## PDHonline Course M507 (3 PDH)

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# Microbiologically Influenced Corrosion

*Instructor: Semih Genculu, P.E.*

**2020**

**PDH Online | PDH Center**

5272 Meadow Estates Drive
Fairfax, VA 22030-6658
Phone: 703-988-0088
www.PDHonline.com

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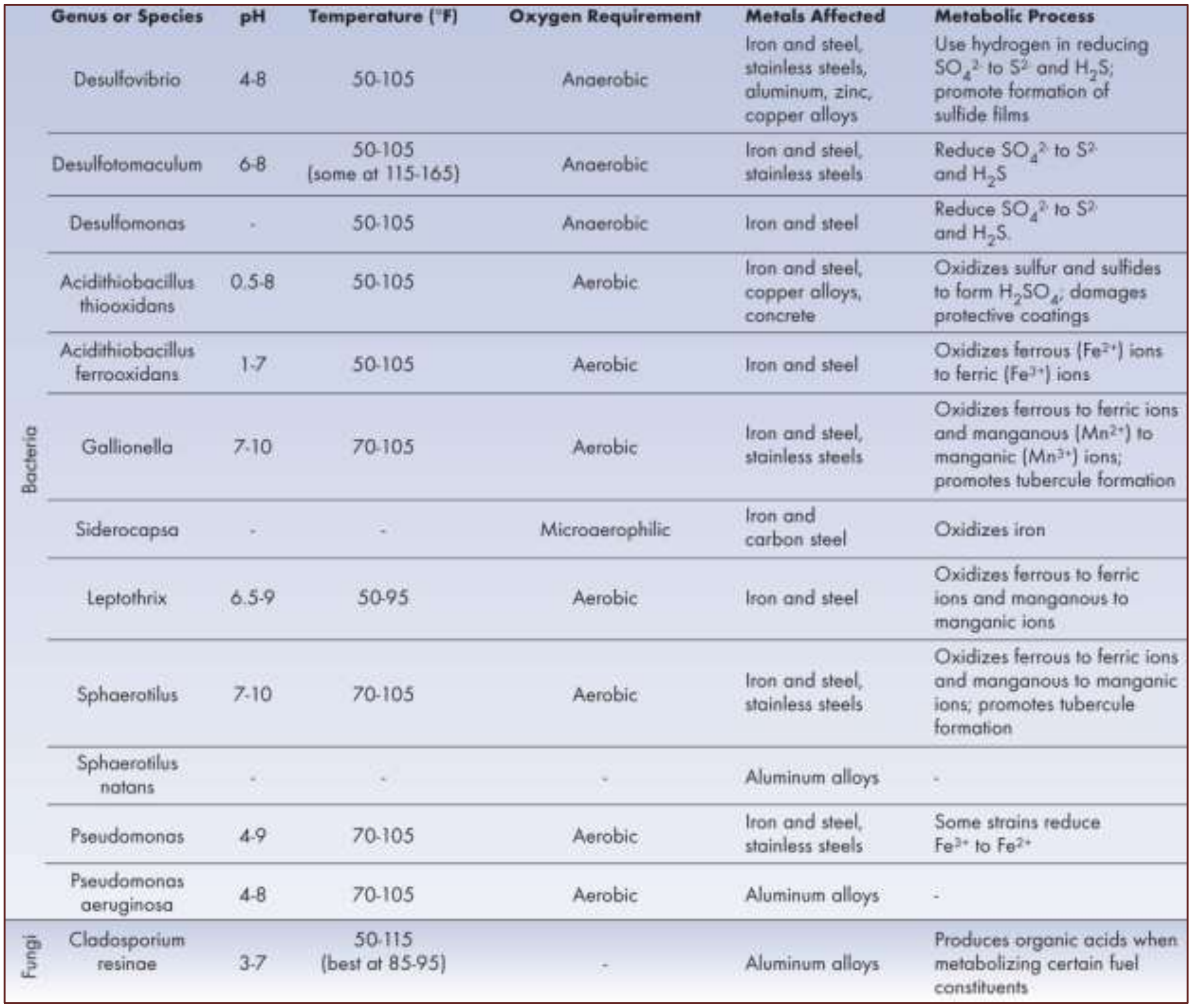
## Course Content

Microbiologically influenced corrosion (MIC) is corrosion that is influenced in some way by the presence and activities of microorganisms or their metabolites. It typically acts in conjunction with other corrosion mechanisms and may appear to be crevice corrosion, under deposit attack, oxygen concentration cell corrosion, carbon dioxide corrosion, etc.

Microorganisms pervade our environment and readily "invade" industrial systems wherever conditions permit. These agents flourish in a wide range of habitats and show a surprising ability to colonize water rich surfaces wherever nutrients and physical conditions allow. Microbial growth occurs over the whole range of temperatures commonly found in water systems, pressure is rarely a deterrent and limited access to nitrogen and phosphorus is offset by a surprising ability to sequester, concentrate and retain even trace levels of these essential nutrients.

### MICROORGANISMS THAT ACCELERATE CORROSION

Many engineers continue to be surprised that such small organisms can lead to spectacular failures of large engineering systems. The microorganisms of interest in MIC are mostly bacteria, fungi, algae and protozans. The most common ones are listed below:



| | Genus or Species | pH | Temperature (°F) | Oxygen Requirement | Metals Affected | Metabolic Process |
|---|---|---|---|---|---|---|
| Bacteria | Desulfovibrio | 4-8 | 50-105 | Anaerobic | Iron and steel, stainless steels, aluminum, zinc, copper alloys | Use hydrogen in reducing $SO_4^{2-}$ to $S^{2-}$ and $H_2S$; promote formation of sulfide films |
| | Desulfotomaculum | 6-8 | 50-105 (some at 115-165) | Anaerobic | Iron and steel, stainless steels | Reduce $SO_4^{2-}$ to $S^{2-}$ and $H_2S$ |
| | Desulfomonas | - | 50-105 | Anaerobic | Iron and steel | Reduce $SO_4^{2-}$ to $S^{2-}$ and $H_2S$. |
| | Acidithiobacillus thiooxidans | 0.5-8 | 50-105 | Aerobic | Iron and steel, copper alloys, concrete | Oxidizes sulfur and sulfides to form $H_2SO_4$; damages protective coatings |
| | Acidithiobacillus ferrooxidans | 1-7 | 50-105 | Aerobic | Iron and steel | Oxidizes ferrous ($Fe^{2+}$) ions to ferric ($Fe^{3+}$) ions |
| | Gallionella | 7-10 | 70-105 | Aerobic | Iron and steel, stainless steels | Oxidizes ferrous to ferric ions and manganous ($Mn^{2+}$) to manganic ($Mn^{3+}$) ions; promotes tubercule formation |
| | Siderocapsa | - | - | Microaerophilic | Iron and carbon steel | Oxidizes iron |
| | Leptothrix | 6.5-9 | 50-95 | Aerobic | Iron and steel | Oxidizes ferrous to ferric ions and manganous to manganic ions |
| | Sphaerotilus | 7-10 | 70-105 | Aerobic | Iron and steel, stainless steels | Oxidizes ferrous to ferric ions and manganous to manganic ions; promotes tubercule formation |
| | Sphaerotilus natans | - | - | - | Aluminum alloys | - |
| | Pseudomonas | 4-9 | 70-105 | Aerobic | Iron and steel, stainless steels | Some strains reduce $Fe^{3+}$ to $Fe^{2+}$ |
| | Pseudomonas aeruginosa | 4-8 | 70-105 | Aerobic | Aluminum alloys | - |
| Fungi | Cladosporium resinae | 3-7 | 50-115 (best at 85-95) | - | Aluminum alloys | Produces organic acids when metabolizing certain fuel constituents |

Common microorganisms found in conjunction with MIC

Bacteria are generally small, with lengths of typically under 10 µm. Collectively, they tend to live and grow under wide ranges of temperature, pH and oxygen concentration. Carbon molecules represent an important nutrient source for bacteria. Microorganisms are classified according to their ability to grow in the presence or absence of oxygen. Organisms that require oxygen in their metabolic processes are termed aerobic (for example sulfur-oxidizing bacteria, such as thiobaccilus ferrooxidans and gallionella); they grow only in nutrient media containing dissolved oxygen. Other organisms, called anaerobic (for example, sulfate reducing bacteria such as desulfovibrio desulfuricans), grow most favorably in environments containing little or no oxygen.

Aerobic bacteria oxidize elemental sulfur or sulfur-bearing compounds, thus producing sulfuric acid. They are known to oxidize ferrous iron to ferric. The formation of acid can drive the pH to 1 or less if not neutralized by reaction with its surroundings. Gallionella have uniquely corrosive tendencies. They tend to concentrate chlorides, with the result that their deposits are rich in ferric chlorides. This acts like dilute hydrochloric acid and causes general corrosion of steel. On austenitic stainless steels, the effect is much more catastrophic, with rapid, subsurface pit cavities that have been known to penetrate walls of piping and vessels within a few weeks at ambient temperature.

Sulfur reducing bacteria (SRB) use sulfate ion as an oxidizing agent. Sulfur reduced from sulfate reacts with available hydrogen and iron to form hydrogen sulfide and iron sulfide thus creating, in general, an alkaline environment. While the mechanisms of corrosion by sulfate reducers are not fully agreed upon, the very nature of the colonies presents several possibilities: (a) generation of hydrogen sulfide, which is corrosive, (b) an extreme oxygen differential cell resulting from strongly anaerobic conditions, (c) a favoring of the kinetics of metal dissolution caused by tying up of metal ions at the surface as insoluble sulfides, and (d) cathodic depolarization by the hydrogenase-induced reaction of hydrogen with sulfates.

SRB have been implicated in the corrosion of cast iron and steel, ferritic stainless steels, 300 series stainless steels (also very highly alloyed stainless steels), copper nickel alloys, and high nickel molybdenum alloys. They are almost always present at corrosion sites because they are in soils, surface water streams and waterside deposits in general. Their mere presence, however, does not mean they are causing corrosion. The key symptom that usually indicates their involvement in the corrosion process of ferrous alloys is localized corrosion filled with black sulfide corrosion products.

Slime-Forming Bacteria are commonly found in circulating and once-through cooling water systems. They produce extraordinary amounts of a gelatinous, sticky capsulation. This biofilm adheres to heat transfer surfaces causing loss of operating efficiency of heat exchangers and condensers. The biofilm is resistant to the shear effect and frictional forces of high flow velocity water. This enables the slime-forming bacteria to exist in environments where other non-slime-forming organisms cannot grow. When this occurs, the isolated slime formers have no competition for food or space and can rapidly grow to a level where severe operational problems can develop in a very short time, e.g., 4 to 8 hours. Siderocapsa sp. is an example of a slime-forming bacteria that not only causes slime problems, but is also important in MIC. This bacterium excretes enzymes into the slime layer as it adheres to metal surfaces. The enzymes are capable of attacking the metal and initiating an anodic corrosion site on both ferrous and non-ferrous metals.

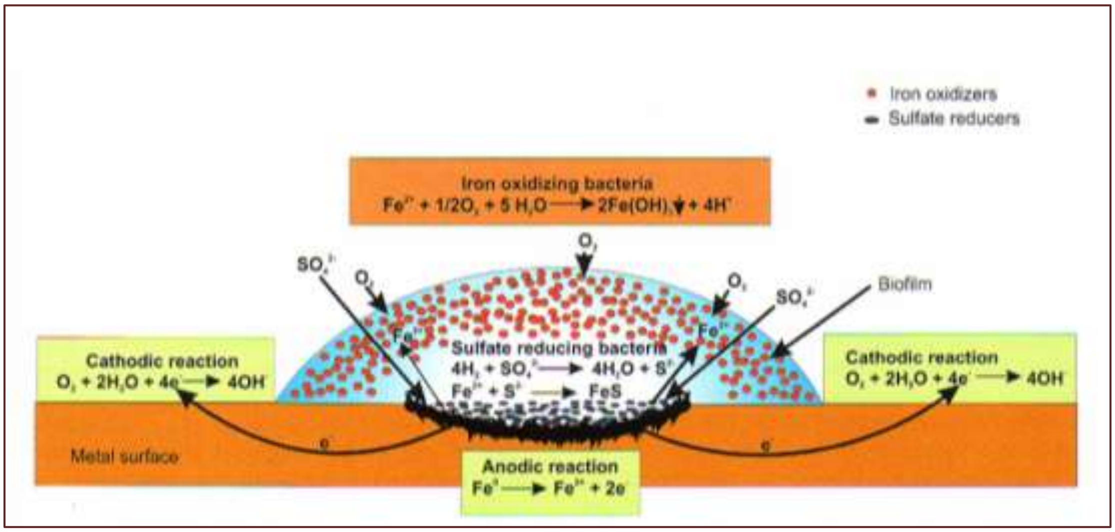


Figure showing the general representation of MIC of a metal surface

Bacteria can exist in several different metabolic states. Those that are actively respiring, consuming nutrients, and proliferating are said to be in a "growth" stage. Those that are simply existing, not growing because of unfavorable conditions, are said to be in a "resting" state. Some strains, when faced with unacceptable surroundings, form spores that can survive extremes of temperature and long periods without moisture or nutrients, yet produce actively growing cells quickly when conditions again become acceptable. The latter two states may appear, to the casual observer, to be like "death", but the organisms are far from dead. Cells that actually die are usually consumed rapidly by other organisms or enzymes. When looking at an environmental sample under a microscope, therefore, it should be assumed that most or all of the cell forms observed were alive or capable of life at the time the sample was taken.

