



Biofouling

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MANGANESE BIOFOULING AND THE CORROSION BEHAVIOR OF STAINLESS STEEL

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Manganese- and iron-oxidizing bacteria (MFOB) are widely implicated in microbially influenced corrosion, often in association with sulfate-reducing bacteria (SRB). Traditionally MFOB have been assigned a passive role in the corrosion process, promoting differential aeration cells, and providing oxygen depleted conditions conducive to the growth and corrosive attack of SRB. Recent work, summarized in this article, demonstrates that manganese biofouling alters the electrochemical behavior of stainless steel (SS), and suggests that MFOB are more active in localized corrosion than traditionally held. The paper discusses the chemistry and potentially corrosive impact of manganese and iron oxides on SS, explores the possible relationship between MFOB and SRB, and proposes a model to describe the synergistic influence these organisms may exert in the corrosion process.

KEYWORDS: manganese-oxidizing bacteria, sulfate-reducing bacteria, MnO₂, stainless steel, corrosion, pitting

INTRODUCTION

A survey of the literature on microbially influenced corrosion raises several notable points: 1) sulfate-reducing bacteria (SRB) have an unparalleled reputation as agents of localized microbial attack of ferrous metals; 2) manganese and iron -oxidizing bacteria (MFOB) are often present within the tubercles surrounding the corrosion sites, and 3) MFOB are considered to promote corrosion primarily by forming mineral deposits that occlude the metal surface. Consequent corrosion is attributed to differential aeration, colonization succession by SRB, and the SRB related processes thought to occur within the corrosion tubercle (*e.g.* diminished redox potential, cathodic iron sulfide formation, hydrogen depolarization, chloride counter-ion accumulation, acidifying metal-ion hydrolysis).

During the past decade, a few reports have suggested that MFOB play a more active electrochemical role in localized corrosion of SS. Duquette and Ricker (1986) proposed a chemical basis for MFOB attack entailing formation of aggressive ferric and manganic chlorides and Linhardt (1994) demonstrated that MFOB can induce massive pitting failure of SS. In addition, it is known that manganese oxides exhibit strong cathodic activity when coupled to passive metals (Tomashov & Chernova, 1967). Despite these considerations, the electrochemical basis for MFOB induced corrosion has as yet received little attention. Recent work in the authors' laboratory (Dickinson *et al.*, 1995) has demonstrated that manganic oxide biofouling can account for the phenomenon known as Ennoblement, in which corrosion potential (E_{corr}) and cathodic current density increase significantly during microbial colonization of passive metals. The findings support the electrochemical role of MFOB in corrosion processes and invite closer

consideration of the corrosive influence of MnO_2 . The present work summarizes the authors' findings concerning the nature and electrochemical consequences of manganese biofouling and outlines the possible scope of MFOB related corrosion. The paper also proposes a mechanism for MFOB induced pitting of SS, and suggests a basis for synergistic corrosive attack by MFOB and SRB.

MFOB AND LOCALIZED CORROSION

Reports linking MFOB to localized corrosion consist largely in detection of MFOB and elevated iron and manganese levels at the corrosion site. A quote from Tatnall is illustrative (Tatnall, 1990); "scattered throughout the (corrosion) mound will often be found filamentous or stalked iron-oxidizing bacteria ... high numbers of *Gallionella* iron-oxidizing bacteria and *Siderocapsa* iron- and manganese-concentrating bacteria...and high levels of iron, manganese, and chloride. Under each of these mounds was found a subsurface pit... Failures of this sort have been reported at numerous sites world-wide." While reports of corrosion attributed solely to MFOB activity are becoming more numerous (Kobrin, 1986; Tatnall, 1990; Linhardt, 1994) by far the majority of case histories still note an association between MFOB and SRB at the corrosion sites. Thus Videla and Characklis (1992) state that "metal-oxidizing microorganisms create environments for the accumulation of chloride ions and form acidic ferric chloride and manganic chloride, which are corrosive to SS. However the main mechanism used by this kind of tubercle-forming bacteria is the production of differential aeration cells. In all cases, corrosion enhancement is largely due to the presence of SRB in the inner area of the tubercle." Although there is an increasing awareness that "in cases of anaerobic corrosion, SRB are seldom if ever the sole organisms present, and other mechanisms of microbial corrosion are at least potentially active" (Hamilton & Maxwell, 1986), the prevailing opinion remains that MFOB promote corrosion primarily by establishing differential aeration cells and oxygen-depleted conditions conducive to SRB growth. The authors' recent work on Ennoblement suggests that another mechanism is indeed "potentially active".

Stainless Steel Ennoblement

Ennoblement refers to the several hundred millivolt noble shift in E_{corr} and the accompanying 2 to 3 decade increase in cathodic current density that develop when SS or other passive metals are colonized by microorganisms in natural waters. Figures 1 and 2 illustrate this behavior for Type 316L SS (UNS 31603) during *in situ* exposure to fresh river-water. The apparent limiting potential between +300 and +400 mV (all potentials vs the saturated calomel electrode, SCE) is characteristic of nearly all reported cases of Ennoblement. In a series of recent experiments (Dickinson *et al.*, 1995; Dickinson & Lewandowski, 1996) the following points concerning these phenomena were demonstrated: 1) MFOB and Mn-rich mineral deposits accumulate during Ennoblement; 2) chemical dissolution of the manganese deposits shifts E_{corr} to pre-exposure values; and 3) SS coated with MnO_2 paste exhibits electrochemical behavior nearly identical to that displayed by Ennobled coupons (Figs 1 and 2 include the electrochemical behavior of MnO_2 paste coated coupons). Based on these results and the thermodynamic potential for one-electron reduction of MnO_2 it was concluded that biomineralized manganese, reacting according to Equation 1, is responsible for the increase in potential and cathodic current density observed during Ennoblement.

