Identifying microbially influenced corrosion on surfaces contacted by mill waters

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ABSTRACT: This introduction to microbiologically influenced corrosion (MIC) describes how bacteria can cause MIC where inadequate disinfection of mill water or white water allows biofilms to grow on metal surfaces. Although planktonic bacteria (that float in solution) rarely cause corrosion, sessile bacteria (that adhere to surfaces) can produce corrosive chemicals or promote under-deposit corrosion. The diagnosis of MIC requires knowledge not only of corrosion processes, but also of microbiology, water treatment, and plant operations. Although the presence of bacteria does not prove that the corrosion was caused by MIC, factors such as the presence in the corroded area of bacteria that can cause MIC, of chemical indicators of MIC, of features of the corrosion damage that are characteristic of MIC, and recent operational changes that could have enhanced the activity of microorganisms can combine to provide compelling evidence. Because of the complexity of mill water environments, test data must be reviewed with care because of the possibility that other components of the water could have interfered with the analytical results.

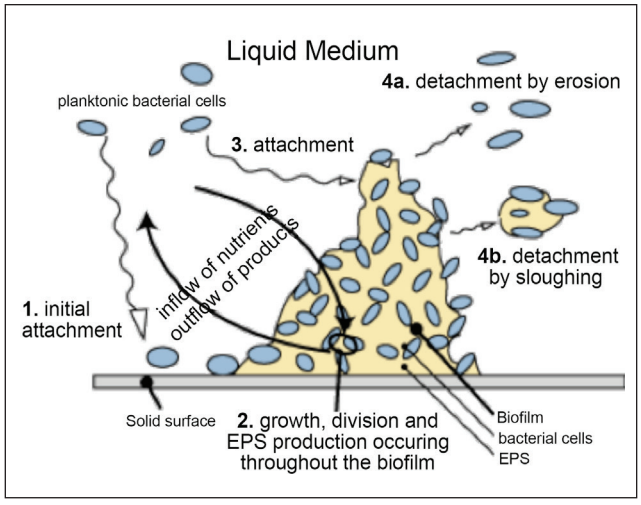
Application: Although MIC is one of the most difficult types of corrosion to diagnose, the characteristic features and tests described in this paper can help identify it as the cause of corrosion damage in cooling water or white water systems.

Before the 1960s, North American cooling water treatment used phosphate and sulfuric acid to prevent calcium carbonate and calcium phosphate scaling [1]. Lowering the pH increased the corrosivity of the water, but this was counteracted by adding chromates to inhibit corrosion. To avoid bacterial growth, biocides were added — typically gaseous chlorine or sodium hypochlorite. This situation changed in the 1960s, when chromate corrosion inhibitors were found to be carcinogenic, when the discharge of phosphates and chlorine became regulated, and when the conservation of water and heat became more important. The water treatment industry responded by introducing new chemicals to inhibit calcium carbonate and calcium phosphate scaling. However, the less acidic industrial waters offered breeding grounds for bacteria.

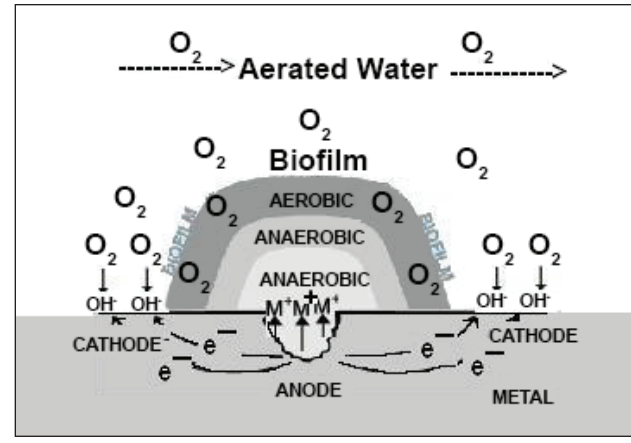
Many cooling water systems provide warm, neutral pH waters that can support microbial growth (i.e., pH between 7 and 9 and temperatures between 80°F and 120°F). Bacteria can also live in more extreme conditions (e.g., by creating their own local environment). Bacteria enter mill water systems either from make-up water or from the air. The basic nutrients they require (carbon, nitrogen, and phosphorus) can come from the same sources, or occasionally from chemical additives or process contamination. Many environmentally acceptable oxidizing and non-oxidizing biocides have been developed to treat these neutral-to-alkaline cooling water systems. Microbial control in cooling waters had been reviewed by Kobrin [2], Freedman and et al. [1], Dillon [3], Herro and Port [4], and Bartholomew [5]. Lutey and Piluso have reviewed locations vulnerable to MIC in pulp and paper mills [2], and Thorpe has reviewed microbiological corrosion of stainless steel in paper machines [6].

