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MIC OF STAINLESS STEELS AS A MODEL SYSTEM TO STUDY METAL- MICROBE INTERACTIONS

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ABSTRACT

Accumulated evidence clearly demonstrates the influence of attached microorganisms in an array of natural and engineered processes, e.g. biomineralization, microbially influenced corrosion of metals (MIC), biomining, and bioremediation. Our knowledge of the mechanisms behind these interactions is limited because they are complex, and because we lack suitable model systems to study the interactions. We have been studying ennoblement of stainless steel - a phenomenon that can lead to a specific yet pervasive form of MIC. Biofilms on stainless steels constitute an ideal system to study microbe-metal interactions, since the redox reactions involving biofilm and stainless steel are relatively slow. Progression of the processes can be easily monitored in real time, since rates are significantly limited by the electrical properties of the passive films.

INTRODUCTION

When studying a case of material failure suspected of being caused by microbial corrosion, a reasonable question to ask is: "How do we know that the corrosion was microbially stimulated?" To answer this question research groups have attempted to find fingerprints of MIC ie. specific characteristics distinguishing biological corrosion from ordinary galvanic corrosion. Despite significant research efforts, no such fingerprints for MIC have yet been found, and there are good reasons to believe that such indicators of some universal mechanism do not exist. Common threads in known MIC mechanisms are, however, evident. It appears that the accelerated corrosion of metals in the presence of microorganisms stems from microbial modifications to the environment near metal surfaces. Such

modifications may depend on a number of possible factors, including the kind of metal used, the surface treatment employed, water chemistry, water microbiology, and the flow regime to which the metal is exposed. When biofilms accumulate on metal surfaces, their metabolic reactions affect both water and metal chemistries, both of which may interfere with the electrochemical processes naturally occurring at the interface between the metal and its environment. Taking place at the same location in the immediate proximity to the metal surface, the microbial and electrochemical processes interact in a complex way. It is difficult both to predict the nature of these interactions, and to gain experimental verification of these predictions. The reasons for these difficulties are many, and most of them are related to the complexity of the system under consideration. The deposits on metal surfaces are composed of microbes (bacteria, fungi, algae; both dead and alive), insoluble products of microbial metabolism and cell lysis, corrosion products, precipitated minerals, and particulate matter within the system under study, and each of these components has the capacity to modify the near surface environment. Therefore using a system where some of these effects can be reduced or eliminated is beneficial. We have found that studying microbial corrosion of stainless steels offers the benefit of working with a "cleaner" system that is easier to monitor than corrosion of mild steel. Therefore, if we make the assumption that many mechanisms by which microorganisms modify the metal/solution interfaces are similar even in different systems, using stainless steels as a substratum offers undeniable advantages for the study of metal microbe interactions in general.

In systems where everything affects everything else it is difficult to find patterns. Therefore, it is important to develop a systematic approach in which hypothetical mechanisms by which the near surface environment is modified can be tested and verified both in vitro and in vivo.

This paper presents a system we have developed and have been using to test MIC mechanisms. After identifying the problem we use a sequence of the following steps:

1. field observations,
2. constructing hypotheses based on the field observations,
3. testing the hypotheses under well defined laboratory conditions,
4. conceptual modeling of a proposed mechanism,
5. constructing hypotheses based on the conceptual model
6. testing the hypotheses based on the conceptual model
7. refining the conceptual model of the process
8. constructing hypotheses based on the refined model of the process
9. testing the hypotheses under well defined laboratory conditions
10. constructing hypotheses for field testing the mechanisms identified in the laboratory
11. field tests

Since the hypotheses testing steps usually bring additional information, we repeat this sequence of steps as many times as needed, and is practical, arriving at the final conclusions by iteration. Our experience indicates that MIC problems tend to be open ended, and the complexity of the conceptual model increases with the number of iterations. We will demonstrate the utility of this approach using as an example a study of microbial corrosion of stainless steels caused by biomineralized manganese oxides.

THE PROBLEM

Numerous researchers[1, 2,3,4] have shown that biofilm formation influences the electrochemical behavior of stainless steels (SS). These researchers described a dramatic increase in Open Circuit Potential (OCP) of microbially colonized stainless steels and termed the phenomenon "ennoblement" because the potential shift was in the noble direction. The ennoblement due to biofilm formation has been observed in a wide variety of environments. Mattila et al.[5] along with Dexter and Gao [6] described ennoblement in sea water, Dickinson et al.[3] reported its occurrence in a fresh water stream, while Linhardt[7] attributed the pitting corrosion of SS turbine runner blades in a hydroelectric power plant to microbially induced ennoblement.

Several hypothesis have been suggested to explain ennoblement: microbially generated protons near the surface[6]; microbially generated hydrogen peroxide, possibly combined with low pH [8]; microbially produced organometallic catalysts of oxygen reduction[9, 10] ; specific enzymes[1]; and passivating siderophores[11].