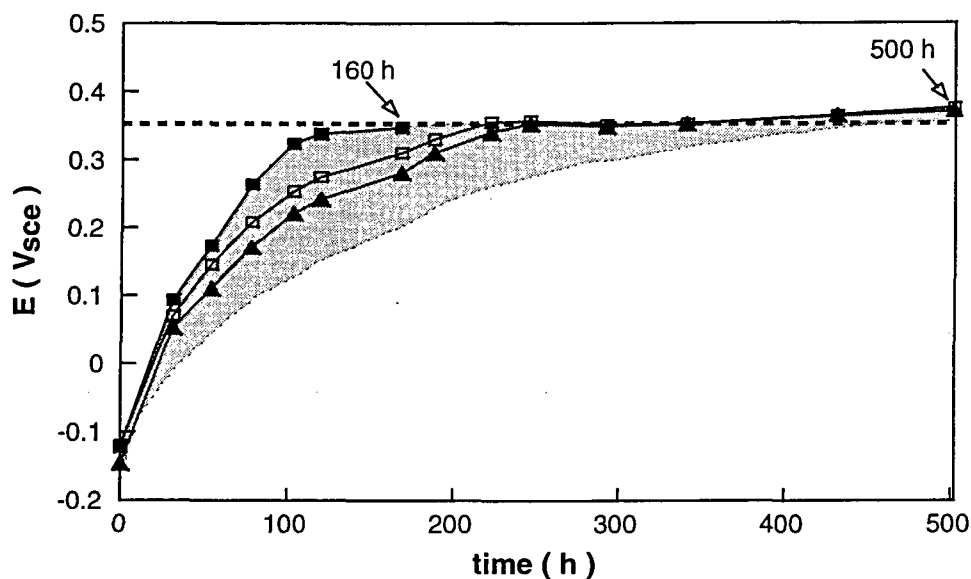


Fig. 1 E_{corr} vs time for 316L stainless steel coupons during *in situ* exposure to fresh riverwater. Data points for 3 coupons used for polarization measurements are shown, while shaded area envelopes curves for 23 coupon set. At times denoted by arrows, cathodic polarization curves were measured. Horizontal dashed line indicates potential for MnO_2 -paste coated coupon. (From Dickinson *et al.*, 1995; reprinted by permission, Elsevier Science Ltd.)

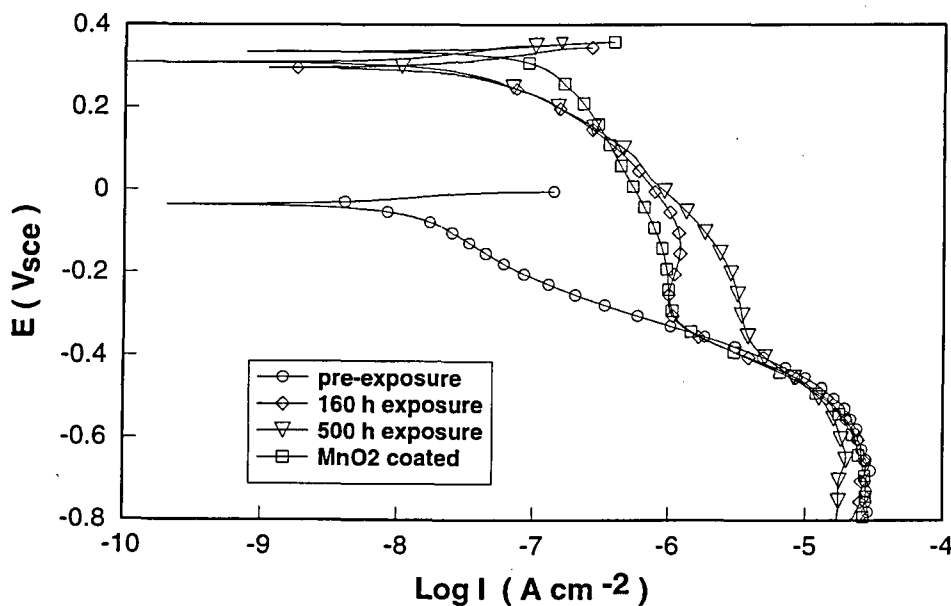
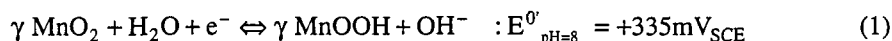
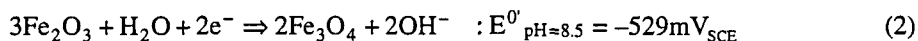


Fig. 2 Cathodic polarization curves for 316L stainless steel coupons after different exposure intervals in fresh river-water, and for an unexposed coupon coated with a $10 \mu m$ thick film of MnO_2 covering 20% of the coupon surface. Measurements were made in air saturated $0.01M Na_2SO_4$ / pH 8.4. (From Dickinson *et al.*, 1995; reprinted by permission, Elsevier Science Ltd.)



MnO_2 deposited on the metal surface acts as an attached cathode to depolarize the metal. The increasing cathodic current density shifts E_{corr} in the noble direction until the reduction potential for MnO_2 at the experimental pH is reached; at this point E_{corr} remains fixed by the solid-phase redox equilibrium. The experiments confirmed that once sufficient MnO_2 was applied to shift E_{corr} to +350 mV, application of additional material caused no further increase in potential.

The electrochemical influence of metal-oxide biofouling very likely extends to iron-oxides as well. The thermodynamic potential for reduction of ferric oxide to magnetite (Dickinson & Lewandowski, 1995) is given as:



Typical values of E_{corr} for mild steel at neutral pH lie near -700 mV, significantly more negative than the reduction potential shown in Equation 2. Thus, ferric oxides are thermodynamically unstable on mild steel in aerated media and may accelerate corrosion by cathodically depolarizing the metal. The possibility has been investigated for wet/dry rust cycles (Evans & Taylor, 1972; Carpio *et al.*, 1995) but the influence of ferric oxide biomineralization on the corrosion of mild steel has yet to be investigated. In contrast, the potential in Equation 2 is lower than E_{corr} for SS in aerated media, indicating that under aerobic conditions, ferric oxides will not cathodically depolarize SS.