EFFECTS OF BIOFILM FORMATION ON CORROSION PROCESSES

Many types of bacteria found in industrial cooling waters exude slimy extracellular polysaccharides (EPS) as part of their life processes. When bacteria adhere to metal surfaces, these sticky slimes can trap particles that float by, incorporating them into the biofilm. Although planktonic bacteria (floating in solution) do not cause corrosion in cooling water systems, sessile bacteria (attached to a metal surface) can influence corrosion directly and indirectly [7,8]. Sessile bacteria can cause corrosion directly by exuding acidic metabolic products (e.g., sulfuric acid) or other corrosives (e.g., ammonia). They can also influence corrosion indirectly by restricting the transport of oxygen, which is required for a metal surface to remain passive beneath a deposit. The formation of sessile microbial films, often referred to as biofouling, is particularly undesirable on heat transfer surfaces because it reduces the efficiency of heat transfer and increases corrosion rates by increasing the temperature of the metal sub-



1. Schematic representation of processes involved in biofilm formation.



2. Schematic diagram of corrosion caused by a biofilm in an aerated water system.

strate. Because the individual bacteria that hold biofilms together are too small to be visible, the resulting deposit typically looks like a solid mound of rust.

If the environment is hospitable, the equivalent of a monolayer of bacteria can attach to a clean metal surface within a few minutes of exposure to cooling water [9]. The EPS produced by this initial film promotes the adherence of other bacteria and can trap other floating materials, such as mineral scales and corrosion products. Surface shear produced by solution flow tends to detach small and large particles from the outside of the biofilm in processes called erosion and sloughing, respectively. **Figure 1** presents a schematic view of these processes [10]. Because bacteria need a continuous supply of nutrients and continuous removal of waste products to continue growing, living biofilms are typically porous.

Biofilms in cooling water systems usually contain many different types of bacteria living in co-operative ecosystems. One type of microorganism might break down a particular chemical that is available in the system. A second organism could further degrade the chemical and a third type could use the degradation products to obtain energy.

Corrosion of a metal under a deposit consumes oxygen that cannot quickly be replaced by diffusion through the deposit. **Figure 2** illustrates the case where the deposit is a biofilm [11]. Because aerobic bacteria consume oxygen, the biofilms they form prevent oxygen from reaching the metal surface. The oxygen-starved area under the biofilm becomes anodic and corrodes more, while deposit-free surfaces in contact with oxygenated water become cathodic and corrode less. Because the rate-limiting step in the corrosion process is the cathodic reaction — the reduction of dissolved oxygen to hydroxyl ions — combinations of small anodic areas and large cathodic areas are the most damaging. The concentration of the corrosion current in a small area produces rapid pitting corrosion.

Inorganic scale deposits and corrosion products floating in the water tend to become incorporated into the sticky biofilm and to form a solid crust over the corrosion site. The oxidation of dissolved metal under the biofilm produces solid inorganic reaction products (e.g., rust) that further hinder the access of oxygen to the under-deposit environment. As the oxygen concentration beneath the biofilm falls, the conditions there become less hospitable to aerobic bacteria and more hospitable to anaerobic bacteria (Fig. 2). If anaerobic bacteria release acidic byproducts at the base of the biofilm, this will accelerate the under-deposit corrosion. Corrosive anions attracted by the accumulation of dissolved metal ions hydrolyze, making the under-deposit solution more acidic and more corrosive. This can make the localized corrosion self-sustaining. Low pH and accumulated halide anions form under-deposit environments that are particularly aggressive toward stainless steel substrates.

The presence of scale-forming minerals or contaminants such as greases and oils in mill waters promotes the deposition of inorganic (hardness) scales. If these scales are coherent and adherent, they tend to inhibit corrosion, but if they are porous or incoherent, they can accelerate corrosion by providing a home for bacteria.

The most effective way to prevent microbiologically influenced corrosion (MIC) in a mill water system is to add biocide chemicals to the water system that kill or deactivate bacteria. Biofilms that have been allowed to thicken and to incorporate inorganic materials are much more difficult to remove because they are much more coherent. The removal of these mature deposits typically requires shock treatments using high concentrations of oxidizing biocides based on chlorine or bromine or mechanical removal by high pressure water jetting. Note that the application of strongly oxidizing biocides that release halide ion byproducts (e.g., chlorine compounds) can introduce additional corrosion problems.

DETECTION AND IDENTIFICATION OF MIC

Of all the forms of corrosion that an engineer might encounter in a pulp and paper mill, MIC might be the most difficult to identify. Little, a world leader in this field, has said, "MIC does not produce any unique type of corrosion and there are no definitive tests or specific observations that can be used to

detect MIC" [12]. For example, because almost all types of MIC-causing bacteria can be found almost everywhere, the detection of MIC-producing microorganisms in liquid or solid samples associated with MIC does not prove that the corrosion was caused by MIC.

Fortunately, there is increasing agreement about the approaches that should be taken to determine whether MIC is the cause of corrosion in industrial equipment. A recently published NACE International test method for detection, testing, and evaluation of MIC on internal surfaces of (oil) pipelines [13] proposes the following as indicators of MIC:

1. Much higher concentrations of living microorganisms at the location of the corrosion than at other locations.
2. Detection of significant concentrations of chemical indicators in the corroded area that support the microbiological evidence (e.g., sulfides where sulfate-reducing microorganisms are suspected or acids where acid-producing bacteria are suspected).
3. Corrosion damage with an appearance that is consistent with a mechanism involving MIC as a primary cause.

