



## ELECTROCHEMICAL INTERACTIONS OF BIOFILMS WITH METAL SURFACES

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### ABSTRACT

Two mechanisms of microbially influenced corrosion (MIC) are discussed and compared: corrosion modified by the presence of (1) sulfate-reducing bacteria (SRB) and (2) manganese-oxidizing bacteria (MOB). It is demonstrated that the nature of MIC in both cases depends on the nature of inorganic materials precipitated at the metal surface, iron sulfides and manganese oxides. Those materials are electrochemically active and, therefore, modify the electrochemical processes naturally occurring at the metal-solution interface. Some of these modifications may lead to accelerated corrosion. © 1997 IAWQ. Published by Elsevier Science Ltd

### KEYWORDS

Biofilms; corrosion; microbially influenced corrosion.

### INTRODUCTION

Microbially Influenced Corrosion (MIC) has been absorbing the attention of many research groups representing quite diverse and frequently disparate disciplines (Kearns and Little, 1994). It has been a goal of many studies to find "fingerprints of MIC", the specific features distinguishing "biological corrosion" from ordinary galvanic corrosion. Despite significant efforts no unique mechanism of MIC has yet been found and reasonable doubt has been cast on whether such a mechanism exists at all (Crolet, 1991). It appears that the accelerated corrosion of metals in the presence of living microorganisms stems from a modification of the near-surface chemistry due to microbial metabolism. In particular, when biofilms accumulate on metal surfaces, the metabolically induced changes in near-surface water chemistry interfere with electrochemical processes occurring at the interface between the metal and its environment. By taking place in immediate proximity to the interface, both microbial and electrochemical processes simultaneously influence the near-surface water chemistry. Changes in water chemistry caused by microbial activity are superimposed on changes caused by electrochemical reactions occurring at the metal-solution interface. The resulting changes in water chemistry influence, in their turn, the dynamics of biofilm processes and the dynamics of electrochemical processes at the metal-solution interface. Further complexity is introduced to the system by the structural and physiological heterogeneities of biofilms (Lawrence *et al.*, 1991; Lewandowski *et al.*, 1993; De Beer *et al.*, 1994) that cause metabolic reaction rates and even the nature of

these reactions to vary from one location in the biofilm to another. The structural and physiological heterogeneities may locally increase corrosivity of the environment by forming concentration cells that result in deposition of corrosion products, further increasing the heterogeneous character of the entire system (Lewandowski *et al.*, 1995).

This paper describes the train of events resulting from microbial colonization of metal surfaces by sulfate-reducing bacteria (SRB) and manganese-oxidizing bacteria (MOB), that can, under certain circumstances, lead to accelerated corrosion of metals and alloys. These two cases were chosen because current understanding of the experimental observations is based on well established concepts and because both cases illustrate the benefits of studying MIC systematically, using principles of process analysis.

#### Corrosion of iron in abiotic systems in the presence of oxygen and hydrogen sulfide

For abiotic systems in the presence of oxygen, the anodic dissolution of iron is followed by deposition of iron oxide corrosion products, in a sequence of reactions:



While iron is being oxidized the cathodic reaction may be the reduction of oxygen:



or in the absence of oxygen, the decomposition of water:



Hydrogen sulfide, if present in the system, adsorbs at metal surfaces. Such adsorption may be followed by anodic discharge (Shoesmith *et al.*, 1980)



the  $\text{FeSH}_{\text{ads}}^+$  may be incorporated into the growing layer of mackinawite,  $\text{FeS}_{1-x}$ , (Hamilton, 1985).



The above sequence of reactions may stimulate corrosion if associated with an adequate cathodic reaction. Such a cathodic reaction may be provided by the reduction of hydrogen sulfide (Costello, 1974; Bolmer, 1965).

