci. Tech.* 20, 161-165
- 12 Geesey GG, Mittelman MW, Iwaoka T, Griffiths PR (1986) Role of bacterial exopolymers in the deterioration of metallic copper surfaces. *Mat. Perform.* 25, 37-40
- 13 Geesey GG, Bremer PJ (1990) Application of Fourier transform infrared spectrometry to studies of copper corrosion under bacterial biofilms. *Mar. Tech. J.* (in press)