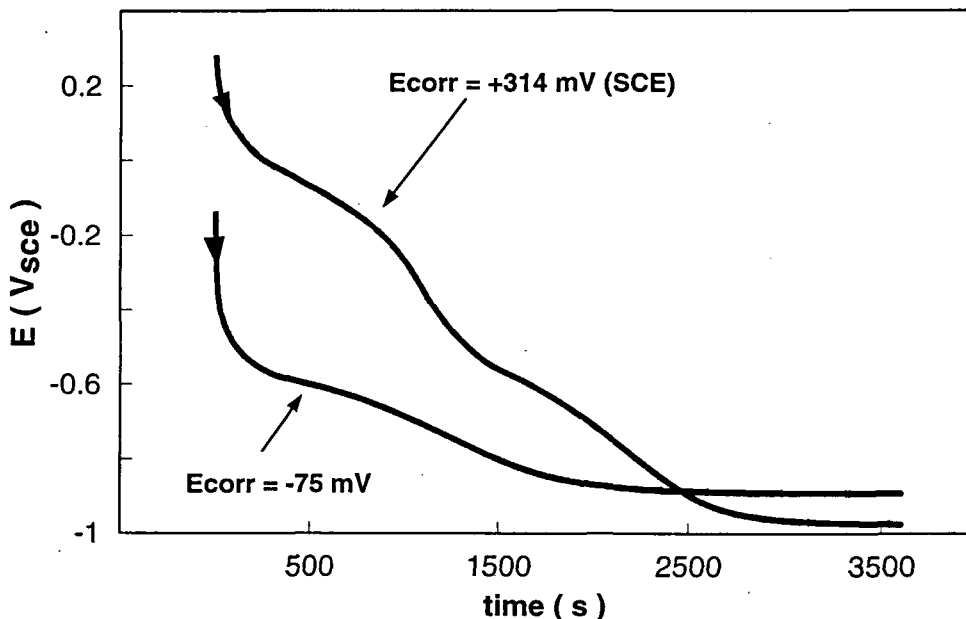


Fig. 3 Galvanostatic reduction behavior for two 316L stainless steel coupons in deaerated 0.1 M Na_2SO_4 / pH 8.5, after microbial colonization during 4 months exposure to fresh riverwater. $2.5 \mu\text{A cm}^{-2}$ applied current. E_{corr} values are at the end of the exposure period. (From Dickinson *et al.*, 1996; reprinted by permission, National Association of Corrosion Engineers.)

Galvanostatic reduction behavior shown in Figure 3, for 316L SS in the presence and absence of Ennoblement illustrates the cathodic character of surface oxides. Galvanostatic reduction is commonly applied to investigations of passive films (Ramasubramanian *et al.*, 1985) and in battery research (Bates *et al.*, 1995), and is carried out by applying constant cathodic current to samples in deaerated (depolarizer-free) electrolyte. In the absence of dissolved faradaic reactants, the electrode is rapidly polarized to the stability potential of adsorbed surface phases, followed by a potential lag as the surface phase is reduced. The potential lag near -550 mV visible in Figure 3 is attributed to ferric oxide reduction (Ramasubramanian *et al.*, 1985) and shows the close agreement between thermodynamic stability potential (cf. Eqn 2) and onset of oxide reduction. The lag at more positive potential exhibited by the Ennobled coupon is assigned to MnO_2 reduction. While, in this latter case, lag potential and stability potential (cf. Eqn 1) do not match, the difference can be attributed to polarization effects, and indeed, the potentials converge as the applied current density is diminished (Dickinson & Lewandowski, 1996).

Proposed Mechanism of Pit Formation by MFOB

MIC of SS is characterized by reddish-brown mound-shaped or volcano-like deposits connected by pin-hole perforations to large subsurface cavities (Kobrin, 1976; Tatnall, 1990). In some cases, the surface perforations can be microscopic (Stoecker, 1984; Dexter, 1995). Based on Ennoblement studies, it is proposed that this form of MIC may result from the electroactivity and specific taxonomy of the manganese deposits produced by MFOB.

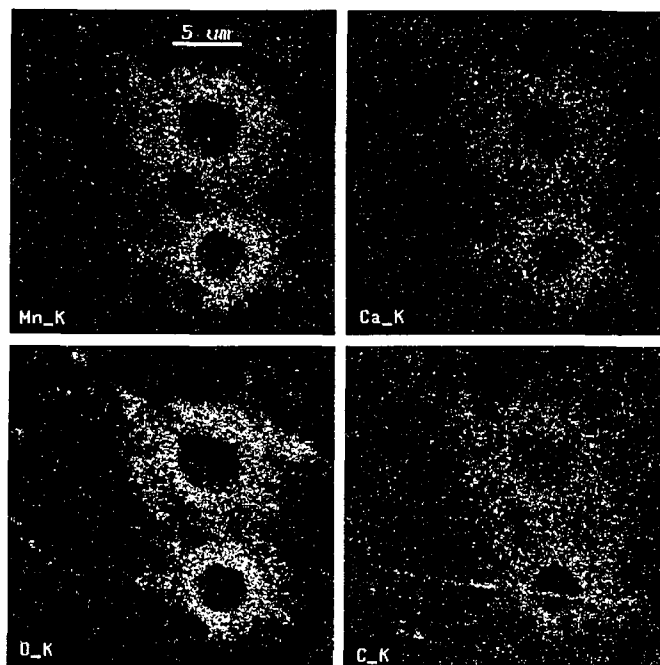


Fig. 4 EDS maps of annular deposits on 316L stainless steel coupons confirming the presence of Mn, Ca, O, and C. (From Dickinson *et al.*, 1995; reprinted by permission, Elsevier Science Ltd.)

