

## **Microbiologically Influenced Corrosion**

Microbiologically Influenced Corrosion is defined as corrosion at a metal surface that is associated with microorganisms, or the products of their metabolic activities including enzymes, exopolymers, organic or inorganic acids, and ammonia or hydrogen sulfide compounds.

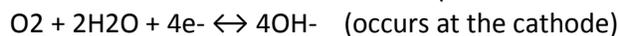
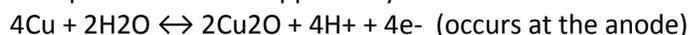
Microorganisms associated with MIC can be found over a wide range of temperature, pressure, salinity, and pH, and MIC attack appears to be climate related with warmer climates more affected. Most metals, including iron, copper, nickel, aluminum, and their alloys, are more or less susceptible to MIC. Only titanium and its alloys appear to be generally immune.

## **Corrosion Mechanisms**

Most alloys rely on protective corrosion product films for their corrosion resistance (chromium oxide in stainless steels and cuprous oxide in copper alloys). In order for these protective films to form, some corrosion must occur. Corrosion is basically an electrochemical process. At the anode, metal goes in to solution. As positively charged metal cations are created, electrons are released and flow through the metal towards a cathode. At the cathode, an electron acceptor (e.g. oxygen) is reduced to form negatively charged oxygen anions. These anions migrate through the electrolyte (the cooling water) towards an anode, where they combine with positively charged metal cations to form metal oxides.

### Electrochemical Corrosion Mechanism

The anodic and cathodic half-reactions, and the overall reaction for the formation of cuprous oxide on copper alloys are as follows:



The anode and cathode areas on a single metal surface are so small as to be invisible and so numerous as to be inseparable; they continuously shift, thus permitting the corrosion products to uniformly cover the metal surface. It is these uniformly distributed corrosion products (sometimes referred to as a corrosion product film or as a protective oxide layer) that give metals their resistance to corrosion. If, for some reason, an anode was to become stationary at one location, localized corrosion at the stationary anode would occur.

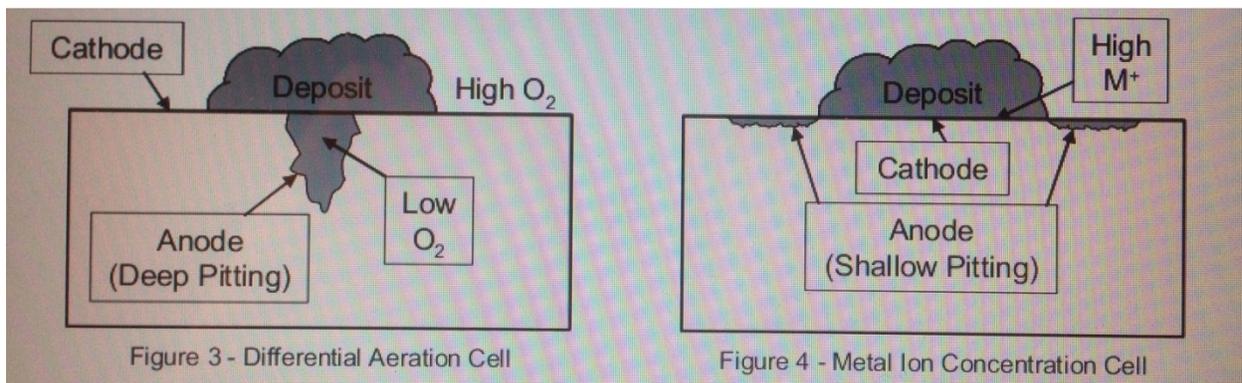
There are two widely accepted theories, or mechanisms, that explain why anodes and cathodes stop shifting, thus resulting in a stationary anode. The first mechanism is known as Concentration Cell Corrosion, and the second involves Alteration of the Protective Metal Oxide Layer. Pitting is the end result of both mechanisms. The rate of corrosion and the depth of attack associated with each of these mechanisms are generally much higher than that seen for general corrosion because of the large cathode to anode ratios that result.

