

Corrosion of metals in natural waters influenced by manganese oxidizing microorganisms

Paul Linhardt

Institute for Testing and Research in Materials Technology (TVFA); Technical University of Vienna, Karlsplatz 13, A-1040 Wien, Austria

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Abstract

Case histories and proposed mechanisms for microbiologically influenced corrosion of metals and alloys by metal depositing microorganisms are reviewed. Mechanisms with indirect participation of these microorganisms, usually iron- and manganese oxidizing species, are distinguished from another mechanism which accounts specifically for the electrochemical properties of deposits containing oxides and hydroxides of Mn in higher oxidation states. The possible influence of such deposits which were formed microbiologically is evaluated. The evaluation is based on the principles of electrochemical corrosion of metals and on the electrochemical properties of $\text{Mn}^{3+}/4+$ compounds. After briefly reviewing the microbiological Mn-oxidation, experimental evidence for the predicted corrosion by such deposits is provided and a model for microbiologically influenced corrosion by manganese oxidizing microorganisms is proposed for stainless steel. Possible consequences of the model and practical aspects of such a corrosion are discussed.

Abbreviations: Eoc – open circuit potential; Epit – critical pitting potential; MIC – microbiologically influenced corrosion; MOMO – manganese oxidizing microorganism; SHE – standard hydrogen electrode; SCE – saturated calomel electrode, $E_{SHE} = E_{SCE} + 242 \text{ mV (25}^\circ\text{C)}$; SS – stainless steel

Introduction

Among the various mechanisms of MIC of metals there is a group which is often designated as MIC by metal depositing microorganisms (Little et al. 1991). These microorganisms are able to deposit oxides or hydroxides of metals, usually iron or manganese, by biological oxidation of Fe^{2+} or Mn^{2+} ions dissolved in the ambient water. If such microorganisms and their deposits are attached to the surface of metals or alloys they may significantly influence the corrosion behaviour of components made of this material.

Although this is a well known phenomenon we find different explanations, some of which are rather vague and lack of practical verification. It is the aim of this paper to deduce a model for the case of corrosion, influenced by MOMOs, by a combination of corrosion prin-

ciples, electrochemical properties of Mn-oxides and practical results from corrosion cases. Experimental evidence for the proposed mechanism will be given.

Case histories

Technical problems with iron- and manganese-oxidizing microorganisms have been known since several decades in water distribution systems. Mass population of these organisms in pipes may lead to clogging or related phenomena. The corrosive properties were recognized more recently and most case histories report on unusual corrosion of SS, mainly of austenitic SS of the type AISI 304 (Fe-18Cr-9Ni) or AISI 316L (Fe-18Cr-12Ni-2.5Mo) (Kobrin 1976, 1986; Tatnall 1981a; Little et al. 1991). Attack was often restricted

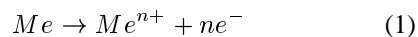
to weld seams. Many of the failures were attributed to insufficient draining after hydrotesting pipes or tanks combined with stagnant conditions. However, it is also known to occur under flow conditions (Renner 1996). Corrosion of AISI 904L steel and copper alloys with participation of metal depositing microorganisms was also reported (Little et al. 1991).

A corrosion case in a hydropower plant in the Netherlands (Linne, NL) with martensitic SS (Fe-13Cr-4Ni) was reported (Linhardt 1994a, 1996b). Recently a very similar case from Thailand was investigated by the author. In both cases, no activity of sulphate reducing bacteria was detected, but films or even massive deposits with high amounts of manganese oxides were identified. Pitting of SS occurred at chloride levels which are normally not considered as too high for this type of steel.

In another instance, massive deposits of MnO_2 were detected on the organic coating in a tunnel carrying freshwater of a hydropower plant subsystem. An extremely high corrosion rate of carbon steel (ca. $2 \text{ mm} \cdot \text{a}^{-1}$) was observed on mechanical defects of the coating. Neither blistering of the coating nor acidification of the corroding area was observed, and no sulphides were present in the corrosion products. In the same system, unusual pitting of Al-bronze was found whereas SS (type AISI 304) remained unaffected at chloride levels of 5 ppm. Although a direct relationship between the evident activity of MOMOs and the corrosion phenomena was not established in this case, the subsequent considerations indicate a connection. Enhanced corrosion of unalloyed steel in the presence of MOMOs has also been known from another hydropower plant (Luchina 1981).

Metal corrosion as an electrochemical process

From the electrochemical point of view, the corrosive dissolution of a metal is considered as the (anodic) dissolution of metal atoms to ions according to:



Subsequent reactions of the metal ions with the medium form the corrosion products usually observed.