It was shown (Dickinson *et al.*, 1995; Dickinson & Lewandowski, 1996) that Ennoblement develops when as little as 10% of the metal surface is covered by annular, manganese-rich, bio-deposits. Figure 4 shows the manganese enrichment within these deposits and Figure 5 shows the distinctive ring-shaped deposit morphology. The rings are 10–20 μm in diameter, approximately 3 μm thick, and frequently contain clusters of individual bacterial cells within the 3–4 μm diameter central void. Figure 6 shows the microbial characteristics associated with the rings for biofilm formed on 316L SS in fresh river-water. The photograph, obtained using epifluorescence microscopy, reveals sheathed cells characteristic of the *Leptothrix-Sphaerotilus* group and cell clusters within the rings characteristic of *Siderocapsa* bacteria. Both genera are known to deposit manganese, and manganese-oxidation was exhibited by separate cultures of both filamentous and sheath free cells isolated from Ennobled coupons.

The ring-bacterial cell taxonomy, in the presence of MnO_2 , suggests the following mechanism as the basis for the characteristic subsurface pitting observed in MIC of SS. Ennobled potential due to cathodic MnO_2 depolarization, coupled with diminished redox potential caused by microbial respiration, increases the interfacial potential difference within the rings to a value exceeding the critical pitting potential (E_{pit}). This occurs before E_{pit} for metal exposed to bulk solution is reached and leads to preferential pit nucleation within the rings. Enhanced pit nucleation in turn increases the probability that stable pit growth will develop. The fixed MnO_2 cathode would initially prevent the pit from spreading but would support relatively large anodic currents, leading to the microscopic

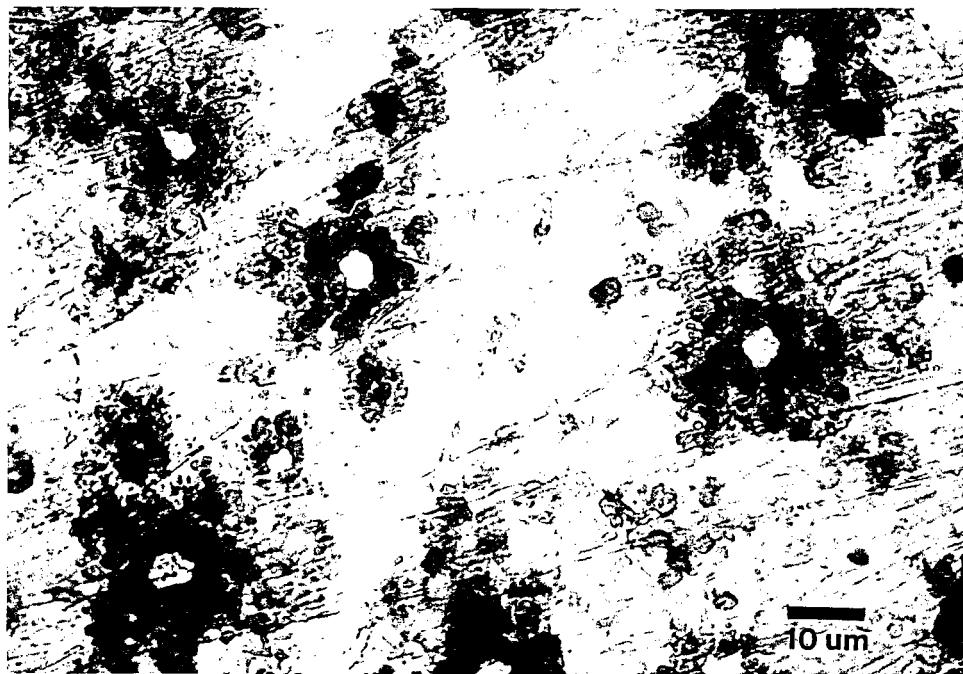


Fig. 5 Reflected-light micrograph of annular deposits on 316L stainless steel coupon after 13 d *in situ* exposure to fresh river-water. Stainless steel substratum is visible outside the rings and within the central void. (See Color Section.)

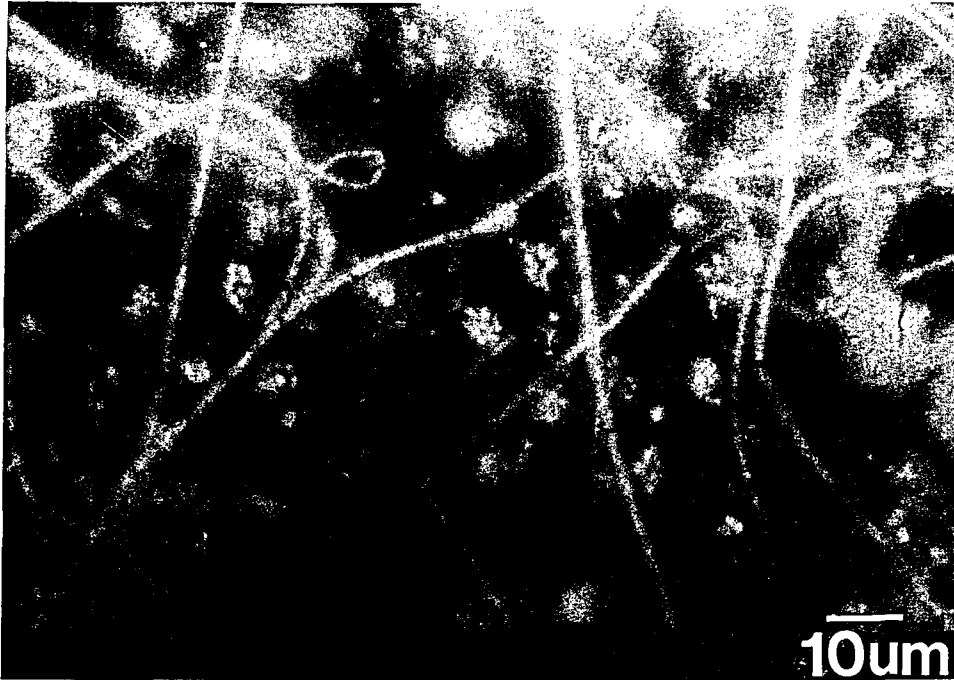


Fig. 6 Epifluorescence micrograph of acridine-orange stained biofilm on 316L stainless steel coupon after 4 d *in situ* exposure to fresh river-water. Individual bacterial cells centrally located within annular deposits as well as sheathed filamentous bacteria can be seen. (See Color Section.)