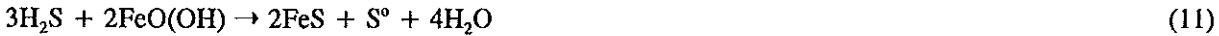


It has been demonstrated that corrosion rate in the presence of hydrogen sulfide is stimulated by the corrosion products, iron sulfides (Wikjord *et al.*, 1980). Evolution of the corrosion products on steel progresses from iron-rich to sulfur-rich phases according to the sequence, mackinawite (tetragonal  $\text{FeS}_{1-x}$ )  $\rightarrow$  ferrous sulfide (cubic  $\text{FeS}$ )  $\rightarrow$  troilite (hexagonal  $\text{FeS}$ )  $\rightarrow$  pyrrhotite (hexagonal  $\text{Fe}_{1-x}\text{S}$ )  $\rightarrow$  pyrite (cubic  $\text{FeS}_2$ ). For corrosion to occur by this mechanism, iron sulfides must have electrical contact with the bare steel surface. Once contact is established, mild steel behaves as an anode and proton discharge and electron transfer occur on and through the iron sulfide. Iron sulfides increase the rates of corrosion by stimulating the cathodic reaction through a decrease in hydrogen overvoltage and/or by adsorbing the cathodically produced hydrogen.

Simultaneous presence of oxygen and hydrogen sulfide further accelerates the corrosion process. The corrosion rate of steel in  $\text{H}_2\text{S}-\text{O}_2$  bulk liquid is higher than that in the presence of  $\text{O}_2$  or  $\text{H}_2\text{S}$  alone, and the prevalent corrosion product is ferrous sulfide,  $\text{FeS}$ . Oxidation of iron sulfides results in generation of highly corrosive products, mainly elemental sulfur, according to the reaction:



Hydrogen sulfide can also react with the oxidized iron to form ferrous sulfide and elemental sulfur (Schmitt, 1991).



Elemental sulfur, the main product of these reactions, accelerates corrosion rate. Schmitt (1991) has shown that corrosion rate caused by the elemental sulfur can reach several hundred mpy.

#### The corrosive influence of bioprecipitated iron sulfides

In the absence of oxygen, the metabolic activity of SRB causes accumulation of hydrogen-sulfide near the metal surface. This is particularly evident for sessile microbial growth that generates biofilms. Under such conditions, iron sulfide nuclei form quickly and cover the steel surface as a result of the availability of sufficient ferrous and sulfide ions. At low ferrous ion concentrations, adherent and temporarily protective films of iron sulfides are formed on the steel surface with a consequent reduction in the observed corrosion rate. High rates of SRB corrosion are maintained only in media containing high concentrations of ferrous ion. The corrosion rate of mild steel is controlled by the nature of the iron sulfide corrosion products, the same way as in abiotic systems. As noted before, these products stimulate corrosion by accelerating the cathodic reaction. The role of SRB in the corrosion process in oxygen-free environments is then principally dependent on their ability to produce ferrous sulfides.

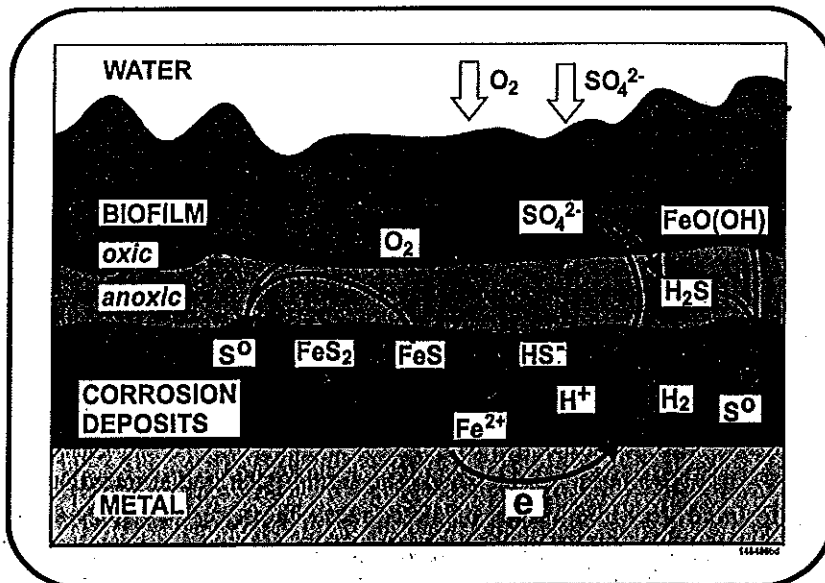


Figure 1. Diagram of transport and transformation processes contributing to corrosion of mild steel under an aerobic/anaerobic biofilm.

