

Microbiologically Influenced Corrosion (MIC) Of Condenser & Heat Exchanger Tubing

Microbiologically Influenced Corrosion, commonly referred to as MIC, has been the subject of many papers in the recent past. Many of these papers have been written from the viewpoint of the microbiologist. It is the intent of this paper to explain the MIC literature in the context of classical corrosion theory, with the ultimate goal being to provide the power plant engineer with guidance on heat exchanger material selection and how to prevent MIC in heat exchanger tubing.

Microbiologically Influenced Corrosion, as used in this article, will be defined as corrosion at a metal surface that is associated with microorganisms, or the products of their metabolic activities (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 pH¹, and MIC attack appears to be climate related². 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 resistant.

Types of Bacteria Causing MIC include Sulfate Reducing Bacteria (SRB), Metal Reducing Bacteria (MRB), Metal Depositing Bacteria (MDB), Slime Producing Bacteria, Acid Producing Bacteria (APB), and Fungi³.

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 corrosion-resistant oxide films on metal surfaces. This results in the protective passive layers (e.g. on stainless steel surfaces) being lost or replaced by less stable reduced metal films; thus, significantly reducing the metal's resistance to corrosion.

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 local consumption of oxygen by bacterial respiration within such deposits, can lead to pitting corrosion in stainless steels.

Slime Producing Bacteria produce Extracellular Polymeric Substances (EPS) that have been implicated in the localized attack of stainless steel, and of copper in drinking water systems.

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 corrosion¹. Organic acid-producing bacteria were suggested 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.

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. On a single metal surface, this corrosion normally proceeds by means of electrochemical corrosion which involves the flow of electrons between anodes and cathodes on the metal surface and the flow of ions through a conductive solution called an electrolyte (i.e. the cooling water). For electrons to flow, and for corrosion to occur, a potential difference must exist between the anode and cathode

areas. Thus, the basic elements of a corrosion cell – an anode, a cathode, an electrolyte, and a path for electron flow – are all present as illustrated in Figure 1.

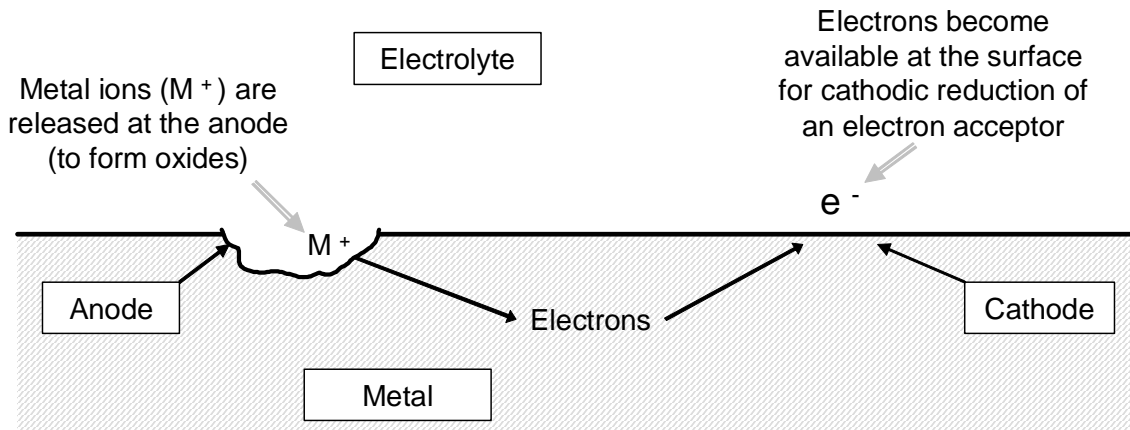
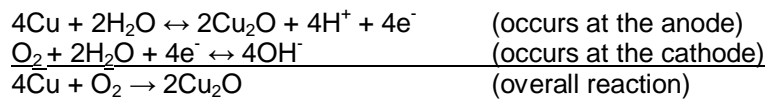