Concentration Cell Corrosion can develop under deposits, within crevices, or under biofilms. The terms “under-deposit corrosion” and “crevice corrosion” are often used in lieu of the term “concentration cell corrosion” to more accurately describe the geometry associated with the concentration cell. Two types of concentration cells can form and the type of cell that forms is alloy dependent.

Differential Aeration Cell Corrosion is common in stainless steel and high nickel alloy and carbon steels. The very small amount of corrosion that occurs across the protective corrosion product film consumes (and depletes) the oxygen within the shielded area of the deposit or crevice causing that area to become anodic, while the area outside of the deposit or crevice becomes cathodic since a ready supply of oxygen

is available. Concurrently, electrochemical action within the shielded area causes the preferential dissolution of the metal resulting in positively charged metal ions. These metal ions hydrolyze, thus depleting hydroxyl ions, and the pH in the shielded area decreases. Subsequently, chloride ions from the bulk solution migrate into the shielded area to neutralize the charge imbalance which resulted from the depletion of hydroxyl ions. If the pH decreases sufficiently, and the chloride ion concentration increases sufficiently, a critical level is reached whereby the protective film breaks down and pitting is initiated. Pitting associated with this type of concentration cell is self-propagating due to the large cathode to anode ratio, and is usually rapid and catastrophic in nature.

Unlike the stainless steels, “under-deposit corrosion” or “crevice corrosion” in copper alloys proceeds via the Metal Ion Concentration Cell mechanism . With this mechanism, copper ions released by surface reactions concentrate under a deposit or within a crevice. Metals in the presence of their own ions become enobled (cathodic) and therefore the anode area develops outside of the crevice or deposit. Thus, unlike stainless steel, corrosion occurs adjacent to the deposit and tends to be shallow in nature .



The corrosion resistance of metals to “under-deposit corrosion” or “crevice corrosion” varies. The best performance is shown by titanium and the copper-nickels, while the austenitic stainless steels exhibit the poorest performance. In general, those metals that corrode via the differential aeration cell mechanism show the worst performance, while those metals that corrode via the metal ion concentration cell mechanism show the best performance.

### **Alteration of the Protective Metal Oxide Layer**

Most metals are protected from corrosion by the formation of passivating metal oxide films. If these protective oxide films are altered, such that the anode-cathode relationships at the surface change and result in a stationary anode corrosion is likely to occur. Changes in the composition of a protective oxide film or the introduction of a biofilm at a metal surface are two common MIC scenarios associated with this corrosion mechanism. When corrosion results from the alteration of the protective oxide film, attack is generally very severe because of the large cathode to anode ratio that results

### **Types of Bacteria Causing MIC**

Sulfate Reducing Bacteria (SRB), Metal Reducing Bacteria(MRB), Metal Depositing Bacteria (MDB), Slime Producing Bacteria (SPB), Acid Producing Bacteria(APB), and Fungi .

- Sulfate Reducing Bacteria are anaerobic bacteria that reduce sulfates, sulfites, thiosulfates, and even elemental sulfur to sulfides in the absence of oxygen. There are multiple theories on how SRB causes corrosion, but the generally accepted theory is that the sulfides substitute in the corrosion product films and that a stationary anode is created under the newly formed sulfide layer. Sulfate Reducing Bacteria can affect almost all metals including cast iron, carbon steel, mild steel, stainless steel, and copper alloys. Mild steel is particularly susceptible to attack by

SRB, and SRB related sulfide pitting has been widely reported on copper alloys in stagnant deaerated waters.

