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MICROBIOLOGICALLY INFLUENCED CORROSION: CAUSATIVE ORGANISMS AND MECHANISMS

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Summary: The relationship between microorganisms and corrosion is both predictable and complex. In aquatic environments and under some atmospheric conditions, microorganisms settle on surfaces and alter the surface chemistry controlling the rates of corrosion or shifting the mechanism for corrosion. The result is corrosion where none could be anticipated based on the composition of the bulk medium, e.g., low-chloride waters, and rates that are exceptionally fast. Under some circumstances microorganisms can also inhibit corrosion. The influence of microorganisms on corrosion depends, not only on the presence and activities of the microorganisms, but also the nature of the metal/alloy and the specific environment in which the organisms are growing, e.g., aerobic vs. anaerobic, ratio of aggressive anions to non-aggressive anions and nutrients.

Keywords: Causative microorganisms, Mechanisms, Microbiologically Influenced Corrosion

1. INTRODUCTION

Several mechanisms for microbiologically influenced corrosion (MIC), including ennoblement of passive alloys and degradation of corrosion inhibitors, are not attributed to specific types of microorganisms, but to microorganisms in general. Other mechanisms for MIC are associated with specific microorganisms. The organisms known to influence corrosion are physiologically diverse and have frequently been grouped by either an electron acceptor or an energy source that is linked to the resulting corrosion, e.g. sulfate-reducing and iron-oxidizing. While a corrosion mechanism may be attributed to a single group of organisms, the most aggressive MIC occurs with natural populations made up of many types of microorganisms. Furthermore, a single type of microorganism can simultaneously affect corrosion via several mechanisms. Cell death within a well-developed biofilm does not necessarily mean an end to the influence on corrosion. For example, pitting corrosion of some alloys continues under deposits of iron-oxidizing bacteria independent of bacterial activity. Similarly, microbiologically generated iron sulfide accelerates corrosion of some materials in the absence of viable cells.

Identification of specific microorganisms associated with corrosion products may not provide insight into failure mechanisms. Under some circumstances, microorganisms are attracted to corroding sites and their accumulation is the result of corrosion (Franklin et al. 2000). In addition, Jigletsova *et al.*, (2004) and Rodin *et al.* (2005) demonstrated that the corrosive properties of biofilms varied with culture conditions. They used mild steel coupons exposed to a natural consortium of bacteria isolated from oil-processing waters. The organisms included oil-oxidizing aerobes and sulfate-reducing bacteria (SRB). During biofilm formation in glucose-mineral medium with peptone, corrosion losses, as measured by weight loss, increased vs. sterile control. Corrosion decreased when the same coupons with biofilms were transferred into enriched Luria-Bertani medium. An increase in corrosion was observed when coupons were transferred from Luria-Bertani to the minimal medium. Their data indicate that environmental conditions determine the specific microbiological effect on corrosion processes – not the individual organisms.

The types of microorganisms involved in corrosion, and consequently the mechanisms for MIC, are continuously being updated. The following sections provide an overview of potential MIC mechanisms, causative microorganisms and the environments in which they could be important.

2. MIC MECHANISMS THAT ARE COMMON TO ALL MICROORGANISMS

2.1 Consumption of Oxyanions

Molar ratios of aggressive ions to inhibiting ions (e.g., Cl^- to $\text{NO}_3^- + \text{SO}_4^{2-}$) are used to predict whether an electrolyte can sustain a localized corrosion reaction. The relationship between the concentration of inhibitive and aggressive anions