The situation is more dramatic when the bulk water contains dissolved oxygen and the bottom of the biofilm is anaerobic and contains SRB. This is also the most frequently encountered scenario in natural and engineered systems. The effect is analogous to that described for abiotic systems, i.e. corrosion in the presence of hydrogen sulfide and oxygen. Processes contributing to the corrosion of mild steel in adjacent

oxic and anoxic biofilms are summarized in Figure 1. There are more processes active in the aerobic/anaerobic system than in a totally anaerobic systems. In addition to ferrous sulfide production, oxygen uptake in the aerobic system plays a vital role (Lee *et al.*, 1993 a,b; Nielsen *et al.*, 1993). The mechanism of this increase in the corrosion rate is related to the microbial and chemical reoxidation of sulfides and ferro compounds (e.g.  $\text{Fe}^{2+}$ ,  $\text{FeS}$ , and  $\text{FeS}_2$ ) and possibly to the cathodic depolarization process. Oxidation of sulfides and ferro compounds produces more corrosive sulfur compounds that facilitate the cathodic reaction.

The possible cathodic depolarization process can also be attributed to oxygen reacting with hydrogen atoms adsorbed on the ferrous sulfide lattice. Atomic hydrogen produced from the cathodic reaction can be adsorbed onto the bare steel surface or dissolved within the ferrous sulfide lattice. Theoretically, it is easier to depolarize ferrous sulfide than it is to depolarize steel, since atomic hydrogen is usually quite strongly adsorbed onto steel surfaces (Stott *et al.*, 1988). Whether cathodic depolarization can influence the corrosion rate remains debatable, however (Crolet, 1991).

#### Anodic polarization of metals by ferric and manganic oxides

The feasibility of using metal oxides to anodically protect stainless steel was demonstrated as early as the 1950s (Tomashov, 1967). Under strongly acidic conditions, galvanically coupled ferric and manganic oxides provide the cathodic current density required to shift the corrosion potential,  $E_{\text{corr}}$ , above the passivation potential. The effect stems from the high standard reduction potential for these oxides:



While protection can be achieved in this way, the possibility that  $E_{\text{corr}}$  will shift into the transpassive region is also of concern. In neutral media these oxides can have similar effects, shifting  $E_{\text{corr}}$  in the noble direction, and increasing the risk of localized corrosion. This behavior may also be induced by various solid phase redox couples:



as well as by mixed phase reactions involving poorly crystalline ferric oxides (Evans and Taylor, 1972),



where the formal potentials in equations 14 and 15 refer to pH 8. The tendency for these reactions to anodically polarize metals will depend on  $E_{\text{corr}}$  for a specific metal-solution system and on the oxide reduction potential. Oxides with potentials more positive than  $E_{\text{corr}}$  will serve as cathodes, while those with values less than  $E_{\text{corr}}$  will be stable with respect to reduction. At the pH and dissolved metal concentrations typical of natural waters (pH = 8,  $[\text{Mn}^{2+}] = 10^{-7} \text{ M}$ ,  $[\text{Fe}^{2+}] = 10^{-6} \text{ M}$ ) reactions 12 and 13 have reduction potentials of +253 and -562  $\text{mV}_{\text{SCE}}$  respectively.  $E_{\text{corr}}$  for stainless steel under these condition lies in the range -100 to -200  $\text{mV}_{\text{SCE}}$ , indicating that  $\text{MnO}_2$  will anodically polarize the metal but  $\text{Fe}_2\text{O}_3$  will not. On the other hand,  $E_{\text{corr}}$  for mild steel in the same media is near -700  $\text{mV}_{\text{SCE}}$ , suggesting that both manganic and ferric oxides may serve as cathodes. Reduction potential for reactions involving amorphous ferric oxides (e.g. equation 16) can vary widely depending on the free energy of the specific hydrous mineral phase (Stumm and Morgan, 1970), making it difficult to anticipate the cathodic behavior of these materials.

