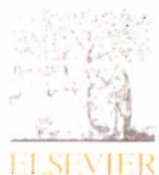


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Review article

The influence of marine biofilms on corrosion: A concise review

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ABSTRACT

The following is a concise review of the literature that addresses the impact of marine biofilms on two phenomena—ennoblement of corrosion potential and sulfide derivitization due to sulfate-reducing bacteria. A universally defined mechanism of potential ennoblement has not been established. Extent of ennoblement varies among locations and the extent of ennoblement for a particular material cannot be used to predict an increased likelihood of localized corrosion. There is some controversy as to the susceptibility of low- and medium-grade stainless steels. Carbon steel and copper alloys are susceptible to sulfide derivitization but thermodynamic models cannot predict the susceptibility of these materials. Laboratory experiments designed to provide data on susceptibility to sulfide derivitization have produced conflicting results because of the following: (1) laboratory media can contain anions that inhibit localized corrosion, (2) laboratory media can contain yeast extract that interferes with electrochemical measurements, and (3) deaeration procedures can produce environments that are not conducive for the growth of sulfate-reducing bacteria. In general, alloys that undergo ennoblement are not vulnerable to sulfide derivitization and conversely, alloys that are subject to sulfide derivitization do not become ennobled.

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1. Introduction

Two microbiologically mediated processes dominate the literature on microbiologically influenced corrosion (MIC) in natural marine environments—ennoblement of corrosion potential values (E_{corr}) and sulfate reduction that leads to sulfide derivitization. Ennoblement and sulfate reduction are global phenomena which have been studied intensely since the 1980s producing extensive literature on both mechanisms. High-grade stainless steels (e.g., Ni–Cr–Mo alloys), titanium alloys, and noble metals (e.g., platinum, gold) are generally accepted throughout the literature to be capa-

ble of sustaining ennobled E_{corr} without increased susceptibility to localized (crevice) corrosion and resistant to sulfide derivitization. Medium-grade stainless steels (e.g., UNS S31725, N08904) are also capable of sustaining ennobled E_{corr} . However, due to their intermediate resistance in marine environments, these alloys are highly susceptible to increased crevice corrosion propagation at ennobled E_{corr} [11]. Low-grade stainless steels (e.g., UNS S30400 and S31603) also experience ennobled E_{corr} . With their high susceptibility to localized corrosion in marine environments, maximum ennoblement values are generally not obtained prior to the onset of localized corrosion [11,15]. In regards to sulfide derivitization, it is impossible to make predictions as to the impact on low- and medium-grade stainless steels exposed in marine environments.

The well-known toxicity of cuprous ions does not mean that copper alloys are immune to microbial colonization. However, only those organisms with a high tolerance for copper are likely to have

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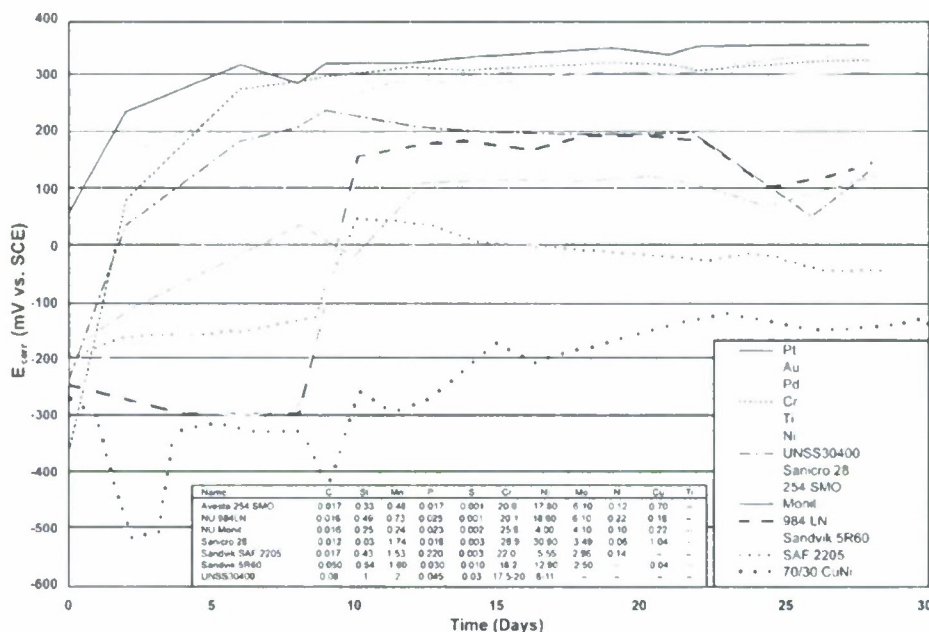


Fig. 1. Composite of E_{corr} vs. time data for materials exposed in natural seawater [1–12].

a substantial effect. Some copper alloys exposed in natural seawater do enoble, but to a lesser extent than do stainless steels, titanium, and platinum [12]. Most of the reported cases of MIC of copper alloys in marine environments are not related to potential ennoblement, but are caused by the reaction of the alloys with microbiologically produced sulfides [16–19].