A recent presentation by Jenneman [12] suggests that the identification of MIC should only be made if the following four questions can all be answered affirmatively:

1. Are environmental conditions conducive to microbial growth and metabolism?
2. Can the observed corrosion not be explained by abiotic mechanisms?
3. Are corrosion products and features characteristic of MIC present?
4. Have recent operational changes occurred that could enhance the activity of microorganisms?

These lists emphasize that the diagnosis of MIC should be based on multiple pieces of corroborative evidence rather than on any single factor. We will now review the tools available to us to determine whether the four different types of evidence listed by Jenneman are present.

Analysis of microorganisms in water and at the location of corrosion

The first indicator that MIC is possible in a system is the identification of types of microorganisms capable of causing MIC in water samples. Analysis of water samples themselves can show whether the pH, temperature, dissolved salts, and bacterial nutrients could support bacterial life. If deposit samples can be retrieved from the corrosion site, their analysis will offer much more detailed information about the types of bacteria that are present, but will require greater care and will cost more.

Historically, planktonic microbial populations in pulp and paper mill waters were identified by counting viable bacteria cultured on nutrient media after serial dilutions. However, laboratory nutrient cultures rarely simulate the complexity of plant environments. In addition, laboratory cultivation methods are slow and labor-intensive, require substantial technical skills, and do not quantify all the microorganisms present. Because of these limitations, many field tests have been developed to rapidly characterize planktonic bacteria. We will first describe a traditional field test that provides a rapid indication of the total population of microorganisms in water samples and then review tests that offer more detailed information.

Analysis of total microbial activity in water samples

An example of a field test for measuring the total microbial activity in water samples is the adenosine triphosphate (ATP) test, which quantitates ATP, a molecule found in all living cells. Water samples suspected of containing bacteria are reacted with the enzyme and reagents that produce light in fireflies. If bacteria are present, their ATP reacts with the firefly materials and produces light. The amount of light generated is proportional to the amount of ATP in the sample volume of water and can be used to estimate cell numbers. Although ATP tests can be made by mill technicians, the test data must be evaluated very carefully because many compounds found in pulp and paper mill water systems can interfere with the bioluminescence reaction.

Analysis of bacteria that can cause MIC in water samples

We will now describe an example of a field test kit (MICkit5, BTI Products LLC; Bayfield, CO, USA) that offers semi-quantitative analysis of the five classes of bacteria that can cause MIC. The test involves collecting water samples in sterile hypodermic syringes and injecting them through rubber seals into each of five inoculant culture media. Each inoculant is designed to nurture the growth of a particular class of MIC-producing bacteria (i.e., low-nutrient bacteria, iron-related bacteria, anaerobic or facultatively anaerobic bacteria, acid-producing bacteria, and sulfate-reducing bacteria). The sample/inoculant mixture is then diluted 10-fold, 100-fold, and 1000-fold in three more sets of the five inoculants, using the same hypodermic-needle-through-rubber-seal method to avoid introducing contamination. **Figure 3** shows the various parts of this test kit. These include the sterile packaged

3. Components of the MICkit5 test kit.

4. A complete set of inoculated nutrient solutions.

hypodermic syringes (left), the packaged needle covers (center), and the nutrient bottles, covered by colored caps (right). Above and to the right in Fig. 3 is the single bottle used to store the original water sample.

Figure 4 shows a complete set of inocultated test solutions. The bottles labeled 1 contain the most concentrated solutions in each inoculant, the bottles labeled 2 contain 10 times less of the water sample, the bottles labeled 3 contain 100 times less of the water sample, and the bottles labeled 4 contain 1000 times less of the water sample. The bottles on the right hand end of each row are unopened nutrient solutions.

The appearance of the inoculant solutions is documented after 2, 5, and 15 days. Samples that contain the bacteria that grow in the particular inoculant show visible changes, as follows:

- *Low-nutrient bacteria:* Cloudiness in solution, with or without slime.
- *Iron-related bacteria:* Rust color in the solution, with or without rust-colored or black deposits.
- *Anaerobic or facultatively anaerobic bacteria:* Cloudy solution.
- *Acid-producing bacteria:* Cloudy orange or yellow solution.
- *Sulfate-reducing bacteria:* Black solution, with or without black slime on iron nail in inoculant bottle.

The greatest dilution at which a color change appears provides a semi-quantitative indication of the concentration of each class of bacteria, expressed as a decade of concentration (e.g., between 100 and 1000 counts/mL of low-nutrient bacteria).

Data obtained with this type of test kit indicate the concentration of planktonic bacteria in each of the five classes to the nearest decade of concentration. Note that concentrations of planktonic bacteria rarely correlate with concentrations of sessile bacteria [14]. Although the presence of high concentrations of types of planktonic bacteria that could cause MIC indicates that MIC could have occurred, the converse is not true (i.e., the absence of high concentrations of a particular type of MIC-causing bacteria in the water does not prove that corrosion was not influenced by the life processes of that type of bacteria under a deposit).