Ennoblement poses a potential threat for material integrity since the elevated OCP can reach the critical pitting corrosion, particularly when the material is exposed to seawater, or other waters with elevated chloride concentration (Figure 1).

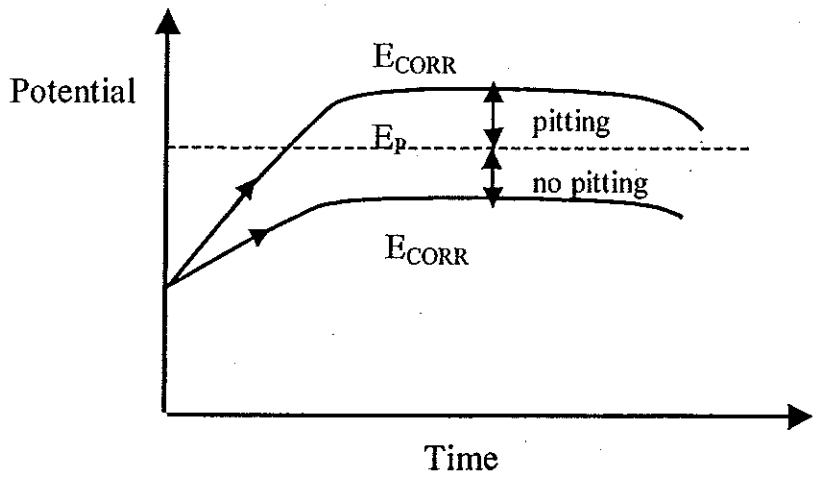

Figure 1. When the corrosion potential, E_{corr}, reaches the pitting potential, E_p, of the metal in the given solution, pits may be initiated. The data show the relation between the corrosion potential, pitting potential, and probability of pits initiation, redrawn from Sedrix[12].

THE APPROACH

Step 1. Field observations

Dickinson et al.[3,4] exposed a set of 23 epoxy-embedded 316L SS coupons (UNS S31603; 1.59 cm dia) to fresh, flowing stream-water at a field site near Bozeman, MT, by mounting the coupons in a 2 cm wide x 60 cm long open-channel polycarbonate reactor and submersing the reactor below the stream

surface. E_{corr} was measured vs. the saturated calomel electrode (all potentials are reported vs. the SCE) at roughly 1 to 3 day intervals. E_{corr} for the set of 23 coupons exposed *in situ* began to increase within 24 hours of exposure and reached steady-state values near +350 mV within one to two weeks (Figure 2).

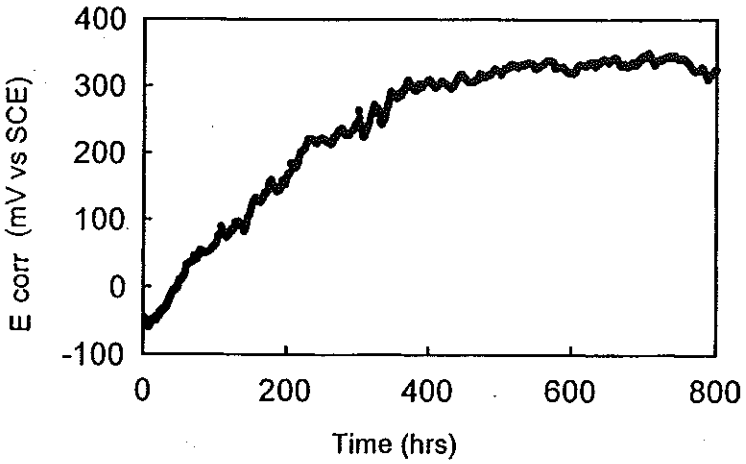

Figure 2. Corrosion potential of 316L SS immersed in natural waters for 30 days showing an increase from -50 mV to 350 mV SCE.

The ennobled coupons were covered with characteristic circular deposits, which were identified as being a diagnostic feature of *Siderocapsa* bacteria.[4]

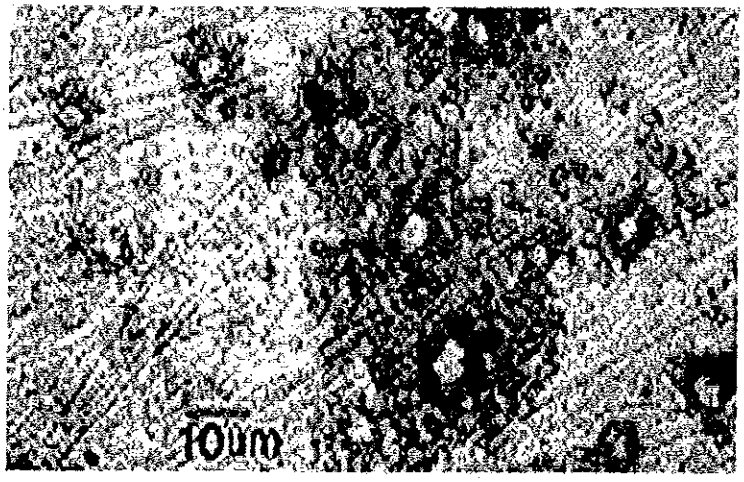

Figure 3. Reflected light micrograph showing bio-deposits on stainless steel after 13-day exposure to fresh river water. Deposits are typically 3-4 μm thick, and are characteristic of *Siderocapsa* bacteria. Stainless steel substratum is visible outside the rings and within the central void[4].