The aim of this paper is to concisely review the literature on ennoblement and sulfate reduction in the marine environment and present some reasons for the persistent confusion as to whether either phenomenon is important in the corrosion of specific materials.

1.1. Ennoblement

At temperatures below 60 °C, resistance to crevice corrosion is the limiting factor for selecting alloys for seawater service and crevice corrosion is the most critical issue affecting the performance of stainless steels in seawater. Marine biofilms cause a noble shift, or ennoblement of E_{corr} for most passive alloys [1–7,9–11]. Theoretically, E_{corr} ennoblement should increase the probability for pitting and crevice corrosion initiation and propagation of some passive alloys. Numerous researchers have shown that increased cathodic reduction rates accompany ennoblement of E_{corr} [2,5,9,11]. However, attempts to relate ennoblement to increased localized corrosion have been inconsistent. Much of the on-going research in the area of ennoblement in marine waters is directed at identifying a unifying mechanism for the global observations.

Ennoblement of E_{corr} has been reported in fresh, brackish and seawaters around the world. The alloys tested include, but are not limited to: UNS S30400, S30403, S31600, S31603, S31703, S31803, N08904, N08367, S44660, S20910, S44735, N10276, N06625, platinum, gold, palladium, chromium, titanium, and nickel. Fig. 1 is a composite graph [1–12] indicating E_{corr} ennoblement for these alloys over a 1-month period. Fig. 1 should only be viewed as an illustration of E_{corr} ennoblement since water conditions (e.g., salinity, temperature, chemical composition, immersion depth, and flow rate), and exposure sites varied. In addition, maximum E_{corr} ennoblement values often are not achieved in the 1-month time frame shown [8]. In fresh and brackish water, ennoblement is the result of

microbial deposition of manganese and localized corrosion of 300 series stainless steels has been related directly to the biomineralized deposits on the surface [20–23].

A mechanistic interpretation of ennoblement in marine waters does not exist. Little and Mansfeld [13] categorized the proposed mechanisms for ennoblement in marine environments into three categories: thermodynamic, kinetic, and alteration of the nature of the reduction reaction itself. Thermodynamic arguments for ennoblement suggest that either a pH decrease at the metal/biofilm interface or a local increase of the partial pressure of oxygen (p_{O_2}) raises the reversible potential of the oxygen electrode ($E_{\text{O}_2}^0$). For aerobic biofilms, changes in $E_{\text{O}_2}^0$ due to changes in p_{O_2} would be small. For seawater, a decrease of local pH from 8 to 3 would account for an ennoblement of about 300 mV, assuming that the exchange current density for the oxygen reduction reaction ($i_{\text{O}_2}^0$), specifically $i_{\text{O}_2}^{0,1}$, and the cathodic Tafel slope remain constant (Fig. 2) where the initial E_{corr}^1 changes to E_{corr}^2 as $E_{\text{O}_2}^0$ increases to $E_{\text{O}_2}^{0,2}$.

Little et al. [15] measured the pitting potential (E_{pit}) in abiotic chloride solutions at pH 4 and 2 and observed that E_{pit} decreased below ennobled E_{corr} values determined in natural seawater, and therefore dismissed the possibility that ennoblement is due to reduction of surface pH. This conclusion was challenged by Chandrasekaran and Dexter [24] who suggested that E_{pit} for a stainless steel covered by a biofilm might be different from that measured in an abiotic solution. Nevertheless, the same authors conceded that “all the observed ennoblement on stainless steel, particularly in low salinity waters, cannot be explained by pH alone.” Mollica et al. [7] analyzing field test data, concluded, “the phenomenon of oxygen depolarization on active-passive alloys covered by slime does not depend on acidification of the substrate but, on the contrary, on a light (sic) alkalization.”