#### The corrosive influence of biomineralized ferric and manganic oxides

Biomineralization of iron and manganese oxides occurs widely in natural waters, and is a dominant control in the geochemical cycling of these elements (Gounot, 1994). Mineralization can be carried out by a variety of organisms including bacteria, yeast, and fungi, (Nealson *et al.*, 1988) but is particularly associated with

genera of the so called iron and manganese group, *Siderocapsa*, *Gallionella*, *Leptothrix-Sphaerotilus*, *Crenothrix* and *Clonothrix*. These bacteria accelerate oxidation of dissolved iron and manganese to form highly enriched mineral-biopolymer encrustations. Deposits form on submerged materials including metal, stone, glass, and plastic and can occur in natural waters with manganese levels as low as a 10-20 ppb (Dickinson *et al.*, 1996). Deposition rates of  $1 \text{ mcoul cm}^{-2} \text{ d}^{-1}$  on stainless steel have been observed (Dickinson and Lewandowski, 1996). Under-deposit corrosion is frequently associated with these minerals and is generally attributed to differential aeration (with the under-deposit regions serving as anodes) and to the corrosive influence of SRB that grow in the oxygen depleted conditions. In view of the cathodic reactivity of ferric and manganic oxides, the area under the deposits is more likely to serve as a microgalvanic cathode to surrounding areas that are made anodic by biological oxygen depletion.

Biominedralized manganic oxides are efficient cathodes and increase cathodic current density on stainless steel by several decades at potentials between roughly -200 and +400  $\text{mV}_{\text{SCE}}$ . The extent to which the elevated current density can be maintained is controlled by the electrical capacity of the mineral which reflects both total accumulation and conductivity of the mineral-biopolymer assemblage (only material in electrical contact with the metal will be cathodically active). Oxide accumulation is controlled by the biominedralization rate and by the corrosion current, in that high corrosion currents will discharge the oxide as rapidly as it is formed. This variation in accumulation causes the oxides to exert different modes of influence on the corrosion behavior of active compared with passive metals.

For mild steel corrosion, under anodic control, the oxides can elevate corrosion current, but will cause little positive shift in  $E_{\text{corr}}$ . The increase in corrosion current may be significant, particularly for mild steel covered with biominedralized oxides and corrosion product tubercles that provide large mineral surface areas. Given sufficient conductivity in the tubercle (e.g. by magnetite), much of this material may serve as an oxide cathode to support corrosion at the oxygen depleted anode within the tubercle. Continued biominedralization within the large tubercle may sustain a significant if not dominant amount of the cathodic current.

While biominedralized manganic oxides are expected to elevate corrosion current on mild steel, for passive metals they serve primarily to initiate localized attack. Passive metal corrosion currents of the order  $10 \text{ nA cm}^{-2}$ , allow biominedralized material to accumulate.  $E_{\text{corr}}$  then shifts in the noble direction as increasing areal coverage anodically polarizes the metal. For coverage of roughly 20%, the couple given in equation 14 fixes  $E_{\text{corr}}$  at values between +300 and +400  $\text{mV}_{\text{SCE}}$ . These values exceed the pitting potential for low molybdenum alloys in dilute chloride media, increasing the risk of pit nucleation. Once nucleation occurs, cathodic current sustained by the  $\text{MnO}_2$  cathode impedes repassivation by holding  $E_{\text{corr}}$  above the protection potential,  $E_{\text{prot}}$ . More available cathode material will support a greater number of pitting sites, increasing the probability that a metastable site will become fixed. Localized corrosion current that exceeds the biominedralization rate will discharge the oxide cathode so that eventually the corrosion rate becomes limited by the oxide biominedralization rate and by availability of other cathodic reactants (typically dissolved oxygen).

#### Corrosion in the presence of manganese-oxidizing bacteria and sulfate-reducing bacteria

MOB and SRB are frequently found together at sites of corrosion on iron and stainless steel (Videla and Characklis, 1992; Tatnall, 1981). As noted, corrosion at these sites is generally attributed to differential aeration and SRB attack, and as described in this paper, to the cathodic reactivity of manganic oxides.  $\text{MnO}_2$  exhibits a rich redox chemistry however, and is likely to play a role in the corrosion process that goes beyond promoting differential aeration and serving as a cathodic reactant. Figure 2 depicts some of the possible processes.