Figure 1 –Electrochemical Corrosion Mechanism

Electrochemical action in the corrosion cell causes the preferential dissolution of metal at the anode area. Positively charged ions of metal detach themselves from the metal surface at the anode and enter the electrolyte generating a counterflow of electrons. These electrons travel through the metal to the cathode area where they take part in the cathodic reaction. The metal ions formed at the corroding anode area react directly with oxygen dissolved in the electrolyte (the cooling water) to form a metal oxide, or hydrated metal oxide, corrosion product film. For illustrative purposes, the anodic and cathodic half-reactions and the overall reaction for 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 as shown in Figure 2, thus permitting the corrosion products to uniformly cover the metal surface. 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 almost always the end result of both mechanisms. The rate of corrosion and the depth of attack associated with pitting are almost always much higher than that seen for general corrosion.

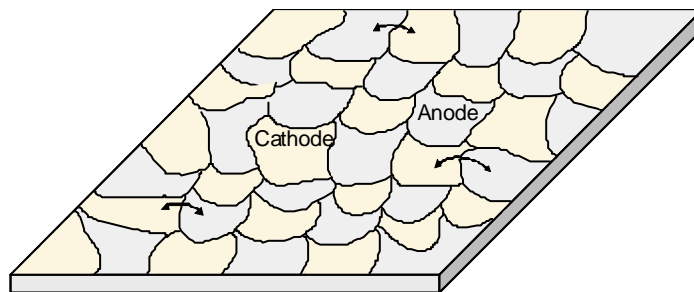


Figure 2 –Shifting Anodes and Cathodes on a Metal Surface

Concentration Cell Corrosion – Concentration cells 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 as depicted in figures 3 and 4; and the type of cell that forms is alloy dependent.

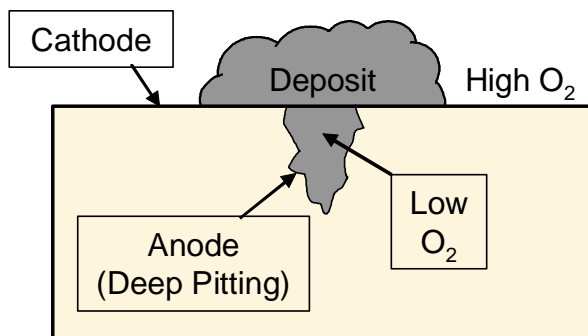


Figure 3 - Differential Aeration Cell

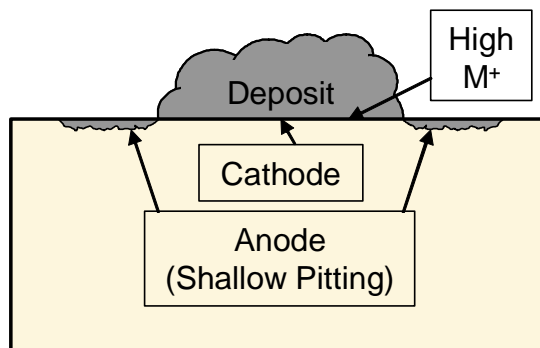


Figure 4 - Metal Ion Concentration Cell

Differential Aeration Cell Corrosion (depicted in Figure 3) is common in stainless steel and high nickel alloys. 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 initiated⁴. 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 (depicted in Figure 4). With this mechanism, copper ions released by surface reactions concentrate under the deposit or within 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 nature⁵.

The corrosion resistance of several alloys to “under-deposit corrosion” or “crevice corrosion” is shown in the following table. The best performance is shown by titanium and the copper-nickels, while the worst performance is exhibited by the stainless steels. 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.

Table 1 - Under Deposit & Crevice Corrosion Resistance of Various Alloys in Quiet Seawater⁶

Inert	Best	Neutral	Less	Deep Pitting
Titanium	90/10 Copper-Nickel	Cast iron	Incoloy Alloy 825	Type 316 Stainless
	70/30 Copper-Nickel	Carbon Steel	Nickel-Copper Alloy	Ni-Cr Alloys
	Bronze		Copper	Type 304 Stainless
	Brass			400 Series S/S

Alteration of the Protective Metal Oxide Layer - Most metals are protected from corrosion by the formation of passivating metal oxide films. Alteration of these protective oxide films, such that the anode-cathode relationships at the surface are changed, can lead to corrosion. 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.