Kinetic arguments for ennoblement suggest that the rate of oxygen reduction at a given potential can also increase due to an increase of $i_{\text{O}_2}^{0,1}$ to $i_{\text{O}_2}^{0,2}$ leading to an increase of E_{corr}^1 to E_{corr}^3 (Fig. 1). Dexter and Gao [25] suggested that increased oxygen reduction rates may be due to an increase of $i_{\text{O}_2}^0$, mediated by biopolymer metal complexes known to catalyze oxygen reduction. The nature of these organometallic catalysts has been the topic of wide dis-

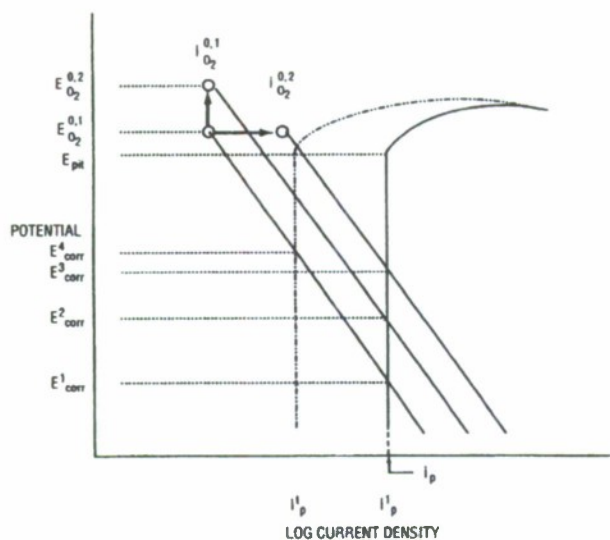


Fig. 2. Schematic polarization curves for stainless steel in seawater [13].

cussion [5]. Holthe et al. [2] referred to biofilm catalysis of oxygen reduction. Scotto et al. [10] attributed catalysis to the presence of microbial enzymes and based this assertion on the abrupt drop in ennobled E_{corr} that accompanied addition of a respiratory inhibitor, sodium azide, to a microbial film. Srinivasan et al. [26] pointed out the ability of enzymes to accelerate electrochemical reactions and noted the inhibitory effect of sodium azide on enzyme electrocatalysis of oxygen reduction. They further reported that lactase increased $i^0_{\text{O}_2}$ on platinum approximately 40 times above that observed in the absence of the enzyme. Johnsen and Bardal [4] observed that the presence of a biofilm dramatically increased the current density required to polarize stainless steel to a potential of -400 mV vs. saturated calomel electrode (SCE), adequate to provide cathodic protection in seawater. They attributed this increase to a lack of calcareous deposits and an enhanced oxygen reduction rate beneath the biofilm due to an increase of $i^0_{\text{O}_2}$. The mechanism of organometallic catalysis has been criticized, however, because ennoblement is also observed on more noble metals, including titanium and platinum, which lack transition elements thought to be necessary to form catalyzing complexes [27]. The nature of the passive layer has also been suggested to play a role in ennoblement by altering the reduction rate of oxygen [28]. Differences in the semi-conductive properties of the passive film has also been suggested to effect an alloys susceptibility to ennoblement [14,29].

In the previous discussion it was assumed that microorganisms change the rate of the cathodic reaction and for neutral, aerated solutions, the cathodic reaction is reduction of oxygen. It is possible that microorganisms change the rate-determining step in an electrochemical reaction or produce an entirely different mechanism. Chandrasekaran and Dexter [24] suggested that reduction in surface pH and production of hydrogen peroxide (H_2O_2) at low oxygen concentration are important contributory factors for ennoblement. The contribution of H_2O_2 to ennoblement is related to its relatively noble thermodynamic potential at low pH. Theoretically, at pH 2.9 and $p_{\text{O}_2} = 0.5$ ppm (0.015 mM), the presence of 8.2 mM H_2O_2 would produce an increase in the reversible potential of 0.5 V. These specific conditions have not been measured in an actual biofilm. The authors measured H_2O_2 concentrations ranging from 1.3 to 6.6 mM on biofilmed platinum coupons after a 1-year exposure. Dupont et al. [30] observed ennoblement of stainless steels exposed in "biochemical artificial seawater," artificial seawater amended with glucose and glucose oxidase. The enzyme catalyzes the oxidation

of glucose to gluconic acid and H_2O_2 [31]. Washizu et al. [32] examined the role of H_2O_2 in ennobling biofilms by addition of catalase and peroxidase, enzymes that are known to decompose H_2O_2 . Concentrations ranging from 10 to 30 ppm (0.29–0.88 mM) H_2O_2 were identified in natural biofilms that produced ennobled E_{corr} values. Addition of catalase or peroxidase to the bulk solution decreased H_2O_2 concentrations to below 0.5 ppm (0.014 mM) and ennoblement was decreased resulting in E_{corr} values observed in sterile conditions. An important point should be made here. The previous work by Scotto et al. [10] indicated that addition of sodium azide resulted in some loss of ennoblement. In more recent work, Scotto and Lai [33] tabulated enzymes inhibited by sodium azide, including catalase and peroxidase which are identified as being reversibly inhibited by sodium azide. These results would seem to contradict, the enzymatic mechanism of ennoblement. Addition of sodium azide to ennobled biofilms containing catalase or peroxidase would inhibit the decomposition of H_2O_2 and result in higher ennobled E_{corr} values, not a sharp decrease in E_{corr} values as reported earlier [10,33]. These results suggest that neither enzymatic activity nor H_2O_2 production is solely responsible for ennoblement.