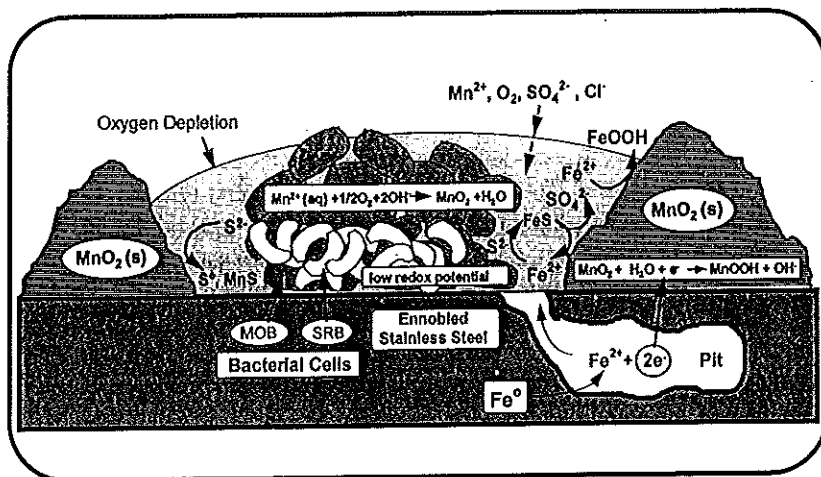


Figure 2. Hypothetical model of corrosion processes on stainless steel at sites of biomineralized  $\text{MnO}_2$  containing SRB. Anodic polarization by  $\text{MnO}_2$  shifts  $E_{\text{corr}}$  to values exceeding  $E_{\text{pit}}$  at local sites of diminished redox potential. The biomineralized deposits may further react with corrosion products and SRB metabolites. All chemical components necessary for this process can be detected in environmentally exposed samples. We assume that such combined action of these two groups of organisms is enough to elevate the potential above the pitting potential. We will verify this assumption in our future work.

The corrosion of steel in  $\text{H}_2\text{S}$ - $\text{O}_2$  systems is accelerated by deposition of elemental sulfur (Eq. 10), and Eq. 11 indicates that ferric oxides can deposit sulfur as well. Manganese dioxide is a substantially more potent oxidizer than ferric oxide, and produces sulfur according to (Burdige and Nealson, 1986):



Divalent manganese may then form manganese sulfide



which is an aggressive nucleant of pitting attack on stainless steel (Jones, 1992).  $\text{MnO}_2$  oxidization of sulfide and ferro compounds can be expected to yield a variety of intermediate sulfur oxidation states. As a result, manganese biomineralization may influence the iron-sulfur mineralogy described earlier in this paper, as well as opening the possibility of a series of  $(\text{MnFe})\text{S}_x$  phases with as yet unknown corrosion properties.

MOB and SRB also may exert a concerted influence on breakdown of the passive film on stainless steel. Heterotrophic respiration by MOB consumes oxygen, providing conditions that foster SRB growth. Regions of low redox potential develop due to sulfide production and these regions are in contact with metal that is anodically polarized by the  $\text{MnO}_2$  cathodes. The interfacial potential difference in these regions exceeds that of metal exposed to aerated bulk solution and the regions become preferential sites for pit nucleation. Close proximity of the  $\text{MnO}_2$  cathodes sustains the high current density required to exceed the pit stability product, increasing the risk that metastable pits will stabilize.

## CONCLUSIONS

The two cases considered here, SRB corrosion and MOB corrosion, show important similarities and important differences. Closer analysis of these features may shed light on the electrochemical interactions between biofilms and metals and on the nature of MIC in general. The important similarity: the influence on electrochemical processes is in both cases facilitated by microbially deposited inorganic materials in close proximity to the metal surface. The important differences include the nature of precipitated material and the electrochemical state of the metal necessary to initiate the process of accelerated corrosion. In the case of

SRB the precipitated material, a mixture of iron sulfides and iron oxides, is the product of biologically generated sulfide combining with ferrous ion from pre-existing corrosion. It is an autocatalytic mechanism where the products of galvanic corrosion enter chemical and biochemical reactions modifying the near-surface environment and making it more corrosive. To initiate this mechanism the metal has to be initially in the active state. In the case of MOB the formation of cathodically active manganese oxide deposits is possible only if the metal is in the noble state. It is the accumulation of these deposits that leads to passive film breakdown and localized corrosion. Although active corrosion can be at least partially supported by cathodic conversion of manganese dioxide to manganese oxyhydroxide, the process is not autocatalytic, and will consume rather than generate the aggressive mineral.

In conclusion, the characteristic factor contributing to MIC appears to be the bioprecipitation of materials influencing the thermodynamics and/or kinetics of processes contributing to galvanic corrosion. Those materials may be products of corrosion, such as the iron sulfides, e.g. SRB corrosion, or, as in the case of MOB corrosion, they may be formed entirely by the microbial process.

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