Fungi can be separated into yeasts and molds. Corrosion damage to aircraft fuel tanks is one of the well-known problems associated with fungi. Fungi tend to produce corrosive products as part of their metabolisms; it is these by-products that are responsible for corrosive attack. Many of the problems caused by the growth of fungi are similar to those associated with algae; the primary difference is the location where the fungi grow. Algae need light to grow before they become problem causing. The fungi do not. Therefore, the fungi are not limited to the location in the system where they can colonize and contribute to plugging and fouling problems, to deposition problems, etc. Quite frequently, the filamentous fungi establish colonies, which entrain and “bind” suspended solids into masses that cause operational difficulties. These masses frequently are found in low-flow areas in the circulating water systems, in “dead” or stagnant flow areas, and on screens or filters. Often colonies of fungi develop on the surface of the fill in cooling towers to the extent that the evaporative capacity of the tower (cooling efficiency) is significantly reduced.

A problem caused by fungi that is often overlooked involves the situation where fungal colonies provide an optimum growth environment for other problem-causing microorganisms, particularly bacteria. Because of the fungal growth, the bacteria can grow protected from external environmental factors that would normally limit bacterial growth. Fungi also provide essential nutrients for other microorganisms in the microenvironment created by the fungal colony.

Most fungi are aerobic and consume available oxygen in the microenvironment within a fungal mycelium or colony. This creates an anaerobic environment within or underneath the fungal mass where anaerobic bacteria, such as the sulfate-reducing bacteria (SRB) can live and perhaps initiate MIC. Under extreme conditions, fungi contribute to the formation of deposits that serve as a barrier to the diffusion of oxygen in the circulating water to the metal surface on which the fungal colony is attached. This creates an oxygen diffusion concentration gradient and a high potential for under-deposit corrosion.

Algae range in size from microscopic forms that are approximately the same size as some bacteria, to very large “seaweeds” that may be many meters in length. Most important types in industrial process water problems are caused by algae that are microscopic in size, requiring magnification of at least 100X for identification. Many species occur as single-celled forms (referred as unicellular algae), which may be spherical, rod-shaped, or variations of these. Other types of algae are multi-cellular, which appear in numerous forms and shapes, including slimy masses of several cells or long strands, forming specific functional structures (referred to as filamentous algae).

All algae contain colored materials called pigments. The most important of these are the chlorophyll pigments, which are responsible for the green color displayed by most forms of algae. In fact, the common names for the largest groups of algae are derived from the pigmentation: i.e., green algae, blue-green algae, yellow-green algae, etc. Algae are found almost anywhere essential requirements for growth are found. The basic requirements include sunlight, water, and air. In addition, pH, temperature, and certain chemical requirements are also important.

The primary problem associated with the growth of algae is plugging and fouling of screens, filters, and cooling tower components. Microbiological slime and MIC, as a direct result of the presence of algal masses, are not encountered very often. The filamentous forms of algae have the capability of entraining large amounts of non-microbiological material and, subsequently, forming troublesome deposits. Very often, these deposits create a favorable environment for other types of microorganisms to grow and to cause slime or MIC problems. The unicellular forms of algae are easily washed away from the sites where they grow and are transported to other areas of the system, thus providing a nutrient source for bacteria and fungi. These microorganisms, using the algae as a food source, may cause slime and MIC problems. Therefore, it is generally recognized that unless algal growth is controlled, prevention of microbiological, biological deposits, and MIC is not readily accomplished.

Protozans are predators of bacteria and algae and therefore potentially mitigate microbial corrosion problems. Typically none of these organisms is found alone in isolated cultures. Instead they often are found in communities influencing each other's growth as well as creating plugging, fouling, and in some cases contributing to corrosion.

Bacteria, fungi and other microorganisms can also play a major part in soil corrosion. Spectacularly rapid corrosion failures have been observed in soil due to microbial action and it is becoming increasingly apparent that most metallic alloys are susceptible to some form of MIC. The mechanisms potentially involved in MIC are summarized as:

- Cathodic depolarization, whereby the cathodic rate limiting step is accelerated by microbiological action.
- Formation of occluded surface cells, whereby microorganisms form "patchy" surface colonies. Sticky polymers attract and aggregate biological and non-biological species to produce crevices and concentration cells, the basis for accelerated attack.
- Fixing of anodic reaction sites, whereby microbiological surface colonies lead to the formation of corrosion pits, driven by microbial activity and associated with the location of these colonies.
- Underdeposit acid attack, whereby corrosive attack is accelerated by acidic final products of the MIC "community metabolism", principally short-chain fatty acids. Certain microorganisms thrive under aerobic conditions, whereas others thrive in anaerobic conditions. Anaerobic conditions may be created in the micro-environmental regime, even if the bulk conditions are aerobic. The pH conditions and availability of nutrients also play a role in determining what type of microorganisms can thrive in a soil environment.

## PRINCIPALS OF MICROBIAL LIFE

Numerous studies have shown that microorganisms in their natural environments are associated with surfaces. Biofilm formation commences with microbial adhesion to a surface. Growth of adherent organisms results in the formation of microbial clusters, referred to as microcolonies. Continued microbial colonization and growth of adherent organisms will cause a surface to be covered by a surface community referred to as a biofilm. The extent of bacterial adhesion and the adhesion pattern depend on bacterial characteristics, including cell-surface hydrophobicity and charge, cell size, presence of flagella and pili, and properties of the substratum such as chemical composition, surface roughness, crevices, inclusions, and coverage by oxide films or organic coatings, the composition and strength of the aqueous medium, and the hydraulic flow regime.

Biofilms are a predominant mode of microbial growth in nature. They are associated with processes including leaf decomposition, fiber digestion in the digestive tract, colonization of marine surfaces by barnacles, and the formation or weathering of rocks. In contrast to planktonic bacteria, one significant characteristic of biofilm bacteria is their heightened resistance to antimicrobial agents, including disinfectants and antibiotics, making them difficult to eradicate.

MIC can only occur when microorganisms are present and active. They also need water, although it is not enough to sustain growth. Growth requires an electron donor, which is oxidized, an electron acceptor, which is reduced, an energy and a carbon source. They may be grouped as below based on these prerequisites:

| Prerequisite | Provided by | Kind of growth |
|---|---|---|
| Energy source | Light, Chemical substances | Phototrophic, Chemotrophic |
| Carbon source | $CO_2$, Organic substances | Autotrophic, Heterotrophic |
| Electron donor | Inorganic and organic substances | Lithotrophic, Organotrophic |
| Electron acceptor | Oxygen, $NO_2^-$, $NO_3^-$,$SO_4^{2-}$,$CO_2$ | Aerobic, anaerobic |

Light is a very important energy source as it promotes photosynthesis. A very good place to live for an anaerobic organism is below an active colony of aerobic organisms as these consume the oxygen and create anaerobic zones, which serve as habitats for the anaerobics. This is the reason why these two organisms can be found in close proximity of one another. Obligate anaerobes such as sulfate-reducing bacteria (SRB), which are very sensitive to oxygen, can therefore survive and multiply in aerobic habitats as they are protected by aerobic organisms. SRB is responsible for most instances of accelerated corrosion damage to ships and offshore steel structures. Iron and manganese oxidizing bacteria are aerobic and are frequently associated with accelerated pitting attack on stainless steels at welds.

Chemical energy can be drawn from practically all reduced chemical species. A well-known example that is of importance for MIC is the oxidation of sulfide, which can be accomplished by sulfur oxidizing bacteria. A result is a steep decrease in pH value. Temperature influences greatly the growth and survival of microorganisms. There is a minimum temperature below which growth no longer occurs, an optimum temperature at which the growth is most rapid and a maximum temperature above which growth is not possible. There are about a dozen of bacteria known to cause microbiologically influenced corrosion of carbon steels, stainless steels, aluminum alloys and copper alloys in waters and soils with pH 4~9. MIC-related bacterial growth typically occurs in systems within specific temperature ranges, depending on the type of bacteria; an “ideal” range is often reported as approximately 10° to 50°C. Bacterial growth typically hibernates below 5°C. Some types of bacteria favor other temperature ranges; for example, most common strains of SRB grow best at 25° to 35°C. A few thermophillic types of SRB grow more efficiently at more than 60°C, and one type is capable of growing at more than 100°C. While MIC more favorably grows in their typical temperature ranges, growth in other temperature ranges should not be discounted. MIC has been found in extremely cold environments such as freezers or piping systems.

## ECOLOGICAL INTERACTIONS ASSOCIATED WITH MIC

There are many types of microorganisms that have roles in the MIC process. Their simplicity, short regeneration cycle, and tolerance to a variety of environments mean they can successfully colonize a wide variety of locations. Once a colony has started they can isolate or protect themselves in the event of an adverse environmental change. If conditions become intolerable, many can form spore-structures that are impervious to most harsh conditions.

The following is a list that includes many of the ecological interactions that have been established as important to the phenomenon of MIC:

Microorganisms are small, a quality that allows them to penetrate into small crevices easily. It also allows them to multiply to large numbers in a very small space while carrying on the processes leading to MIC.

Microorganisms are actively or passively motile, which aids them in migrating to more favorable environments or away from adverse environments, i.e., seek food sources or away from toxic conditions. Physiologically, they have receptors for certain chemicals, which allows them to seek out higher concentrations of those substances that are required for growth, i.e., food sources. It is important to understand that many essential nutrients are in limited supply in most aqueous environments. In process water systems, the nutrients that are available absorb on surfaces or locate in specific sites, creating areas of relative plenty. Microorganisms seek out these sites and establish themselves into self-sustaining colonies. The individual microorganisms are readily dispersed by wind, moving water, or other mechanisms, providing a high potential for widely distributed inoculum sources.

MIC microflora can exist in a relatively wide range of temperatures, pH, and oxygen concentrations. Those members of the microflora most suited to the existing environment dominate and establish self-sustaining colonies.

MIC microorganisms exist in consortium with the total microflora of the system. They can grow in the form of colonies of a highly diverse microflora, which often helps to interact with the individual types in the colony. This ensures the survival of at least part of the microflora under adverse conditions.

Most microorganisms involved with MIC are able to multiply into enormous numbers of individuals in a short period of time. This allows them to become an established colony during a short period of favorable conditions. Once established, they “take over the environment” and maintain favorable growth conditions for the dominant types, even under unfavorable conditions.

Most MIC microorganisms have a relatively simple metabolic process that enables them to adapt to the use of a wide variety of food sources. For example, the bacterium Pseudomonas sp. can use over 100 different organic compounds as an energy source, including sugars, lipids, alcohols, phenols, organic acids, etc. This flexibility provides the advantage of having a food supply in spite of a constantly changing environment.

Many microorganisms form extra-cellular biofilm composed of polysaccharides, lipids, and other organic polymeric materials (referred to as capsules or slime layers). This material adheres to system surfaces and can accumulate rapidly to massive quantities, causing problems in heat transfer, fluid movement, and creating sites where MIC can occur. The biofilm is typically a sticky mass that entrains other debris existing as suspended solids in the bulk water. When this occurs, the slime layer provides some degree of resistance for the microorganisms against adverse environmental conditions and provides protection against toxic substances that may exist in the bulk water. The slime layer provides a means for the concentration of food sources and a medium for the concentration of extra-cellular enzymes produced by the microorganisms. Very often, these enzymes are involved in the initiation of MIC. The presence of the biofilm on system surfaces may lead to fouling and the deposition of other materials that affect heat transfer, fluid flow, and provide sites for MIC.

Many types of microorganisms involved with MIC produce endospores (bacteria), clamydospores, (fungi and algae), or filamentous mats (bacteria, fungi, and algae) that provide a significant degree of resistance to adverse environmental conditions. As a result, many microorganisms are resistant to exposure to boiling water; and they can survive extremes in pH, salinity, and the presence of inhibiting gases and naturally occurring toxic substances. This mechanism provides a means of resistance to many biocides and biostats by virtue of the cells being in a static stage of metabolism or by the fact that the toxic material cannot penetrate the individual cells or the filamentous mat. Endospores and clamydospores may last for hundreds of years and then germinate to produce typical vegetative cells when favorable conditions occur.

Many types of microorganisms produce acids or alkali that affect the pH within the micro-environment where they grow. Some produce organic acids, e.g., formic, succinic, lactic, butyric, which may initiate or accelerate corrosion. Others produce mineral acids, such as sulfuric or nitric acids, which, of course, are extremely corrosive. Certain bacteria, fungi, and algae metabolize protein, peptides or amino acids, producing ammonia as an end product. The ammonia can raise the pH of the micro-environment to extremely high alkaline levels, e.g., 13.0+. The result of this is subsequent corrosion of copper alloys and other non-ferrous alloys. In some cases, the high pH inactivates biocides, both oxidizing and non-oxidizing, thereby ensuring survival of the microorganisms within the micro-environment.