Theoretically it is also possible that E_{corr} becomes ennobled due to a decrease of passive current density (i_p) at constant $E^0_{\text{O}_2}$, $i^0_{\text{O}_2}$, and Tafel slope, leading to a change from E^1_{corr} to E^4_{corr} (Fig. 2). Eashwar et al. [34,35] proposed a mechanism in which siderophores (iron chelators) produced by microorganisms within biofilms at neutral pH act as inhibitors and enhance passivity of the stainless steel by reducing i_p . Siderophores, produced by all microorganisms, have been shown to possess excellent corrosion inhibition properties. Hansen and McCafferty [36] demonstrated that a bacterial siderophore, parabactin, has an inhibitive effect on E_{ph} for aluminum in NaCl. Eashwar et al. [35] predicted that siderophore production and maximum ennoblement occur at pH 8. Their proposed model has not been rigorously tested, but it does explain Scotto's [10] observations of a drop in E_{corr} with the addition of sodium azide. The respiration inhibitor would prevent formation of siderophores. The theory involving enhanced passivation is also consistent with the observation that very noble E_{corr} values are often maintained for long periods of time without any indication of localized corrosion. Eashwar has called the theory "imaginary, but ... based on careful analysis of both the literature on ennoblement and ecological factors inherent in marine biofilms."

Martin et al. [14] compared ennoblement of several Ni–Cr–Mo alloys (N06625, N10276, N06059, N064555 and N06686) and S30403 at two coastal seawater locations—Key West, Florida and Delaware Bay (Fig. 3a and b). The two exposure sites have different temperatures and different salinities. Martin et al. [14] demonstrated that E_{corr} ennoblement is site-specific, varying 100 mV vs. SCE between locations, with higher potentials at Delaware Bay. Localized corrosion was observed for alloy S30403 (attached to an Alloy 59 rod) exposed in Key West (Fig. 4), but not in Delaware Bay. In summary, the authors demonstrated that extent of ennoblement varied between two locations and that the extent of ennoblement for a particular material could not be used to predict an increased likelihood of localized corrosion for a crevice corrosion prone alloy, i.e. 304 stainless steel.

Most experiments on ennoblement have been conducted in coastal environments. Dexter et al. [37] had previously reported that manganese was found within biofilms on UNS S20910 coupons exposed in Delaware Bay. Manganese has not been reported in other marine biofilms. Delaware Bay is an estuary, which is strongly influenced by the Delaware River. Water at this location has been referred to as estuarine [1], coastal seawater [11], seawater [24] and marine [38]. Salinity in Delaware Bay water varies from 25–31 parts-per-thousand (ppt) [1,11] to 26–33 ppt [38]. Manganese distribution maps prepared by the U.S. Geological survey

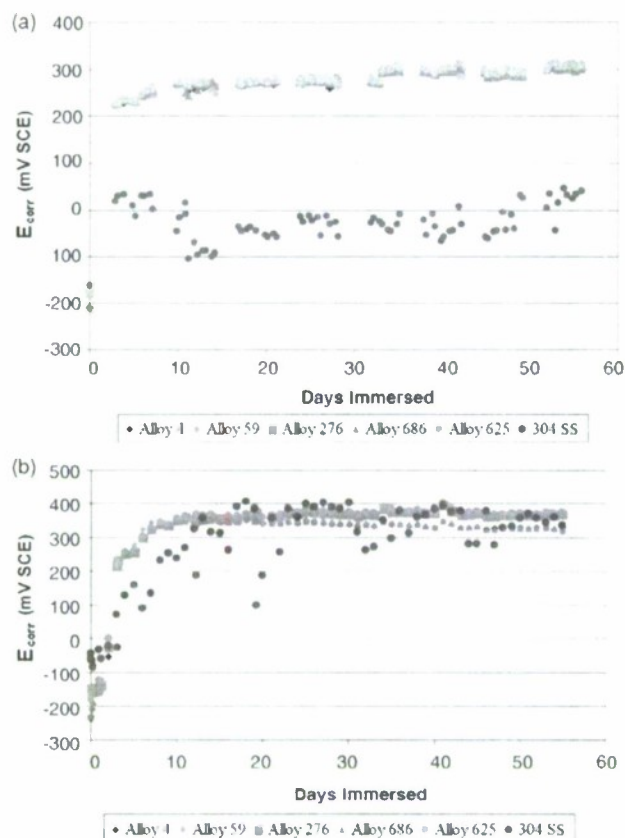


Fig. 3. E_{corr} Ni–Cr–Mo alloys and 304SS during 60-day exposure at (a) Key West, FL, showing corrosion potential ennoblement approaching 300 mV in the first 30 days [14] and (b) Delaware Bay, showing corrosion potential ennoblement approaching 300 mV in the first 7 days [14].