Molecular microbiological methods

Tests for planktonic bacteria provide only a general classification of the types of organism present. In the last 5 years, molecular microbiological methods (MMMs), which had been used for many years in health care and forensics, have increasingly been used for the diagnosis of MIC [13,15]. By analyzing the genetic content of water samples these tests eliminate many of the problems introduced by culturing. MMMs can be applied to very small samples of liquids, and to wet or dry solids such as biofilms. The test methods extract genetic materials from the samples and use genetic sequencing to determine the concentrations of the various types of bacteria that are present. Because of the sensitivity of these tests, samples must be handled and stored with great care to avoid contamination and degradation of the nucleic acids. The analysis of the DNA extracted from the samples allows the total content and identity of virtually all of the microorganisms present to be determined rapidly and accurately throughout large concentration ranges. **Table I** compares four MMMs commonly used to evaluate MIC [16].

4',6-diamidino-2-phenylindole (DAPI), a fluorescent DNA stain, offers a visual count of all cells that have lived in a deposit or biofilm, but does not distinguish which bacteria were alive in the deposit when it was sampled. The fluorescence in situ hybridization (FISH) test attaches a fluorescent tag to a specific DNA sequence in chromosomes. Test materials can be designed to color different types of bacteria with different-colored fluorescent tags. The FISH test differentiates active from dead and inactive cells. Denaturing gradient gel electrophoresis (DGGE) is a molecular fingerprinting method that identifies particular DNA sequences to compare the microbial populations in an ecosystem. It does not quantitate specific genes. The quantitative polymerase chain reaction (qPCR) quantifies one or more specific sequences in a sample of DNA. It quantitates a chain reaction that uses the enzyme DNA polymerase to amplify the DNA while the reaction proceeds.

Although care must be taken to avoid false-positive results caused by the introduction of nucleic acid contaminants, MMMs appear likely to replace many traditional laboratory assays. We can expect the reliability of MMM data to improve as these new tests become standardized and codified.

Chemical indicators of bacteria that cause MIC

The second marker of MIC is the presence of chemicals produced by the life process of the bacteria that are causing MIC. These indicators are important because we need to determine whether the observed corrosion could have occurred in the absence of bacteria. We will discuss the indicators produced by each of the five types of MIC bacteria categories that are frequently analyzed (iron- and manganese-

MMM	Basis of Method	Living Cells Counted?	Dead Cells Counted?	Quantitative Method?	Information Obtained
DAPI	Microscopy	Yes	Yes	Yes	Total cell count (live and dead)
FISH	Microscopy	Yes	No	Yes	Total numbers of live bacteria Total numbers of live *Archaea* Total numbers of live SRB Total numbers of live sulfate-reducing *Archaea*
DGGE	PCR	Yes	Yes	No	Comparisons of populations Identifications of abundant microrganisms
qPCR	PCR	Yes	Yes	Yes	Numbers of total bacteria Numbers of total *Archaea* Numbers of SRB Numbers of live sulfate-reducing *Archaea* Numbers of three groups of methanogens

MMM = molecular microbiological methods; DAPI = 4′,6-diamidino-2-phenylindole; FISH = fluorescence in situ hybridization; DGGE = denaturing gradient gel electrophoresis; PCR = polymerase chain reaction; qPCR = quantitative polymerase chain reaction; SRB = sulfate-reducing bacteria.

I. Comparison of molecular microbiological methods.

related bacteria, low-nutrient bacteria, aerobic or facultatively anaerobic bacteria, acid-producing bacteria, and sulfate-reducing bacteria).

Iron- and manganese-related bacteria

Iron- and manganese-related bacteria derive energy by oxidizing Fe^{++} to Fe^{+++} or Mn^{++} to Mn^{+++}. Increasing concentrations of ferric or manganic ions increase the corrosion rate of steel surfaces beneath a biofilm. Reaction products of iron-related bacteria include orange-red or brown slimes and hardened tubercles. Tubercles, which often are shiny or slimy, can appear either as blisters of corrosion products or as free-standing narrow iron oxide tubes like very fine stalks. Beneath the tubercles, steel surfaces are pitted. Manganese-related bacteria produce black deposits and corrosion where they exclude oxygen from the metal surface.

In the presence of oxidizing biocides that produce hypochlorous or hypobromous acids and reactions with the manganese that produce permanganic chloride compounds, distinctive pitting and sub-surface tunneling are produced in stainless steels [2]. Thus, severe corrosion under biofilms containing high concentrations of manganese can occur on ferrous alloys and stainless steels, even in water systems treated with chlorine or bromine biocides. For example, *Gallionella* are iron-oxidizing bacteria that produce deposits containing iron and manganese oxides and chlorides. MIC initiated by *Gallionella* has caused at least two major plant failures after untreated water used for hydrostatic testing was left in new stainless steel equipment for a few months [5].

Low-nutrient bacteria

Low-nutrient bacteria (sometimes called oligotrophs) are the most common group of microbes found in aerated waters containing low concentrations of organic nutrients (e.g., potable water, well water, demineralized water, fire-protection water, or condensates). These bacteria adapt to the lack of food by having low metabolic rates and by living in low population densities. Low-nutrient bacteria produce extracellular slime (EPS) that can bind other cells to a metal substrate and trap floating particulates (Fig. 1). Although these bacteria could also be classified as aerobes, facultative anaerobes, or slime-formers, their unique characteristic is their ability to live in low-nutrient environments. *Pelagibacter ubique*, possibly the most abundant organism in salt and fresh water, is an oligotroph.