The generation of e^- by reaction (Equ. 1) is balanced by the (cathodic) reduction of an oxidant consuming the electrons. In acidic media this may be the evolution of hydrogen according to:

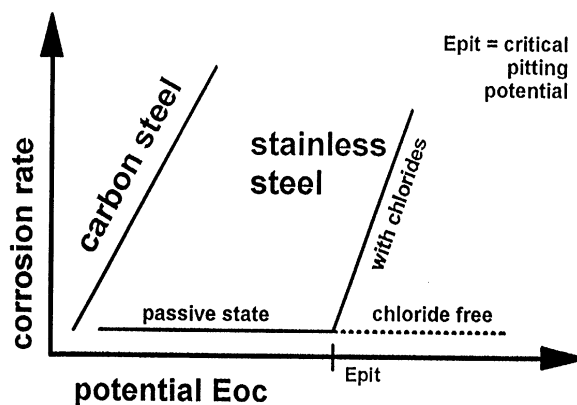
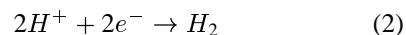
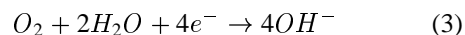


Figure 1. Qualitative relation between E_{oc} and the corrosion rate of carbon steel and SS.



Dissolved oxygen is usually the predominant oxidizing agent in natural waters. The formal reaction is:



The ability of the medium to oxidize a metal is reflected by the electrochemical (open-circuit) potential E_{oc} of the metal in this medium. For non-passivating metals such as carbon steel, we can qualitatively assume an increase in the corrosion rate with higher potentials (Figure 1).

The passivating SS (alloyed steel with $Cr \geq 12\%$) are protected against corrosion by the so-called passive layer. This very thin, electronically conductive layer is spontaneously formed at the metals surface under air and consists mainly of chromium oxide protecting the metal even at relatively high E_{oc} . According to the current models, certain aggressive ions such as chloride may adsorb preferentially at surface defects and may penetrate the passive layer if E_{oc} is above a critical potential ($Epit$). This leads to localized corrosion (see Figure 1). $Epit$ is primarily determined by the alloy composition, the surface condition (type, density and size of defects), the chloride concentration and pH. The pits are the sites of anodic metal dissolution. The cathodic reaction can take place at the surrounding passive areas (see Figure 2). Local acidification occurs due to hydrolysis reactions within the pit. The cations formed in the pit attract anions from the medium. Chlorides which have a relatively high diffusion rate are preferentially enriched within the pit which becomes covered by porous corrosion products. Acidi-

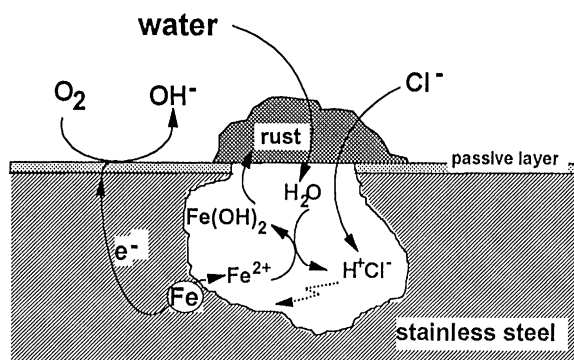


Figure 2. Schematic diagram of pit growth indicating acidification and chloride enrichment in the pit.

fication and chloride enrichment reduce the probability of repassivation by lowering E_{pit} within the pit. Stable pitting corrosion at relatively high penetration rates may develop.

Under crevice conditions (e.g. under deposits or washers) the gradient in oxygen access to the surface and similar enrichment processes lead to preferential attack in the crevice. The critical potential for corrosion in this case is lower than E_{pit} of the free surface.

Corrosion mechanisms in the presence of MOMOs

It is generally accepted that under MIC conditions the same basic mechanisms are valid as in the case of abiotic (electro-) chemical corrosion of metals. This results in the same modes of failure. From today's view, the main feature of MIC seems to be the modification of the medium of the corrosion system due to (i) the creation of strong concentration gradients and (ii) generation of unexpected chemicals at the metals surface. In the case of MIC by metal depositing microorganisms the following mechanisms are presently proposed:

- (a) Under-deposit- or crevice-corrosion (Kobrin 1976; Tatnall 1981b; Pope et al. 1984; Duquette 1986; Little et al. 1991), which is based on the differential aeration at the metal surface. Corrosion is caused in the oxygen depleted area under a deposit. Aerobic organisms consuming oxygen may favour such a condition.
- (b) Corrosive attack by sulphate reducing bacteria (SRB) or acid producing bacteria. It follows from (a) that areas under deposits are anaerobic climates

and therefore well suited for SRBs or acid producing bacteria which may cause corrosive attack. (Kobrin 1976; Tatnall 1981b; Pope et al. 1984; Duquette 1986; Little et al. 1991). Such organisms were identified in some and absent or unidentified in others of the above mentioned case histories. MnO_2 in the deposits may be the terminal electron acceptor for anaerobes, supporting such a situation.