[37] indicate that the Delaware River basin is high in manganese concentration. Therefore, E_{corr} ennoblement in Delaware Bay may be due to microbial manganese deposition and the data generated at that site may have little in common with data collected from other coastal locations. In fact there may be other site-specific

environmental parameters that influence ennoblement at other locations. Oceanographers recognize that the major constituents of seawater do not change their ratios with changes in salinity. This principal of constant proportion of seawater applies to the open ocean and is not applicable in brackish water influenced by river water [39].

Comparison of ennoblement data among investigators is complicated because extent of ennoblement is affected by sample size [40], flow rate [2,4,41], and temperature [2,6,41,42]. Furthermore, ennoblement in marine waters has been measured for boldly exposed metals with a crevice free surface, metals incorporated in crevice assemblies and polarized metals. In some cases, anodes have been initiated galvanostatically and cathodes have been pre-ennobled with biofilms to demonstrate some influence of ennoblement. There are no reports of localized corrosion on crevice-free surfaces even in the presence of ennoblement above pitting potentials for the material [34].

1.2. Sulfate reduction

Susceptibility of metal substrata to derivatization by microbiologically produced sulfides is predicted by a thermodynamic model proposed by McNeil and Odom [43]. The model for predicting SRB-influenced corrosion is based on the likelihood that a metal would react with microbiologically produced sulfide. The model assumes that SRB MIC is initiated by sulfide-rich reducing conditions in the biofilm and that under those conditions, the oxide layer on the metal (or the metal itself) is destabilized and acts as a source of metal ions. At the outer surface of the SRB, sulfide ions react to produce sulfide compounds in micron-sized particles that are in some cases crystalline. The consumption of metal ions at the microbe surface is balanced by release of surface ions until the oxide is totally consumed. If the reaction to convert the metal oxide to a metal sulfide has a positive Gibbs free energy under surface conditions, the sulfides will not strip the protective oxide and no corrosion will take place. If the Gibbs free energy for that reaction is negative, the reaction will proceed, sulfide microcrystals will redissolve and reprecipitate as larger, generally more sulfur-rich crystals, ultimately altering the sulfide minerals stable under biofilm conditions. The following is a summary of the mineralogical products produced during SRB-influenced corrosion reactions:

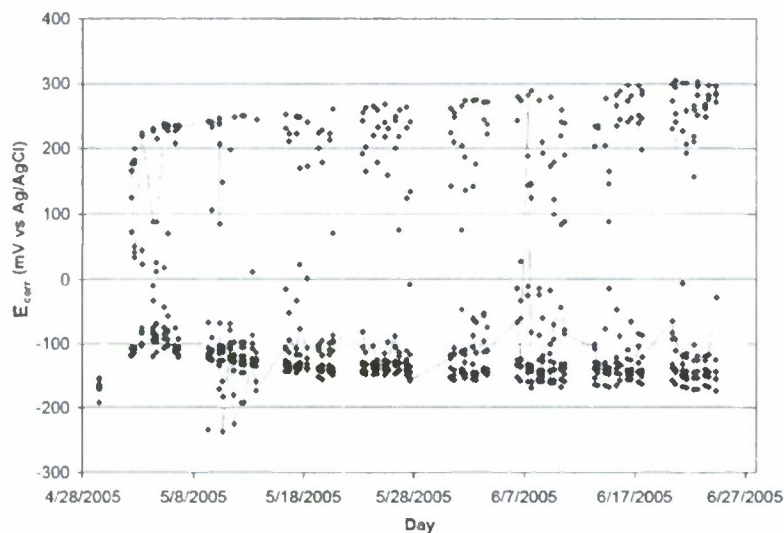


Fig. 4. E_{corr} of 304SS control specimens at Key West, FL, showing periods of active corrosion, with ennoblement-driven E_{corr} values visible between active corrosion episodes. Measurements referenced using a Ag/AgCl/seawater electrode [14].

- Ag—acanthite (Ag_2S).
- Ag—Cu alloys—acanthite, argentite (the high temperature polymorph of Ag_2S or jalpaite (Ag_3CuS_2)).
- Cu—complex suites of sulfide minerals: the most common product is chalcocite (Cu_2S). Final product in many cases is blue-remaining covellite (CuS_{1+x}).
- Cu—Ni alloys—sulfide corrosion products similar to those of Cu but with significant djurleite ($\text{Cu}_{31}\text{S}_{16}$). No Ni minerals observed.
- Cu—Sn alloys—corrosion products similar to those in Cu.
- Fe (carbon steel)—final product is pyrite (FeS) with numerous intermediates.
- Fe (stainless alloys)—rates are slower than pure Fe or carbon steel. No Ni minerals have been detected. Stainless steels with 6% or more Mo appear to be very resistant.
- Ni—millerite (NiS).
- Pb—galena (PbS).

