Biocorrosion: towards understanding interactions between biofilms and metals
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The term microbially influenced corrosion, or biocorrosion, refers to the accelerated deterioration of metals owing to the presence of biofilms on their surfaces. The detailed mechanisms of biocorrosion are still poorly understood. Recent investigations into biocorrosion have focused on the influence of biomineralization processes taking place on metallic surfaces and the impact of extracellular enzymes, active within the biofilm matrix, on electrochemical reactions at the biofilm–metal interface.

**Introduction**

Physicochemical interactions between a metallic material and its environment can lead to corrosion. Electrochemical corrosion is a chemical reaction involving the transfer of electrons from zero valent metal to an external electron acceptor, causing release of the metal ions into the surrounding medium and deterioration of the metal. This process proceeds through a series of oxidation (anodic) and reduction (cathodic) reactions of chemical species in direct contact with, or in close proximity to, the metallic surface. In aerated solutions, the cathodic reaction is the reduction of oxygen, whereas in anoxic solutions it is, usually, the evolution of hydrogen. The rate of the anodic reaction (metal dissolution) decreases gradually with time, because the oxidation products (corrosion products) adhere to the surface forming a protective layer that provides a diffusion barrier to the reactants.

The stability of such layers depends on their chemistry and morphology and determines the overall susceptibility of the metal to corrosion. Microbial activity within biofilms formed on surfaces of metallic materials can affect the kinetics of cathodic and/or anodic reactions [1] and can also considerably modify the chemistry of any protective layers, leading to either acceleration or inhibition of corrosion [2,3].

The deterioration of metal due to microbial activity is termed biocorrosion or microbially influenced corrosion (MIC). Owing to its economic and environmental importance, MIC has been the subject of extensive studies for the past five decades and several models have been proposed to explain mechanisms governing biocorrosion [4].

Bacteria are considered the primary colonizers of inanimate surfaces in both natural and man-made environments. Therefore, the majority of MIC investigations have addressed the impact of pure or mixed culture bacterial biofilms on corrosion behavior of iron, copper, aluminium and their alloys. The main types of bacteria associated with metals in terrestrial and aquatic habitats are sulfate-reducing bacteria (SRB), sulfur-oxidising bacteria, iron-oxidising/reducing bacteria, manganese-oxidising bacteria, and bacteria secreting organic acids and slime [5]. These organisms typically coexist in naturally occurring biofilms, forming complex consortia on corroding metal surfaces [6–8]. The mixed biotic/abiotic manganese oxide reduction mechanisms and their importance for biocorrosion have been extensively described in MIC literature [9–12]. The impact of microbial iron respiration on corrosion processes has also been recently reviewed [13*]. Hence, these mechanisms are not discussed here.

Biocorrosion is a result of interactions, which are often synergistic, between the metal surface, abiotic corrosion products, and bacterial cells and their metabolites (Figure 1). The latter include organic and inorganic acids and volatile compounds, such as ammonia and hydrogen sulfide. There is an ongoing dispute as to which component, biotic or abiotic, is of greater relevance to corrosion reactions [14]. The importance of microbial synergy has recently been reconfirmed in studies of carbon steel corrosion in the presence of bacteria isolated from rock samples obtained from the proposed high-level nuclear waste repository site at Yucca Mountain [15*] and in the presence of thermophilic and thermotolerant bacteria from a hot spring in Mexico [16]. The rates of corrosion obtained with different combinations of mixed bacterial cultures were considerably higher than those measured in pure cultures.
Progress in microbial molecular ecology and microbial genomics is changing our perception of the composition of bacterial consortia associated with corroding metals and has furthered our understanding of the type of substrata that these bacteria are capable of utilizing as electron donors and acceptors. These advances have also revealed the existence of previously unsuspected biochemical pathways. The elucidation of the genome sequence of the SRB Desulfovibrio vulgaris Hildenborough [17**] and studies of the corrosion of iron in the presence of novel anaerobic microorganisms [18**] are the best examples of current discoveries pertinent to MIC.