- (c) Accumulation of chlorides under deposits containing Fe^{3+} and Mn^{4+} (Kobrin 1976, 1986; Tatnall 1981b; Pope et al. 1984). Ferric and manganic chlorides are formed which are aggressive to SS.

- (d) $Fe^{2+}/3+$ and $Mn^{2+}/4+$ redox couples from the substances in the deposits may influence the potential E_{oc} and lead to pitting of SS (Pope et al. 1984; Duquette 1986).

Mechanisms (a) and (b) are not specific for MOMOs and may also be the consequence of other organisms such as slime formers. The deposits formed by MOMOs are treated as inert material with respect to the corrosion reactions. The attack is finally attributed to the crevice effect or to other organisms. From this point of view, we will consider mechanisms (a) and (b) not as MIC by MOMOs.

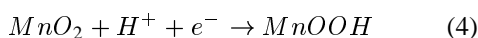
Mechanism c appears to be unrealistic with respect to the proposed manganic chloride, $MnCl_4$, which is not stable in aqueous systems. The accumulation of chlorides in deposits by microorganisms may be real in certain cases, but in the author's experience, high chloride concentrations are often the consequence of the corrosion reaction rather than its cause and are not found in deposits free of corrosion products. However, this mechanism indirectly tries to take into account the oxidative properties of Fe^{3+} and Mn^{4+} compounds.

The following considerations will concentrate more on the consequences of mechanism d which is based on the redox-properties of the deposits. It is the proposed mechanism for a corrosion case (Linhardt 1994a, 1996b) and has been supported by subsequent laboratory experiments (Linhardt 1994b, 1996a). Recently similar conclusions based on experiments with SS in river water were published (Dickinson & Lewandowski 1996). The considerations will be restricted to Mn-deposition by MOMOs only, being the relevant process in the corrosion case and the investigations mentioned.

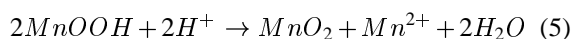
Properties of higher Mn-oxides relevant to corrosion processes

Manganese is a transition metal and may exist in a number of oxidation states ranging from +2 to +7. In nature only the states +2, +3 and +4 are commonly observed. The mineralogy of their oxides, hydroxides and hydrous oxides is varied and complex since more than one oxidation state may be present in a certain compound (Bricker 1965). A wide range of non-stoichiometric compounds MnO_2H_x (yH_2O) exists and the situation is even more complicated due to a possible uptake of ions like protons, alkali and others. Furthermore, Mn^{3+} is known to be unstable as a free ion and may undergo disproportion to Mn^{2+} and Mn^{4+} . In the following we will only consider MnO_2 and $MnOOH$ with an idealized stoichiometry.

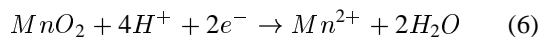
MnO_2 is well known as a strong oxidant and exhibits a moderate electronic conductivity. One of the most important practical applications of MnO_2 is that of an oxidizing agent in the Leclaché-type primary battery where metallic zinc is anodically dissolved and MnO_2 reduced. The reduction mechanism of MnO_2 which depends on pH, appears to be relatively complicated and is the subject of numerous publications most of which relate to battery applications and deal with strong electrolytes (Amarilla et al. 1994, Bodoardo et al. 1994). For simplicity we may assume a 2-step mechanism, first the reduction of Mn^{4+} to Mn^{3+}



and the subsequent disproportion of Mn^{3+} to Mn^{4+} and Mn^{2+}



so that the cathodic net reaction is:



The standard potential of reaction (Equation 6) is $E_0 = +1.23$ V. By applying Nernst's equation we find $dE/dpH = -120$ mV/pH. We may calculate a redox-potential of MnO_2 in natural water ($pH = 7.5$, $c(Mn^{2+}) = 0.1$ ppm) of around $+510$ mV_{SHE}. A much more detailed treatment of equilibrium electrode potentials is given by (Pohl 1986; Atlung&Pohl 1986).

The consequences for corrosion processes seem not to be serious at the first sight. For the reduction of oxygen (Equation 3) we find a standard potential $E_0 =$

$+0.401$ V with $dE/dpH = -60$ mV/pH and by applying Nernst's equation we derive for $p(O_2) = 2 \cdot 10^{-4}$ Pa redox-potentials being generally higher than those of reaction (Equation 6) under practically relevant conditions of pH and $c(Mn^{2+})$. Therefore, oxygen dissolved in natural waters should be the stronger oxidizing agent, overriding a possible effect of MnO_2 in corrosion processes.