Many microorganisms produce $C0_2$, $H_2S$ and/or $H_2$ as a result of their metabolism. Carbon dioxide in solution becomes carbonic acid. Hydrogen could depolarize metal alloys, such as stainless steel, and result in corrosion. Some microorganisms, which normally use $CO_2$ or $H_2$ as their carbon and energy source, can live autotrophically without organic carbon food sources. The biochemical reactions taking place in the colonies of autotrophic microorganisms can result in the depolarization of the cathodic site and promote corrosion. This is one of the proposed mechanisms whereby sulfate-reducing bacteria (SRB) obtain hydrogen to reduce sulfate to sulfide, initiating corrosion of steel in anaerobic environments. The hydrogen sulfide produced by the SRB’s can, in itself, be corrosive to many metals.

Some bacteria oxidize or reduce metals or metallic ions directly. For example, Gallionella sp. and Sphaerotilus sp. oxidize ferrous ions to ferric ions. The ferric ions complex and precipitate into a sheath formed around the individual bacterial cells. As the sheaths form, the bacteria scavenge the oxygen in the microenvironment, produce more sheath material, and, subsequently, form oxygen concentration gradients between the metal surfaces and the bulk water (localized corrosion cell). Whether the removal of the ferrous ion from the bulk water directly affects the corrosion is not clear. It is clear, however, that if the microorganisms “co-accumulate” ferric or ferrous ions with chloride ions, aggressive corrosion of stainless steels and other ferrous metals occurs.

Other microorganisms, such as Pseudomonas sp., have been shown to reduce the ferric ion to a soluble ferrous form. This strips ferric compounds from the passivated surface leaving it more likely to form an anodic site and more prone to corrosion. In some cases, the same bacteria can oxidize or reduce manganese in the same manner as done with iron. This, along with the iron transformations, results in considerable tubercle formation and subsequent fouling or occluding of the pipes. The deposition of the corrosion products and tubercle formation often provides a microenvironment favorable for the growth of anaerobic microorganisms, such as Desulfovibrio sp., and subsequent pitting corrosion under the deposits.

The microflora found in industrial process water systems readily form synergistic or mutualistic communities that result in the accomplishment of things that the individual members of the microflora, alone, cannot perform. For example, certain fungi break down wood to sugars and organic acids. In the process, they consume the oxygen in the microenvironment. This provides an organic food source and an oxygen-free environment for the growth of the anaerobic sulfate-reducing bacteria. These communities also change their structure and dominant types to meet changes in the external or internal environment, and in response to the natural competition that exists between the microorganisms within the community. At the so-called “biological equilibrium,” the total community provides protection or a favorable ecology for all the individuals within the community. The community, therefore, increases the potential of microorganisms to accomplish many feats otherwise not possible, among them the corrosion of many types of metals.

## INCREASED FREQUENCY of MIC

While MIC problems have been around for many years, recent awareness and procedural changes have created increased potential for problems. Environmental impact concerns and new operating parameters have contributed to the changed conditions that encourage microbial growth. Plant designs, construction delays (resulting in wet lay-ups), and redundant systems with stagnant or intermittent flow rates contribute to increased MIC in the electric power generating industry.

Virtually all aqueous environments in industrial raw water, process cooling water, process water, and wastewater systems can support the growth of at least some of the types of microorganisms now known to be involved in the corrosion process. As stated earlier, there has been an increased awareness of MIC and this has contributed to the perception that MIC problems are now occurring at a greater frequency than in the past. There appears to be no limit to the inoculum sources for MIC microorganisms. There are widespread environments in which the MIC microorganisms grow. These facts contribute to the conclusion that MIC problems are more common today than thought to be in the past.

The reasons for the increased occurrence of MIC are many. Recent changes in the procedures used for scale and corrosion control in cooling water systems are important factors. The traditional approach used in open-recirculating systems to prevent scaling had been to add acid (usually $H_2SO_4$) to the circulating water to maintain the pH in a non-scaling range. At a pH of 5.5 to 6.5, it was often necessary to add corrosion inhibitors, such as chromates, to control electrochemical corrosion caused by the addition of the acid. Typical chromate inhibitor concentrations ranged from 50 ppm to as high as 2000 ppm (as $CrO_4$). At these concentrations, the corrosion inhibitor not only prevented electrochemical corrosion, but was also toxic to many of the microorganisms that would have been involved with MIC. In other words, both non-MIC and MIC corrosion problems were being inhibited concurrently by the same treatment. The literature reports bacteria, such as the SRB, are not readily cultured/isolated from systems treated with 50 ppm or more chromate corrosion inhibitor.

Recent environmentally-related limitations on the use of chromates and other heavy metal treatment chemicals in cooling water systems have eliminated the opportunity to capitalize on their inhibitory effect on the growth of those microorganisms involved with MIC. The corrosion inhibitor chemicals and treatment procedures that are now used to replace chromates typically do not inhibit MIC. In some situations, the chemicals used to inhibit electrochemical corrosion may actually accelerate or stimulate MIC. Without additional preventive measures to specifically control MIC, it is not unusual to anticipate increased frequency of MIC when using non-chromate corrosion inhibitors.

Another consideration has also contributed to increased frequency and severity of MIC. This relates to changes that have occurred in the types of chemicals used for general microorganism control and to changes in the operating conditions where they are used. For example, the traditional microorganism control technology used with the acid-chromate treatment program at a pH range of 5.5 to 6.5 was to use shock or breakpoint chlorination. When necessary, the chlorination treatment was supplemented with the application of a non-oxidizing biocide such as a pentachlorophenate or one of the various quaternary ammonium compounds. Not only was this effective in controlling the microorganisms that caused slime or plugging and fouling problems, but it also was effective in eliminating most of the microflora that induced or influenced corrosion. However, in conjunction with the transition to non-chromate treatment programs or to low chromate use concentrations (5 to 25 ppm as $CrO_4$), the operating pH of many systems was increased to above 7.5. This affected the potential MIC problem in two ways.

First, the effectiveness of chlorine as an oxidizing biocide was reduced to a level of less than 10% of what the same concentration would be at a pH of 6.5 or less. When the pH of the water is greater than 8.5, the effectiveness of chlorine as an oxidizing agent to control microorganisms is essentially zero.

Secondly, the effectiveness of many non-oxidizing biocides in controlling MIC microorganisms may be much less at the alkaline pH ranges. Laboratory and field studies confirmed that many of the commonly-used biocides developed for use at acidic pH did not adequately control MIC at pH above 8.0. Unfortunately, the technology of biocide development did not keep pace with the changes in the ecology of MIC. Without taking this factor into consideration when developing a coordinated program for water treatment, it should be expected that the frequency and severity of MIC will increase.

A third consideration may have contributed to the increased frequency of MIC. This relates to the increased level of suspended solids in the water contained in the operating system. Presently, a procedure for the control of scale formation at pH above 8.5 is the “pro-precipitation” technology. This procedure includes the “all organic,” “stabilized phosphate,” “multifunctional scale/corrosion,” etc., inhibitors. The technology is based on operating the system at non-corrosion conditions, inducing the precipitation of potential scale forming substances, and mechanically purging the precipitate from the treated water by bleed off or side stream filtration. The pro-precipitation technology is different in many ways from the anti-precipitation threshold/sequestration technology used at neutral to slightly alkaline pH. The significant difference is that the concentration of suspended solids in the pro-precipitation treated water is consistently higher. The high levels of suspended solids may result in the formation of sedimentary deposits or sludge at low-flow sites within the system. The deposits and sludge provide optimum environments for the growth of that microflora capable of contributing to MIC. In many cases, microorganisms “influence” corrosion under these conditions by functioning as binding agents, entraining suspended solids into deposits. Under-deposit corrosion subsequently occurs as a result of the differential oxygen diffusion concentration gradient created by the aerobic microorganisms and the suspended solids they bind into deposits on metal surfaces. The biofouling, sludge, and deposits also provide optimum environments consisting of “micro-anaerobic cells” where the anaerobic MIC microorganisms are able to grow and cause problems. Therefore, under present conditions where excessive suspended solids exist and without adequate control of the sludge and deposits caused by the suspended solids, the frequency and severity of MIC will increase.

Limited supplies of water for makeup and more stringent environmental discharge requirements have contributed to increased water re-use, "zero-discharge operation", and use of wastewater for makeup. Each of these situations has reduced the quality of water used for process cooling. The change in makeup water characteristics (lower quality) has increased the occurrence of conditions promoting MIC.

The electric power generating industry faces certain unique conditions that have contributed to the increased frequency of MIC at plant sites. These conditions relate primarily to design and construction considerations and are particularly evident in nuclear power plant systems. The length of time required for plant construction, the extensive time required to get into operation, and the routine practice of wet lay-up contributes to an environment with a high potential for MIC. Nuclear power plant construction/engineering design includes a large number of standby and redundant systems. This results in a number of situations where stagnant or intermittent flow conditions exist; yet the backup system, if “safety-related,” must be maintained continuously in an immediate conformance-operating condition. The stagnant and intermittent flow conditions provide optimum environmental conditions for MIC. It has been only recently that MIC has been identified by the industry as a potential problem under these conditions.

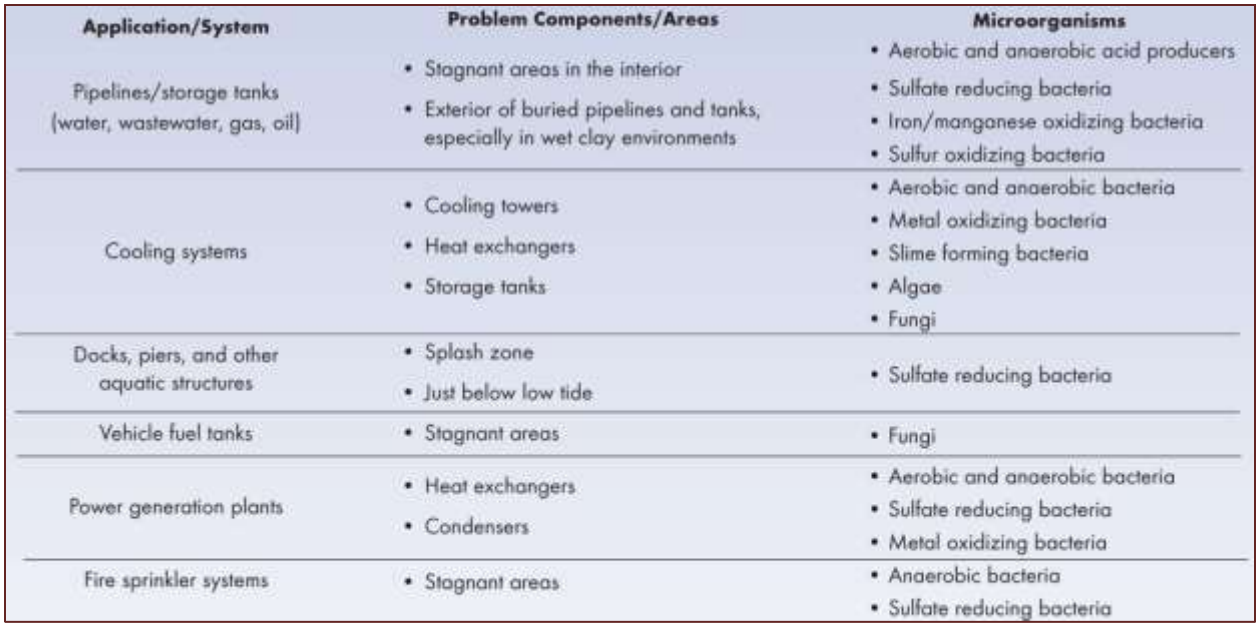
## SPECIFIC SYSTEMS and COMPONENT ENVIRONMENTS WHERE MIC OCCURS

MIC is responsible for the degradation of a wide range of materials in various industries, such as:

- Chemical processing industries: stainless steel tanks, pipelines and flanged joints, particularly in welded areas after hydrotesting with natural river or well waters.
- Nuclear power generation: carbon and stainless steel piping and tanks; copper-nickel, stainless, brass and aluminum bronze cooling water pipes and tubes, especially during construction, hydrotest, and outage periods.
- Onshore and offshore oil and gas industries: mothballed and waterflood systems; oil and gas handling systems, particularly in those environments soured by sulfate reducing bacteria-produced sulfides
- Underground pipeline industry: water-saturated clay-type soils of near-neutral pH with decaying organic matter and a source of SRB.
- Water treatment industry: heat exchangers and piping
- Sewage handling and treatment industry: concrete and reinforced concrete structures
- Highway maintenance industry: culvert piping
- Aviation industry: aluminum integral wing tanks and fuel storage tanks
- Metal working industry: increased wear from breakdown of machining oils and emulsions
- Marine and shipping industry: accelerated damage to ships and barges

Most piping and components, regardless of material types, in plant water systems are potential candidates for biofouling and/or MIC. Documented cases of attack of almost any material type including stainless steel, copper, brass, Monels (Cu-Ni alloys), and others have been noted. Careful control of water chemistry is also not a guarantee for avoiding biofouling or MIC. Although it may be a rather broad generalization, the localized ecological conditions within the environment of the system are the determining factors for the establishment of MIC. This means that the source or the chemistry of the water in the system does not appear to be a determining factor as to the existence of MIC. Systems containing sea water, raw well or surface water, treated fresh water, demineralized water, or treated municipal/domestic water all have experienced MIC.