surface openings. Once stable pitting develops, active corrosion currents may consume the available MnO_2 , removing the fixed cathode and allowing the surface openings to broaden. The combination of ferrous corrosion products and continued iron and manganese biomineralization around these sites would result in visible red-brown mounds. By this mechanism, MFOB can be expected to promote SS pitting even in fresh waters. The combined influence of MFOB and colonization succession by SRB would be potentially even more damaging, since the risk of pit nucleation would increase as SRB activity further decreases redox potential within the rings.

Evidence to support the above model can be obtained by considering the anodic current required to sustain SS pitting. The "pit stability product" required for stable pit growth on 304 SS is 3 mA cm^{-1} (Pistorius & Burstein, 1992). For hemispherical pits constrained to the 3–4 μm diameter area within the rings (Fig. 5), this would correspond to about $5 \mu\text{A}$. Figure 2 shows that Ennobled SS of a few cm^2 area would support this current at potentials that still exceed E_{pit} (-50 mV at 0.5N NaCl ; Uhlig, 1971), indicating that a greater density of metastable pits can be sustained by manganic oxide depolarization than by oxygen depolarization alone. The greater density, increases the probability that a metastable pit will stabilize. In addition to increasing the density of metastable pits, the ring shape would serve as a barrier to diffusion of cations from the metastable site, lowering the "pit stability product" required to maintain the high cation anolyte concentrations required for pit growth

The mechanism described above has some similarities to previous arguments relating SS pitting to manganese biofouling (Duquette & Ricker, 1986), but differs in a fundamental way, and, contrary to the previous discussions, is based on experimental evidence that manganese biofouling strongly shifts E_{corr} in the noble direction. In past discussions, the corrosive agents produced during MFOB biofouling are considered to be ferric and manganic chlorides. The argument assumes that metal ions produced during oxidation of the substratum necessitate accumulation of counter anions (typically chloride) at the metal surface to maintain charge neutrality. Chloride accumulation in the presence of MnO_2 presumably results in an aggressive manganic chloride solution. While this proposed mechanism would implicate manganese biofouling in active corrosion, it does not address the possible role of MnO_2 in fostering corrosion by enhancing pit nucleation and sustaining greater metastable pit density.

MnO₂ Induced Corrosion

To demonstrate that MnO_2 can induce corrosive attack of SS, chemically prepared MnO_2 paste (Dickinson *et al.*, 1995) was coated over approximately 30% of a 304L SS coupon, and the coupon was immersed in 0.05N NaCl solution carbonate buffered at pH 8.2, while E_{corr} was monitored and linear polarization resistance (R_p) was periodically measured. As shown in Figure 7, E_{corr} exhibited a series of negative excursions that were accompanied by a sharp decrease in R_p . The behavior is interpreted as follows: 1) cathodic depolarization by MnO_2 elevates E_{corr} above E_{pit} ($E_{\text{pit}} = 0.12$ V in 0.05N NaCl/pH 8.2, unpublished data); 2) increased corrosion current caused by pit initiation anodically depolarizes the electrode, with MnO_2 furnishing the cathodic current; 3) as E_{corr} falls below the protection potential (E_{prot}), anodic current drops, and E_{corr} again

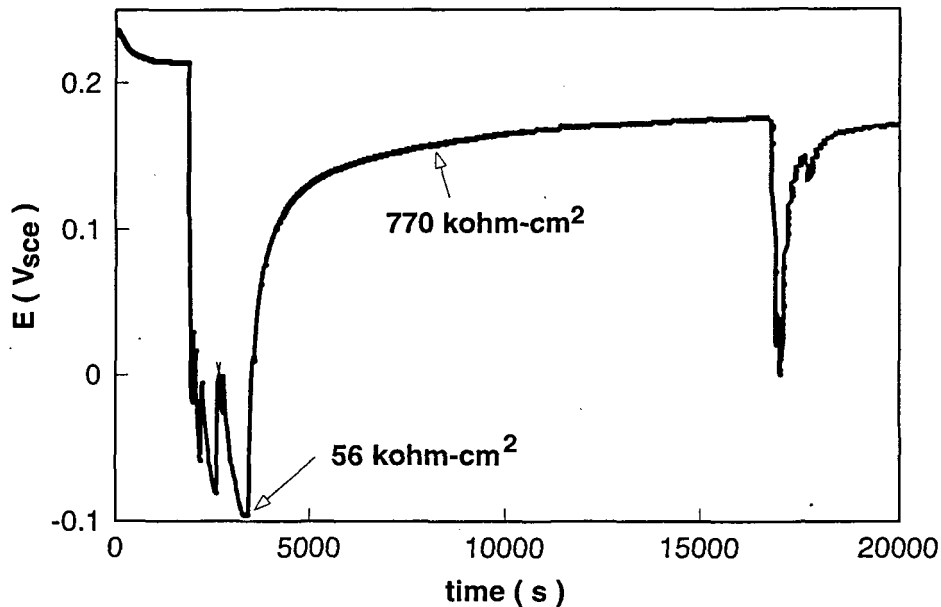


Fig. 7 E_{corr} vs time for MnO_2 -paste coated 304L stainless steel coupon in 0.05N NaCl / pH 8.2. Polarization resistance at two points during exposure is shown.