On the other hand, it is well known that reaction (Equation 3) is a kinetically hindered reaction. Measured redox potentials are always several 100 mV below the theoretical value. This is true for platinized platinum and even more for SS in the passive state. Usually we find E_{oc} for SS in natural waters with oxygen as the predominant oxidizing agent not higher than ca. $+350$ mV_{SHE}, which indirectly determines the maximum tolerable chloride concentration for a certain SS-alloy by the condition $E_{oc} \ll E_{pit}$. Furthermore, oxygen as a dissolved species has to diffuse from the bulk to the reaction site (metal's surface) where it is consumed. This results in a diffusion-limited cathodic current density. Such an effect is not found for a solid, cathodically active material attached to the metal as long as it is in direct contact.

From these considerations, MnO_2 seems to be a very effective cathodic material since: (i) Its redox potential appears to be significantly higher than practical oxygen-potentials. (ii) It is not diffusion-limited, if reduced, but the disproportion reaction (Equation 5) may be rate-limiting for the second reduction step. (iii) In addition it may act as an oxygen-electrode (Matsuki&Kamada 1986). (iv) The electronic conductivity allows a layer of MnO_2 to be reduced from the outer surface and not only just at the interfacial layer, thus spalling of the deposit may not occur by reduction if the local current densities are not too high.

From these properties we may deduct possible consequences for pitting corrosion of SS:

- In an application E_{pit} may not be exceeded by E_{oc} because of oxygen but by the influence of MnO_2 -deposits which shift the metal to more anodic potentials (ennoblement).
- Corrosion in the pit may be more effectively driven into the active state by such a deposit than by oxygen because relatively high currents are supplied, at least for a limited time, in the critical phase of the beginning pit growth.

The effect of the anodic potential shift has been observed in the increase of the redox-potential in a suspension of commercial MnO_2 (Schweissfurth 1976).

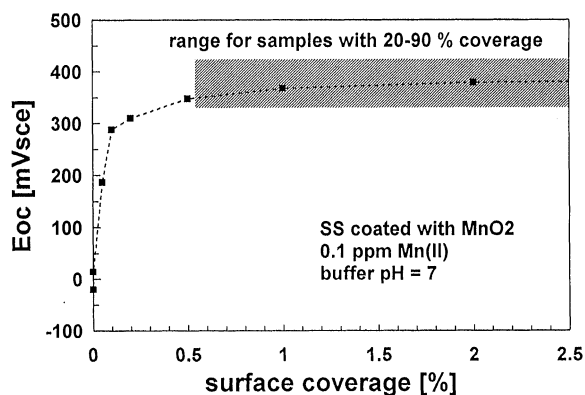


Figure 3. Anodic potential shift of SS by a layer (1.3–1.4 μm) of artificial MnO_2 as a function of surface coverage.

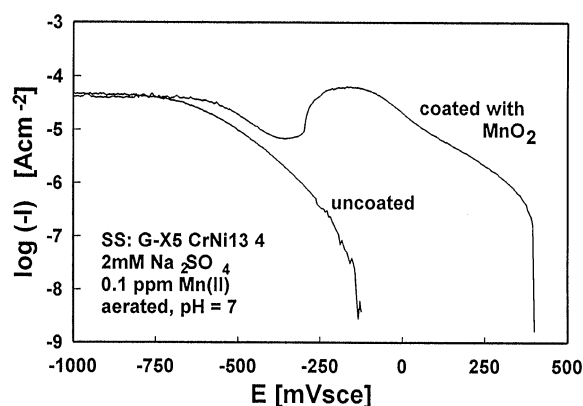


Figure 4. Cathodic polarization curves of bare SS and SS fully coated with a layer (1.3–1.4 μm) of artificial MnO_2 .

(Dickinson & Lewandowski 1996) achieved ennoblement of SS with an artificial layer of MnO_2 -paste and in our laboratory we have carried out some work on the question how effective small amounts of MnO_2 can influence the potential of SS (Ball 1997). For this experiment a coupon of SS (similar to AISI 304) was coated with a layer (1.3–1.4 μm) of MnO_2 by anodic deposition from a solution of $\text{Mn}(\text{NO}_3)_2$. The surface coverage was decreased step by step by carefully grinding off the black deposit to the desired area. For each coverage, measurements of E_{oc} were carried out in a $\text{KH}_2\text{PO}_4/\text{NaOH}$ buffer solution with 0.1 ppm Mn^{2+} (as sulphate) at pH = 7.0 for typically 1 day. The data in Figure 3 demonstrate clearly that even minute amounts of MnO_2 attached to the surface may have a considerable influence on E_{oc} of SS in the passive state.