Factors for fouling to occur are: The content of organisms in the water, water temperature and pH, flow rate (stagnant conditions are very unfavorable). Once fouling has started, other factors make the conditions worse; amount of inorganic particles – may settle on top of the fouling (sediment) – as well as chloride content and sulfide ions. Pitting or crevice corrosion is a risk under the fouling.



| Application/System | Problem Components/Areas | Microorganisms |
|---|---|---|
| Pipelines/storage tanks (water, wastewater, gas, oil) | • Stagnant areas in the interior<br>• Exterior of buried pipelines and tanks, especially in wet clay environments | • Aerobic and anaerobic acid producers<br>• Sulfate reducing bacteria<br>• Iron/manganese oxidizing bacteria<br>• Sulfur oxidizing bacteria |
| Cooling systems | • Cooling towers<br>• Heat exchangers<br>• Storage tanks | • Aerobic and anaerobic bacteria<br>• Metal oxidizing bacteria<br>• Slime forming bacteria<br>• Algae<br>• Fungi |
| Docks, piers, and other aquatic structures | • Splash zone<br>• Just below low tide | • Sulfate reducing bacteria |
| Vehicle fuel tanks | • Stagnant areas | • Fungi |
| Power generation plants | • Heat exchangers<br>• Condensers | • Aerobic and anaerobic bacteria<br>• Sulfate reducing bacteria<br>• Metal oxidizing bacteria |
| Fire sprinkler systems | • Stagnant areas | • Anaerobic bacteria<br>• Sulfate reducing bacteria |

Systems with persistent MIC problems

Investigations of situations where MIC has occurred have established a list of conditions most likely to support the initiation and perpetuation of MIC. It must not be assumed this list is complete. It merely provides a general definition of the environments conducive to MIC.

### *Primary and Auxiliary Service Water Systems*

Service water systems (SWS) are typically constructed using carbon steel, with stainless steel piping used in components directly associated with critical or safety-related functions. Heat exchanger tubes may be stainless steel, copper/copper alloy, or other high-efficiency heat transfer materials. The system components include piping, heat exchangers, tanks, coolers, condensers, open basins, cooling towers, and reservoirs. SWS are open-recirculating, closed-loop, open-loop, or once-through systems. Makeup water includes at least one of all the available sources.

MIC affects SWS functions by reducing water flow due to the massive deposition of corrosion products in piping and heat exchangers, by forming deposits on heat transfer surfaces, or by causing pitting (through-wall failures) at welds, in heat exchanger tubes, and piping. Failures in the SWS may also contribute to MIC in safety-related systems via heat exchanger leaks into high purity cooling water circuits.

### *Condenser Cooling Water Systems*

Main condenser cooling water systems are usually once-through cooling processes. Materials of construction include carbon and low-alloy steels (often coated), with condenser tubes made of a variety of materials, including stainless steels, copper/copper alloy, carbon steel, titanium etc. Selection of construction materials depends on the water source and the water chemistry of the cooling water. Most condenser cooling systems are characterized by extremely high-volume flow rates with little or no recycling of the cooling water.

Fouling of the condenser and deposits on the heat transfer surfaces are critical to the function of the main condensers. MIC is directly associated with the severity of both micro- and macro-fouling, as well as plugging, in condenser cooling systems. Biofouling provides an optimum environment for MIC to exist in the system and MIC provides optimum conditions for fouling to occur by modifying the surfaces of the components, e.g., tube sheets and piping. In certain conditions, through-wall pitting of the condenser tubes has occurred, resulting in system failures.

### *Fire Protection Water Systems*

Microbiologically influenced corrosion causes leaks and plugging of fire protection sprinkler system (FPS) components, often within months of installation. MIC affects all types of FPS and system components and is accompanied by other forms of corrosion, principally those related to the action of oxygen. The principal source of microbes, oxygen, inorganic and organic nutrients for microbial activity are materials left in the FPS during construction and make-up water. Water is added to most FPS frequently, thereby adding new microbes, nutrients, and oxygen on a regular basis. MIC in FPS can be very severe due to microbial and chemical formation of deposits and a generous supply of oxygen, especially to the areas of the FPS closest to the make-up water source. Proper diagnosis and treatment of MIC in FPS requires biological and chemical analyses of water and deposits from the FPS and make-up water to the FPS.

Pipe samples from various locations in the FPS should be examined to determine the distribution and severity of MIC and the chemical nature of deposits and corrosion products. These data will provide information necessary to determine what type of treatment, if any, is necessary to keep or return the FPS to fully functional and safe status. New FPS should be treated to remove oils, dirt, and other materials, which harbor bacteria, provide food for microbes, and shield bacteria from the action of biocides. FPS having existing, advanced deposits and corrosion should be cleaned to remove these materials. All FPS should be equipped with a device to deliver anti-microbial and oxygen scavenging chemicals to the FPS and all water entering the FPS. Traditional treatments using oxidizing biocides such as chlorine, even at levels far in excess of those required to control microbial growth in waters, do not control microbes or corrosion in FPS pipes and, in fact, contribute to general corrosion. This is due to the inability of the biocides to penetrate oils, dirt, and other materials on the internal surface of the FPS components. Tetrakishydroxymethyl phosphonium sulfate (THPS), a biocide used in other industries, has proven to help clean oils, etc. from the pipe surface, kill all MIC bacteria, and eliminate oxygen in water added to the FPS. These actions lead to control of microbes, slimes, deposits, MIC, and oxygen-related corrosion. THPS also has very favorable environmental and toxicity profiles which should make its use in FPS acceptable to authorities having jurisdiction over FPS and water suppliers.

The fire protection system must be maintained in operable condition, prior to and continuously, during plant operation. The systems are typically constructed from carbon steel with some copper/brass or similar alloy components. The pipes (some which may be buried) range in size from over 30 inches to less than 1 inch I.D. Most fire protection systems involve miles of small bore piping. Raw water, treated fresh water, or potable/domestic water is commonly used as makeup for the system. Some plants have modified systems, which include the use of treated fresh water contained or stored in large on-site storage tanks. In terms of its function, the fire protection system is considered a standby system. Therefore, a stagnant status exists in most “wet” systems. This provides an ideal environment for macro- and micro-fouling, as well as for MIC. These problems result in decreased flow at hydrants, hoses, and, in many cases, total plugging of sprinklers. The result is an overall loss of system function and efficiency. MIC has produced through-wall pitting to the extent that total failure of the system occurred.

Photograph showing corrosion on sprinkler pipe

Sectioned head area showing MIC around the weld joint

### *Spray Pond Piping and Tanks*

Many spray pond systems, constructed of carbon or stainless steel, experience severe MIC of the piping and tank components. Intermittent flows and stagnant conditions are typical in these systems. The water is very often a composite of streams from several different sources and often is highly aerated. In many cases, the level of suspended solids is high, and there is a potential for the accumulation of sludge and deposits at low flow sites within the system.

Inoculum may be introduced into the process when the system is hydrostatically tested, often with untreated water, and then left standing until the system is put into operation. During operation, the system is contaminated with MIC microorganisms by the inclusion of untreated waters from other locations in the plant.

Failures due to MIC are usually located at the welds and other “stress” sites in the tank and piping components. Pitting that produces sub-surface cavities in the weld metal are common in carbon steel piping and stainless steel tanks. Occasionally, tubercles and mounds of corrosion products are found on the floors of tanks. Failures of the piping components are relatively non-specific in location. However, the first locations that seem to be attacked by MIC are flanges, weld butts, “stressed” sites, heat-affected zones (HAZ), and sites where deposits and sludge are likely to accumulate.

### *Essential and Non-safety Related Heat Exchangers*

Heat loads from various pieces of plant equipment are transferred to the plant’s ultimate heat sink by a variety of pathways through “essential” and “non-safety related” heat exchangers. The cooling water in contact with the equipment may range from untreated brackish or sea water, to demineralized water, or treated/untreated freshwater, often depending upon the safety function of the equipment in question. Many of the component heat exchangers are subject to standby or intermittent operation. Many are situated where the potential for biofouling or fouling from silt and mud is great.

The smaller heat exchangers, particularly those subjected to stagnant or intermittent flow conditions of untreated water, are particularly prone to severe MIC. The construction materials selected for heat exchangers are based on the need for heat transfer efficiency, specifically for the heat exchanger tubes, and on the material’s resistance to conventional electrochemical corrosion. Copper/copper alloys or stainless steels are commonly used for tubes. Muntz metal, carbon steel, and, occasionally, stainless steels are used for tube sheets. Carbon steel is often used for the heat exchanger shells and tube supports. Unfortunately, no practical criteria exist for selecting materials totally resistant to MIC.

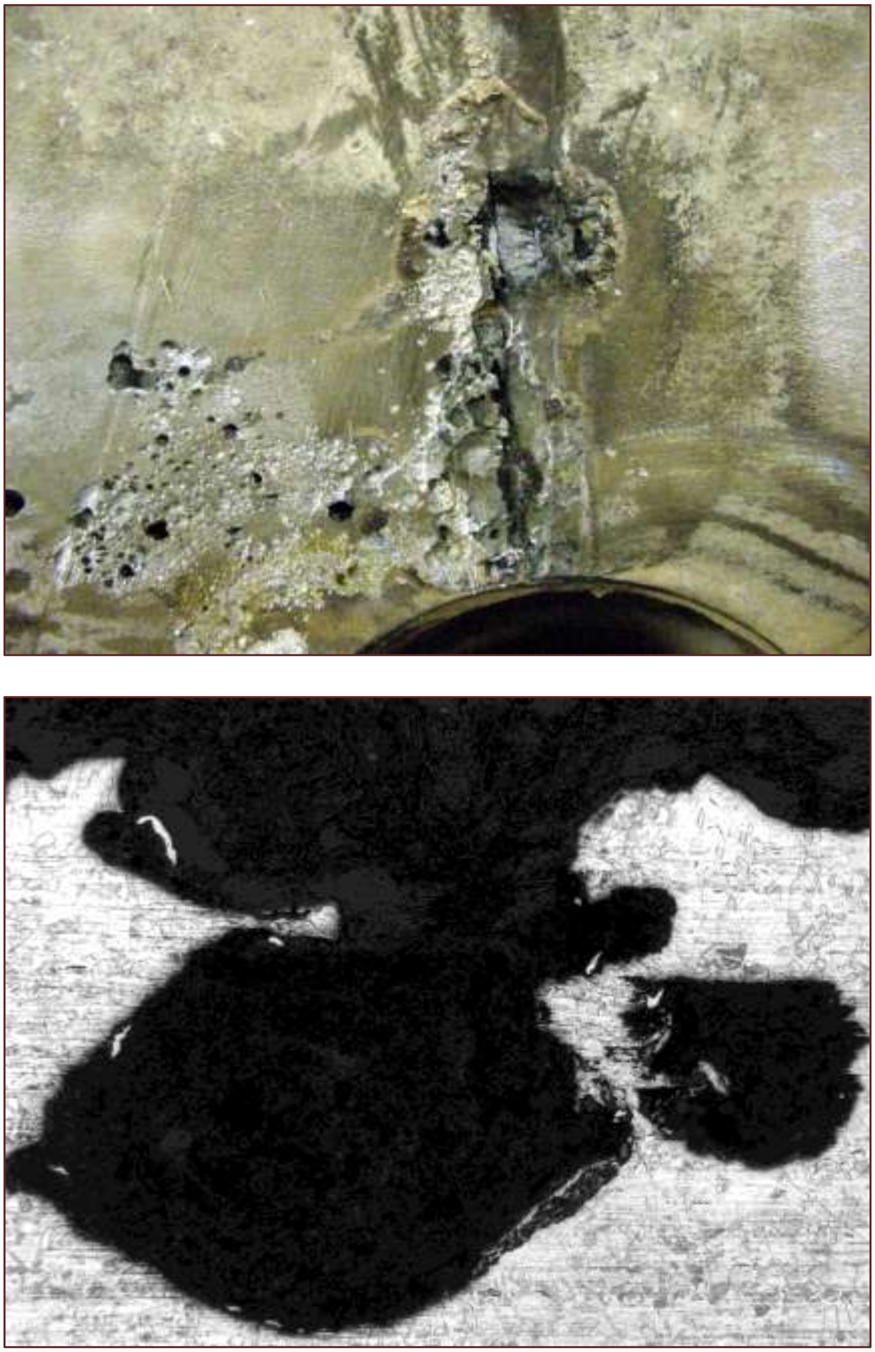
Through-wall pitting of tubes and fouling at the tube sheet area are the most common failures in heat exchangers. Deposition of corrosion products on heat exchange surfaces also result in a loss of heat transfer efficiency. Heat exchanger tube walls and tube/tube sheet joints can be critical boundaries for the separation of high-purity water circuits from the highly contaminated open cooling water circuits in many “essential” components. In the event of a leak in the heat exchanger, contaminated water may be introduced into the high-purity circuit. Corrosion on the high-purity water side would less likely be the cause of the initial leak. (MIC on the contaminated water side could readily be the cause of the leak.) However, because of the leak and subsequent contamination of the high-purity water, MIC must be considered a potential problem in high-purity water circuits.

### *Seawater Service*

In seawater macro-fouling is building up of oysters, barnacles, mussels, tube worms and the like. The immersion of stainless steels, as well as any kind of material, in natural seawater induces the development of a microbial film called biofilm, which is established after 1-3 weeks. The biofilm can attach to any material in seawater and macro-fouling helps this process.