- Metal Reducing Bacteria react with elements in the corrosion product films on metal surfaces such that the protective film is lost or replaced by a less stable film; thus creating a stationary anode in the affected area.
- Metal Depositing Bacteria participate in the biotransformation of oxides of metals such as iron and manganese. These types of bacteria are capable of oxidizing manganous ions to manganic ions with the concomitant deposition of manganese dioxide. These types of bacteria can also oxidize ferrous ions to ferric ions. The deposition of cathodically reactive ferric and manganic oxides, and the consumption of oxygen by bacterial respiration under such deposits, can lead to differential aeration cell pitting in stainless steels.
- Slime Producing Bacteria produce Extracellular Polymeric Substances (EPS), or biofilms, under which differential aeration concentration cells can form.
- Acid Producing Bacteria can produce large quantities of either inorganic or organic acids as by-products of their metabolism. Acetic, formic and lactic acids are common metabolites (metabolic by-products) of APB. Acid-producing bacteria may also have a role in providing nutrients to SRB and are often found in association with SRB related corrosion. Organic acid-producing bacteria have been found as the primary cause of carbon steel corrosion at an electric power station.
- Fungi are known to produce organic acids, and are therefore capable of contributing to MIC. In one case, the biocorrosion of aluminum was theorized to be related to fungal contaminants of jet fuel.

### **MIC in Stainless Steels**

Austenitic stainless steels including both Type 304 and Type 316 are susceptible to MIC attack associated with metal depositing bacteria, metal reducing bacteria, sulfate reducing bacteria, and slime producing bacteria.

Metal depositing bacteria are the most troublesome for stainless steel. Iron oxidizing bacteria can oxidize the ferrous ion ( $Fe^{+2}$ ) to the ferric ion ( $Fe^{+3}$ ) and promote the deposition of hydrated ferric hydroxide.

Manganese oxidizing bacteria can oxidize the manganous ion ( $Mn^{+2}$ ) to the manganic ion ( $Mn^{+3}$ ) and promote the deposition of manganese oxide. Pitting corrosion via a Differential Aeration Cell Mechanism can occur under such deposits. The iron and manganese oxidizers also have the ability to concentrate chlorides and to convert ferrous and manganous chlorides to ferric and manganic chlorides. The latter two are strong oxidizers and well known pitting agents of stainless steel; when present, the protective oxide film, already weakened by the exclusion of oxygen, breaks down and deep pitting follows. Unlike conventional under-deposit corrosion, this type of microbiologically influenced under-deposit corrosion does not require set chloride conditions (typically,  $> 200$  ppm for Type 304 and  $> 1000$  ppm for Type 316) and can occur at both very low and high chloride levels.

Metal reducing bacteria can also be problematic for stainless steel. They can lead to the localized depletion of chromium and iron content (relative to the nickel content) in the subsurface region of the

superficial oxide 9. It has been theorized that such changes weaken the oxide layer, thus predisposing the metal to a higher frequency of pitting due to attack by chlorides.

Anaerobic sulfate reducing bacteria are also responsible for corrosion of the austenitic stainless steels. Massive failures due to pitting in utility condensers were identified as a sulfate reducing bacteria MIC problem in the 1970's. Corrosion damage was ascribed to metastable sulfur oxyanions produced by SRB in the reduction of sulfate, or formed in the oxidation of biogenic iron sulfide to elemental sulfur in oxygenated water. Sulfur oxyanions, such as thiosulfate and tetrathionate, reduce the pitting potential of stainless steel and promote localized corrosion, with or without the presence of chloride 10, 11. In another example, severe intergranular pitting of 304L stainless steel condenser tubes in a geothermal electrical power plant operating at a temperature greater than 100° (212° was attributed to the presence thermophilic SRB 12.

It has also been noted that microorganisms can produce organic acids and/or create conditions for the formation of HCl or FeCl<sub>3</sub> under biofilms, and that these agents can cause the passivating layer on stainless steel to fail, allowing pitting and crevice corrosion to proceed.

In another example, corrosion in heat exchangers tubed with Type 304 stainless steel and cooled with lake water was described as microbially induced underdeposit corrosion. Pitting was found under calcium carbonate deposits after one year. Anaerobic methanogens (methane producers) promoted the deposition of calcium carbonate. After a period of stagnation, oxygen introduced with flow on start-up then oxidized biogenic sulfides that were produced by SRB during stagnation when anaerobic conditions prevailed. Formation of thiosulfate through oxidation stabilized metastable pitting, thus promoting corrosion at even lower chloride levels.