Anaerobic or facultatively anaerobic bacteria

Anaerobic bacteria can only live in the absence of molecular oxygen. Facultatively anaerobic bacteria can live with or without oxygen. This enables them to continue growing under a biofilm after MIC has consumed all the oxygen in the liquid under the deposit. Layers of anaerobic bacteria can exist in

the inner portion of a corrosion deposit while aerobic bacteria live in the outer portion of the same deposit. Anaerobic bacteria include slime-forming, acid-producing, and sulfate-reducing bacteria.

Acid-producing bacteria

Some bacteria and some fungi produce acids as part of their respiration process. These organisms may be anaerobic, facultatively anaerobic, or aerobic. The acids they produce might be inorganic or organic. For example, *Thiobacillus thiooxidans* oxidizes sulfur-containing compounds to form sulfuric acid. It can live symbiotically with sulfate-reducing bacteria, with the *Thiobacillus* oxidizing sulfide to sulfate and the sulfate-reducing bacteria reducing the sulfate back to sulfide. *Clostridia* feed on organic nutrients and produce short-chain organic acids that can cause severe pitting on deposit-covered steel. They are often found inside corrosion tubercles. The detection of large concentrations of acid-producing bacteria often indicates the presence of mature biofilms that cause MIC and suggests that pitting corrosion is likely to be severe.

In waters that are anaerobic and highly acidic, organisms called methanogens consume hydrogen and produce methane. These organisms are not bacteria, but *Archea*. They accelerate corrosion by consuming hydrogen formed in the cathodic process required for corrosion.

Sulfate-reducing bacteria

Sulfate-reducing bacteria (SRB) are anaerobic bacteria that reduce sulfates to sulfides. Their presence is indicated by sulfide or sulfur deposits and sometimes by hydrogen sulfide gas. Even a small amount of hydrogen sulfide production can support self-sustaining corrosion. SRB corrosion of steel forms black iron sulfide (FeS) and can also liberate hydrogen sulfide gas. A galvanic couple is created between the steel substrate as anode and the iron sulfide as cathode. The SRB sustain the corrosion reaction by consuming electrons liberated by iron dissolution. The presence of these organisms in many natural waters suggests that they are not killed by the oxygen in aerated waters. Some SRB live at temperatures up to 100°C. They typically rely on other bacteria to develop micro-anaerobic sites where they can grow and can live symbiotically with acid-producing bacteria. Common sulfate-reducing bacteria include *Desulfovibro* and *Desulfotomaculum*.

Corrosion features characteristic of MIC

Susceptible materials and susceptible locations

The presence of characteristic features provides a third indication that corrosion damage was caused by MIC. MIC only occurs on metals that are in contact with water. Within pulp and paper mill water systems, sites vulnerable to MIC include heat exchangers, cooling water systems, mill water systems, and fire water systems. Papermaking equipment is also susceptible to MIC because cellulose can provide bacterial nutrients. Bacterial slime on paper machines is often pink. Sticky deposits on paper or pulp machines are particularly troublesome because they can accumulate fibers and break away from their substrate, producing lumps or holes in the paper. In addition, many fluids stored in a mill, such as gasoline, oil, and cutting lubricants, contain enough water to support bacteria that could initiate MIC.

Low flow areas in circulating water systems are particularly susceptible to MIC because the shear stresses that could remove the biofilm by erosion or sloughing are much lower. Low flow areas exist in crevices and joints, under biofilm-bound deposits or hardness scales, in micro-crevices at the surface of welds, and under delaminated coatings. If untreated water is stagnant (e.g., in a fire water storage system, or in equipment that is out of service), biofilms can form rapidly. Areas where deposits are particularly difficult to remove are also more vulnerable to MIC. Once a biofilm is established, corrosion processes can continue even after the fluid flow is restored. Hydrostatic testing (in which a system is filled with water, pressurized, leak-tested, and drained but often not completely dried) is a frequent cause of MIC. When a leak appears months after the hydrostatic test, the condition of the water used for hydrostatic testing is often not considered, so the cause of failure might be misdiagnosed.

MIC can occur on almost all industrial alloys except stainless alloys containing more than 6% molybdenum and titanium. As early as the 1950s, corrosion in aluminum fuel tanks in jet aircraft was found to be caused by MIC in condensed water. The interface between condensed water and non-water-soluble fluids was particularly susceptible. Copper and copper alloys can be corroded by the products of many microbial life processes, 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 bacterially produced ammonia. Nickel-based stainless alloys show some resistance to MIC, but are vulnerable during shutdowns when process waters are stagnant.

Corrosion morphologies characteristic of MIC

MIC can produce general and localized corrosion. However, localized corrosion is more typical and more likely to cause leaks. Corrosion pits produced by MIC are typically isolated. They often include one deep pit or hole surrounded by shallower pits that make the metal surface look like a sponge.

SRB can produce isolated pits that open into large and connected sub-surface cavities. Sub-surface cavities under discrete deposit mounds provide a tell-tale sign that MIC might have been the cause of the corrosion. Discoloration of a metal surface around a deposit might indicate that corrosive solutions are leaking out from pits under the deposit. Note that because MIC frequently initiates on the process side of equipment materials, severe corrosion and even perforation might occur before any evidence of attack can be seen from the outside of the vessel or pipe. Subsurface cavities are frequently found alongside weld seams under the base of narrow tubercles.