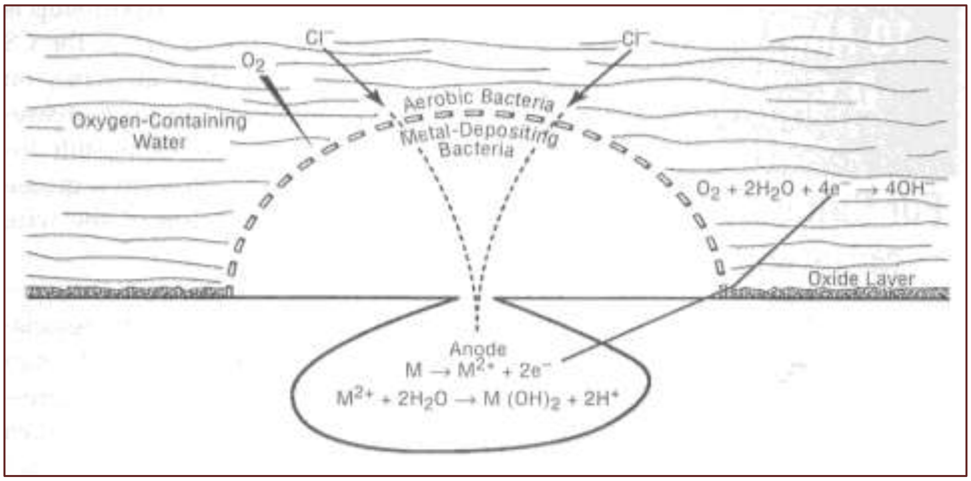
The activity of the micro-organisms in the biofilm causes the electrochemical open circuit potential of the stainless steel to increase. This increase is called potential ennoblement that will increase the risk of crevice corrosion or pitting if the resistance to pitting and crevice corrosion of the steel grade is exceeded.

The presence of an active biofilm on the stainless steel surface may result in that the seawater is more corrosive at temperatures below 35-40ºC (95-104ºF) than at a few degrees in temperatures above, and the seawater becomes more aggressive as the temperature dependence in corrosivity develops. MIC of stainless steel is characterized by pitting, most commonly at weldments. The weld areas are favored MIC failure sites because their dual structure and alloy segregation make them more susceptible than the base metals. Small leaks resulting from though-wall pitting is the most common consequence of MIC of stainless steels. Pits often exhibit very small entrance and exit penetrations, with very large subsurface cavities and pitting occurring under tubercles. Although not clearly defined, austenite and delta ferrite phases are preferentially more susceptible to attack.



Photographs showing typical MIC attack around a stainless steel weld and corresponding pit morphology

Mechanisms for MIC are different for stainless and carbon steels. Therefore, attempts to upgrade carbon steel systems with 304 or 316 type stainless steels to alleviate MIC problems have often been ineffective. Failures in carbon steels are often attributed to SRB and acid-producing bacteria (APB). Failures in stainless steels are most often due to the formation of differential aeration cells resulting from the activities of metal depositing bacteria. These organisms create environments that are conducive to corrosion, especially on metals that are prone to crevice corrosion. Dense deposit of cells and metal ions create oxygen concentration cells that effectively exclude oxygen from the area immediately under the deposit and initiate a series of events that are extremely corrosive.



Possible reactions under tubercles created by metal depositing bacteria

### *Oil and Gas Industry*

Microbiologically influenced corrosion is a big concern in the oil and gas industry. MIC pitting attacks tend to result in reservoir souring, equipment and pipeline failures that are of great problems in oil field. Collection of sulfate-reducing bacteria (SRB) is almost always the responsible factor for these problems. SRB are nonpathogenic and anaerobic bacteria, but SRB can act as a catalyst in the reduction reaction of sulfate to sulfide. It means they are able to cause severe corrosion of metals in a water system by producing enzymes, which can accelerate the reduction of sulfate compounds to $H_2S$. However, for this reduction to occur, three components namely SRB, sulfates, free electrons as an external energy source must be present and the water temperature must be less than approximately 65°C. Stainless steel and carbon steel are the most commonly exploited materials in the petroleum realm which are known to undergo MIC.

### *Hydrostatic Test Water*

Hydrotesting is a routine test in industry to check for leakage and weld joint integrity in systems that will operate under pressure. The test entails introducing water into the system and applying internal pressure to some factor of the operating pressure. Hydrotesting typically uses untreated water, which may carry corrosion enhancing bacteria. Special emphasis should be made for the selection of hydrostatic testing water with regards to preventing MIC. A system's first encounter with conditions that may lead to MIC usually occurs during its initial exposure to an aqueous environment, such as during hydrotesting. There are numerous case histories that illustrate severe MIC problems, which occurred as a result of ignoring the quality of the makeup water used for hydrostatic tests and other pre-operational activities. The water sources for hydrostatic tests are not necessarily limited by plant or component design. Therefore, very few excuses exist for using makeup water with an undesirable quality that would contribute to potential MIC. Those quality factors that are important for hydrostatic testing are the same as those to be considered for operational makeup waters. If the available sources are not of adequate quality, provisions for treatment should be made available. Treated hydrostatic test water may be stored on site and reused as required. Use of a high quality water for hydrostatic and leak testing is critical to preventing MIC. There are other factors that are also important.

One of these relates to how well the system or component was cleaned prior to adding the test water to the process. Often, if there is residual debris in the system, it can be transported to a site where it accumulates and provides an optimum environment for MIC. Provisions must be made to prevent this from occurring or to have the capability of purging these materials following testing.

System design is another factor that plays an important role during hydrostatic testing. Hydrostatic testing is usually done in stages, where each segment of the system or individual component is tested as construction is completed. The system must be designed in such a way that individual segments can be drained completely and dried immediately after hydrostatic testing. Segments should not be allowed to stand idle even for only a few days with test water still in them. Tanks and vessels should be completely drained after leak testing as well. The design of these components should enable them to be completely drained. This means that any standing water below the drain point should also be removed. Planning and scheduling the hydrostatic testing sequence must take into consideration how long the system will stand idle after hydrostatic testing and before the normal operation. Every effort should be taken to do the testing as near as possible to the time when the process will be put into operation. When it is known that an extended period will occur between testing and startup, appropriate measures to reduce the potential for MIC must be taken. The ideal situation, as pointed out, is to drain and dry.

Chemical treatment of the testing water also provides some degree of assistance in preventing the initiation of MIC during hydrostatic testing, especially when the considerations mentioned earlier cannot be managed to the extent needed to prevent MIC. However, it must be re-emphasized that water treatment alone should not be expected to reduce the potential for MIC to zero.

Pitting corrosion failures in austenitic stainless steel tanks and piping systems are often misdiagnosed as attack caused by conventional chloride crevice/pitting corrosion. Rapid failure rates with extremely localized attack at weld regions should be investigated thoroughly with microbiological analysis techniques to determine the root cause of the failures.

## INFORMATION NEEDED to DETECT and IDENTIFY LOCATION OF MIC

Ideally the MIC specialist should have enough information available to confidently state, “If MIC was to occur in this system, it should first appear at these sites.” It would then be possible to monitor those sites on a routine maintenance schedule to ensure that preventive MIC procedures are functioning. If already established, the MIC can be mitigated while mitigation is still practical, using the most effective and appropriate procedures. The information required for this ideal scenario would include the following sources discussed below.

*Comprehensive/Current System Diagram of the Water Flow from Makeup through Discharge*: Initial engineering prints, etc., may not be adequate, especially if there have been revisions and maintenance work done on the system since it was put into service.

*Materials of Construction*: Most all materials of construction are subject to MIC. However, it is important to know materials of construction of various components to help define MIC if it should occur. This will help locate potential sites based on degree of susceptibility to MIC.

*Fabrication Methods*: The method of fabrication of a specific component may relate to the susceptibility of the component to MIC attack. Information about welds, “stress bends,” flange torqueing, pipe threading, butt vs. socket weld joints, etc., are some of the factors about fabrication methods that can be useful to locate potential MIC sites. Background information related to the presence of coating materials existing on surfaces in the system is useful. When and how the coating was applied (i.e. factory or field applied), and the condition of the surface to which the coating was applied, would be of interest.

*Operating History*: A detailed operating history of the entire system and of individual components of the systems is useful. The data should include information on the hydrostatic testing, stagnant flow, low flow velocities, intermittent flow, lay-up procedures, standby or intermittent operation, and routine operating time. Maintenance records dealing with repair or replacement of system components should be part of the history. Reviewing component operating/function efficiency yields interesting insights into predicting potential MIC situations. The MIC specialist should be aware of all changes or deviations from normal operation that have occurred. Routine photographic records should be made of selected internal sites of the system, taken whenever the opportunity for visual inspection arises. Any history of mechanical or chemical cleaning operations and any potential modification of the internal surfaces of components (e.g. brushing of tube surfaces) can be important in the characterization of non-conformance situations and assessing if MIC is involved.

*Water Chemistry*: It is sound practice to make routine analysis of makeup water chemistry. Analyses can be made of samples taken at the intake, immediately upstream and downstream of critical components, and at discharge from the system. Factors to determine include; pH, Turbidity, Calcium Hardness, Sulfates, Residual concentration of treatment chemicals (if used), Alkalinity, Total Hardness, Chlorides, Phosphates ($PO_4$), Conductivity, Total soluble iron Manganese, Nitrite (nitrate). Other factors to determine periodically include; Total organic carbon (identify the source of TOC), Metal sulfides (or sulfide ion concentration if it exists), Total organic nitrogen (identify the source of N), Oils and greases, Total sulfur, Identify composition of suspended solids, Equate oxygen concentration to water temperature at intake and discharge.

The cumulative data from these tests should be reviewed quarterly to identify any significant changes in water chemistry and to determine if seasonal variations significantly affect the microbiological equilibrium in the system. When diagnosis of a non-conformance situation (root cause failure analysis) is necessary, the water chemistry data is useful in determining whether the corrosion could be due to non-microbiological causes. Tests trended over a long period of time provide data of the frequency and extremes of variations that occur. They also tend to substantiate the values obtained at any given time. Any operational or environmental condition that is unique to a specific site in the system should be identified. Important conditions include locations where sludge or suspended solids accumulate, local anaerobic or oxygenated sites, chloride or sulfide cell concentrations, isolated areas of high or low pH, sites of extreme redox potential, areas of malodors, etc.

*Biological/Microbiological History*: A one-time characterization of the microflora in bulk water samples taken at various locations in the system does not provide useful information for characterizing non-conformance situations. However, repeated microbiological surveys made over an extended time period will provide insight into trends or changes that occur in the total microflora of the bulk water. This microbiological history can be correlated to periodic visual inspections of the system and to other operational data that are related to potential microbiological problems, such as slime formation, plugging/fouling, and MIC. Specific tests for determining the presence of those microorganisms known to be involved with MIC should be done. This may include testing for the presence of SRBs, metal oxidizing bacteria, slime-formers, etc., in the bulk water and the makeup water. These tests will indicate whether the inoculum source for MIC exists in the system. However, these tests will not indicate the existence of MIC. Changes in the microflora may indicate that changes in the environment have occurred which might have an effect on increasing the potential for MIC.

Periodic testing at several different locations within the system will help identify specific locations where the potential for MIC problems is greatest. It should be emphasized that microbiological data alone cannot be used to make assumptions on the presence of MIC. It must be correlated with other observations and tests. It does, however, provide supportive information that can be used to characterize a non-conformance situation and help answer the question, “Is this MIC?”

*Historical and Current Treatment Program for Microbiological Control*: A review of the past treatment programs for microbiological control helps interpret current conditions. Precise documentation of what the treatment programs were (i.e., what chemicals were used, how much, where added, what frequency, what were the results, etc.) is needed. Similar information about the current treatment program should be available for review. In many situations, information relating to scale and corrosion control treatment programs will provide supporting information important to successfully characterizing MIC.

## POTENTIAL PROBLEMS and COMMON MONITORING ERRORS

### *Water Quality Parameters*

Water quality parameters important to MIC are sometimes ignored. It is crucial to measure all parameters relevant to the growth of microorganisms, including temperature (especially wall temperature), pH, nitrate, phosphate, sulfate, suspended and dissolved solids, organic carbon, iron, turbidity, and microorganisms (bacteria, algae, and fungi). Dissolved oxygen often is not helpful because it gives misleading data about microenvironments where corrosion may be occurring. Biofilms can sequester anaerobic bacteria in waters supersaturated in oxygen. Additional parameters may be measured in specific systems, for example, sulfide, nitrite, and ammonia. Changes in these numbers should be cause for concern.

### *Measuring the Wrong Organisms*

The classic mistake is to measure only planktonic bacterial numbers, which repeatedly have been shown to have a very poor correlation with sessile bacteria on metal surfaces. Microbes sometimes are measured for convenience, not for their importance as potential corrodants. SRB's are not the only important corrosion-causing organisms, although they have been given a lot of attention.

### *Incorrect Sampling of Planktonic Organisms*

Planktonic bacteria can provide useful data but only if measured consistently. Samples should be collected from the same place, incubated for the same time, at the same temperature, and counted by the same operator. Errors introduced by changing these variables are so large they can mask any changes in the system, rendering the monitoring program useless. This important point is often overlooked by the technicians in the field. The culture medium used should not be changed unless strictly necessary. There is a very poor correlation between bacterial numbers counted using different commonly used culture media and the resulting differences are not consistent or predictable. Microorganisms grow selectively on various media, so it is necessary to use several culture conditions appropriate for a wide variety of potentially corrosion-causing microbes, including general aerobic bacteria, sulfur-oxidizing bacteria, sulfur producing bacteria, fungi, algae, and any other groups that have been suspected of being a problem in the system.