Finally, slime producing bacteria produce biofilms under which differential aeration concentration cells can form. Figure 6 compares the propensity of various materials to form bioslimes in seawater. Type 304 stainless steel is 100 times more likely to develop a bioslime than is 90/10 copper-nickel.

### **MIC in Copper Alloys**

Although known to exhibit superior resistance to biological macro and micro fouling, copper alloys are susceptible to some forms of MIC. The predominant type of MIC attack that occurs on copper alloys (including 90/10, 70/30, and admiralty) is SRB related; the literature is filled with examples. With this type of attack, sulfides are produced from the action of anaerobic sulfate reducing bacteria on naturally occurring sulfates during periods of stagnation (e.g. during a wet lay-up). In the presence of sulfide ions, cuprous sulfide forms on the metal surface instead of cuprous oxide, and pitting occurs because the sulfides are cathodic to the base metal. Sulfides can also be found in polluted water in the form of hydrogen sulfide.

In a related SRB example, preoperational leaks from pitting and denickelification were reported for 90/10 copper-nickel and 70/30 copper-nickel in an open loop heat exchanger. The leaks were attributed to SRB embedded in a bioslime and resulted from alternating periods of oxygenation and stagnation. In another example, the failure of admiralty brass condenser tubes in a nuclear power plant was determined to be MIC related. Nitrate-reducing bacteria present in the lake water used for cooling produced high levels of ammonia when established in biofilms, and the resultant ammonia levels at the metal surface were found to be 300 times higher than the background levels in the lake water. Since Admiralty Brass is susceptible to stress corrosion cracking in ammoniated environments, stress corrosion cracking failures resulted.

## **Prevention and Avoidance of MIC**

Microbiologically Influenced Corrosion can be prevented and/or avoided, to a large degree, knowing the types of attack that occur and the corrosion mechanisms associated with each type of attack.

SRB attack in copper alloys and stainless steels related to anaerobic bacteria can be prevented if stagnant conditions are avoided. Extended wet lay-ups at start-up, during regularly scheduled outages, following a hydrotest, etc. should absolutely be avoided. If the unit cannot be returned to normal service within several days, the cooling water should be drained and the inside of the tubes should be dried with forced air. If system draining is not practical, the circulating water system should be run at the maximum design flow at least every 3-4 days, preferably more often.

Unlike copper alloys, stainless steels are highly susceptible to bioslime formation and biological fouling from mussels, algae, barnacles, etc. Chlorination is effective in controlling biofoulers, but many hard shelled biofoulers are able to retreat into their shells at the first sign of a biocide and remain until the biocide has dispersed; thus making intermittent chlorination considerably less effective than continuous chlorination. Continuous chlorination, or intermittent chlorination supplemented with periodic shock treatments of chlorine, is recommended for stainless steel.

The use of treated water for hydrotesting is also very effective for the prevention of MIC. The water may be treated with a biocide or disinfected by an alternative method. However, attention to water treatment before hydrotesting or layup is necessary as the effectiveness of biocide additions made after layup will likely be limited due to poor distribution throughout the system and because bio-organisms will have had time to become established. Large doses of biocide (e.g. 2 ppm Cl<sub>2</sub>) are recommended for hydrotest waters or for extended wet layup provided that potential incompatibilities with other system components have been properly considered. Extended wet layups may also require periodic additions of biocide to maintain an effective concentration.

MIC attack related to under-deposit pitting can be avoided if deposits and sediment buildup are not allowed to form, or if they are regularly removed; a clean, well maintained system will also be much less susceptible to other forms of corrosion. Wherever possible, system design should provide for continuous operation at a lower limit velocity where MIC will be prevented or at least delayed. The selected velocity should be high enough to keep particulates and organisms suspended in the fluid stream. Crevice corrosion, macrofouling, and microbiological corrosion can generally be avoided with flow velocities in excess of 4 fps, and microfouling (slime formation) can generally be avoided with flow velocities in excess of 8 fps, as shown in figure 7. Although low velocities should be avoided with stainless steels, there are no practical upper velocity limits like there are for copper alloys (in the range of 9-10 fps). With stainless steel, the use of continuous cleaning systems (sponge ball cleaning) or regularly scheduled cleanings with non-metallic brushes or high pressure water is recommended. Routine cleaning can also prevent slime build-up associated with slime producing bacteria.