While the origin of the manganese-rich material deposited on stainless steel coupons exposed to Bozeman stream water was not rigorously established, mineral-encrusted bacterial sheaths characteristic of *Leptothrix sp.* and mineralized capsules characteristic of *Siderocapsa treubii* were abundant on the surface of the ennobled stainless steel coupons, and manganese-oxidizing bacteria were

isolated from the manganese-rich deposits[4]. In parallel with these findings, Linhardt[7] also demonstrated that manganese-oxidizing biofilms were responsible for pitting corrosion of SS.

Although biomineralization of manganese can be carried out by certain genera of the so-called iron and manganese group, *Siderocapsa, Leptothrix, and Crenothrix,* in fact the property is widely distributed in a variety of organisms including bacteria, yeast, and fungi[13]. These organisms can oxidize dissolved manganese to form highly enriched mineral-biopolymer encrustations. Deposits of manganese oxides form on submerged materials including metal, stone, glass, and plastic and can occur in natural waters and sediments with manganese levels as low as a 10-20 ppb[3, 4,14].

Extensive studies of microbial sediment ecosystems have shown that the cyclic oxidation and reduction of manganese, and of iron, play a critical role in the transfer of electrons from anaerobic sulfate reduction to the oxic zone where oxygen serves as the terminal electron acceptor[15, 16,17]. Of particular interest in the present context is the finding that the high chemical reactivity of manganese dioxide has the consequence that significant proportions of reduced sulfide and ferrous iron are re-oxidized by abiotic reaction with manganese dioxide[17]. The manganese redox cycle involves microbial oxidation and chemical reduction.

As shown in this study, biomineralized manganese oxides are also efficient cathodes and increase cathodic current density on stainless steel by several decades at potentials between roughly -200 and +400 mV_{SCE}. Their cathodic efficiency stems from the fact that they are in solid state, and therefore (1) do not decrease activity as reaction progresses, and (2) are not subjected to mass transport limitations.

Step 2. Constructing hypotheses based on the field observations

In the first step we have documented that the annular deposit morphology and the presence of MOB in the biofilm pointed to *Siderocapsa* activity as the cause of the manganese deposition in samples exposed in field environments. Although these findings strongly suggested that stainless steel electrochemistry was altered by the presence of manganese oxides deposited by manganese-oxidizing bacteria, this conclusion has to be verified by direct experimentation. Therefore we use this observation to construct the following hypotheses:

Hypothesis #1: Manganese oxides abiotically deposited on the SS surface can ennoble the potential.
Hypothesis #2: Manganese oxides deposited on the surface of SS by pure culture of manganese oxidizing bacteria have the same effect.

Step 3. Testing the hypotheses under well defined laboratory conditions

Cathodic polarization behavior is a characteristic feature of ennoblement. To ensure that noble shifts in E_{corr} observed in our work were similar to the changes observed in other laboratories, potentiodynamic polarization measurements were carried out. The measurements were made using a conventional three-electrode system by applying current between the stainless steel specimen (the working electrode) and a graphite or platinum counter electrode, and measuring the potential difference between the working electrode and an SCE reference

electrode located within a few mm of the metal surface. A computer controlled, model 273A potentiostat and 352 SoftCorr™ software (EG&G Instruments, Princeton, NJ) were used to generate the polarization curves. Figure 4 demonstrates that coupons covered with electroplated MnO_2 have the same characteristics as coupons ennobled microbially. Consequently, hypothesis #1 has been verified with the conclusion that the biofouling deposits and electroplated MnO_2 on the SS surface have the same cathodic characteristics.