### *Sampling Organisms in the Wrong Location or for Insufficient Time*

Sessile bacterial numbers may not be sampled in areas most susceptible to corrosion problems. The most successful monitoring programs include removable, in-process probes. Similar side-stream devices also have been successful and have the additional advantage that biocide levels and process conditions can be altered experimentally under controlled conditions, giving reasonably fast and reliable information on their effects on the system. Monitoring should be carried out over a long period. Large seasonal and annual changes can occur in bacterial counts and in bactericide demand.

### *Ignoring Direct Examination of Surfaces During Shutdowns*

Examination of metal surfaces during planned or unplanned shutdowns is an often ignored but extremely important component of biological corrosion monitoring. Direct examination of equipment surfaces is the best method to determine the success or failure of biocide programs. As soon as vessels, equipment, pipes, etc. are opened, samples should be collected before the system has a chance to change in condition. MIC-monitoring technicians should be the first people into the equipment before it dries out and/or contaminated by exposure to air and other activities.

### *Incorrect Measurement of Biocides*

Biocides often are incorrectly and inaccurately measured. The most common biocide used in industry is some form of chlorination. Biocides are typically added automatically according to fixed schedules or by dosing pumps. Dosage information, however, gives few details on the amount of effective biocide received by the system, particularly with oxidizing biocides. So many intangible factors affect the chlorine/bromine demand that the residual free chlorine/bromine delivered to the system rarely is predictable. This is particularly important for chlorination because chloramines have poor biocidal properties compared to free chlorine. Changes in weather, sunshine, temperature, organic content, pH, etc. affect the ratio of residual free chlorine to total chlorine. Therefore, it is necessary to measure free residual biocide in the system. The half-life of chlorine is extremely short. Inexperienced plant operators often make the error of not measuring the chlorine in a water sample as soon as it is taken. If samples are collected and taken to the laboratory to be measured after half an hour or more, the numbers obtained may be meaningless.

### *Failure to Correlate Biocide Dose with Microbial Counts and Corrosion Rates*

Another obvious but curiously common error in biocide efficacy monitoring is the failure to correlate microbial numbers or corrosion rates with biocide dosage. Microbial numbers must be checked before, during and for frequent periods after biocide addition. Corrosion rates from coupons should be measured during new biocide regimes to ensure effectiveness of the program.

### *Errors in Estimating Corrosion Rates*

The major difficulty with corrosion monitoring is that there are no quick, reliable methods to measure corrosion by microorganisms. Electrochemical methods have been tried repeatedly, however attempts to use them in the field have met with limited success and do not generally repay for the expense, effort and time required for reliable predictability. Electrical resistance and linear polarization techniques are not particularly efficient at detecting localized corrosion and MIC, and are not recommended. Electrochemical noise and impedance methods have been found to be better for monitoring corrosion by MIC, but are difficult to interpret. Ultrasonic thickness testers are good at measuring pits, but only if the pits are found. In stainless steels, only one aggressive, through-wall pit is necessary to cause a leak, even though it only constitutes a fraction of a percent of the total surface in the system. The most reliable techniques seem to be corrosion and fouling coupons. These must be carefully placed in the process stream or in representative side-stream conditions. The most common error with side-stream devices is that they are maintained at incorrect flow rates, temperatures, or other conditions that do not represent the worst-case scenario present in the system.

## IDENTIFYING and DIAGNOSING MIC

Determining the cause of a corrosion site can be an involved and multi-step process. Visual examination is the first step and should reveal the characteristic colors and deposit texture associated with MIC. Verification continues with different levels of microscopic examination. Assuming the sample is properly taken, a chemical analysis should reveal the presence of chlorides, sulfides, manganese, iron salt complexes, etc. that are typical for MIC. Field and laboratory culturing procedures are also used to isolate and identify the presence of MIC causing microorganisms. A metallurgical analysis can also be performed which would provide additional data to help determine the cause of the corrosion deposit. The results of all these steps should be considered when making a conclusion as to the cause of the corrosion site.
To answer the question "Is this MIC?", the foregoing discussion emphasizes that confirming data in three categories must be obtained. These are:

- Visual appearance (it must look like MIC)
- Microbiological involvement ("MIC bugs" must be present at the site); and
- Chemical data (analysis must detect materials associated with MIC mechanism).

### *Physical Appearance (Visual examination)*

The physical characteristics of many types of MIC can be detected by sight, smell, and touch. The appearance of MIC is often sufficiently different from non-microbiological corrosion to make the distinction between the two. The general appearance of the non-conformance site, including the size and shape of the associated deposits, the appearance of the anodic sites (pits and laterally corroded surfaces), the color of the deposits, the color of the base metal beneath deposits and at the corrosion site, the presence of specific odors, and in many cases, the location of the non-conformance can be indicative of MIC. The diagnosis of MIC by visual examination is more difficult when the MIC is associated with non-microbiological electrochemical corrosion. In these situations, it is necessary to employ every available technique in assembling the data and information required to diagnose MIC. The possibility must also be considered that the failure may have been initiated by microorganisms, but the corrosion occurring at the time of the examination may not be due to microbiological activity. Under these circumstances, very often, the evidence of microbiological involvement is obscured or eradicated.

Visual inspection will disclose certain characteristics consistent with MIC. For example, SRBs produce a characteristic black deposit of metal sulfide on carbon steel and stainless steels. Carbon or low alloy steels often have shallow pits covered by a hard crust (especially if the deposit has dried), with a soft powdery black paste inside or beneath the crust. A pit and black iron sulfide, surrounded by a dark outer ring and a shiny bluish ring, with shiny bare metal beneath, are associated with SRB surface attack of stainless steel. Without SRB growth, the existence of sulfides in most environments would be highly unlikely; thus appearance related to sulfides is probably MIC related.

The deposits produced by iron oxidizing bacteria typically result in the development of orange or reddish brown tubercles on the surface of carbon steel. At sites of low flow velocity or in areas protected from shear forces, “stalks” produced by Gallionella are often observed. The tubercles are generally hemispherical or conical in shape, often less than 1/4 inch high, but can be much larger (occasionally, the size of a golf ball).

Photograph showing tubercle formation in a water line

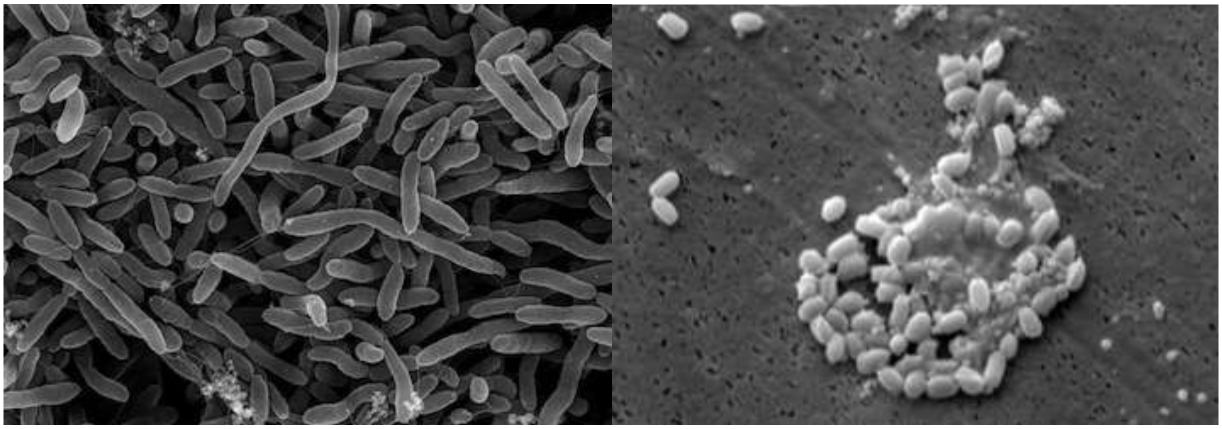
In pipe and other sites of constant water flow, the individual tubercles can grow together into a large mass where the individual tubercle shape is lost. A concentric layering effect can often be seen when discrete smaller tubercles are picked off the metal surface and the underside of the tubercle is examined. A matching pattern of concentric rings is occasionally seen on the metal surface from which the tubercle was removed. A cavity in the undersurface of the tubercle is typical. Occasionally, the cavity is covered with a white or tan material. The cavity inside the tubercle can also be observed through the top, without removing the tubercle from the metal surface, when the crust is ruptured. Corrosion of stainless steel due to MIC usually results in rust-colored streaks emanating from the penetration and staining the surfaces near the penetration. Through-wall penetrations or pitting of copper and copper alloy due to metal oxidizing bacteria, such as Siderocapsa sp., is characterized by the lack of an accumulation or deposition of corrosion products.

***Microscopic Appearance***

The use of a stereomicroscope at magnifications of 4 to 40X increases the capability of visually distinguishing the unique characteristics of MIC as compared to non-microbiological corrosion. It is important to observe the specimen as soon as possible after the system is taken out of operation. Some stereomicroscopes are designed to use for examination of specimens in place, not requiring the affected component to be disassembled and brought into the laboratory. In other cases, it may be necessary to remove the specimens and bring them to the laboratory. In these situations, the specimens should be kept wet, preferably with the actual water from the process, and examined as soon as possible. If the microscopic examination cannot be done within 8-12 hours, the specimens should be allowed to air-dry and then wrapped or enclosed in plastic film.

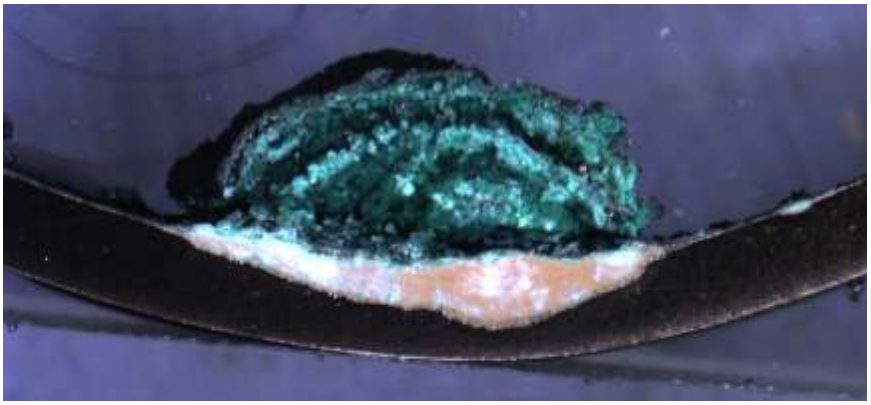
Samples of the materials adhering to the surfaces of the specimens should be removed and placed into separate air-tight sterile plastic bags. These will be examined by using a compound microscope at magnifications up to 1500 X. When removing the specimens from the system, the use of cutting torches or any other procedure that would heat the specimen, should be avoided. Cooled metal saws or “hack” saws are preferred. The compound microscope can be used to detect the presence of those specific microorganisms known to be involved with MIC. The development of tubercles by bacteria, such as Gallionella sp., can readily be identified by microscopic techniques.

In many cases, the presence of SRBs, such as Desulfovibrio sp., can be confirmed by the direct microscopic examination of the fluid found in pits or embedded in sludge collected at the corrosion site. Filamentous bacteria, such as Sphaeratulus sp., can be readily identified by microscopic examination. The presence of certain types of sulfur-oxidizing bacteria can be detected by examination of materials collected at the corrosion site. Confirmation of the presence/origin of biofilm or slime, as produced by bacteria such as Siderocapsa sp., can be done by microscopic examination.



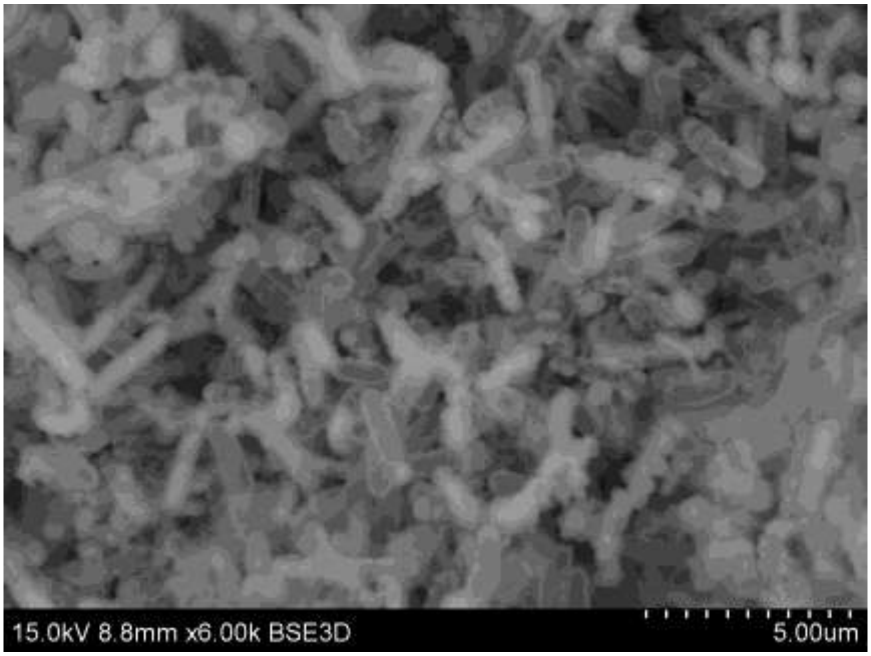
Desulfovibrio (left) and Siderocapsa (right)

SEM and radiographic procedures are useful when characterizing the surfaces of MIC sites. It is possible to define the appearance of the corrosion site and relate it to that typically associated with MIC. SEM defines the location and morphology of any attack on the metal surface. Examination of a cross section of a corrosion site illustrates the nature of the attack, particularly a pitting type attack. The general morphology of the pits (e.g. round vs. angular or flat bottomed); the shape (e.g. small entry and exit holes with bulbous cavities beneath); and any change in direction of pit propagation can be noted. Intergranular attack or preferential attack of one phase, such as attack of austenite or delta-ferrite in stainless steel welds, is readily characterized with SEM.



