THE INFLUENCE OF MARINE MICROFOULING ON THE CORROSION BEHAVIOUR OF PASSIVE MATERIALS AND COPPER ALLOYS

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ABSTRACT

The influence of marine biofilms on corrosion varies with alloy composition. At temperatures below 60°C, resistance to crevice corrosion is the limiting factor for selecting alloys for seawater service and is the most problematic issue affecting the performance of passive alloys in seawater. Several investigators have documented the tendency for biofilms to cause a noble shift, or an ennoblement, in open-circuit potential (OCP) of passive alloys exposed in marine environments. Ennoblement in marine waters has been ascribed to depolarization of the oxygen reduction reaction due to organometallic catalysis, acidification of the electrode surface, the combined effects of elevated $\text{H}_2\text{O}_2$ and decreased $\text{pH}$ and the production of passivating siderophores. 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. Theoretically, potential ennoblement should increase the probability for pitting and crevice corrosion initiation and propagation, especially for alloys with pitting potentials within 300 mV of the OCP. The relationship between passive alloy composition and ennoblement will be discussed.

The well-known toxicity of cuprous ions toward living organisms does not mean that the copper-based alloys are immune to microbial colonization and microbiologically influenced corrosion (MIC). It does mean, however, that only those organisms with a high tolerance for copper are likely to have a substantial effect. Most of the reported cases of MIC of copper alloys in marine environments are not related to ennoblement of OCP, but are caused by the reduction of sulfate (concentration $>$ 2 gm L$^{-1}$) to hydrogen sulfide. Sulfate-reducing bacteria (SRB) produce sulfide-rich conditions in the biofilm and 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 these 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. Susceptibility of copper alloys to derivatization by microbiologically produced sulfides depends on alloying elements. However, 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 of copper alloys cannot be decoupled easily. 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 contrast, many passive alloys are immune to sulfide-induced corrosion.

Keywords: Marine biofilms, passive alloys, copper alloys, and ennoblement

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INTRODUCTION
Exposure of any engineering material to naturally occurring seawater initiates a series of sequential and parallel biological and chemical events that culminate in the formation of a complex layer of inorganic, organic, and cellular components known as biofouling. Biofouling is a general term used to describe both the microbiological and macrobiological growths that develop on exposed surfaces. Gubner and Beech (1999) evaluated the parameters that affect the corrosivity of natural seawater and concluded that the general microbial population, in addition to specific types of marine microorganisms, i.e., sulfate-reducing (SRB), sulfur-oxidizing bacteria (SOB) and chemo-organotrophic bacteria, could affect corrosivity. The influence of micro- and macrofouling on corrosion rate can range from acceleration to inhibition.

DISCUSSION
Microfouling

Natural seawater surrogates, including sodium chloride (NaCl) solutions (3.5 wt%), buffered NaCl solutions, artificial seawater and artificial seawater to which nutrients and microorganisms have been added, have been used in microbiologically influenced corrosion (MIC) experiments. It is generally recognized that artificial seawater mixtures do not approximate the complexity of natural seawater, especially the organic material and the microflora. The assumption has been that NaCl solutions were free of organics and microflora. Dexter (1988) concluded that NaCl solutions were not free of organics. Instead, the organics in NaCl solutions were just different from those found in natural seawater. Over time, NaCl mixtures become contaminated with bacteria, fungi and microalgae. Yet the presence and activities of these organisms are usually not quantified or considered in corrosion experiments. Most corrosion experiments conducted in artificial seawater do not reproduce rates and in some cases the mechanism for corrosion in natural seawater (LaQue, 1975).

Zobell and Anderson (1936) and Lloyd (1937) demonstrated that when seawater was stored in glass bottles, the bacterial numbers fell within the first few hours followed by an increase in the total bacterial population with a concurrent reduction in the number of species. Lee et al. (2007) demonstrated dramatic changes in the chemistries and microflora of two natural coastal seawaters as a result of storage and environmental conditions (Figure 1). Exposure to an anaerobic atmosphere containing a mixed gas of nitrogen (N2), carbon dioxide (CO2), and hydrogen (H2) generated the highest microflora concentration, especially SRB. Biotic dissolved sulfide levels were also highest in the mixed gas atmosphere. In contrast, sulfides were not detected in anaerobic seawater maintained with bubbled N2. The pH of natural seawater is controlled by CO2. The concentration of dissolved gases (O2 and CO2) in surface waters is determined by their solubilities, which are functions of salinity and temperature (Dexter, 1998). As more CO2 is dissolved the pH decreases. If CO2 is removed from solution (by N2 purging), pH increases. Lee et al. (2007) demonstrated that bubbling N2 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.