In the same study, the cathodic activity of MnO_2 was demonstrated by cathodic polarization curves,

recorded potentiostatically at 60 mV/h with SS-specimens uncoated and fully coated with MnO_2 . The electrolyte was aerated 2 mM Na_2SO_4 with 0.1 ppm Mn^{2+} (as sulphate) at pH = 7. The results in Figure 4 reveal a cathodic current peak due to the MnO_2 -layer. The current decrease at about -300 mV_{SCE} was coincident with the observed delamination of the MnO_2 -coating. Another explanation for the decrease may be the intermediate formation of MnOOH , passivating the deposit (Dickinson & Lewandowski 1996).

Formation of deposits containing manganese oxides produced by MOMOs

It is widely accepted today, that MnO_2 is formed only very slowly by chemical reaction of dissolved Mn^{2+} and oxygen in natural waters, although it is the thermodynamically stable phase. We find that below pH = 8 and $c(\text{Mn}^{2+}) = 0.1$ ppm the reaction rate can be neglected compared to that of the formation of deposits (Nealson et al. 1988; Ehrlich 1990).

The formation of higher manganese oxides and hydroxides via a biological route by MOMOs is very fast. There is a wide variety of ubiquitous organisms capable of converting Mn^{2+} to solid $\text{Mn}^{3+}/\text{Mn}^{4+}$ -oxides (Ghiorse 1984). This variety is reflected by various mechanisms which may lead to a biochemically induced transformation of Mn (Ehrlich 1990). The oxidation process may be either enzymatic or non-enzymatic. The non-enzymatic mechanism refers to changes in the environment of a microorganism promoting the autooxidation of Mn^{2+} or direct oxidation by metabolic end products. The enzymatic processes are classified by three groups of organisms: (i) Those which oxidize dissolved Mn^{2+} and (ii) organisms which oxidize Mn^{2+} prebound to certain solids. Both groups utilize oxygen as the terminal electron acceptor and certain organisms may derive useful energy from this reaction. Group (iii) organisms oxidize dissolved Mn^{2+} by the metabolic H_2O_2 via catalase.

All MOMOs known so far are aerobes and the oxidation of Mn^{2+} is often closely related to the oxidation of Fe^{2+} . It should be noted here that microorganisms may also be able to reduce manganese oxides. Some of these are aerobes or facultative organisms, others are anaerobes. A few organisms are known to be capable of both, oxidation of Mn^{2+} and reduction of manganese oxides.

The manganese oxides produced by MOMOs are mainly of the type birnessite (MnO_2) or manganite

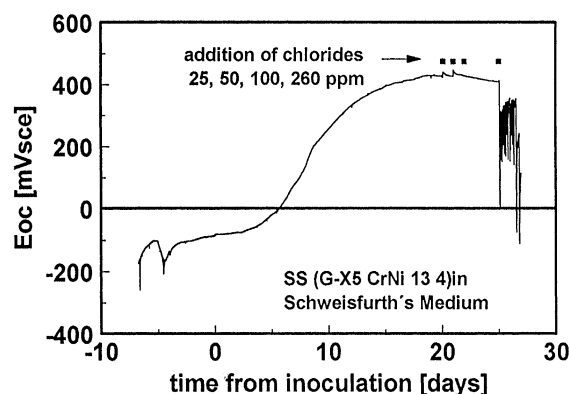


Figure 5. Anodic potential shift of SS under the influence of MOMOs and subsequent induction of unstable pitting by addition of chlorides.

(MnOOH), but other compounds such as hausmannite (Mn_3O_4) may also be found (Schweisfurth & Gattow 1966). The similarities between MnO_2 formed by certain microorganisms and the material used in batteries have already been recognized. An attempt to quantitatively synthesize MnO_2 for potential use in batteries via a biological route has been undertaken (Greene & Madgwick, 1991).