corresponds to competitive uptake of the anions by adsorption or ion exchange at a fixed number of sites at the oxide surface. Microorganisms can alter the corrosivity of an electrolyte by consuming inhibiting anions (Little 2003). Increasing chloride concentration shifts the critical pitting potential to more active (negative) values. The potential is shifted to more noble (positive) values by the presence of other anions, particularly oxyanions (ClO_4^- , SO_4^{2-} , NO_3^- , PO_4^{3-} , NO_2^- and OH^-). The concentrations and types of anions required for corrosion inhibition are extremely specific for both metals and environments. To be fully effective, inhibitor anions must be present in certain minimum concentrations. "In many service applications excursions in solution chemistry, temporary loss of inhibitor or transient increases in temperature may give rise to localized corrosion in an otherwise inhibited system" (Turnbull et al. 2002). At concentrations below the critical value, inhibitive anions may act aggressively and stimulate breakdown of oxide films. Salvarezza and Videla (1984) used pitting potential to assess MIC of aluminum alloys. During growth of the fungus *Cladosporium resinae*, nitrate and phosphate were incorporated into the biomass increasing the chloride/inhibitor ion ratio. In their experiments, fungal uptake of inhibitors was the principal cause of the pitting potential decrease during microbial growth.

2.2 Inactivation of Corrosion Inhibitor

Biofilms reduce the effectiveness of corrosion inhibitors by creating a diffusion barrier between the metal surface and the inhibitor in the bulk solution. Furthermore many of the compounds used as corrosion inhibitors can provide nutrients. Amines and nitrites used as corrosion inhibitors can be degraded by microorganisms, decreasing the effectiveness of the compounds and increasing the microbial populations. Cooke *et al.* (1995) reported that chromate (K_2CrO_4) was ineffective as a corrosion inhibitor in an electricity generating station because chromate-reducing bacteria blocked pipes with precipitated chromium (III) oxide.

2.3 Ennoblement

Microbial colonization of passive metals can shift E_{corr} in the noble direction and produce accompanying increases in current density and polarization slope at mild cathodic potentials. Ennoblement has been observed in fresh, estuarine and marine waters with many metals and alloys. The phenomenon is particularly important for alloys which have a pitting potential a few hundred millivolts more noble than the open-circuit potential, e.g., 300 series stainless steels, aluminum and nickel alloys. Ennoblement in marine waters has been attributed to depolarization of the oxygen reduction reaction, acidification of the electrode surface, the combined effects of elevated H_2O_2 and decreased pH and the production of passivating siderophores, but not to specific microorganisms. For a review see Little *et al.* (2008).

2.4 Oxygen Concentration Cells

Any geometrical factor that results in a high oxygen concentration in one area and a low concentration at another will create a differential cell, including the presence of microbial cells on a surface. Adsorbed cells grow, reproduce and form colonies that are physical anomalies on a metal surface, resulting in local anodes and cathodes and the formation of differential aeration cells. Under aerobic conditions, areas under respiring colonies become anodic and surrounding areas become cathodic (Little and Lee 2007).

2.5 Metal Concentration Cells

Microorganisms on surfaces produce polymers and form a gel matrix on the metal. In general, exopolymers are acidic and contain functional groups that bind metals (Geesey et al. 1986). Nivens *et al.* (1986) demonstrated that *Vibrio natriegens* increased the corrosion rate of 304 stainless steel coupons during a six-day incubation. The corrosion rate began to increase when colonies of microorganisms were detected on the surface. The most rapid increase in corrosion rate, however, correlated with the formation of extracellular polymer.

3. THE CAUSITIVE ORGANISMS

The specific microorganisms that can influence corrosion are from all three main branches of the tree of life, i.e., bacteria, archaea and eukaryota (Little and Lee 2009). Archaea and bacteria are single-cell prokaryotes and have no cell nucleus or any other organelles within their cells. Generally, archaea and bacteria are similar in size and shape, although a few archaea have very unusual shapes, such as the flat and square-shaped cells. Despite the visual similarity to bacteria, archaea possess unique biochemistries, genes and several metabolic pathways that are more closely related to those of eukaryotes. The cells of eukaryotes possess a clearly defined nucleus, bounded by a membrane, within which DNA is formed into distinct chromosomes. Eukaryotic cells also contain mitochondria and other structures organelles that, together with a defined nucleus, are lacking in the cells of prokaryotes. Typically, eukaryotic cells are ten times larger in each dimension than bacteria and archaea. Fungi, i.e., yeasts, molds and mushrooms are eukaryotic organisms.