A recently proposed unifying electron-transfer hypothesis offers MIC of ferrous metals as a model system for the study of metal–microbe interactions [19**]. Considering this hypothesis, using as an example biotic and abiotic manganese oxidation/reduction reactions on stainless steel in aerated solutions, biocorrosion is a process in which metabolic activities of microorganisms associated with metallic materials (e.g. manganese oxidation by bacteria) supply insoluble products (e.g. manganic oxides/hydroxides MnOOH, MnO₂), which are able to accept electrons from the base metal. This sequence of biotic and abiotic reactions produces a kinetically favored pathway of electron flow from the metal anode to the universal electron acceptor, oxygen. Anaerobic corrosion of iron in the presence of SRB is explained in a similar manner.

Although the unifying electron-transfer hypothesis offers the most elegant explanation of MIC to date, the hypothesis does not take into account the possibility that the organic component of the biofilm matrix itself can facilitate electron transfer from the metal to an electron acceptor such as oxygen. For example, enzymes active within the biofilm matrix and metal ions bound by bacterial extracellular polymeric substances can catalyze cathodic reactions. Both mechanisms are likely to contribute to the biocorrosion process, as discussed below.

This review addresses the current understanding of MIC, viewed as a consequence of coupled biological and abiotic redox reactions of metals that result from diverse metabolic activities of biofilm bacteria. In addition, a new scheme is proposed for the MIC of ferrous metals, which considers a catalytic function of iron ions bound within the biofilm matrix.

Enzymes and biocorrosion

Enzymatic activities are readily detected in biofilms, nonetheless, the importance of reactions mediated by these enzymes has only recently been considered as relevant to biocorrosion [20–22, 23**]. In particular, studies to determine the mechanisms that increase the free corrosion potential (Ecorr) of stainless steel, widely reported in oxygenated natural waters and referred to as ‘ennoblement’ [24], brought enzymes into focus. A lack of ennoblement was observed when a biofilm was treated with sodium azide, which is an inhibitor of the microbial respiratory chain and enzymes such as catalases, peroxidases and superoxide dismutases. These enzymes are involved in reactions of oxygen reduction, therefore, in principle, they might facilitate corrosion by accelerating the overall cathodic reaction. However, it is imperative to realize that the ability of such enzymes to accelerate oxygen reduction depends on the chemistry of surface films. The effect of extracellular catalase produced by Pseudomonas species on the ennoblement behaviour of aluminium brass is the best example of such a relationship [23**]. The study showed that the presence of catalase strongly influenced the reduction kinetics of H₂O₂ produced during oxygen reduction on aluminium brass. An increase in cathodic currents (up to 60%) was measured.
when the surface film was composed mainly of CuO. With only a submonolayer of Cu2O covering the surface, there was no change in the current density values compared with controls. When Cu2O and CuO were present simultaneously, a 35% increment in the cathodic current was recorded.

**SRB and corrosion in oxygenated environments**

The presence of oxygen gradients within the biofilm matrix can be readily demonstrated, and it is accepted that anoxic niches can be found even within biofilms developed in fully aerated systems. Anaerobic bacteria such as SRB are commonly isolated from natural biofilms found in oxygenated environments and the existence of oxygen resistant proteins in some SRB species has been demonstrated [25]. Nevertheless, the possible use of oxygen as terminal electron acceptor by SRB is a subject of ongoing dispute. The complete genome sequence of *D. vulgaris* Hildenborough revealed genes encoding for oxidases, oxidoreductases, plasmid-encoded catalase and superoxide dismutase [17**]. Furthermore, analysis of the incomplete genome sequence of the Gram-positive SRB *Desulfitothricum hafniense* showed genes encoding three catalases, of which at least one is extracellular. These catalases are homologs of hydroperoxidases I and II (HPI and HPII) and manganese-containing catalase (IB Beech, unpublished). Whether or not these enzymes contribute to oxygen reduction reactions on the metal surface under intermittent oxygenation still needs to be elucidated.

The genome of *D. vulgaris* encodes several sensors with hemerythrine-like domains, which are likely to be involved in the response to iron and/or oxygen [26*,27]. In total, the genome sequence of *D. vulgaris* indicates the presence of 27 methyl-accepting chemotaxis proteins, which include the oxygen or redox potential-sensing proteins DcrA and DcrH [17**]. These proteins might be important in positioning SRB in the gradients across the oxic/anoxic interface; however, their relevance in MIC is yet to be tested.