increases. The process is the same as for active-passive cycles with dissolved oxygen (DO) as the sole depolarizer, with the marked distinction that the elevated cathodic current supplied by MnO_2 (cf. Fig. 2) requires a higher anodic current to polarize E_{corr} to E_{prot} . Thus more numerous or more active pits must form before repassivation can occur, increasing the risk of stable pit formation and localized damage

POTENTIAL SCOPE OF MFOB RELATED CORROSION

In view of the proposed mechanism of microbially induced pitting of SS, the question arises, "how pervasive is MFOB corrosion?" Only a few of the reports published since MIC of SS was first noted in the early 1970's (Stott, 1993) have included manganese analysis of the corrosion products (Kobrin, 1976; Tatnall, 1981; Stoecker, 1984; Tatnall, 1990). Nevertheless, the widely acknowledged role of MFOB in tubercle formation (Miller & Tiller, 1970; Tiller & Corr, 1986; Jones, 1992) indicates that these bacteria are prevalent, and these organisms are known to be broadly distributed in soils and natural waters (Ghiorse, 1984; Nealson *et al.*, 1988; Gounot, 1994). While reports of MFOB related corrosion have most frequently implicated the freshwater genera *Siderocapsa*, *Gallionella*, and the filamentous bacteria *Leptothrix* and *Sphaerotilus*, a far broader range of organisms is known to deposit manganese. These include the bacterial genera *Bacillus*, *Pseudomonas*, and *Micrococcus* (Staley, 1980), numerous marine bacteria, and a variety of algae, yeast and fungi (Nealson *et al.*, 1988). Schuett *et al.* (1986) isolated forty-seven strains of manganese-oxidizing bacteria from manganese nodules, sediments, and seawater in the Pacific Ocean and the Mediterranean Sea; Moffett (1994) demonstrated microbially-mediated oxidation of manganese(II) in seasonally anoxic coastal waters; and Cowen and Silva (1984) established the presence of manganese-oxidizing bacteria and biomineralized manganese on macroparticulate material in the oceanic water column. Such reports underlie the pronouncement that "microorganisms are, either directly or indirectly, the major catalysts of manganese cycling in the natural environment" (Gounot, 1994) and indicate that manganese biofouling can be expected in a variety of natural conditions.

The extent of corrosion caused by manganese biofouling has yet to be assessed. The ability of manganese deposits to depolarize SS is at least partially dependent on where the deposit is located relative to the metal surface since the mineral must be within charge-transfer distance or must be embedded in electrically conductive material. Thus adherent deposits such as those depicted in Figure 5, are effective depolarizers, while deposits broadly distributed within a polysaccharide biofilm matrix may cause E_{corr} to shift only slightly, if at all. Furthermore, the extent of Ennoblement may be influenced by the rate of manganese deposition. That is, MnO_2 accumulation will reflect both the rate of biological and chemical deposition and the rate of removal by discharge through the metal corrosion current. Rates of cathodically active MnO_2 deposition between 0.57 and 3.1 $\text{mCoul cm}^{-2} \text{d}^{-1}$ were found for 316L SS exposed to fresh river-water (Dickinson & Lewandowski, 1996). For a one-electron reduction according to Equation 1, the cathodic material deposited at these rates would be discharged by between 6 and 36 nA cm^{-2} of anodic current. Initially, with E_{corr} near the pre-exposure value, anodic current will be balanced by DO reduction, allowing MnO_2 to accumulate; however as MnO_2 deposition shifts E_{corr} in the positive direction, more and more cathodic current will be supplied by MnO_2 reduction. Only metals with low corrosion currents (*i.e.* noble or passive metals) will allow MnO_2 to accumulate sufficiently to reach Ennobled potentials. MnO_2 accumulation will also depend on the nature and activity of the organisms causing

deposition, and on the redox, chemical, and physical characteristics of the environment. As an example of the possible influence of physical conditions, it is speculated that inhibition of Ennoblement, which has been observed for sunlight-irradiated seawater (Eashwar *et al.*, 1995), may be caused by photo-inhibition of enzymatic manganese oxidation (Moffett, 1990), that prevents MnO_2 deposition.

Manganese oxidation rates (biological plus chemical) have been determined in a number of natural environments (Nealson *et al.*, 1988), but these are typically reported as Mn(II) uptake rates (moles $\text{l}^{-1} \text{h}^{-1}$). It is difficult to relate these rates to deposition of cathodically active material since the surface area of the particulate material (on which the deposition is presumed to occur) is generally not known. Nevertheless, if all Mn(II) oxidation were to deposit MnO_2 on a metal surface placed in solution, the above studies suggest that deposition rates as high as $700 \text{ mcoul d}^{-1} \text{ l}^{-1}$ of solution may be encountered in some natural environments. This would have a very strong influence on the cathodic performance of the metal.

A better perception of the extent of potentially destructive manganese biofouling is gained by considering the reported instances of Ennoblement. In separate studies, the electrochemical behavior of passive metals exposed to fresh, estuarine, and marine waters at twelve different sites world-wide has been examined. In all but two of the reports, E_{corr} was observed to increase to values exceeding +300 mV at rates between five (Scotto *et al.*, 1985) and one hundred (Motoda *et al.*, 1990; Dickinson & Lewandowski, 1996) mV d^{-1} . If these few experiments are representative of the behavior of SS exposed to natural waters, the risk of pit initiation due to manganese biofouling is significant.