MIC in Stainless Steels – Austenitic stainless steels, including Types 304 and 316, are susceptible to MIC attack associated with metal depositing bacteria, metal reducing bacteria, sulfate reducing bacteria, and slime producing bacteria.

Iron oxidizing and manganese oxidizing bacteria are the most troublesome for stainless steel. Both are capable of laying down deposits of metal oxides on metal surfaces. Iron oxidizing bacteria can oxidize the ferrous ion to

the ferric ion and promote the deposition of hydrated ferric hydroxide⁷. Manganese oxidizing bacteria can oxidize the manganous ion to the manganic ion and promote the deposition of manganese oxide¹. 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 316⁴) and can occur at both very low and high chloride levels.

In 316 stainless steel, the presence of *Citrobacter freundii* can lead to the localized depletion of chromium and iron content (relative to the nickel content) in the subsurface region of the superficial oxide⁸. It has been theorized that such changes can weaken the oxide layer, thus predisposing the metal to a higher frequency of pitting due to attack by chlorides. It has also been noted that microorganisms can produce organic acids and/or create conditions for the formation of HCl or FeCl₃ under biofilms⁹, and that these agents can cause the passivating layer on stainless steel to fail, allowing pitting and crevice corrosion to proceed.

Anaerobic sulfate reducing bacteria such as *desulfovibrio desulfuricans* can be responsible for corrosion that occurs in the absence of oxygen⁴. Massive failures due to pitting of stainless steel in utility condensers were identified as a MIC problem in the 1970's¹⁰. 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 water¹¹. Sulfur oxyanions, such as thiosulfate and tetrathionate, have been shown to reduce the pitting potential of stainless steel and promote localized corrosion, with or without the presence of chloride^{10,11}.

In another report, corrosion in heat exchangers tubed with Type 304 stainless steel and cooled with lake water was described as microbially induced underdeposit corrosion¹². Pitting was found under calcium carbonate deposits after one year. Anaerobic methanogens promoted the deposition of calcium carbonate. After a period of stagnation, oxygen introduced with flow on start-up then oxidized biogenic sulfides 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.

In a final example, severe intergranular pitting of 304L stainless steel condenser tubes in a geothermal electrical power plant operating at > 100°C(210°F) was attributed to the presence thermophilic SRB¹³.

Key features of the metallurgical fingerprint ascribed to MIC in stainless steel include corrosion pits composed of several smaller pits with hemispherical appearance, striations in the direction of rolling in the pit bottom, and tunneling into the sides of the corrosion pit. When attack is by SRB, metal sulfides can be expected.

MIC in Copper Alloys - Sulfide Pitting is the most common form of MIC in copper alloys. In the presence of sulfide ions, copper sulfides form on the metal surface instead of cuprous oxide, and pitting occurs because the sulfides are cathodic to the base metal¹⁴. Sulfides, in the form of hydrogen sulfide, can be found in polluted water, but they can also be produced in clean unpolluted water from the action of anaerobic bacteria on naturally occurring sulfates during periods of stagnation (e.g. during a wet lay-up) if the water contains sulfates and is not periodically aerated. Sato¹⁵ reported that a sulfide ion content as low as 0.05 ppm is capable of causing severe corrosion, and EPRI¹⁶ has suggested that sulfide levels even as low as 0.01 ppm can be detrimental. Copper sulfide corrosion product films are black in color and may include digenite (Cu₉S₅), spionkopite (Cu₃₉S₂₈), chalcocite (Cu₂S), and covellite (CuS). Chalcocite, Cu₂S, is the most characteristic corrosion product for sulfate-reducing bacteria MIC scenarios¹⁷.

In another example, stress corrosion cracking of admiralty brass condenser tubes was attributed to the presence of ammonia formed by nitrate reducing bacteria found in the lake water used for cooling¹.