3.1 Sulfide-Producing Prokaryotes

For decades, it has been assumed that microbial sulfide production was the result of the activities of sulfate-reducing bacteria (SRB). However, some archaea can reduce sulfate to sulfide and some bacteria can reduce thiosulfate to sulfide. The inclusive term for microorganisms capable of sulfide production is sulfide-producing prokaryotes (SPP).

The most obvious mechanism whereby SPP influence corrosion is by formation of a metal sulfide on a surface. McNeil and Odom (1994) prepared a model that can be used to predict susceptibility of metals to the formation of various metal-sulfide minerals (derivatization) by microbiologically produced sulfides. The model assumes that SSP MIC is initiated by sulfide-rich reducing conditions in a 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. 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. The model accurately predicts that titanium alloys will be immune to derivatization and that carbon steel and copper alloys will be vulnerable. 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 other factors that influence corrosion rate. The model does not make specific predictions for low and medium grade stainless steel alloys.

Hamilton (2003) concluded that all mechanisms for MIC involved a process of electron transfers from base metal to oxygen as the ultimate electron acceptor through a series of coupled reactions. The specific coupled reactions varied with mechanism and causative organism. He proposed that in the case of SRB and carbon steel, sulphate, an intermediate electron acceptor, is reduced to sulphide that reacts with iron to form a corrosion product that ultimately transfers electrons to oxygen. In the model, sulphate is the terminal electron acceptor in anaerobic respiration, but oxygen is the terminal electron acceptor in the corrosion reaction. 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. Using mild steel and weight loss measurements Hardy and Bown (1984) reported that successive aeration-deaeration shifts caused variation in the corrosion rate. The highest corrosion rates in their experiments were observed during periods of aeration.

Lee *et al.* (2005) designed field experiments to evaluate deoxygenation of natural seawater as a corrosion control measure for unprotected carbon steel seawater ballast tanks. Carbon steel exposed to cycles of hypoxic seawater and oxygenated atmosphere had higher corrosion rates than coupons exposed to either consistently aerobic or deoxygenated conditions.

Additional corrosion mechanisms have been attributed to SRB, including cathodic depolarization, anodic depolarization, release of exopolymers capable of binding metal ions, sulfide induced stress corrosion cracking and hydrogen induced cracking or blistering. Recent reviews suggest that SRB can influence a number of corrosion mechanisms simultaneously (Beech and Chung 1995).

3.2 Acid-Producing Bacteria and Fungi

Elemental sulfur, thiosulfates, metal sulfides, H_2S , and tetrathionates can be oxidized to sulfuric acid by thioacidophiles. Most heterotrophic bacteria secrete organic acids during fermentation of organic substrates. The kinds and amounts of acids produced depend on the type of microorganisms and the available substrate molecules. Organic acids may force a shift in the tendency for corrosion to occur. The impact of acidic metabolites is intensified when they are trapped at the biofilm/metal interface. Organic acids produced by fungi were identified as the cause for pitting failures in painted carbon steel holds of a bulk carrier (Stranger-Johannessen 1986) and aluminum fuel storage tanks (Salvarezza *et al.* 1983).

3.3 Ammonia Production

Many organisms produce NH_3 from the metabolism of amino acids or the reduction of nitrite or nitrate, forming NH_4^+ . Pope *et al.* (1984) documented corrosion failures in copper alloys due to the presence and activities of ammonia-producing bacteria.

3.4 Metal-Depositing Bacteria

Deposition of iron and manganese oxides occurs widely in natural waters, and is a dominant control in geochemical cycling of these elements. Mineralization can be carried out by a variety of organisms including bacteria, yeast and fungi (Nealson *et al.* 1988). Ghiorse (1984) prepared a review of metal-depositing microorganisms in which he identified microorganisms that catalyze the oxidation of metals, others that accumulate abiotically oxidized metal precipitates and still others that derive energy by oxidizing metals.