The McNeil–Odom model [43] predicts that carbon steel and copper alloys will be derivitized by sulfide. The model is limited to thermodynamic predictions as to whether or not a reaction will take place and does not consider metal toxicity to the organisms, tenacity of the resulting sulfide or others factors that influence corrosion rate. In the presence of oxygen, the possible corrosion reactions in a copper sulfide system are extremely complex because of the large number of stable copper sulfides, their differing electrical conductivities, and catalytic effects. Transformations between sulfides, or of sulfides to oxides, result in changes in volume resulting in internal stresses that weaken the attachment scale and oxide subscale leading to spalling. In the presence of turbulence, the loosely adherent sulfide film is removed, exposing a fresh copper surface to react with the sulfide ions. For these reasons turbulence-induced corrosion and sulfide attack cannot be decoupled easily.

McNeil–Odom [43] predict that the rate of sulfide minerals formation from stainless steels will be slower than for pure iron and that stainless steels with more than 6% molybdenum will be very resistant to derivitization. The model does not make specific predictions for alloys. Laboratory experiments have attempted to provide data, however the literature on the subject of SRB-influenced corrosion of passive alloys, particularly stainless steels with less than 6% molybdenum, is contradictory. For example, Brossia and Yang [44] exposed S30400 stainless steel in a deaerated (via nitrogen [N_2] bubbling) 0.5 M NaCl solution with an SRB (*Desulfovibrio vulgaris*) and a slime-forming bacterium (*Vibrio natriegens*). They added unspecified nutrients. They did not observe any significant corrosion. Yang and Cragolino [45] exposed S30400 and S30403 to the same solution inoculated with the same organisms. No pitting was observed on either material. The authors specified that modified Baar's Broth medium and NaCl nutrient broth were added to the test cells. The modified Baar's broth contained 1 g L^{-1} yeast extract. The test cell was not deaerated. Webster et al. [46] concluded that SRB-influenced corrosion in stainless steel is unlikely to occur in the absence of oxygen in the bulk electrolyte. The author's surmised that cathodic current provided by the oxygen reduction reaction (ORR) at discrete cathodic sites was required for high rates of anodic dissolution. In contrast, Neville and Hodgkiess [47] evaluated corrosion of five stainless steels (S32760, S31803, S31603, S31254 and a 25% Cr duplex) in a variation of Postgate's B medium (0.1 wt% yeast extract), inoculated with SRB. The medium was deaerated with bubbling nitrogen. They reported increased susceptibility to localized and general corrosion in marine environments containing SRB for duplex and austenitic grades of stainless steels even in the absence of an efficient ORR cathode.

The reason for the conflicting results may be the varying laboratory conditions and the varying media used to represent seawater. Two media are frequently used for SRB experiments: (1) a variation

of Postgate B medium and (2) artificial or natural seawater to which nutrients and microorganisms are added. The relative consistency of natural seawater, as previously described, has led to the development of recipes for artificial seawaters. It is generally recognized that artificial seawater mixtures do not approximate the complexity of natural seawater, especially the organic material. Dexter [48] concluded that synthetic seawater solutions were not free of organics. Instead, the organics were just different from those found in natural seawater. Webster and Newman [49] examined the impact of media constituents on localized corrosion of Fe–15Cr–10Ni stainless steel crevices and made the following observations: localized corrosion would not readily occur unless chloride (Cl^-) was the predominant anion in the medium. They concluded that Cl^- must be present in a concentration at least comparable to that of all other anions combined, otherwise corrosion was inhibited even at high H_2S concentrations up to 100 ppm. Reduction of the ratio of Cl^- to other anions increased the time to initiation and decreased the rate of propagation of the corrosion. Other corrosion investigators have concluded that extra nutrients cannot be added to stimulate bacterial growth if those nutrients inhibit corrosion by adding too many non-chloride ions [50]. Anions, including sulfate, hydroxide, phosphate, acetate, carbonate, and nitrate can inhibit pitting corrosion. It is possible that bacterial consumption and fixation of nutrients, including sulfate could render an initially inhibiting solution aggressive by removing non-chloride ions [51].

An additional complication in the interpretation of electrochemical measurements in synthetic media is the effect of culture media on the measurement. Webster and Newman [49] observed interferences in electrochemical measurements when yeast extract was included in the culture medium/electrolyte. The interferences were removed when the yeast extract was removed.