Typical MIC Pit Morphology

Scanning electron microscopy can be used to characterize specific microorganisms found at the MIC site. However, optical microscopy is generally considered adequate to characterize the microflora, as it exists naturally. Very often, the techniques used with sample preparation for SEM examination distorts cell structure to the point where direct observation of the microflora is not possible.



Electron Microscope Image of Rod-shaped Bacteria Found in a Corrosion Pit

***Sampling Suggestions***

It is important to make microscopic examinations as soon as possible after the specimen is removed from the system. The deposits should not be allowed to dry. Care must be taken not to contaminate the specimens when removing them for examination. Deposits resulting from microbiological growth generally feel slimy or are soft and pliable, in comparison to non-microbiological oxides or mineral deposits. Detailed descriptions of where and how the deposits were collected should be recorded. This information is required to make valid interpretations of the observations made with both the stereoscope and the compound microscope. Photomicrographs of the observed specimens made from the microscopic examinations are useful in the interpretation of the results of the examinations.

### *Microbiological Culturing Data*

As part of the total data assembly required to detect and identify MIC, it is important to confirm that microorganisms known to be capable of MIC involvement are, or have been, part of the sessile microflora at the corrosion site. This can be determined by using selective microbiological "swab culturing" methods from samples collected at the site. Sessile microflora relates to that microbiological community that adheres to the surface involved in corrosion. The presence of these same types of microorganisms in the bulk water (planktonic microflora) does not necessarily confirm that the corrosion is MIC. The selective isolation techniques should include those which will detect the presence of the following:

Metal (iron/manganese) oxidizing bacteria
Nitrite oxidizing bacteria
Aerobic/anaerobic-acid producing bacteria
Fungi
Sulfide producing bacteria
Slime-forming bacteria
Nitrate reducing bacteria
Aerobic ammonia producing bacteria
Sulfate reducing bacteria
Clostridial spore forming bacteria

The sessile bacterial count as well as planktonic count should not be overlooked. When a system is infected with corrosion-enhancing bacteria, these bacteria would like to find the nutrients already floating in the water. That is why bacteria in this state are called “planktonic” or floating, since they are receiving most of the required nutrients while they are simply swimming around in the system. In this case, they are not doing significant harm to the system unless their by-products can change the electrochemistry of the system locally. When these nutrients become scarce, however (say, by precipitating on the nearby surfaces under their weights), the bacteria will also accumulate on the surfaces to “dwell on the food.” In this state the bacteria are not in their planktonic state anymore and are referred to as “sessile bacteria.” Most of the damage from MIC comes from sessile bacteria. So, to monitor your system in the most ideal way possible, you need to know the condition (numbers) of both planktonic and sessile bacteria-a sudden increase in the number of the planktonic bacteria is a sign of the start-up of system contamination.

Sampling sites must be selected to obtain representative samples. Ideally these sites should be swabbed immediately after draining, or when the component surfaces are still moist ("as-found" condition). When sampling sites that are associated with sludge and/or biofouling, swabs should be made of both the outer and inner mass of the deposit. Unless multiple sampling sites at relatively similar environments can be done, it is necessary to take replicated samples at the available site.

### *Chemical-Physical Analysis*

Under ideal situations, the aqueous environment will be defined in detail prior to any investigation. If MIC specialists will sample the bulk water at the water intake point and at locations immediately before and downstream of the suspected MIC site, at the time when the investigation is done, they will obtain optimum background information. Random grab/composite samples are satisfactory for general water chemistry determinations.

After the suspected MIC site has been examined visually and microscopically, as discussed earlier, samples should be removed for detailed chemical and physical analysis. Typically, items of interest are deposits, tubercles, and quantities of the adhering corrosion products located at the corrosion site. Removal of these specimens requires care in ensuring that the material is not physically damaged nor chemically contaminated. No water or other fluid should be added to any samples. If the sample is dry upon removal, it should be kept dry. If wet, the sample should be kept moist by adding a wet paper towel to the sample container. Either water from the sample area or sterile distilled water should be used as the moisture source.

Chemical analysis of deposits and other materials collected at the corrosion site, used in conjunction with visual observations and historical information of the suspected MIC site, provides creditable data toward confirming MIC. MIC leaves a particular unique set of chemical and physical fingerprints that, when analyzed, can be used to determine whether the non-conformance was MIC or not. Elemental analysis by any of several techniques, such as X-ray fluorescence, energy dispersive X- ray spectroscopy, atomic absorption, ICP, etc., in conjunction with specific wet chemistry techniques, provides useful insight into the cause of the corrosion. Determination of the amount of organics by "weight-loss on ignition" and by total organic carbon analysis indicates the degree of potential involvement of microorganisms in the process of the deposit formation (an organic carbon content greater than 20% indicates likely microbiological involvement). Accumulation of certain compounds (e.g., manganese, chlorides, copper, organo-phosphorus complexes, etc.) coupled with a high iron salt complex, such as ferrous carbonate, hydroxide, or phosphate, would indicate that iron-oxidizing bacteria are implicated in the formation of the deposit. A high sulfur content, the presence of iron sulfide, the release of hydrogen sulfide when acidified, the presence of black slimy deposits, or the existence of a characteristically yellow deposit, are usually associated with the presence of sulfate-reducing or sulfur-oxidizing bacteria. When a properly collected and maintained sample exhibits a very low organic content and essentially no concentration of sulfur, chloride, phosphide, or phosphate (as compared to the base metal and/or the water analysis) is evident, MIC is unlikely to be a contributor to the corrosion.

## DESIGN CONSIDERATIONS

The most effective approach to MIC control is through MIC prevention. During construction or retrofit, flow rates, water chemistries, bypass lines, etc. should be considered to reduce system susceptibility to MIC. Fire safety water systems deserve special consideration for make-up water, chemical treatment, periodic testing, purging, etc. Along with appropriate design considerations, the materials used in construction should be carefully chosen to match service conditions and for MIC prevention.

System design (whether re-design of an existing system or an original design of a new plant or system component) must incorporate sound engineering concepts for total corrosion control. This includes MIC prevention considerations. Items to be coordinated into the total system design include elements from pre-construction engineering, the construction phase, pre-operational phase, hydrostatic testing phase, operational phase, and preventive maintenance. Important factors incorporated with each of these items are:

- Consideration of source water chemistry (including pH, salinity, hardness, levels of suspended solids or turbidity, organic contamination)
- Typical temperature ranges
- Flow rates (including the increase/decrease of flow rates within a single circuit)
- Type of operation (continuous, intermittent, normally stagnant)
- Once-through vs. Closed-loop circulation

Original system design and system re-design must include provisions that allow accessibility for cleaning and implementation of water treatment programs. Neither of these considerations should be dealt with as "afterthought" factors. Stagnant or low flow conditions provide optimum environments for the growth of microorganisms and subsequent corrosion. These flow conditions also make it more difficult to use traditional microorganism control procedures. Where possible, the system design should provide control of the flow velocity within a range that will serve as a limiting factor to the growth of microflora. Generally, this would involve a lower limit on flow velocity to the extent that suspended solids will remain suspended in the bulk water stream. Continuous flow is preferred to intermittent flow conditions. Dead legs and bypass circuits should be avoided wherever possible. Do not allow "dead-spots" in the design of your system, which will cause the water's velocity to fall below 1.5 m/s. This water, literally referred to as "stagnant water," will provide an ideal environment for the bacteria to grow and develop biofilm and extra-cellular material, which can help entangle chemicals that can then serve either as nutrients to the bacteria or establish electrochemical cells. Biofilm has also been held responsible for developing oxygen gradients that lead to the formation of differential cells where areas of low oxygen partial pressure (established mainly under the biofilm) will constitute anodic sites from which corrosion in the form of pitting will commence.

When they are required and when standby components are part of the system, the system design should include provisions for drains, traps, recycle circuits, monitoring equipment, and the capability to permit periodic draining and cleaning when necessary without interrupting the operation of the system. Design details should consider those local sites likely to create optimum environments for microorganism growth. When possible, the design of these sites should be changed. For example, crevices generated by weld-backing rings may act as a means to trap accumulations of organic and inorganic deposit-forming materials. These crevices can be eliminated with proper design.

Provisions should be made for circulating water periodically (or flushing the system) in those components that typically remain stagnant for long periods of time, such as fire safety water systems. Side-stream filtration and in-line filters/screens should be included in the design when it is known the water flow will contain high levels of suspended solids. Provisions must be made, to purge accumulations of suspended solids from the system when it is not possible to prevent their existence. Facilities for planned maintenance and routine "housekeeping" procedures should be developed, and the system design should include considerations of effective implementation of this type of preventive maintenance. System design should consider the need for periodic removal of deposits by physical or mechanical cleaning. This involves providing access ports for the insertion of pigs, air-bumping, or hydrolasing equipment. System design should also include the development of a totally coordinated water treatment program, which includes corrosion control, scale and deposit control, and microorganism control (i.e., slime, plugging/fouling, and MIC). The system design must provide facilities where the water treatment program can be implemented in the most effective manner possible. Included with these facilities should be equipment that monitors the control-parameters used in the water treatment program and detects any variation from the criteria on which the water treatment program is based. Designed processes that provide the capability for on-line cleaning of those isolated components that are particularly susceptible to biofouling or MIC also must be considered, especially when there are no other alternatives to prevent potential problems. Serious consideration to the use of closed-loop design should be made for those circuits with high susceptibility to MIC and with serious failure consequences.

In a closed-loop, contaminants can more readily be controlled, and chemical treatments can be used because they are less restricted by environmental effluent limits. This approach, although initially more costly, may prove to be, in the long run, the most economical approach for preventing MIC for safety-related or critical components. Within fire safety water systems there are certain design considerations that should be included for purposes of preventing MIC. These include:

- Eliminate the possibility of non-essential use of hydrant water, which will reduce the need for adding makeup water to the system
- Include a makeup water reservoir which facilitates chemical treatment of the system
- Design the capability to purge suspended solids for the bulk water via bypass circulation and side-stream filtration
- Design facilities that enable monitoring and inspecting the system for potential or existing MIC.

### *Materials of Construction Selection*

The selection of those materials used in construction is usually done without direct consideration of MIC prevention. Other criteria, including the initial cost of the materials, were given a higher priority. It was believed that in many systems, MIC could be controlled through proper water treatment, i.e., the use of biocides, dispersants, and corrosion inhibitors. This was particularly true, and may still be true, in closed-loop and recirculating systems. However, in open-loop and once- through systems, such as raw water or service water systems, chemical treatment alone is not adequate to prevent MIC. It very often proves to be economically impractical and difficult because of the increased limitations on water treatment due to environmental restrictions. Consequently, in once-through systems, proper selection of construction materials has become more important. Materials selection alone though is not usually sufficient to assure prevention of MIC. This criterion must be combined with proper system design and an effective coordinated water treatment program. Still, appropriate material selection can provide a margin of resistance to MIC and complement other preventive measures.

It is recognized that no materials can be assumed to be totally resistant to MIC. Resistance exists as a manner of degree and is related to the environment and service of the materials. For example, titanium (and possibly zirconium and tantalum) does appear to have a greater degree of resistance to MIC than other commonly-used materials of construction. However, the cost, susceptibility to biofouling, and other metallurgical properties have limited their use.

Stainless steels exhibit an inherently greater degree of resistance to general electrochemical corrosion in most service situations as compared to carbon or other low-alloy steels. However, numerous case histories have illustrated that MIC can be significant at weldments, in heat-affected zones, and crevice sites in stainless steel components. Most cases of MIC on stainless steel are characterized by the formation of pits or “tunneling,” most commonly at weldments, crevices, and other stressed-metal sites. The metal loss is often associated with attack of the weld material near the fusion line or with sensitization in the heat-affected zone (HAZ). Base metal attack is much less common. Two-phase weld metal appears to be the most susceptible, although the relative susceptibilities of austenite and delta ferrite phases have not been clearly defined. The severity of stainless steel corrosion is difficult to assess visually until component failure has occurred. This is because the pits and metal loss are sub- surface and result in “cavities or tunnels” within the wall of the component. Extreme severity is represented by through-wall penetration, leaks, and loss of structural strength.