MIC caused by anaerobic iron-related bacteria in low flow areas in piping systems typically produces tubercles that look like blisters of corrosion product. They can also appear as free-standing, narrow iron oxide tubes like fine stalks. Pitting propagates under these tubercles.

Corrosion rates

Because bacterial processes accelerate corrosion processes such as under-deposit or crevice corrosion that occur without bacteria, rates of wall penetration caused by MIC can be much higher than abiotic corrosion rate – as high as 20 mm per year.

Evidence of operational change that could enable microorganisms to multiply

Many analyses of corrosion problems traced to MIC report that the corrosion failures appeared after changes in biocide treatment or dosage, or after changes in process temperatures or oxygen concentrations. This is not surprising. Water systems are typically treated with biocides and scale prevention chemicals. If treatment programs are changed in ways that increase limited food sources, slow flow rates, enable increased formation of inorganic deposits, increase the concentration of suspended material that could be incorporated into biofilms, or reduce the efficiency of disinfection, we can expect microorganisms to take all the opportunities that these changes provide for new or accelerated biofilm formation.

Programs to prevent MIC typically involve the addition of oxidizing or non-oxidizing biocides that are chosen in light of the materials of construction and the process requirements. Microbiological populations of plant waters should be routinely monitored in representative locations within the water systems to provide early warning of changes in planktonic ecosystems. Corrosion monitoring methods rarely predict the occurrence of MIC, but might be important to verify that the biocide additions are not themselves causing corrosion.

PREVENTING MIC

Although the prevention of MIC is beyond the scope of this paper, we will present four general comments. First, the cause and mechanism of individual MIC failures must be clearly understood to develop a remediation plan. Second, the primary method for preventing MIC is applying biocides that kill or deactivate bacteria that could otherwise form biofilms and support MIC. Surveillance programs should be maintained to evaluate the effectiveness of the biocides that are applied. Third, although changing materials of construction might be prohibitively expensive, minor system redesign might minimize vulnerable areas (e.g., low-flow areas, crevices at flange joints, and even welds). Jenneman replaced carbon steel with duplex stainless steel where the risks and consequences of MIC were particularly high [15]. Fourth, we should note that, although advances in the remediation of MIC during the last 20 years have greatly improved our ability to identify conditions that could cause MIC, it remains very difficult to predict where MIC might occur and impossible to predict how rapidly it will penetrate a vessel or pipe wall.

CASE HISTORY OF MIC IN MILL COOLING WATER SYSTEM

The following case history of corrosion in a mill cooling water system is presented as an example of how multiple pieces of consistent evidence can establish MIC as the cause of corrosion. **Table II** shows the time to failure of various items touched by this mill's cooling water or white water. All of these items failed from the water side (or the white water side).

The first leaks occurred at welds in the shells of three type 304L stainless steel heat exchangers or in the discharge piping that removed hot cooling water from these heat exchangers. No leaks were found in the supply piping that delivered cool water to the same heat exchangers, typically at 113°F (45°C).

The investigation of these corrosion problems included a detailed review of the equipment and processes used to treat the make-up water drawn from a river beside the mill and to

Item	Materials of Construction	Operating Temperature	Service until First Leak
Heat exchanger 1	Type 304L stainless steel	208°F (98°C)	9 months
Heat exchanger 2	Type 304L stainless steel	221°F (105°C)	12 months
Heat exchanger 3	Type 304L stainless steel	185°F (85°C)	24 months
White water storage tank	Type 316L stainless steel*	149°F-158°F (65°C-70°C)	<36 months
Hot mill water piping 1	Type 304L stainless steel	185°F-221°F (85°C-105°C)	36 months
Hot mill water piping 2	Type 304L stainless steel	185°F-221°F (85°C-105°C)	48 months

* This tank was constructed from carbon steel but had a welded-in, loose ("wallpaper") lining of type 316L stainless steel sheet.

II. Time to failure of various items in a mill cooling water system.

Water	Low-Nutrient Bacteria, counts/mL	ATP Analysis, relative light units
Filtered make-up water	$>10^4$	Not tested
Biocide treated make-up water	10^3–10^4	55, 35, 27
Recirculated cooling water downstream from cooling towers after biocide treatment	10^3–10^4	62, 49, 52
Potable water	10^0–10^1	70, 85, 86

ATP = adenosine triphosphate.

III. Analysis of mill waters.

treat the recycled cooling water. Samples of mill waters were analyzed and their scaling and corrosion tendencies were calculated. Corrosion samples from scrapped heat exchangers were analyzed in several laboratories. We report the findings of these studies in the same categories that we previously identified as indicating the presence of MIC.

Analysis of microorganisms in the water and at the location of corrosion

Bacterial concentrations in water samples from four sources in the mill were analyzed using MICkit5 test kits. The data are presented in **Table III**. Substantial concentrations of low-nutrient bacteria were found in the recirculated mill water and in the treated make-up water, but not in the mill's potable water supply, which received an additional disinfection treatment with sodium hypochlorite.