Evidence of participation of MnO_2 from deposits formed by MOMOs in the corrosion of SS and possible consequences

An increase of Eoc of a metal under the influence of MOMOs was already been observed about 20 years ago (Schweisfurth 1976) when potential measurements with a platinum electrode were performed in cultures of *Pseudomonas manganoxidans*, but these findings were never related to corrosion. In the corrosion case of Linne (NL) a model of the corrosion mechanism has been developed based on the assumption of an anodic potential shift caused by MnO_2 , which was supported by the determination of high redox potentials for original deposits (Linhardt 1994a, 1996b). This led to some laboratory experiments in order to verify the influence of MOMOs on Eoc of SS. It was possible to demonstrate the effect of ennoblement in a nutrient medium containing Mn^{2+} with test specimens made of SS and gold when the inoculum was taken from river water (Linhardt 1994b, 1996a). In one experiment with a martensitic SS (Fe-13Cr-4Ni) a shift in Eoc of more than +500 mV relative to the usual Eoc of the steel in this medium was observed (Figure 5). By stepwise

increasing the chloride concentration strong potential fluctuations were induced. This is usually interpreted as unstable pitting corrosion.

Subsequent SEM/EDX study of the surface of the specimen revealed tiny, unstructured accumulations (Figure 6) containing high amounts of Mn. However, no corrosion sites were found. After removal of the deposits, sites of possible corrosive attack were identified, ca. 10 μm wide. This size may correlate with the short time of pit growth during unstable pitting.

Similar results of ennoblement could be obtained with an inoculum from the parallel corrosion case in Thailand at the river Pak Mun (Figure 7). This figure also contains data for Eoc of the steel in the nutrient medium under sterile conditions for a longer period of time (23 days). There is no indication for an abiotic process which may cause significant ennoblement in this timescale.

Dickinson & Lewandowski (1996) report on electrochemical measurements carried out with MnO_2 -deposits grown under natural conditions. The galvanostatic polarization curve is qualitatively comparable to the one obtained in our laboratory with artificial MnO_2 (see Figure 4). From coulometric titration curves taken after various deposition times, the deposition rates and possible corrosion rates were determined. However, the coulometric titration was carried out in an aerated electrolyte and Mn-reduction may have been accompanied by reduction of O_2 which could influence quantitative data.

These results indicate strongly that microbiologically formed manganese oxides may indeed play a significant role in the electrochemical processes of corrosion, at least of SS. Figure 8 represents this model for MIC by MOMOs and refers to a special case of MnO_2 -containing deposits of a calcarous nature (Linhardt 1994a, 1996b) which are not found in all instances. The preferential attack beneath the biofilm may be expected due to the crevice effect as is also proposed in the very similar model of (Dickinson & Lewandowski, 1996). The applicability of this model to marine corrosion, where ennoblement is observed repeatedly (Little et al. 1991), is unclear at present. The fact that marine Mn-nodules are the result of bacterial activity (Ehrlich 1990) may indicate such a possibility.

It has to be pointed out that the model presented here can only be applied to deposits containing MnO_2 which are in electrical contact with the metal. If MnO_2 excreted by MOMOs is embedded in or on a layer of organic matter, i.e. within sheaths or slime, and no direct contact to the metal is possible, it will not influ-

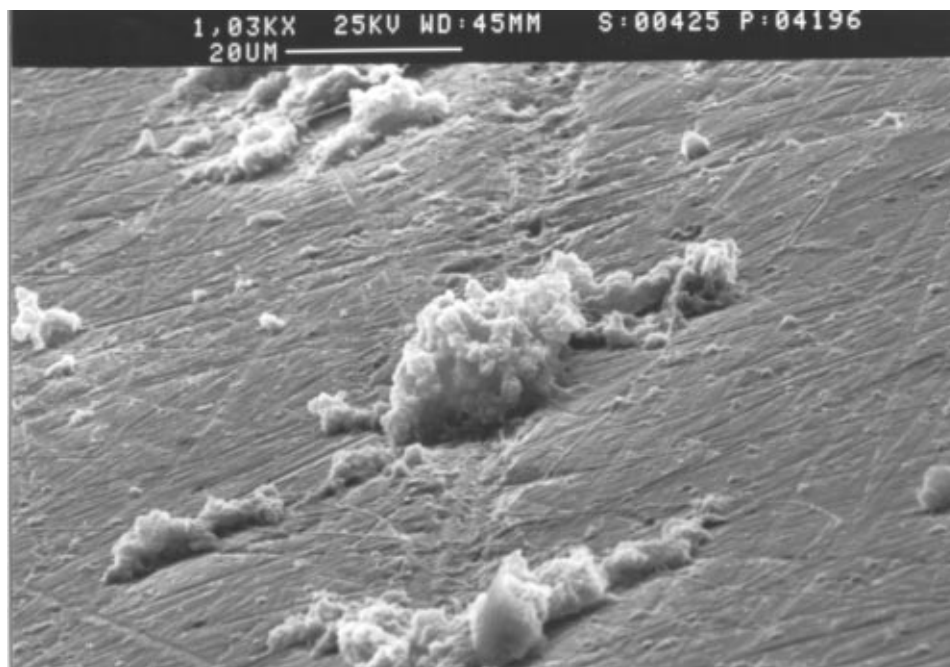


Figure 6. SEM observation of Mn-rich deposits attached to SS formed by MOMOs in a nutrient medium.