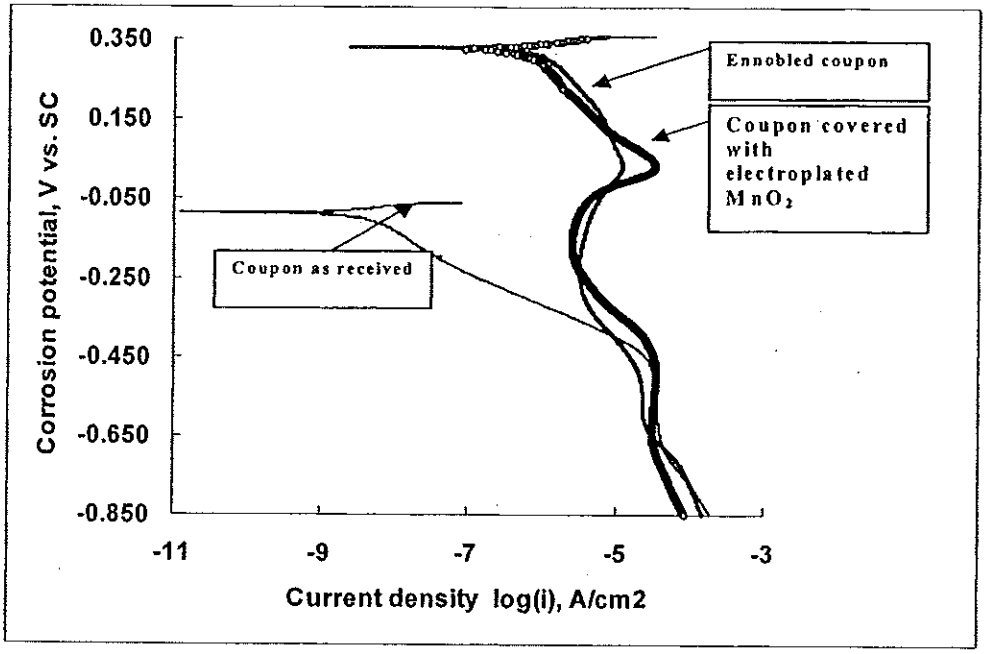

Figure 4. Potentiodynamic polarization curves (316L SS, 0.01M Na_2SO_4, pH 8.30; scan rate: 0.167mV/s) show typical behavior of non-ennobled, fully ennobled, and MnO_2-plated stainless steel coupons. Both the microbial ennoblement and electroplating of MnO_2 on the metal surface shift corrosion potentials by approximately 300 mV in the noble direction and cause a corresponding increase in cathodic current density at modest overpotentials (around -100 mV). Figure 4 was generated using an electroplated MnO_2 for the purpose of this presentation. However, it was first demonstrated by Dickinson[2] that SS coated with MnO_2 paste displayed electrochemical behavior nearly identical to that of ennobled samples, which at that time was a convincing demonstration that biomineralized manganese oxides are responsible for ennoblement.

To test the second hypothesis pure culture biofilms of the manganese oxidizing bacterium, *Leptothrix discophora,* were grown on 316L stainless steel coupons under well-defined conditions, and the rate and extent of ennoblement measured as functions of the parameters, oxygen, pH, and temperature. As controls, coupons were also exposed under identical conditions but with the absence of manganese or the manganese-oxidizing bacterium (Figure 5).

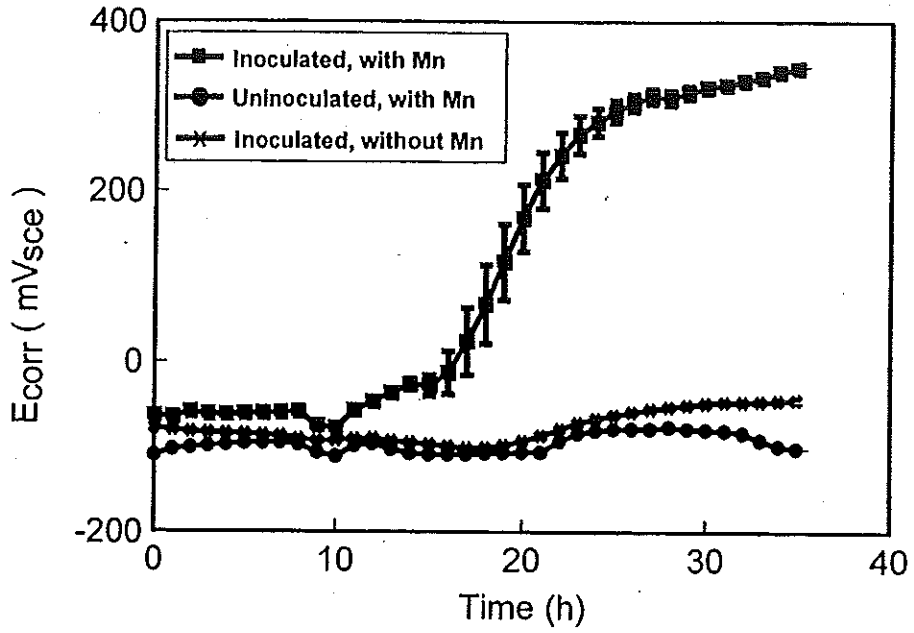

Figure 5. The results verify that the biomineralized manganese oxides deposited by the manganese oxidizing bacteria *Leptothrix discophora* can cause the noble shift potential of 316L SS, analogous to the potential shift seen in samples exposed in field situations The control coupons exposed to the same growth media but in the absence of manganese oxidizing bacteria or manganese ions did not ennoble[14].