MNO₂ AND SRB: CHEMISTRY WITHIN THE DEPOSITS

A possible symbiotic relationship between MFOB and SRB has been noted above. SRB are obligate anaerobes and under natural conditions, depend on the action of aerobic and facultative anaerobic microorganisms to generate oxygen depleted conditions. MFOB respiration coupled with a deposit morphology that impedes oxygen transport can reasonably be expected to provide such conditions, and this point has been raised repeatedly in the literature (Kobrin, 1976; Tatnall, 1981; Tiller & Corr, 1986). In light of the chemical and electrochemical reactivity of MnO_2 however, a number of possible chemical aspects of MFOB/SRB symbiosis also bear consideration.

Hamilton (1990) has noted the limited nutritional spectrum of SRB. The bacteria can utilize small organic acids and alcohols, but are generally unable to grow on carbohydrates or biopolymers. To quote from Hamilton (1990), "Although SRB are strict anaerobes, it has been noted that in sediment systems they demonstrate maximal activity within a few centimeters of the aerobic/anaerobic interface. Almost certainly this reflects nutrient input from the metabolic activities of other aerobic and facultative organisms also present but with greater biodegradative capability than the SRB, and the availability of biotic and abiotic oxidation of the produced sulphide to which the SRB are themselves sensitive."

Nutrient Production

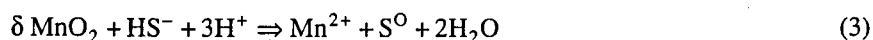
Sunda and Kieber (1994) have recently reported significant levels of pyruvate formation by MnO_2 oxidation of humic substances in natural waters. These authors speculate that manganese oxidation has evolved as a means by which abundant but biologically refractory humic and fulvic acids can be converted to low-molecular-weight biological

substrates. Sunda and Kieber (1994) measured pyruvate formation rates of 10 nM h^{-1} for 2 mg l^{-1} fulvic acid in the presence of 55 mg l^{-1} of suspended MnO_2 , and noted that total production of small organic substrates including alcohols and short chain organic acids is likely to be considerably greater. MnO_2 biofouling rates greater than $1 \text{ } \mu\text{g cm}^{-2} \text{ d}^{-1}$ on 316L SS exposed to river water have been measured (Dickinson & Lewandowski, 1996). The MnO_2 is contained almost completely within the annular deposits shown in Figure 5, which number approximately $1600 \text{ rings mm}^{-2}$ after 7 d exposure. From these values, a mass of 44 ng MnO_2 per ring is calculated. Treating each ring as a tiny reaction vessel, and applying the following simplifying assumptions: 1) stagnant solution containing 2 mg l^{-1} fulvic acid permeates the roughly $15 \text{ } \mu\text{m}$ diameter \times $3 \text{ } \mu\text{m}$ thick volume of the ring plus central void (volume of ring plus void, $5 \times 10^{-13} \text{ l}$; substratum area beneath central void, $1.2 \times 10^{-11} \text{ m}^2$); 2) all MnO_2 in a ring is accessible for reaction with the stagnant solution; 3) the 10 nM h^{-1} rate for 55 mg l^{-1} of MnO_2 can be extrapolated to the grossly larger MnO_2 wt/vol ratio within the rings; and 4) pyruvate removal by mass transfer can be ignored; a pyruvate production rate of $15 \text{ } \mu\text{M h}^{-1}$ within the rings can be estimated. For a ring volume of $5 \times 10^{-13} \text{ l}$, a production rate of $7.5 \times 10^{-18} \text{ moles h}^{-1}$ per ring is estimated. Characklis and Marshall (1990) reported glucose removal rates of about $2.8 \times 10^{-4} \text{ moles m}^{-2} \text{ h}^{-1}$ for a $10 \text{ } \mu\text{m}$ thick mixed culture biofilm. Converting this to a pyruvate removal rate based on a pyruvate/glucose ATP ratio of 0.4 for aerobic metabolism, gives a value of $7 \times 10^{-4} \text{ moles m}^{-2} \text{ h}^{-1}$. For a biofilm area of $1.2 \times 10^{-11} \text{ m}^2$, a pyruvate consumption rate of about $8 \times 10^{-15} \text{ moles h}^{-1}$ within each ring is calculated. Thus, pyruvate produced by MnO_2 oxidation of fulvic acid is estimated to furnish roughly one-tenth of one percent of the substrate demand within the rings, and as noted, pyruvate may represent only a small fraction of the total assimilable organic carbon produced during fulvic acid degradation. This coarse calculation provides a modest test of Sunda's hypothesis concerning the evolutionary selection of manganese biomineralization, and suggests that MFOB activity could generate modest levels of organic substrates for SRB growth.

Sulfide Removal

Sulfide is known to diminish SRB growth (Brock *et al.*, 1984; Hamilton, 1990) and standard culture technique for these organisms includes addition of ferrous iron that detoxifies the media by formation of FeS (Brock *et al.*, 1984). This same process may protect SRB during growth in the presence of active ferrous metal dissolution, as would occur during corrosion of mild steel. For SS in the passive state, however, ferrous iron production will be negligible, and the above mechanism of sulfide removal will not be operative. Under these conditions, other sulfide removal mechanisms may be important to SRB growth, and one such mechanism is sulfide removal by reaction with MnO_2 .

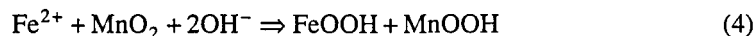
MnO_2 is reduced by bisulfide ion in natural waters according to Equation 3 (Burdige & Nealson, 1986):



and may further oxidize elemental sulfur to sulfate (Aller and Rude, 1988). Reaction 3 is rapid and quantitative, and provides a substantial removal mechanism for microbially produced sulfides in anoxic waters. The same process may be the primary mechanism controlling sulfide toxicity during initial SRB growth on passive SS, and so may promote pit nucleation by fostering SRB growth as described under the Proposed Mechanism of Pit Formation above.