## **Mitigation of MIC**

Treatments for MIC generally fall in to three categories ; biocides, cleaning, and operational controls. Biocides can effectively control MIC but they need to be able to come in contact with the metal surface to be effective; therefore mechanical and/or chemical cleaning to remove deposits is usually recommended as a first step. Biocidal treatments used for mitigation are typically much stronger than those used in normal operation, for example 0.2 ppm ozone for 12 hours or 20 ppm chlorine for 2 hours was reported to be effective for a bioslime containing SRB 19. Once the metal has been cleaned and treated with a biocide, standard operating procedures should be revised to include a minimum flow

velocity, keeping the tubes clean, and draining of the tubes during shutdowns or treating the cooling water with biocides prior to layup.

For the unique case of SRB related sulfide pitting in copper alloys, acid cleaning of the tubes followed by reconditioning with ferrous sulfate will aid in the reformation of a protective cuprous oxide film and significantly help to minimize further damage. Ferrous sulfate is most effective when injected into the cooling water for several hours per day over a period of 20-40 days.

### **Material Replacements**

Material replacement may be required if MIC damage is excessively severe or where design, environmental, or economic constraints prevent full implementation of recommended preventive measures. Material replacement generally represents the last resort as a means to eliminate MIC failures and should only be considered after the source of the problems has been identified and controlled. Otherwise, MIC may continue to be a problem with the replacement material. In situations where Type 304 or Type 316 stainless steel has experienced MIC damage, Super Austenitics and Super Ferritics are often specified as replacements. "AL-6XN", the most commonly specified Super Austenitic, offers improved resistance to pitting versus 304 and 316, and has been found to exhibit good resistance to MIC. Super Ferritics include "Sea-Cure" and Alloy 29-4C. They also offer improved resistance to pitting and to MIC. Copper alloys, with their inherent resistance to biofouling and bioslime formation, have also replaced 304 and 316 stainless steel. In the copper alloys, 90-10 Copper-Nickel is often specified as an upgrade over Admiralty Brass; it offers improved resistance to bioslime formation and is essentially immune to stress corrosion cracking in ammoniacal environments. Finally, if the cost can be justified or if the MIC problem is exceptionally severe, titanium is considered generally immune to MIC.

Replacement in kind, or the replacement of the corroded material with a material of the same basic specification, is an often overlooked alternative. With increased attention to cleanliness, flow velocities, and shutdown procedures, MIC can be significantly reduced, if not eliminated. Further, this alternative precludes concerns for vibrational mid-span collision, heat transfer degradation, and galvanic incompatibilities that might result with a different material.

### **Summary**

Most metals including iron, copper, nickel, and their alloys are susceptible to MIC, but most forms of MIC can be avoided. The ideal situation is one where water treatment, a relatively high fluid velocity, and regular cleanings are combined to make the attachment of bio-organisms to metallic surfaces extremely difficult, if not impossible

Specific preventive actions to avoid MIC include:

- Avoid stagnant waters; they can be catastrophic to both copper alloys and stainless steels. This can be accomplished with good commissioning, hydrotesting, and shutdown practices.
- Avoid low flow conditions. With stainless steels, to prevent sediment build-up, macrofouling, and microbiological corrosion, never allow the water velocity to fall below 4 fps.
- Maintain tubes in a clean condition; this is probably the single most important action that can be taken to prevent MIC. With flow velocities less than 8 fps, on-line cleaning systems should be considered for stainless steel tubes.
- Use biocides during normal operation, and prior to and during wet layup; this is important for all materials.

Finally, a change in materials can introduce an entirely new set of unexpected operational problems. Fully evaluate if the implementation of MIC preventive measures could have prevented MIC with the current material.