Finally, in a situation unrelated to heat exchanger tubing, the corrosion of copper water tube in a potable water system was theorized to be the result of the incorporation of EPS into the copper oxide on the metal surface, thus disrupting the passivating film¹⁸.

Prevention and Control of MIC - Almost all reports of MIC in copper alloys are related to sulfide pitting which has resulted from the action of anaerobic sulfate reducing bacteria in stagnant waters. Extended wet lay-ups at

start-up, during regularly scheduled outages, following a hydrotest, etc. that will last for more than 3-4 days should be avoided. If the unit cannot be returned to normal service within 3-4 days, the cooling water should be drained and the unit dried with forced air. If system draining is not practical, the cooling water should be circulated and aerated. As a minimum, the circulating water system should be run at the maximum (design) flow at least every 3-4 days. If stagnant water is left in a unit for more than 4 days, sulfide pitting may not necessarily result, but if it does, acid cleaning of the tubes followed by reconditioning with ferrous sulfate will aid in the reformation of a protective cuprous oxide film¹⁹ and significantly help to minimize further damage. For those not familiar with the use of ferrous sulfate, it is most effective when injected into the cooling water for several hours per day over a period of 20-40 days²⁰.

Other than SRB associated sulfide pitting, the only other report found in the literature for MIC on copper alloys was for the stress corrosion cracking of Admiralty Brass. Admiralty Brass is known for its susceptibility to stress corrosion cracking in ammoniated environments. Thus, where nitrate reducing bacteria (that can result in ammonia) are known to be of concern, the use of 90/10 copper-nickel should be considered as it is essentially immune to ammonia-related stress corrosion cracking.

Prevention and avoidance of MIC in stainless steel is also possible, although it is a little more difficult. As previously noted, stainless steels are susceptible to MIC attack associated with metal depositing bacteria, sulfate reducing bacteria, slime producing bacteria, and metal reducing bacteria. MIC attack related to under-deposit pitting can be avoided if deposits are not allowed to form or if they are regularly removed. Sediment formation and macrofouling can generally be avoided with flow velocities in excess of 6 fps and microfouling (slime formation) can generally be avoided with flow velocities in excess of 9 fps⁴. Deposits can also be avoided, or minimized, with the use of continuous cleaning systems (sponge ball cleaning) or through regularly scheduled cleanings with non-metallic brushes or high pressure water. Routine cleaning can also prevent slime build-up associated with slime producing bacteria.

Like copper alloys, SRB attack in stainless steels related to anaerobic bacteria can be prevented if extended periods of stagnation are avoided. Unlike copper alloys, stainless steels are susceptible to 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 or ineffective.

The ultimate solution may be to select a tube material, such as titanium, that is not susceptible to MIC attack. However, this is a very expensive solution, especially in light of the fact that most all MIC problems can be avoided with good operating and maintenance practices. In addition, with titanium, chlorination will still be required to control biofouling, it is customary to weld the tubes to the tubesheet versus roller-expanding the tubes, the tubes may need to be staked to avoid vibration-related mid-span collision, and cathodic protection to avoid galvanic corrosion of the tubesheet is almost always necessary.

Summary and Conclusions

- 1.) Copper alloys used for condenser and heat exchanger tubes are susceptible to MIC attack from SRB associated sulfide pitting in anaerobic (stagnant) conditions.
- 2.) Stainless steels are susceptible to MIC attack from metal depositing bacteria, metal reducing bacteria, sulfate reducing bacteria, and slime producing bacteria.
- 3.) Most, if not all, forms of MIC can be avoided. Particularly important for copper alloys is the avoidance of stagnant waters conducive to anaerobic sulfate reducing bacteria. This can be accomplished with good commissioning, hydrotesting, and shutdown practices. For stainless steels, the use of water flow velocities in excess of 9 fps generally prevents sediment build-up, macrofouling, and microfouling. With flow velocities less than 9 fps, the tubes should be cleaned regularly and continuous chlorination employed.

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