Reactions with Corrosion Products

Once pit nucleation occurs within a ring, MnO₂ chemistry may continue to influence the corrosion process. Thermodynamically favored reactions such as 4 and 5, would serve to oxidize ferrous corrosion products and deposit hydrous ferric oxides. Oxide accumulation near the pit nucleation site would serve as an added barrier to metal cation diffusion (Cr³⁺, Fe²⁺, Ni²⁺), and so would promote the high cation concentrations required for metastable pit growth. The result would be similar to porous cap formation that occurs in conventional pitting of SS when ferrous ion is oxidized by dissolved oxygen (Jones, 1992). The role of MnO₂ in forming the barrier may be particularly important for processes occurring in the low oxygen conditions at the base of a biofilm where ferric oxide deposition might not otherwise occur.



In the presence of sulfides, an additional process may occur as insoluble FeS is oxidized by MnO₂ to produce SO₄²⁻, and regenerate Fe²⁺ (Aller & Rude, 1988). Fe²⁺ may then be oxidized further by reactions 4 and 5. The net result would be to shift the location of surface occlusions that form during the corrosion process. The actual influence of MnO₂ on the corrosion chemistry will very likely depend on the spatial relationship between the deposit and the nucleation site; near surface pH and oxygen gradients; the geometry of the ferrous ion plume emanating from the pit; counter-ion access; and whether SRB are present. Microbiological analysis coupled with micro-electrode measurements of DO, S²⁻, redox potential, and pH within the rings before and after pit initiation would help clarify the actual pitting process.

Model for MFOB/SRB Induced Corrosion

The proposed chemical interactions between MnO₂ and SRB, together with the electrochemical effects already described, make it possible to propose an overall synergistic relationship between MFOB and SRB in promoting SS corrosion. The following model is put forth:

- 1) SS is colonized by heterotrophic MFOB which consume oxygen and produce MnO₂-rich deposits;
- 2) the deposits i) physically impede oxygen transport, allowing oxygen depleted conditions to develop; ii) oxidize natural polymeric substances to produce organic substrates suitable for SRB growth; and iii) elevate metal potential by depolarizing the cathodic process;
- 3) SRB colonization, which develops under the favorable growth conditions, lowers redox potential within the deposits by producing sulfides;
- 4) sulfide toxicity is controlled by oxidation at the MnO₂ deposits, furthering SRB growth;
- 5) the combined electrochemical effects of elevated metal potential and diminished redox potential raise the interfacial potential difference within the deposits above the critical pitting potential, causing pit nucleation;
- 6) elevated cathodic current density provided by the MnO₂ prevents repassivation of the nucleation sites and increases the probability of stable pit growth by supporting a greater density of metastable pits.
- 7) MnO₂ chemistry promotes the high anolyte cation concentrations required for stable pit growth by forming insoluble ferric corrosion products that serve as a diffusion barrier.

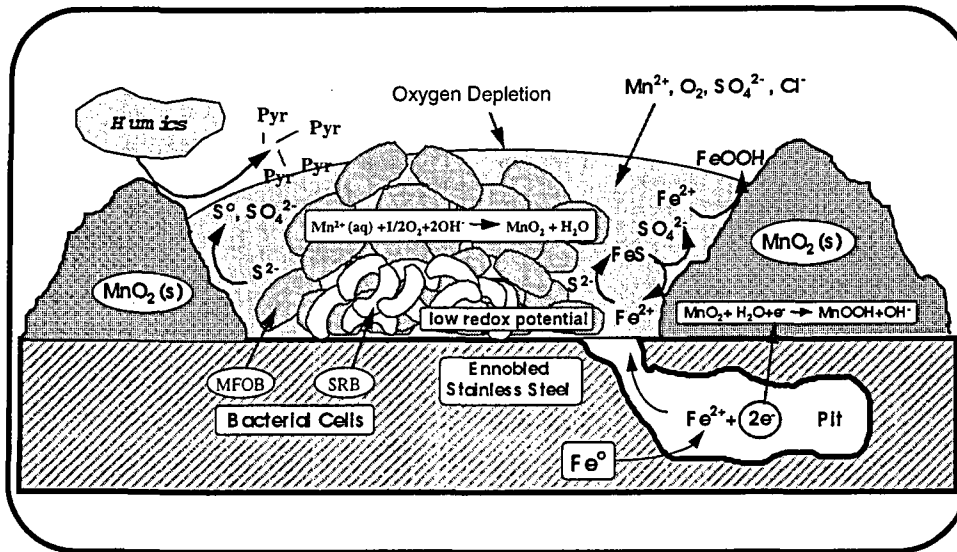


Fig. 8 Proposed model of corrosion processes within biomineralized MnO_2 deposit containing SRB. MnO_2 depolarization shifts E_{corr} to values exceeding E_{pit} at local sites of diminished redox potential. Cross-section through annular ring is shown.

Figure 8 shows the overall nature of this process. While the key role of MnO_2 in depolarizing SS has now been established, several of the steps in the model are based on theoretical arguments that clearly invite continued research.

CONCLUDING REMARKS

Manganese biomineralization is a widely distributed process in natural waters. Results from recent experiments on Ennoblement have demonstrated that this process profoundly alters the electrochemical behavior of SS and suggest that biomineralized MnO_2 may be responsible for widely observed pitting corrosion of microbially colonized SS. It has been shown that, at modest chloride concentrations, MnO_2 coated SS exhibits behavior typical of pit initiation, and it is suggested that an annular deposit morphology may compound the corrosive effect by serving as a barrier to oxygen penetration and cation removal. SRB succession within manganese biofouling deposits may intensify the corrosive effect of MnO_2 by diminishing redox potential; and both chemical and physical interactions between MnO_2 and SRB are expected to promote SRB succession. In light of similarities between the microbial ecology at natural aerobic/anaerobic interfaces and the MFOB/SRB relationship proposed here, it is likely that data on manganese cycling in natural waters will be a useful tool in evaluating MIC of SS.

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