Step 4. Conceptual modeling of a proposed mechanism

The first conceptual model we proposed to explain the ennoblement by biomineralized manganese oxides was based on one electron transfer reaction (Reaction 1) [3,4]. Data from figures 4 and 5 demonstrate that bacterial MnO_x deposition induces this process and confirm that manganese biomineralization by *Leptothrix discophora* results in ennoblement. This conclusion coincided with Linhardt's conclusions about the involvement of manganese oxidizing bacteria in pitting corrosion[7].

The model was predicting that the reaction

$$MnO_2 + H_2O + e^- \Leftrightarrow MnOOH + OH^- \qquad (1)$$

which has a reduction potential of +335 mV_{SCE} at pH 8.0 fixes E_{corr}.
The model explains that 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.

Actually, our field measurements indicated that coupons could ennoble to potentials higher than 335 mV. However, it had been reported that the Mn oxidation state for MnO_x formed by *Leptothrix discophora* increases as the oxide ages, from a value of 3.32 after 11 hours to 3.62 after 30 days[20]. Such a change would increase the oxidizing power of the oxide and thus shift the reduction potential to more positive values, and perhaps explain why in the field we measure potentials exceeding the equilibrium potential given by reaction 1. Such findings are consistent with an increase in Mn oxidation state that would occur as microbially deposited MnO_x ages

Step 5. Constructing hypotheses based on the conceptual model

The model allows us to make a number of predictions of which the following were tested:

Hypothesis #1: The rate and extent of ennoblement is related to the amount of biomineralized manganese deposited on the surface.
Hypothesis #2: Manganese oxides deposited on a surface of stainless steel are progressively reduced to manganese oxihydroxide.

The first prediction was tested in the field, and the second in the laboratory using surface analysis.

Step 6. Testing the hypotheses based on the conceptual model

Testing hypothesis #1. The purpose of the study was to quantify the rate and extent of ennoblement and to test whether they are proportional to the amount of manganese deposited on the metal surface. In the field, OCP of the coupons was measured at regular intervals. Also, coupons were retrieved and the amount of manganese deposited on their surfaces estimated. The manganese oxides were reductively dissolved from the surface of the coupons, and the dissolved manganese was measured by inductively coupled plasma emission spectrophotometer (ICP).

We exposed 316L SS coupons in four fresh water locations near Bozeman, Montana (Roski Creek, Bracket Creek, Hebgan Reservoir, and the Madison River). The sites were selected based on limnological factors such as depth and flow characteristics, and to an extent on location and human impact factors. The corrosion coupons were exposed for several weeks at each site by attaching them to plastic frames. Exposure sites were visited at approximately 2-week intervals. At each site visit, open circuit potential (OCP) of the coupons vs. Saturated Calomel Electrode (SCE), dissolved oxygen (DO), dissolved manganese, 15 other metals concentrations, temperature, pH, and total organic carbon (TOC) were recorded. Two SS coupons were periodically collected for surface analysis. The manganese oxides were dissolved from the surface of the coupons, and the dissolved manganese measured by inductively coupled plasma emission spectrophotometer (ICP).

Coupon holders were constructed from a modified ½ inch threaded PVC plug. The top of the PVC plugs were fitted with ¼ nylon plugs that could be removed for access to the backside of the SS coupon. The frames holding the coupons were constructed of ¼ inch PVC sheets, 3x12 inches. Twelve holes were drilled and taped through each frame.