Extracellular iron biomineralization has been studied extensively in fresh water. Some iron-oxidizing microorganisms extrude polymeric structures upon which they deposit the ferric iron derived from their metabolism. Chan *et al.* (2004, 2009) concluded that polymer directed iron hydroxide mineralization is a general phenomenon that can occur in any system containing acidic polysaccharides and iron. Banfield *et al.* (2000) suggested that negatively charged polymers (e.g., *Gallionella* stalks) served as templates for aggregates of enzymatically produced iron oxides. Ghiorse and Ehrlich (1992) suggested that microbial mineral formation can take place in intimate association with cells forming mineralized structures.

They further concluded that the resulting structures could be used to identify a biological role in the formation in the absence of viable cells. Working with hyphal budding bacteria, Gliorse and Hirsch (1979) described the accumulation of positively charged iron hydroxides on negatively charged bacterial polymers. Once deposited, the iron oxides carried negative charges so that such a process could continue indefinitely without any biological activity. The only required biological input is the initial production of a negatively charged polymer. Sogaard *et al.* (2001) described a similar process for biological iron precipitation by *Gallionella* in a polluted ground water (pH 5). Iron precipitated on the surface of the stalks until the negative charge effect was eliminated. The colloidal iron was condensed and the result was a dense deposit. Miot *et al.* (2009) demonstrated precipitation of goethite on polymeric fibers extending from the cells of an iron-oxidizing bacterium. They also demonstrated a redox gradient, with the proportion of Fe(III) highest near the cells and the proportion of Fe(II) increasing at distance from the cell.

Bacteriogenic iron oxides, formed in response to chemical or bacterial oxidation of Fe(II) to Fe(III), are made up of intact and/or partly degraded remains of bacterial cells mixed with amorphous hydrous Fe(III) oxides (Ferris 2005). Bacteriogenic iron oxides have reactive surfaces and act as sorbents of dissolved metal ions and enrichments of lead, cadmium, aluminum, chromium, zinc, manganese, and strontium, in addition to copper, have been reported. Sarin *et al.* (2001, 2004) reported the absorption of copper in iron corrosion scales. Gerke *et al.* (2008) demonstrated that heavy metals, including copper, were either trapped within the structure or sorbed onto regions of the tubercles.

The iron-oxidizing genera that are usually cited as causing MIC are *Gallionella*, *Sphaerotilus*, *Crenothrix*, *Siderocapsa*, *Clonothrix* and *Leptothrix*. Iron-oxidizing bacteria (IOB) have been implicated in MIC since the 1960s. It is well established that tubercle formation by IOB produces an oxygen concentration cell. Most of the documented MIC case histories associated with IOB tubercle formation have involved exposure of a 304 or 316 stainless steel in untreated well water (200-300 ppm) and chlorinated drinking water. IOB form dense deposits, excluding oxygen from the area immediately under the deposit. In an oxygenated environment, the area deprived of oxygen becomes a relatively small anode compared to the large surrounding oxygenated cathode. Metal is oxidized at the anode and pH decreases. The extent of the decrease is determined by the alloy composition. For this reason, oxygen concentration cells produce particularly aggressive corrosion on 300 series stainless steels, containing 17.5 to 20 percent chromium. Cl⁻ migrates from the electrolyte to the anode to neutralize charge, forming heavy metal chlorides that are extremely corrosive. Under these circumstances, pitting involves the conventional features of differential aeration, a large cathode: anode surface area and the development of acidity and metallic chlorides.