In the classical theory of SRB-influenced corrosion of metallic iron, electrons are proposed to be transported from the metal surface to the bacterial sulfate reduction pathway through a hydrogen intermediate. This process requires the activity of hydrogenase enzymes. Undoubtedly, hydrogenases of SRB are the most extensively studied group of enzymes in MIC [25]. Recent experiments reconfirmed the role of hydrogenases in anaerobic MIC [28,29]. Furthermore, the direct electron transfer between hydrogenase purified from *Ralfstonia eutropha* and the surface of stainless steel has been shown [21], thus supporting early reports that hydrogenase, when expressed within the biofilm matrix, can have a direct influence on the cathodic reaction even in the absence of viable bacterial cells.

The genome sequence of *D. vulgaris* Hildenborough offers new insight into the energy metabolism of this bacterium, which for decades has served as a model SRB for the study of biocorrosion. It indicates a network of novel *c*-type cytochromes, connecting multiple periplasmic hydrogenases and formate dehydrogenases [17**]. The relative arrangement of the genes encoding enzymes for energy transduction, coupled with the inferred cellular location of these enzymes, offers an expansion of the hydrogen-cycling model and further indicates that the hydrogenase/cytochrome network is likely to participate in cell-scavenging of the cathodic hydrogen or a hydrogen film on iron surfaces in aqueous solutions. Recent studies have reported the isolation of new species of SRB that are capable of reducing sulfate with metallic iron much faster than *D. vulgaris* [18**], showing much greater corrosive potential. According to the authors, their study demonstrates the ability of surface-associated cells of novel SRB species to obtain electrons from zero valent iron in a more direct manner than via hydrogen consumption. Such a process would require the existence, in some SRB species, of a yet unidentified cell-surface-associated redox-active component.

It has to be noted that the metabolic specificity of SRB species is rarely addressed when assessing the effect of biofilms on metal deterioration, despite the overwhelming evidence that species belonging to the same genus can vary considerably in their metal-corroding ability [5,25]. Differences in bacterial species composition of biofilm consortia and resulting differences in metabolic activities within such biofilms could explain why, in two identical systems under the same environmental conditions, corrosion rates can vary significantly; for example, carbon steel corrosion can vary from a rate of 0.05 mm/year in one system to 3 mm/year in another. This phenomenon has been reported for steel piling structures in several European harbours and has also been observed in certain secondary oil recovery systems (IB Beech, unpublished). The discovery of novel SRB species reemphasizes the importance of considering species diversity when investigating MIC failures of ferrous metals.

**Metal binding by extracellular polymeric substances**

The development of a biofilm is facilitated by the production of extracellular polymeric substances (EPS) comprising macromolecules such as proteins, polysaccharides, nucleic acids and lipids. The capacity of EPS to bind metal ions is important to MIC [30–32] and depends both on bacterial species and on the type of metal ion [5]. Metal binding by EPS involves interaction between the metal ions and anionic functional groups (e.g. carboxyl, phosphate, sulfate, glycerate, pyruvate and succinate groups) that are common on the protein and carbohydrate components of exopolymers. In particular, the affinity of multidentate anionic ligands for multivalent ions, such as
Ca\(^{2+}\), Cu\(^{2+}\), Mg\(^{2+}\) and Fe\(^{3+}\), can be very strong. The presence of, and affinity for, metal ions in different oxidation states in the biofilm matrix can result in substantial shifts in the standard reduction potentials. For example, Fe (III/II) redox potential varies significantly with different ligands (from +1.2 V to −0.4 V). EPS-bound metal ions can, therefore, act as electron ‘shuttles’ and open up novel redox reaction pathways in the biofilm/metal system, such as direct electron transfer from the metal (e.g. iron) or a biomineral (e.g. FeS). In the presence of oxygen, acting as terminal electron acceptor, Fe\(^{3+}\) in EPS is reoxidised to Fe\(^{3+}\). Note that a similar type of reaction can take place on the surfaces of corrosion products (CP) such as oxides, hydroxides and sulfides, which contain divalent iron.