A third standard practice that can influence the outcome of an experiment of a marine SRB experiment is the method of deaeration. Lee et al. [52] demonstrated dramatic changes in the chemistries and microflora of two natural coastal seawaters as a result of storage and environmental conditions. Exposure to an anaerobic atmosphere containing a mixed gas of nitrogen (N_2), carbon dioxide, and hydrogen generated the highest number of SRB and dissolved sulfide concentrations. In contrast, sulfides and SRB were not detected in anaerobic seawater maintained with bubbled N_2 . Lee et al. [52] demonstrated that bubbling N_2 into natural seawater produced a pH shift from 8.0 to above 9.0, an environment that was not conducive to the growth of SRB. Maintenance of seawater in an anaerobic hood with an anaerobic mixture of gases produced a pH shift of 8.0 to below 7.0 and a significant increase in SRB numbers.

2. Conclusions

It is impossible to predict the impact of ennoblement and sulfide derivitization on low alloy and medium-grade stainless steels exposed in marine environments. Extent of ennoblement of E_{corr} varies among locations and the extent of ennoblement for a particular material cannot be used to predict an increased likelihood of localized corrosion. A number of thermodynamic and kinetic arguments have been used to explain experimental ennoblement data. Ennoblement of stainless steels in seawater has been shown to be the result of acceleration of the rate of the cathodic reaction in the corrosion process. While it is generally assumed that this reaction is reduction of oxygen as in abiotic solutions, it is possible that reduction of H_2O_2 plays a role in ennoblement phenomenon. It is remarkable that frequently observed significant increases of E_{corr} on crevice-free surfaces does not lead to localized corrosion and sharp decreases in E_{corr} . There may be multiple site-specific

mechanisms for ennoblement of E_{corr} in coastal seawaters. Thermodynamic models cannot predict the susceptibility of low- and medium-grade stainless steels exposed in marine environments to corrosion induced by SRB. Laboratory experiments designed to provide data on susceptibility of these alloys have produced conflicting results.