Natural seawater and passive alloys

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 problematic issue affecting the performance of stainless steels in seawater. Several investigators (Chandrasekaran and Dexter, 1994; Johnsen and Bardal, 1985; Motoda et al. 1990; Ito et al., 2002; Zhang and Dexter., 1995) have documented the tendency for marine biofilms to cause a noble shift, or an ennoblement, in open circuit potential (OCP) of passive alloys. 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 (Figure 2). Ennoblement of OCP has been reported in fresh, brackish and seawaters. In fresh and brackish water, ennoblement is related to microbial deposition of manganese (Dickinson et al.,
1996). Ennoblement in marine waters has been attributed to depolarization of the oxygen reduction reaction due to organometallic catalysis, acidification of the electrode surface, the combined effects of elevated hydrogen peroxide (H₂O₂) and decreased pH and the production of passivating siderophores. Despite the extensive literature on the subject, the exact mechanism of ennoblement of metals in seawater remains unresolved.

Theoretically, OCP ennoblement should increase the probability for pitting and crevice corrosion initiation and propagation. However, attempts to relate biofilms to increased localized corrosion have been inconsistent. Part of the confusion about the significance of ennoblement can be attributed to differences between exposure sites and exposure techniques. Ennoblement has been measured for metals boldly exposed and metals incorporated in crevice assemblies. In some cases, anodes have been initiated galvanostatically and cathodes have been pre-ennobled with biofilms. Martin et al. (2007) compared ennoblement at two coastal seawater locations – Key West, Florida and Delaware Bay (Figures 3a&b). The two locations have different temperatures and different salinities. Martin et al. (2007) demonstrated that OCP ennoblement is site specific, varying 100 mV vs. saturated calomel electrode between locations, with higher potentials at Delaware Bay. Localized corrosion was observed for alloy SS3040 boldly exposed in Key West (Figure 4), but not in Delaware Bay. Zhang and Dexter (1995) used a remote crevice assembly technique to expose a series of metals in Delaware Bay. They initiated polarization in one set of specimens and compared the results with a set that was exposed without prior polarization. Biofilms did not affect initiation times for S31603 and S31725. Biofilms did increase the propagation rate for preinitiated UNS S31603, S31725 and N08904 as measured by maximum and average pit depths, weight loss and current density.

Natural Seawater and non-passive alloys

Most of the reported cases of MIC of non-passive alloys (e.g., carbon steel and copper alloys) in marine environments are not related to ennoblement of OCP, but caused by the reduction of sulfate (concentration > 2 gm L⁻¹) to sulfide by SRB. McNeil and Odom (1994) developed a thermodynamic model for predicting SRB influenced corrosion based on the likelihood that a metal would react with microbiologically produced sulfide. The model is based on the assumption 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 these 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. In the presence of dissolved oxygen, the sulfides may react to form other compounds. Based on their model they prepared the following database:

- **Ag** - acanthite (Ag₂S).
- **Ag-Cu alloys** - acanthite, argentite (the high temperature polymorph of Ag₂S or jalpaite (Ag₃CuS₂)).
- **Cu** - complex suites of sulfide minerals: the most common product is chalcocite (Cu₂S). Final product in many cases is blue-remaining covellite (CuS₁₋ₓ).
- **Cu-Ni alloys** - Sulfide corrosion products similar to those of Cu but with significant djurleite (Cu₃S₁₆). 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).
- **Sn** - No data.
- **Ti** - Not affected by SRB.
- **Zn** - SRB MIC produces a sulfide conjectured to be sphalerite, ZnS.
- **Zr** - Not affected by SRB.

The model accurately predicts that titanium will be immune to reactions of sulfide along with most stainless steels and that carbon steel and copper alloys will be vulnerable to sulfide derivatization. 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.

The severity of the localized corrosion resulting from sulfide derivatization depends on the presence of oxygen. Hamilton (2003) proposed a model for SRB corrosion of carbon steel in which sulfate, an intermediate electron acceptor, is reduced to sulfide. In his model, sulfide reacts with iron to form a corrosion product that ultimately transfers electrons to oxygen. Consistent with that model, most reported cases of SRB induced corrosion of carbon steel in marine waters are in environments with some dissolved oxygen in the bulk medium (Hardy and Bown, 1984; Lee et al., 1993). Others (Lee et al., 2005; Syrett, 1981) have demonstrated that the most corrosive operating condition is one in which carbon steel and copper are exposed to alternating oxygenated/anaerobic seawater.

**Macrofouling**

Macrofouling organisms are found at all depths and in all seas. They are most numerous along the margins of continents where they are sometimes organized in communities of up to 500 species.