In systems where the water is relatively corrosive, independent of MIC, iron loss to the system from stainless steel upstream will be less than for carbon steel. Also, microorganism tubercle formation will be less, and fouling due to corrosion by-products will be less. In spite of these factors, MIC of stainless steel must still be considered a major concern because failures, when they do occur, are highly localized and take place within a relatively short period of time. The MIC of stainless steel often results in weld/structural strength loss, through-wall pitting, and leaks. Recognizing these facts, materials selection should consider the use of alternate filler materials for welds (fully austenitic, iron, or nickel based), or additional preventive treatments, such as cathodic protection. Substitution of stainless steel for carbon steel typically will only “buy time” relative to failure resulting from MIC. Substitution of a “lower-alloyed” material (e.g., copper-nickel) for a presumably more resistant alloy (e.g., nickel and Monel) has, in many cases, increased the degree of MIC resistance, but it has not provided total MIC prevention.

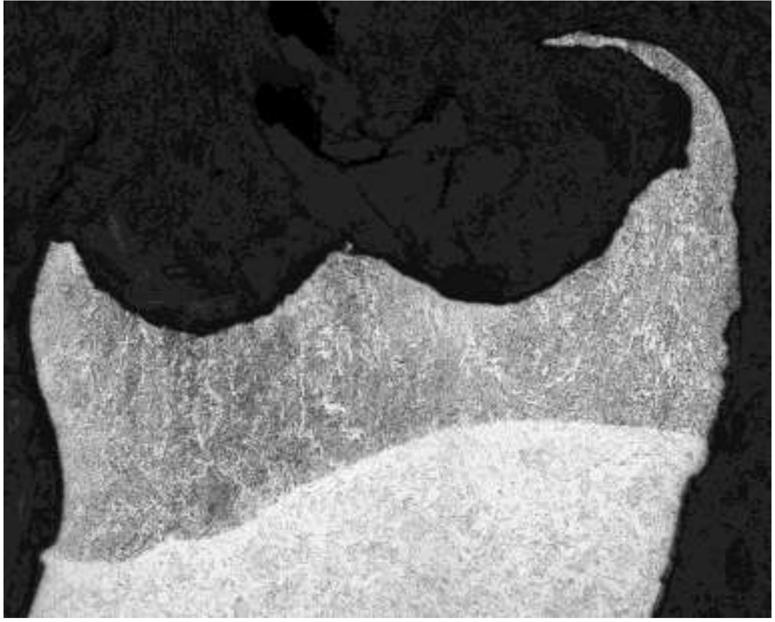
Aluminum Alloys: Corrosion resistance of aluminum and its alloys is due to an aluminum oxide passive film. Anodizing produces thicker films and better corrosion resistance. This oxide film can be attacked locally by halide ions. The susceptibility of aluminum to localized corrosion makes it particularly vulnerable to MIC. One of the earliest recognized high-profile cases of MIC was of aluminum jet aircraft fuel tanks in the 1950s. Water contaminant in the kerosene-based fuel and condensation in the tanks provided the media in which the bacteria multiplied. Research indicates some bacteria species may utilize kerosene and other fossil fuels as a nutrient source. Since this landmark case, MIC has been widely recognized as a significant problem in both tank and structural aircraft components.

Copper alloys are frequently used for seawater piping systems and heat exchangers due to their good corrosion resistance combined with mechanical workability, excellent electrical and thermal conductivity, ease of soldering and brazing, and resistance to macrofouling. Alloying additions may increase mechanical properties but may increase susceptibility to MIC, although relatively pure copper is also susceptible to MIC. Copper and copper alloys are affected by a wide range of bacterial by-products including carbon dioxide, hydrogen sulfide, and organic and inorganic acids. Cold worked or stressed copper alloy components are especially susceptible to stress corrosion cracking from ammonia and the bacteria that generate it. Selective corrosion, such as de-zincification in brass alloys, has also been observed in MIC failures.

In the past copper was believed to be immune to MIC corrosion. In recent years many cases of MIC of copper and copper based alloys have been reported. Microbiologically influenced pitting attack of copper pipes in domestic water systems was reported to affect both cold and hot water lines. The attack is often observed in soft waters. Other factors known to contribute to MIC of copper piping include long-term or periodic water stagnation, high suspended solids content, low or nonexistent chlorine levels, and high organic carbon content. MIC is often identified by the presence of biofilms on the affected surfaces. In the case of sulfate-reducing bacteria (SRB) frequently intense localized attack is present. These bacteria are anaerobic and occur in most natural waters including fresh, brackish, and seawaters. The mechanism of biocorrosion of copper by SRB is not well developed. One of the theories suggests that SRBs promote corrosion by cathodic depolarization due to removal of hydrogen from cathodic sites. SRBs use hydrogen to reduce inorganic sulfates to sulfides. Also they produce $H_2S$, which directly attacks the metal surface. As a result a black copper sulfide (CuS) rich scale forms on the metal surface. This scale is porous and easily removable from the metal surface. Hydrogen sulfide may cause rapid degradation of the parent metal.

Nickel Alloys are often used in high-pressure, high-flow rate applications, such as pumps, turbine blades, valves and evaporators. Nickel alloy components in these systems are vulnerable to MIC during shut down intervals and stagnant water conditions. It has been demonstrated that Nickel-chromium alloys exhibit a degree of resistance to MIC.

MIC attack in weld zones of a stainless steel component



Pitting due to MIC at a weld

Non-metallic materials, such as PVC, fiberglass reinforced PVC, concrete, and various coatings and linings have been used to provide some degree of MIC prevention. Each has its limitations as to its use as a metal substitute. However, on an applications-specific basis, selection of various non-metallic materials, used as pipes or tanks, or for coating applications, may offer some degree of effectiveness in preventing MIC-related failures.

## MIC PREVENTION and CONTROL

One of the classic concepts for maintaining an industrial system free of the deleterious effects of MIC is to keep the system clean. Good housekeeping practices are essential in plant programs intended to minimize the effects of MIC. Specific plant design characteristics may impact the periodicity of housekeeping activities. Accessibility of certain areas within the various systems may also dictate the cleaning activities used. A well conceived plan that includes mechanical cleaning, chemical cleaning, and careful maintenance of water quality is the most effective approach to minimizing the impact of MIC. An additional degree of importance for MIC prevention is addressed when dealing with safety related systems, such as the fire safety water system.

Physical methods include flushing which is perhaps the most simple although of limited efficacy. High pressure water lancing has been successfully used where access is available. The biomass and other deposits can be satisfactorily removed. A special case is the use of flushing supported by cleaners or jointly with chemical agents that induce biofilm detachment. Abrasive or non-abrasive sponge balls are frequently employed in industry. Sponge ball cleaning systems provide an on-line cleaning method for mechanically removing MIC-related deposits from tubes and pipes in both once-through and recirculation systems. Sponge rubber balls (available in various degrees of stiffness, with and without abrasive coatings), of a diameter slightly larger than the pipe or tube, are periodically introduced into the fluid stream, passed through the pipe or tubes, and are then collected in a downstream area of the system and cycled back to the injection area. This type of on-line cleaning can improve the removal of deposits, but it must be used in conjunction with other procedures, such as water treatment (biocides and dispersants).

However, abrasive sponge balls can damage protective passive films and non-abrasive sponge balls are not very effective with thick biofilms. The physical and mechanical cleaning discussed earlier provides a means for removing loose or loosely adhering deposits associated with MIC. Very often, it is necessary to do further cleaning to remove the tubercles and other deposits that are tightly adhered to the metal surfaces. The use of chemical cleaning solutions have become accepted and widely used. Chemical cleaning is generally safer and more economical than mechanical cleaning that requires labor intensive dismantling.

Taking into consideration what pre-treatment procedures were implemented, there are three basic chemical treatment options that can be used. These are:

- Short-duration, shutdown, aggressive cleaning (e.g., acid/chelate) followed by passivation and biocide chemical addition.
- Short-duration, shutdown, non-aggressive cleaning (e.g., neutral/alkaline pH anionic polymer dispersant) followed by penetrant/passivation and biocide chemical addition.
- Extended-duration, on-line cleaning (e.g., passive penetrant/dispersant), followed by biocide chemical addition concurrent to a typical maintenance treatment program.

Chemicals used to mitigate MIC subsequent to each of the options listed fall into the following four general categories:

23. Biocides/Biostats: Chemicals designed to kill existing microorganisms or prevent the microflora from reaching critical population levels.
24. Penetrant/Biodispersants: Chemicals designed to penetrate into the biomass, disperse the materials deposited at or near the corrosion sites, provide a mechanism for the biocide to contact the sessile microflora associated with MIC.
25. Anionic Dispersants: Chemicals designed to disperse and suspend the deposits, corrosion products, and sludge associated with MIC. These materials also provide a mechanism for the biocide

to contact the sessile microflora associated with MIC.

26. Electrochemical Corrosion Inhibitors: Chemicals designed to inhibit the corrosion process by anodic passivation, cathodic passivation, physical (filming) passivation, oxygen scavenging, or neutralization.

Many of the corrosion inhibitors currently in use employ a combination of these mechanisms. The most common chemical method for controlling biocorrosion in systems is the use of biocides. These can be either oxidizing or non-oxidizing biocides. Chlorine, ozone and bromine are three typical oxidizing agents of industrial use for general microorganism control. However, there is no standard application procedure or specific accepted level of chlorination used for microorganism control, including MIC. Practical experience has shown that at a pH of less than 7.8, chlorine treatment of once-through and circulating water systems will provide an effective degree of control of MIC microorganisms in the bulk water; that is, if the water is free of excessive organic contaminants, suspended solids, and other de-chlorinating substances. At a pH greater than 7.8, bromine compounds or chlorine dioxide may be more effective than chlorine used alone. Above pH 8.5, none of the oxidant materials should be relied upon alone to provide consistent prevention of MIC.

Non-oxidizing biocides are reported to be more effective than oxidizing biocides for overall control of algae, fungi and bacteria as they are more persistent and many of them are pH independent. Combinations of oxidizing and oxidizing biocides or of two non-oxidizing biocides are often used to optimize the effect of microorganisms. Typical biocides of the second type are formaldehyde, glutaraldehyde, isothiazolones and quaternary ammonia compounds.

The amount of biocide to use will depend primarily on the volume of water (capacity) in the system, but also on the amount of water lost in drift, blow down, or bleed off. The severity of fouling problems must also be considered. Also to be considered is the need for both effective concentration of biocide and adequate contact time. Concentrations that are too low will not only be ineffective, but may actually stimulate the growth of some microorganisms. Adequate contact time is necessary because many organisms are not killed immediately by the organic, nonmetallic biocides employed in modern water treatment programs. As normally used, the broad-spectrum biocides do not sterilize the system, but merely reduce the microbiological population while maintaining biological competition. However, if contact time is insufficient, the normal biological equilibrium may be upset, and the more resistant organisms may proliferate because of reduced competition. This is the reason for using broad-spectrum biocides that kill many types of microorganisms. It is also the reason for alternating between two biocides, perhaps using one product for two or three weeks and then treating the system with an alternate biocide for one or two weeks. The second biocide may have different degrees of effectiveness against different microorganisms. Ideally, it will be able to kill the organisms that were resistant to the first biocide. The dosage of biocide is based upon whether an initial shock treatment or a maintenance treatment is intended. The initial dosage is often higher than a maintenance dosage. The intention is to reduce the existing level of microorganisms in the cooling water to an acceptable low figure, after which a lower dosage of biocide can be used to maintain this level.

Recognizing the conditions under which the problem has occurred not only helps to understand why the problem exists, but also provides some potential means of mitigating the problem. The most important environmental conditions to investigate are those considered critical to the growth of microorganism, such as pH, aeration, temperature, nutrient source, flow velocity, and the presence of suspended solids. Making appropriate changes in the environment may be the deciding factor in the success of the mitigation program. A thorough understanding of the operating conditions is also necessary to ensure that the chemical treatment to be used is compatible with the environmental conditions.

Microorganism control is the first requirement of preventing MIC. Prevention of MIC is much more practical and achievable than trying to clean up or mitigate a microbiological problem that has gotten out of control. MIC is a problem directly involved with the uncontrolled growth of microorganisms. Most microbiological problems are due to conditions that exist from the time of initial contact of the system with water and the subsequent changes in operating conditions that promote uncontrolled growth of microorganisms that cause problems. Therefore, the procedures for preventing microbiological problems

such as MIC, slime, and plugging/fouling must be implemented before changes take place.
Control procedures must be implemented immediately as the system contacts makeup water. With some plant designs, there is no option as to the source of the makeup water used. When an option is available, factors such as system function, volume required, system design, and discharge quality should be considered as tools to be used as part of MIC abatement programs. Use of oxidants to control contamination by organic materials is limited. With current environmental requirements, the discharge of even low level oxidants can present problems with their use. Non-toxic penetrant/biodispersants are used as replacements for, or in conjunction with, these oxidants, creating less toxic effluents. Other conditions such as treatment of suspended solids, scale deposits, and use electrochemical corrosion control techniques should be considered as important factors in water treatment programs for the prevention of MIC.

Current technology approaches the control of suspended solids in two ways. The first is by preventing suspended solids from entering or being formed in the system (i.e., precipitation of dissolved materials, corrosion products, etc.). The second is by preventing the existence of suspended solids from causing problems in the system. This would be done either by removing them by filtration, bleed/flushing, dissolving them, or by treating the system with chemicals, such as dispersants and deflocculation agents. No single procedure has proved to be entirely effective. Based on the importance of controlling suspended solids as a factor in preventing MIC, system-specific programs must be developed in coordination with all elements of operation to prevent the accumulation of deposits in the system.