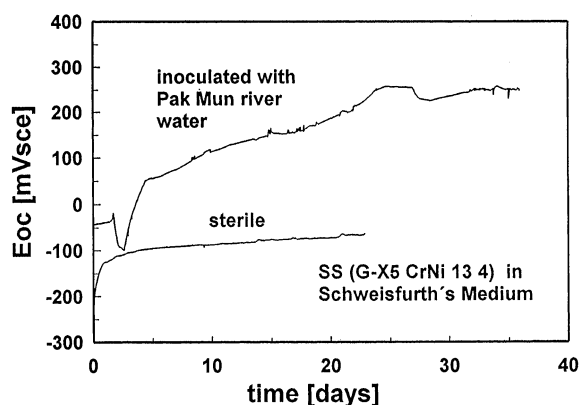


Figure 7. Time dependance of Eoc of SS in a nutrient medium under sterile conditions and under the influence of MOMOs.

ence the electrochemical processes. Such a case has been observed in our laboratory when a fungus capable of Mn-oxidation grew unintentionally on a test specimen of SS in a nutrient medium containing Mn^{2+} . In this case, Eoc of the specimen did not increase but decreased instead, probably due to oxygen depletion. Such a situation supports the corrosion mechanisms a and b, described in the chapter on corrosion mechanisms in the presence of MOMOs.

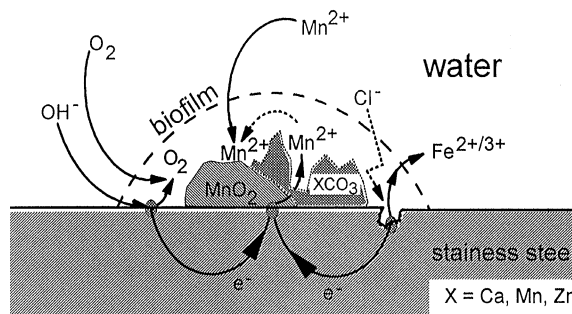


Figure 8. Schematic diagram for the mechanism of pitting of SS under the influence of MOMOs.

Since the formation of manganese oxides by MOMOs is an enzymatic process in many cases, the role of Mn in biochemical systems may also be of interest. This trace element seems to play an important role in biochemical redox processes (Pecoraro 1992). Keeping in mind that most MOMOs form manganese oxides in the cell envelope or completely outside the cell, we may speculate about the possibility of a direct coupling of a Mn redox enzyme to a metal substrate. If this is the case, we could expect anodic potential shifts of passive metals without massive (observable) formation of MnO_2 .

A similar situation arises if we assume that the manganese oxide, produced by cells on the surface of a metal is reduced immediately by corrosion currents when it is formed. In this case we might expect no significant formation of MnO_2 . This could mean large corrosion rates for non-passivating metals such as carbon steel.

Practical aspects of corrosion cases under the influence of MOMOs

The identification of higher manganese oxides in brown to black deposits at a metal surface is usually one of the first tasks in a corrosion case suspected to be influenced by MOMOs. The author found samples of deposits free of corrosion products generally more useful since MnO_2 is easily diluted or masked by corrosion products. At this point we should remember Figure 3, demonstrating that even smallest amounts of deposits containing MnO_2 may have an impact on Eoc and thus on the corrosion initiation on SS. For the purpose of identification of MnO_2 , Feigl's spot test with benzidine (Feigl 1958) is a simple, useful tool in the laboratory and in the field and is widely used according to literature. X-ray diffraction is often used for identification purposes (Schweisfurth & Gattow 1966), but the highly disordered structures of manganese oxides limits its applicability. FTIR was found to be more reliable (Potter & Rossman 1979) and is often used now. SEM/EDX allows elemental analysis of smallest amounts of material, but overlapping signals of Cr, Mn and Fe in EDX spectra may create problems in identifying Mn in corrosion products or at the surface of SS. Furthermore, no information on the oxidation state of Mn is obtained. Since for the investigation of the corrosion process the electrochemical properties of the deposits are of higher interest than structural information, direct assessment of the redox behaviour by an electrochemical method seems desirable. Currently, we are evaluating in our laboratory the method of cyclic voltammetry on carbon paste electrodes (Chouaib et al. 1981) for this purpose.