No other types of MIC-causing bacteria were identified. Three of the water samples were analyzed by ATP testing. The ATP data (also shown in Table III) did not respond to the difference in bacterial concentrations between the mill water and the potable water. This lack of response almost certainly indicates the presence of compounds that interfere with the ATP bioluminescence reaction. Such interferences are common in pulp and paper mill water systems. Four other pieces of evidence supported the hypothesis that ATP indications of low concentrations of living material in mill waters are misleading: 1) potassium permanganate titrations showed that the make-up water treatment removed about two-thirds of the oxidizable organic matter in the water supply, 2) substantial algae growth was observed in biocide-treated cooling waters downstream of the cooling towers (**Fig. 5**), 3) algae were also observed at a leak in a fire water nozzle cap (**Fig. 6**), and 4) pink slime (bacteria) was reported on the pulp machine.

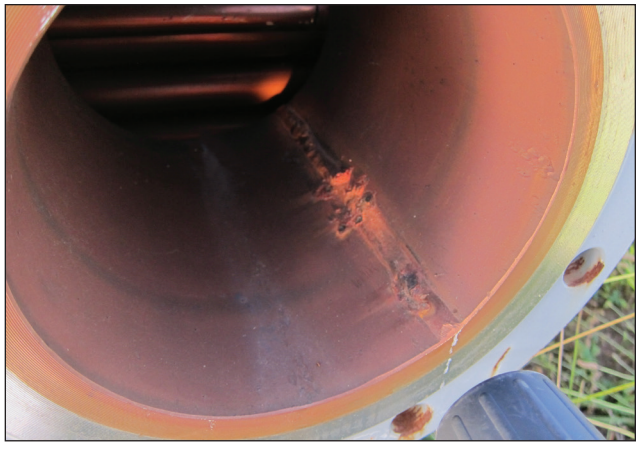
Those bacterial data led to three important conclusions. First, although there was a high concentration of low-nutrient bacteria in the filtered make-up water, treatment of this water with sodium hypochlorite produced effectively disinfected potable water. Second, the application of the mill's biocide treatment to the filtered make-up water produced only a slight reduction in the concentration of low-nutrient bacteria. Third, the addition of the mill's biocide treatment downstream

5. Growth of green algae on the wall of a channel taking recycled water from the cooling towers.

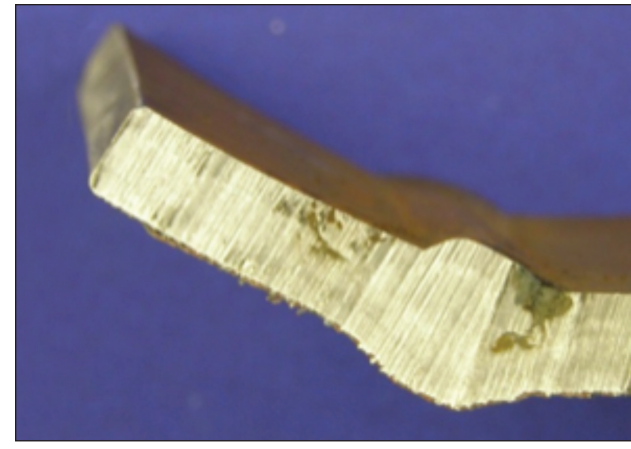
6. Growth of green algae at a water leak where a fire water outlet nozzle cap was screwed to a fire water pipe.

of the cooling towers left the recycled cooling water with a similar concentration of low-nutrient bacteria to that in the water used to make up losses in this system. The general conclusion is that the mill's biocide treatment was not significantly reducing the concentration of low-nutrient bacteria in the mill waters.

Samples taken from the outermost layer of a deposit over a corrosion pit on the inner diameter surface of heat exchanger 1 were sent to an outside laboratory for DGGE testing. Of the organisms identified in this sample, 84% were slime-forming bacteria, 7.6% were nitrifying bacteria, and 1.5% were iron-related bacteria. Nitrifying bacteria consume inorganic

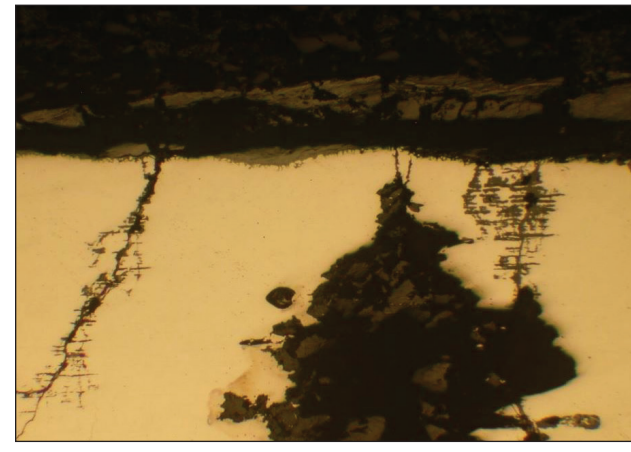


7. Heat exchanger 1: Deposit mounds along a cooling water discharge nozzle weld.



9. Heat exchanger 1: Cross-section through the longitudinal weld in the cooling water discharge nozzle

8. Heat exchanger 1: Pits under deposit mounds on the water-side of the cooling water discharge nozzle.



10. Heat exchanger 1: Narrow surface crack opening to a large subsurface pit, and branched cracking typical of stress-corrosion cracking (75×).

nitrogen compounds and can also oxidize nitrite to nitrate. The slime-forming bacteria in the deposit could have initiated crevice corrosion on the metal covered by the deposit.