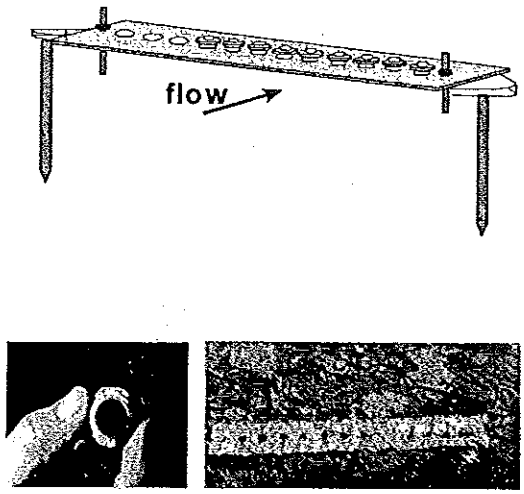

Figure 6. The frame holding corrosion coupons

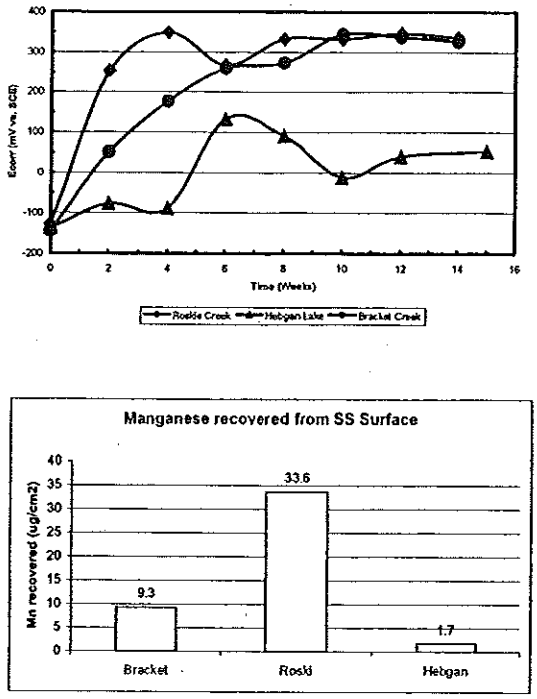

Figure 7. 316L stainless steel coupons exposed to fresh water at three locations in Montana for four months (Braughton *et al.*[21]). The rate and extent of ennoblement are roughly correlated with the amount of manganese retrieved from the surface.

At creek and river exposure sites two twelve inch steel spikes were attached to either end of the frames. These spikes were driven into the streambed, with the coupon faces remaining approximately six inches above the bottom. At lake exposure sites, the frames were suspended from buoys at a depth of three meters. The entire frame apparatus, with SS coupons inserted is seen in Figure 6 while the evolution of the OCP of the exposed coupons is shown in Figure 7.

Testing hypothesis #2. For the kinetic study of manganese reduction, manganese dioxide was galvanostatically plated on stainless steel corrosion coupons in an aqueous electrolyte containing 0.1 M Na_2SO_4 and 5 mM $MnSO_4$ at pH 6.5. The deposited oxide was then slowly reduced by passing a small cathodic current across the metal/deposit/water interfaces. Analyses of the deposits before and after the electrochemical reduction provided information about the kinetics of the manganese oxide reduction. The composition of the deposits was determined at time intervals, by interrupting the reduction process and retrieving coupons, by comparing the XPS spectra of the deposits with the XPS spectra of different manganese minerals of known composition.

To identify the oxides on the surface, six manganese compounds were used as standards: MnO (99%), Mn_2O_3 (97%), Mn_3O_4 (99%), Mn metal (99.98%), MnOOH and MnO_2 (99%). All compounds, except MnOOH, were commercial products from Aldrich Chemical Company, Inc. Manganese oxyhydroxide was prepared by oxidation of manganese sulfate.

Using standard XPS peak fitting routines, the two peaks, one for MnO_2 and one for MnOOH, were deconvoluted. Figure 8 shows the development of the areas under the peaks as the function of time. As the MnO_2 peak decreased, the MnOOH signal increased slightly, reached a maximum and declined by the end of the process of oxide reduction. Such behavior can be explained assuming that the MnOOH was an intermediate product of the reaction. Consequently, MnOOH must be unstable under the experimental conditions; otherwise MnOOH would build up at the surface.

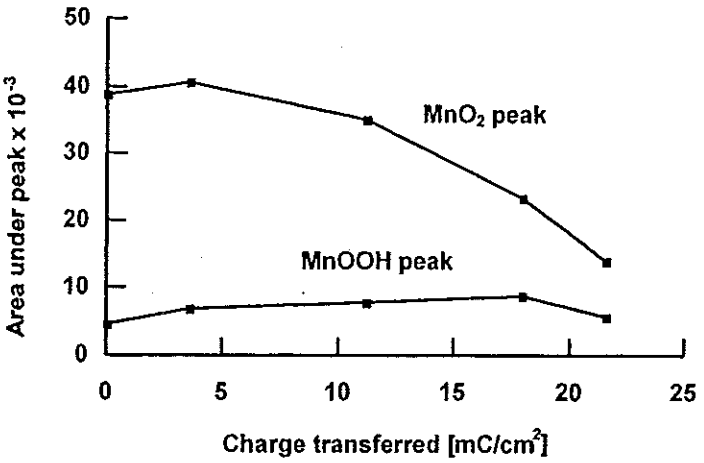

Figure 8. Temporal changes in the amounts of MnO_2 and MnOOH deposited on the 316L surface during galvanostatic reduction. The results show that the amount of MnOOH does not increase, as was expected, but instead initially increases, reaches a maximum, and then decreases. This is consistent with kinetics of sequential reactions during which MnOOH is an intermediate product, not the final product of the reaction[18]

These observations (Figure 8) are not consistent with our initial thermodynamic model (reaction 1). The data shows that MnOOH is an unstable intermediate product and suggests that MnO2 is first reduced to MnOOH gaining one electron, with MnOOH then gaining the second electron and being further reduced to divalent manganese, Mn^{2+}. Consequently, the conceptual model has to be modified.