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References

- [1] S.C. Dexter, H.-J. Zhang, Proceedings of the 11th International Corrosion Congress, Florence, Italy, 1990, p. 4333.
- [2] R. Holthe, E. Bardal, P.O. Gartland, CORROSION/BB, St. Louis, MO, 198B, Paper no. 393.
- [3] K. Ito, R. Matasuhashi, M. Kato, O. Miki, H. Kihira, K. Wantanabe, P. Baker, CORROSION/2002, Denver, CO, 2002, Paper no. 02452.
- [4] R. Johnsen, E. Bardal, Corrosion 41 (1985) 296.
- [5] A. Mollica, Int. Biodeter. Biodegr. 29 (1992) 213.
- [6] A. Mollica, A. Trevis, E. Traverso, G. Ventura, V. Scotto, G. Alabiso, G. Marcenaro, U. Montini, G. De Carolis, R. Dellepiane, Proceedings of the Sixth International Congress on Marine Corrosion and Fouling, Athens, Greece, September 5–8, 1984, p. 269.
- [7] A. Mollica, G. Ventura, E. Traverso, in: N.J.E. Dowling, M.W. Mittleman, J.C. Danko (Eds.), Microbially Influenced Corrosion and Biodeterioration, The University of Tennessee, Knoxville, TN, 1990, p. 2.
- [8] A. Mollica, G. Ventura, E. Traverso, V. Scotto, Int. Biodeter. 24 (1988) 221.
- [9] S. Motoda, Y. Suzuki, T. Shinohara, S. Tsujikawa, Corros. Sci. 31 (1990) S15.
- [10] V. Scotto, R. Di Cintio, G. Marcenaro, Corros. Sci. 25 (1985) 185.
- [11] H.-J. Zhang, S.C. Dexter, Corrosion 51 (1995) 56.
- [12] M.F.L. de Mele, G. Brankevich, H.A. Videla, Br. Corros. J. 24 (1989) 211.
- [13] B.J. Little, F. Mansfeld, in: F. Mansfeld, A. Asphahani, H. Bohni, R.M. Latanision (Eds.), Proceedings of the H.H. Uhlig Memorial Symposium, The Electrochemical Society, Pennington, NJ, 1994, p. 42.
- [14] F.J. Martin, S.C. Dexter, M. Strom, E.J. Lemieux, CORROSION/2007, Nashville, TN, 2007, Paper no. 07255.
- [15] B.J. Little, R.I. Ray, P.A. Wagner, Z. Lewandowski, W.C. Lee, W.G. Characklis, F. Mansfeld, Biofouling 3 (1991) 45.
- [16] V.K. Gouda, I.M. Banat, W.T. Riad, S. Mansour, Corrosion 49 (1993) 63.
- [17] F. Mansfeld, B.J. Little, Electrochim. Acta 37 (1992) 2291.
- [18] B.C. Syrett, Corros. Sci. 21 (1981) 187.
- [19] K.D. Efrid, T.S. Lee, Corrosion 35 (1979) 79.
- [20] W.H. Dickinson, F. Caccavo, Z. Lewandowski, Corros. Sci. 3B (1996) 1407.
- [21] W.H. Dickinson, R.W. Pick, CORROSION/2002, Denver, CO, 2002, Paper no. 02444.
- [22] P. Linhardt, Werks. Korros. 45 (1994) 79.
- [23] M.H.W. Renner, in: W. Sand (Ed.), DECHEMA Monographs, DECHEMA, Frankfurt, 1996, p. S9.
- [24] P. Chandrasekaran, S.C. Dexter, CORROSION/93, New Orleans, LA, 1993, Paper no. 493.
- [25] S.C. Dexter, G.Y. Gao, Corrosion 44 (1988) 717.
- [26] S. Srinivasan, J.O. Bockris, Y.A. Chizmadzhev, B.E. Conway, E. Yeager (Eds.), Bioelectrochemistry, Plenum Press, New York, 1985.
- [27] F. Mansfeld, B.J. Little, S.C. Dexter, Corrosion 45 (1989) 786.
- [28] N. Le Bozec, C. Compere, M. L'Her, A. Laouenan, D. Costa, P. Marcus, Corros. Sci. 43 (2001) 765.
- [29] S.C. Dexter, S. Maruthamuthu, CORROSION/2001, Orlando, FL, 2001, Paper no. 01256.
- [30] I. Dupont, D. Feron, G. Novel, Int. Biodeter. Biodegr. 41 (1998) 13.
- [31] M.E. Lai, A. Bergel, Bioelectrochemistry 55 (2002) 157.
- [32] N. Washizu, Y. Katada, T. Kodama, Corros. Sci. 46 (2004) 1291.
- [33] V. Scotto, M.E. Lai, Corros. Sci. 40 (1998) 1007.
- [34] M. Eashwar, S. Maruthamuthu, Biofouling 8 (1995) 203.
- [35] M. Eashwar, S. Maruthamuthu, S. Sathiyarayanan, K. Balakrishnan, Corros. Sci. 37 (1995) 1169.
- [36] D.C. Hansen, E. McCafferty, J. Electrochem. Soc. 143 (1996) 114.
- [37] S.C. Dexter, K. Xu, G.W. Luther, Biofouling 19 (2003) 139.
- [38] S.C. Dexter, J.P. LaFontaine, Corrosion 54 (1998) 851.
- [39] A.B. Duxbury, K.A. Sverdrup, An Introduction to the World's Oceans, 6th ed., McGraw Hill, New York, 2000.
- [40] G. Salvago, G. Fumagalli, G. Taccani, CORROSION/96, Denver, CO, 1996, Paper no. 511.
- [41] G. Salvago, L. Magagnin, Corrosion 57 (2001) 680.
- [42] G. Salvago, L. Magagnin, Corrosion 57 (2001) 759.
- [43] M.B. McNeil, A.L. Odom, in: J.R. Kearns, B.J. Little (Eds.), Microbiologically Influenced Corrosion Testing, ASTM STP 1232, American Society for Testing and Materials, Philadelphia, PA, 1994, p. 173.
- [44] C.S. Brossia, L. Yang, CORROSION/2003, San Diego, CA, 2006, Paper no. 0357S.
- [45] L. Yang, G. Cragnolino, CORROSION/2004, New Orleans, LA, 2004, Paper no. 0459B.
- [46] B.J. Webster, R.G. Kelly, R.C. Newman, in: N.J.E. Dowling, M.W. Mittleman, J.C. Danko (Eds.), Microbially Influenced Corrosion and Biodeterioration, The University of Tennessee, Knoxville, TN, 1990, pp. 2–9.
- [47] A. Neville, T. Hodgkiss, Br. Corros. J. 35 (2000) 60.
- [48] S.C. Dexter, in: P.E. Francis, T.S. Lee (Eds.), The Use of Synthetic Environments for Corrosion Testing, ASTM STP 970, American Society for Testing and Materials, Philadelphia, PA, 1988, p. 217.
- [49] B.J. Webster, R.C. Newman, in: J.R. Kearns, B.J. Little (Eds.), Microbiologically Influenced Corrosion Testing, ASTM STP 1232, American Society for Testing and Materials, Philadelphia, PA, 1994, p. 28.
- [50] R.C. Salvarezza, M.F.L. de Mele, H.A. Videla, Corrosion 39 (1983) 26.
- [51] B.J. Little, Corrosion 59 (2003) 701.
- [52] J.S. Lee, R.I. Ray, B.J. Little, CORROSION/2007, Nashville, TN, 2007, Paper no. 0751B.