Tubercles have also been observed on carbon steel exposed in fresh water. Ray *et al.* (2009) demonstrated that differential aeration cells alone do not cause aggressive corrosion of carbon steel in fresh water. After examining tubercles on carbon steel from multiple fresh water environments and of varying ages, they reported that tubercles consistently had an outer crust of goethite and lepidocrocite and an inner shell of magnetite. Core regions differed in structure, composition, chemistry and microbiology. The presence of tubercles on carbon steel and cast iron could not be used to conclude localized corrosion directly under the tubercles or a role for bacteria in their formation. Tubercles formed on carbon steel pilings in Duluth-Superior harbor, Minnesota and Wisconsin, did create anaerobic areas under the tubercles causing copper dissolved in the water to precipitate onto the surface and form galvanic cells and localized corrosion.

As a result of microbial action, manganese oxide deposits can form on submerged materials including metal, stone, glass, and plastic and can occur in natural waters with manganese levels as low as 10-20 ppb (Dickinson and Lewandowski 1996). They demonstrated that microbially deposited manganese oxide on a stainless steel in fresh water caused an increase in E_{corr} and increased cathodic current density at potentials above -200 mV (vs. saturated calomel reference electrode (SCE)). Ennobled E_{corr} can enhance the risk of pit nucleation, while elevated cathodic current density impedes repassivation. Biomineralized manganic oxides are efficient cathodes and increase cathodic current density on stainless steel by several decades at potentials between roughly -200 and +400 mV_{SCE}. The extent to which the elevated current density can be maintained is controlled by the electrical capacity of the mineral reflecting both total accumulation and conductivity of the mineral-biopolymer assemblage (only material in electrical contact with the metal will be cathodically active). The biomineralization rate and the corrosion current control oxide accumulation, in that high corrosion currents will discharge the oxide as rapidly as it is formed.

3.5 Metal reduction

Dissimilatory iron and/or manganese reduction occurs in several microorganisms, including anaerobic and facultative aerobic bacteria. Inhibitor and competition experiments suggest that Mn(IV) and Fe(III) are efficient electron acceptors similar to nitrate in redox ability and are capable of out-competing electron acceptors of lower potential, such as sulfate or carbon dioxide. Little *et al.* (1997) used synthetic iron oxides (goethite, αFeOOH ; hematite, Fe_2O_3 ; and ferrihydrite, $\text{Fe}(\text{OH})_3$) as model compounds to simulate the mineralogy of passivating films on carbon steel. Rates of reduction, measured by atomic absorption spectroscopy of Fe(II) in solution as a function of time, for the three minerals indicate that after a 24-hr exposure to *Shewanella putrefaciens*, initial reduction rates for goethite and ferrihydrite were approximately the same and were 5 times faster than the reduction rate for hematite. After 22 days the integrated reduction rates for goethite and ferrihydrite were much faster than those measured at 24 hours. The hematite reduction rate actually slowed

over the exposure period so that after 22 days the overall integrated rate was 50 times slower than reduction rates for goethite and ferrihydrite (Roden and Zachara 1996). Obuekwe *et al.* (1981) observed that *Pseudomonas* sp., an iron-reducing bacterium, accelerated the corrosion of 1018 steel.

3.6 Methane Producers

Boopathy and Daniels (1991) demonstrated that methanogens could use H_2 produced by the "cathodic depolarization-mediated oxidation of elemental iron" to produce methane and influence corrosion. In many environments, methanogens and SRB coexist in a symbiotic relationship: SRB producing hydrogen, CO_2 and acetate by fermentation, and methanogens consuming these compounds. Larsen *et al.* (2011) using molecular microbiology methods to identify microorganisms in water and solids in a producing oil well, found that methanogens sometimes outnumbered SPP and suggested that their numbers should be monitored in MIC risk assessments.

4. SUMMARY

With the introduction of culture-independent molecular microbiology methods it has become possible to detect many microorganisms associated with corrosion that were not previously detected with culture techniques. As a result, the list of causative organisms and mechanisms for MIC is constantly being updated. However, in all cases, the influence of microorganisms on corrosion depends on the nature of the metal/alloy and the specific environment in which the organisms are growing.

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