Step 7. Refining the conceptual model of the process

It is proposed that manganese dioxide, plated on stainless steel corrosion coupons, is reduced electrochemically to divalent manganese, Mn^{2+}, obtaining two electrons from the metal substratum. Manganese oxyhydroxide, MnOOH, is proposed as an intermediate product in this reaction. The presence of biomineralized manganese dioxide may increase the corrosion rate and/or the probability of

active corrosion through these cathodic reactions. The manganese oxidizing bacteria (MOB), active in the process of manganese dioxide biomineralization, may hypothetically use the product of MnO_2 reduction, Mn^{2+}, making the cycle perpetual.

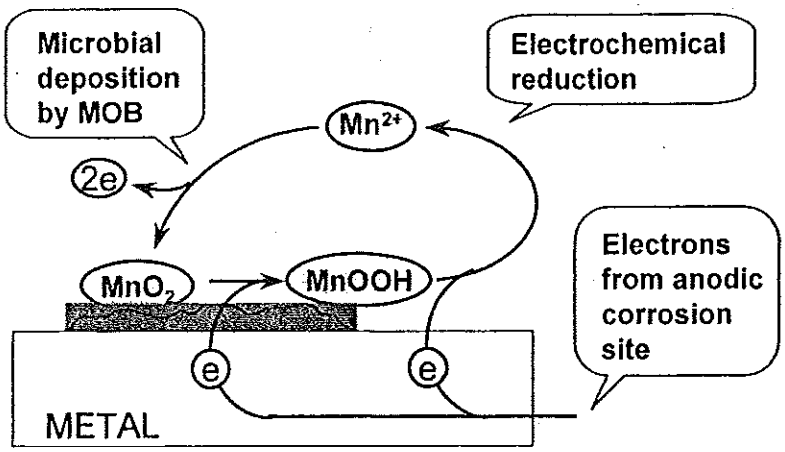

Figure 9. The mechanism indicates that the redox cycling of manganese on metal surfaces may produce a renewable cathodic reactant [18, 19]

Step 8. Constructing hypotheses based on the refined model of the process

Using this refined model, it is possible to identify a hypothesis with regard to the microbial oxidation of manganese.

Hypothesis #1: Divalent manganese is directly oxidized by *L. discophora* to manganese dioxide, MnO_2.

Step 9. Testing the hypothesis formulated in step 8 under well defined laboratory conditions

We attempted to verify the mechanism of ennoblement caused by biodeposited manganese oxides by determining the chemical composition of microbial deposits on stainless steel coupons using Time of Flight Secondary Ion Mass Spectroscopy, ToF-SIMS analysis. Secondary ions with different mass-to-charge ratios have been identified, and the cumulative (typically 5 minutes acquisition time) ion counts for each mass were recorded. However, the presence of alloying elements in the metal surface, especially iron and manganese, interfered with the Mn-related secondary ion peaks in the SIMS spectra of microbial deposits on the ennobled coupons. For example, MnH^+ generated by microbial deposits and the metal substratum could not be differentiated from Fe^+ generated by the metal substratum. The extent of this interference was unknown because we did not have an independent standard without these contributions. To alleviate this problem we used two types of coupons, 316L stainless steel and low-iron titanium alloy (Ti-6Al-4V), and exposed them to the same environments. Assuming that the chemical nature of the deposits was the same on both coupons in terms of manganese oxides, any differences in the SIMS spectra would reflect the effect of iron within the stainless steel coupons. Following this strategy, the SIMS spectra of the deposits on the Ti-6Al-4V coupons were used to verify the information

obtained from the 316L stainless steel coupons.

Pure-culture biofilms of the manganese-oxidizing bacterium *L. discophora* were grown on corrosion coupons made of 316L stainless steel or Ti-6Al-4V under laboratory conditions. The composition of the microbial deposits was determined by comparing the positive/negative ion SIMS spectra of the deposits with the spectra of several manganese standards: MnO_2, MnOOH, Mn_3O_4, $MnCO_3$, MnO, and Mn_2O_3. We identified the manganese oxides on the ennobled metal samples and determined their spatial distribution[22]. Surface analysis of the exposed coupons is in Table 1.

TABLE 1. THE OCP AND SURFACE CHEMISTRY OF THE METAL COUPONS ENNOBLED UNDER LABORATORY CONDITIONS[22]

	Ti-1	SS-1	SS-2	SS-3
OCP	+380 mV_{SCE}	+380 mV_{SCE}	+270 mV_{SCE}	+320 mV_{SCE}
Surface deposits	Mainly MnO_2	Mainly MnO_2	Mainly MnOOH	Mixture of MnOOH and MnO_2

The results in table 1 indicate that as the process progresses, the deposits ennoble the potential. For low ennobled potentials (270 mV), the deposits are composed mainly of MnOOH; as the potential increases (320 mV) the chemistry of the deposits changes to a mixture of MnOOH and MnO_2; and on fully ennobled coupons (380 mV) the deposits are mainly MnO_2. This observation is not consistent with the prediction based on the model in Figure 9, as it now appears that MnOOH is an intermediate product during the oxidation from manganese ions to manganese dioxide. Therefore, the model has to be further modified (Figure 10)[22].