Most of this paper is dedicated to MIC by MOMOs of SS and most of the case histories relate to SS. This is probably due to the nature of SS, being either stable passive (as intended) or corroding locally at high speed (which is usually unexpected and gives rise to investigations). This feature is also very useful for experimental work. Chlorides may be used to switch from the passive to the active state. On the other hand, unpro-

tected carbon steel is known to corrode in natural water. If the usual protection (coating or cathodic protection) fails for some reason, corrosion is expected to occur. Variations in the corrosion rate are usually not noted and therefore such cases remain uninvestigated. The behaviour of other metals or alloys under the influence of MOMOs seems to be quite unknown at present, probably for the same reason.

According to case histories, weldings of SS are most susceptible to MIC by MOMOs. This is not surprising. It is well known that the heat affected zones are usually richer in surface defects than the base material. The situation is even more pronounced if properly passivated parts are welded but the weldings are not passivated afterwards. This is the practice for cooling water tubing (Renner 1996). The weld seams will be significantly more sensitive to pitting (have a much lower Epit) than the base metal. Thus Eoc is more likely to exceed Epit at the welding under the influence of MOMOs. On the other hand, reports on preferential colonization of welds by microorganisms remain unexplained up to date.

Risk assessment for MIC by MOMOs seems to be challenging since no indicators are known at the moment. MOMOs appear to be ubiquitous and identifying them in a water does not mean that corrosive deposits must necessarily develop there. The specific reasons for mass population and formation of deposits in technical systems such as hydropower plants need to be investigated. The concentration of Mn^{2+} in a water seems also not to be a useful indicator. Deposition of MnO_2 is reported at concentrations of as low as 20 ppb Mn^{2+} (Sly et al. 1990). It has to be noted here that determination of Mn^{2+} in natural water may be falsified by MOMOs if no precautions are taken. MOMOs in the sample may remove dissolved Mn^{2+} by oxidation during the time between sampling and laboratory analysis.

Specific countermeasures in cases of MIC by MOMOs are currently not known. The formation of deposits is somehow related to stagnant conditions (e.g. shut down periods in a hydropower plant). Avoiding such conditions was successful in one instance (Linhardt 1994a, 1996b) but had no influence in another case. From the electrochemical point of view, cathodic protection seems to be a promising method by shifting the ennobled potential of the metal to more negative values (lower than Epit). Whether activity of MOMOs does have a noticeable influence on a cathodic protection system, e.g. by the necessity to increase the protection current density, seems to be unknown at present.

Conclusion

Based on the knowledge of the electrochemical properties of higher manganese oxides and supplemented by experimental results we may conclude that there exists a mechanism of MIC by MOMOs for SS. This mechanism is characterized by the direct participation of deposits rich in MnO_2 as cathodic material. The direct contact of MnO_2 with the metal is a prerequisite for this mechanism. This condition may not necessarily be met by all the different types of MOMOs forming such deposits.

If the prerequisite is fulfilled, we may expect for SS in the passive state that values of E_{oc} are significantly higher than under conditions free of deposits. Minute amounts of deposits are necessary for this effect. E_{oc} under the influence of MnO_2 depends strongly on pH in the vicinity of the deposits. This could possibly mean a strong interaction with acid producing bacteria.

In the presence of chlorides, the anodic potential shift may lead to values of E_{oc} more noble than the critical pitting potential E_{pit} , thus initiating pitting corrosion. In crevices and zones affected by heat from welding the critical potential for corrosion is expected to be lower than E_{pit} of the free base metal surface, making these zones more susceptible for corrosive attack.

After pit initiation, the reduction of MnO_2 in parallel to the reduction of oxygen may deliver more cathodic current than without MnO_2 , at least for a certain time, thus lowering the chances for repassivation. If the formation of MnO_2 by MOMOs continues, corrosion rates may be expected to be continuously higher.

If the above mentioned prerequisite is not fulfilled, the classical mechanisms of MIC by metal depositing or slime forming microorganisms can be applied, based on oxygen depletion under the deposits and possibly on the development of acid producing or sulphate reducing bacteria. However, such cases are considered as not specific for MOMOs. A diagnostic tool is needed to classify corrosion cases as MIC by MOMOs or as classical MIC by metal depositing microorganisms.

It seems that we are merely at the beginning of understanding MIC by MOMOs and all the further implications. We even do not know its quantitative relevance in all the cases of MIC. Further work is required to refine the presently proposed model of the corrosion mechanism, to predict the corrosion behaviour of metals and alloys other than SS, and to develop diagnostic tools, methods of risk assessment and strategies for counteracting. It is the author's belief that many of the questions may be answered by properly combining the

existing knowledge of the various scientific disciplines concerned. We have to keep in mind that we always have to deal with consortia of interacting microorganisms in nature, possibly creating additional parameters which influence an idealized corrosion mechanism for a metal.

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