Mineralization was shown to result from the contact between the EPS and oxidized iron, through ferric iron binding with carboxylic groups on the polymer. The authors pointed out that oxidation of ferrous ions and subsequent precipitation of iron oxyhydroxide on the biofilm exopolymers releases protons, leading to a decrease in the pH outside the cell membrane. They inferred that the purpose of polymer production is to localize iron oxyhydroxide mineral precipitation immediately outside the cell to increase metabolic energy generation of the cell through enhancement of the proton motive force.

Apart from demonstrating that mineral precipitation within a biofilm matrix can have a major influence on the activity levels of biofilm organisms, the described phenomenon also has implications for biocorrosion. In the presence of ferrous metal, iron oxyhydroxide surfaces assembled on biofilm polymers would adsorb ferrous iron leading to its oxidation, thus providing an additional contribution to the cathodic reaction. It is rather exciting to think of such biominerals as electron-conducting fibers dispersed within the biofilm matrix.

**Conclusions**

Biocorrosion occurs in aquatic and terrestrial habitats that differ in nutrient content, temperature, pressure and pH.
It results from the presence and physiological activities of microbial consortia on the metallic surfaces. Such biofilms promote interfacial physicochemical reactions, not normally favoured under abiotic conditions. Mechanisms proposed as pertinent to biocorrosion reflect the range of physiological activities carried out by diverse types of microorganisms found within biofilms. These mechanisms vary with microbial species and the chemistry of the colonised metal surface. Progress in molecular ecology and microbial genomics, in parallel with exciting developments in biological imaging and analytical surface techniques, allows for better understanding of the dynamics of the community structure within biofilms. These advances will also help to explain how such dynamics result in spatial and temporal distributions of biotic and abiotic reactions and how these, in turn, govern the electrochemical processes on the surfaces of metals.

Despite considerable research efforts into the MIC phenomenon, there are still general issues that need to be addressed, such as the importance of microbial ecology in MIC (i.e. the differences in microbial population between actively corroding and non-corroding metals exposed in the same environment) and the effect of the biofilm matrix on the electrochemical behavior of metals. More specific questions concern the impact of enzymes active within the biofilm matrix on the kinetics of corrosion reactions and the involvement of organometallic complexes in electron transfer from zero valent metals and from chemically and morphologically diverse metallic surface films to ultimate electron acceptors.

Elucidating biofilm–metal interactions at the molecular level will not only aid understanding of the contribution of the biological component to corrosion processes, but will also facilitate the development of more efficient MIC prevention and protection measures. For example, in oil production, encouraging SRB to switch from the sulfate reducing district heating systems using fluorescence in situ hybridisation and microautoradiography. Water Sci Technol 2003, 47:117-122.


This review focuses on the effect of iron-respiring bacteria on corrosion of steel by showing the influence of the biofilm on the chemistry of the environment at different stages of biofilm development, under static and dynamic flow regimes.


An experimental study of carbon steel corrosion in the presence of various types of microorganisms isolated from rock samples obtained from the proposed high-level nuclear waste repository site at Yucca Mountain. The rates of corrosion caused by mixed bacterial cultures was much higher than those measured in pure cultures. Evaluation of the rates of biocorrosion of materials used for site construction and waste containment is imperative for the safety assessment of the planned repository.


The study of MIC.

Novel marine species of SRB, obtained through isolation with metallic iron as sole electron donor, are reported and their possible contribution to the corrosion of iron described. The existence of yet unidentified cell-surface-associated redox components is suggested as a mechanism to facilitate electron transfer between zero valent iron and these new isolates under anaerobic conditions.

Biocorrosion is viewed in the context of metal microbe interactions. Microbiologically influenced corrosion is a model system for the study of metal microbe interactions: a unifying hypothesis of electron transfer from zero valent metal to oxygen as ultimate electron acceptor is offered as a novel approach to the study of MIC.

Electron transfer between catalases produced by bacteria from the genus Pseudomonas influences the oxygen chemotaxis in D. vulgaris. It is inferred that the cells extrude the polysaccharide strands to localize FeOOH precipitation to harness the proton gradient for energy generation.

The composition of the surface oxide layers strongly influences the oxygen reduction kinetics on surfaces of aluminum brass in the presence of catalases produced by bacteria from the genus Pseudomonas.