A heavy encrustation of macrofouling organisms on structural steel immersed in seawater will often decrease the corrosion rate of the steel as long as the cover of organisms remains complete and relatively uniform. The heavy fouling layer acts as a barrier, limiting dissolved oxygen at the metal surface. A layer of hard-shelled organisms, such as barnacles or mussels, on steel in the splash zone (just above the high tide level) also shields the metal from the damaging effect of wave action. Beneficial effects on general corrosion occur under uniform fouling layers. If coverage is incomplete, the fouling is more likely to cause initiation of localized corrosion by creating oxygen concentration cells. A heavy encrustation of macroorganisms also can have a number of undesirable physical effects on marine structures. The fouling layer will increase both weight and hydrodynamic drag on the structure. Interference with moving parts also may occur. A scatter of individual barnacles on a stainless steel surface will create oxygen concentration cells. The portion of the metal surface covered by the barnacle shell is shielded from dissolved oxygen in the water and thus becomes the anode. The result is crevice corrosion under the base of the barnacle. A similar effect can take place on aluminum and, to a lesser extent, on structural steel.

**Microfouling and Macrofouling**

Accelerated low water corrosion (ALWC) or lowest astronomical tide (LAT) corrosion is a particularly aggressive form of localized corrosion that has become a high profile problem, associated with unusually high rates of metal wastage on unprotected, or inadequately protected, steel sheet pilings. Sheet piles are used as retaining walls, wharfs, and piers. In tidal waters, pilings are exposed to a range of corrosive environments, which can be classified into four zones: splash zone, tidal zone, permanent immersion, and
bed zone (Figure 5). Corrosion rates in the low water level are typically 0.1 mm/year. Average corrosion rates in the range of 0.3 to 1.2 mm/side/year are typically reported for ALWC.

ALWC phenomenon is a global phenomenon reported around the world in all climatic conditions on unprotected steel pilings in contact with saline water (i.e., seawater and brackish water) that is subject to tidal influences. ALWC has a distinct appearance – patches of lightly adherent, bright orange and black (iron sulfide rich) deposits over a clean, shiny and pitted steel surface (Beech et al., 1993; Cheung et al. 1994). As the pits deepen and become more numerous, they overlap, producing a dishing effect in the metal surface, which ultimately develops into a hole. Corrosion products contain magnetite, iron sulfides, and green rust (an unstable iron oxy-hydroxide sulfate complex). ALWC also produces a specific pattern of damage on steel sheet piling. In U-shaped piles the corrosion occurs on the outpans, while in the Z-shaped sheet piles ALWC occurs in the web areas or corners. The pattern of damage is similar for particular pile geometries, irrespective of the geographic location of the installation.

The detailed mechanism of ALWC in marine/estuarine environments continues to be a matter of some debate but several research groups have concluded that it is a form of MIC. Gehrke and Sand (2003) completed a three-year study of pilings in German marine harbors with and without corrosion. They concluded that the ALWC was due to the combination of SRB and thiobacilli in the fouling layers on the pilings. The organisms occurred together, separated by the oxygen gradient in the biofilm. At low tide the biofouling layer was oxygenated whereas at high tide, anaerobic areas developed. The sulfides produced by the SRB in the anaerobic regions and sulfuric acid resulting from the thiobacilli in the aerobic regions combined to produce an extremely corrosive environment (Figure 6).

**Conclusion**

Despite the predictability of ennoblement and sulfide derivatization for passive and non-passive alloys, respectively, exposed in marine waters, their influence on corrosion is determined by environmental factors that are not yet predictable.

![](image)

- General aerobic bacteria
- General anaerobic bacteria
- Acid-producing bacteria
- Sulfate-reducing bacteria

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Figure 2. Composite of OCP vs. time data for materials exposed in natural seawater. Data were taken from Ito et al., 2002; Johnsen & Bardal, 1985; de Mele, 1992. Prepared by Jason S. Lee, Na Research Laboratory.

Figure 3b. OCP of Ni-Cr-Mo alloys and 304SS during 60-day exposure at Delaware Bay, showing corrosion potential ennoblement approaching 300 mV in the first 7 days. (Martin et al., 2007)
Figure 4. OCP ennoblement of 304SS control specimens West, FL, showing periods of active corrosion, with blement-driven OCP's visible between active sion episodes. (Martin et al., 2007)

Figure 5. Typical corrosion profile of steel piling in lal water. Reprinted with permission from sevier. (Cheung et al., 1994)

Figure 6. Schematic summary on the mechanism of MIC, accelerated-low-water corrosion (ALWC), on marine sheet piling structures at the low-water level. © NACE International 2003. (Gehrke and Sand, 2003)

Bibliography