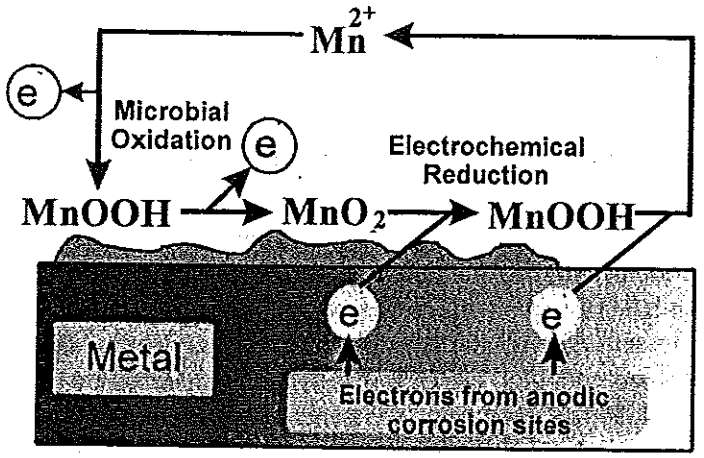

Figure10. Manganese cycling at a surface of passive metals includes biomineralization of divalent manganese and electrochemical reduction of manganese oxides. Manganese oxides are reduced to divalent manganese, which is, again, microbially re-oxidized. This sequence of events, called "manganese cycling on metal surfaces," produces renewable cathodic reactants, manganese oxyhydroxide and manganese oxide, and endangers material integrity[22].

The manganese oxides are in direct electrical contact with the stainless steel, and the metal exhibits the equilibrium potential of the MnO_2 in agreement with the following half-reactions:

$MnO_{2(s)} + H^+ + e^- \Rightarrow MnOOH_{(s)}$ $E^0 = +0.81\ V_{SCE}$ $E'_{pH=7.2} = +0.383\ V_{SCE}$ {1}

$MnOOH_{(s)} + 3H^+ + e^- \Rightarrow Mn^{2+} + 2H_2O$ $E^0 = +1.26\ V_{SCE}$ $E'_{pH=7.2} = +0.336\ V_{SCE}$ {2}

The overall reaction is:

$MnO_{2(s)} + 4\ H^+ + 2e^- \Rightarrow Mn^{2+} + 2H_2O$ $E^0 = +1.28\ V_{SCE}$ $E'_{pH=7.2} = +0.360\ V_{SCE}$

Step 10. Constructing hypotheses for field testing the mechanisms identified in the laboratory

The model of ennoblement and manganese redox cycling in Figure 10 needs to be tested in the field. It was generated based on laboratory experiments, which were designed to test hypotheses generated as a result of field studies. However, the model itself has been generated mostly as a result of studying the system under well-defined conditions and using pure culture of manganese oxidizing microorganisms. It remains to be seen whether these conclusions will withstand field tests. Laboratory tests were conducted to isolate certain variables, and therefore other variables have to be removed. For example we have not tested the role of iron oxides on the ennoblement process, even though we are aware that manganese-oxidizing bacteria in nature are often associated with the presence of iron oxidizing bacteria. Therefore, for the next stage of the work we hypothesize that the model in Figure 10 reflects the characteristics of the ennoblement process in the field.

This hypothesis has been tested and the results are in another paper from our group presented at this conference[23].

Step 11. Field tests

In this regard it is important to point out that the laboratory studies demonstrating the microbial oxidation of manganese to MnOOH and MnO_2 were carried out with pure cultures of the manganese oxidizing bacterium *L. discophora.* There are, however, many microbial species capable of manganese oxidation[13], and biofilms forming on steel samples exposed in natural environments will, in any case, comprise mixed communities of organisms. It is possible, therefore, that additional field observations may identify further levels of complexity that will have to be accommodated within the model. Therefore, step 11 is essentially equivalent to Step 1: Field observations; it begins the next iteration loop.

CONCLUSIONS

We have presented here an approach, a general concept of how MIC can be studied. As expected, this is an open-ended process. We proceed from field observations to conceptual modeling, to laboratory studies testing hypotheses, and back to field studies to verify conclusions of laboratory studies. Clearly, every mechanism of MIC is different and will require modifications of the process. However, we believe that there is a universal validity to our approach. Also, using stainless steels as a substratum offers several advantages to the researcher. The most important are: (1) In this study we have been able to isolate the thermodynamic phenomenon of ennoblement from the kinetic processes of pit initiation; these latter can now be examined with the introduction of saline solutions to the experimental procedures. (2) This is a "clean" system where corrosion products interfere to a much lesser extent than, for example, in SRB corrosion of mild steel.

ACKNOWLEDGEMENTS

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