Evaluation of MIC chemical indicators in corroded areas

Scanning electron microscopy with energy dispersive X-ray (SEM/EDX) analysis of corroded areas in heat exchanger 1 showed that the corrosion products contained mostly oxygen, with up to 11% sulfur and chromium and iron. The deposit immediately above the corroded area also contained elevated concentrations of sulfur, which would be consistent with the presence of bacteria at this location. Although the DGGE analysis detected no SRB in the outer layer of the deposit, SRB activity under the deposit could have produced the accumulation of sulfur.

Chloride concentrations were elevated (up to 1 wt%) in corrosion products on these two heat exchangers and small accumulations of chloride salts were detected in corroded areas of the white water tank. The outer layer of a corrosion product sample from heat exchanger 2 was porous iron oxide. Nearer the surface of the stainless steel, the corrosion product contained chromium and sulfur. This sulfur in the corrosion product suggests that SRB or possibly sulfates were present, as in the sample from a corroded area in heat exchanger 1.

Evaluation of corrosion features characteristic of MIC

Heat exchanger 1

Figure 7 shows deposit mounds alongside a longitudinal weld in the cooling water discharge nozzle from heat exchanger 1. Removal of the outer red-brown layer of these deposits revealed underlying pits filled with black corrosion products (**Fig. 8**). Each pit was surrounded by yellow stains running downward, as if sulfur had leaked out of the pits. A cross-section through this longitudinal weld in the discharge nozzle included deep and irregular pits beside the weld that had small mouths, which opened into large, rounded, sub-surface cavities (**Fig. 9**), typical of MIC. Figure 9 also shows tunnel-like corrosion cavities under the water-side surface. In several locations, narrow cracks had propagated from the bottom of the corrosion pits. **Figure 10** shows a very narrow crack at the nozzle surface that opened into a large sub-surface pit.

Next to this is a branched crack typical of stress-corrosion cracking, which would be consistent with the finding of elevated chloride concentration in the pitted area. Micrographs of the cracks showed that the nozzle material retained substantial cold deformation from its fabrication.

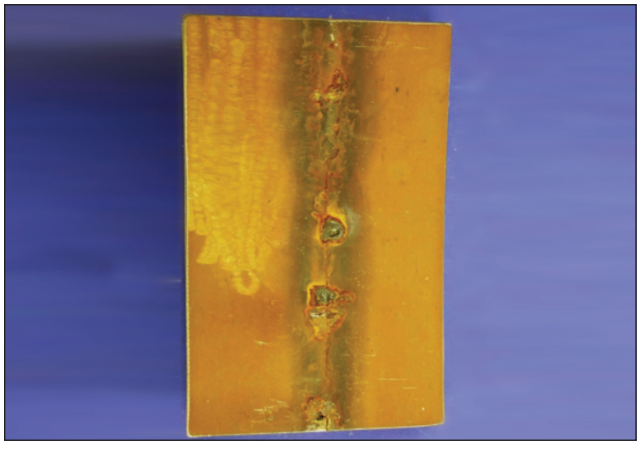
The corrosion of this cooling water discharge nozzle is consistent with the development of MIC under a layer of bacterial slime on the stainless steel surface. The first leaks appeared in the hottest part of the heat exchanger 1, probably because rates of pitting and crevice corrosion initiated by biofilm deposits would increase with the temperature of the corroding alloy. Note that such crevice corrosion could continue even at temperatures above those at which bacteria could live in the biofilm.

A second sample removed from heat exchanger 1 included a girth weld in the shell of this heat exchanger. Adjacent shell plates had been welded together from the outside of the vessel, but this weld penetrated as little as 2/3 of the thickness of the shell. The widest unwelded crevices between the adjacent plates had been weld-repaired on the water side of this seam (**Fig. 11**), although the narrowest crevices would have been most vulnerable to corrosion. Rounded mounds of corrosion products at the girth weld covered rounded pits in the surface of the type 304L stainless steel shell. As on the discharge nozzle, removal of the outer red-brown layer of the deposit revealed a shiny black surface on the corrosion pit underneath, and the corrosion sites were surrounded by yellow stains.

Bacteria could easily have attached themselves to the irregular bottom of the weld in the crevice between the unwelded plates. The rounded deposit mounds, the corrosion pits with narrow openings over large rounded cavities, and the tunnel-like sub-surface cavities were all characteristic of MIC. The lack of penetration defects made the girth weld particularly susceptible to MIC.

Heat exchanger 2

Over a period of years, heat exchanger 2 experienced many leaks at welds where the cooling water was hottest. Many of these leaks were repaired by welding scab patches to the outside surface of the vessel, but the leaks continued. **Figure 12** shows the water-side of the girth weld joining the hot water discharge nozzle to the heat exchanger shell. Corrosion mounds surrounded by yellow deposits and repair weld penetrations can be seen. Eventually, this heat exchanger was replaced and the cooling water discharge pipe upgraded to type 316L stainless steel. The surfaces of the inlet nozzle that delivered cool water to the scrapped heat exchanger 2 had remained deposit-free and still showed heat tints from the original fabrication welding (**Fig. 13**).

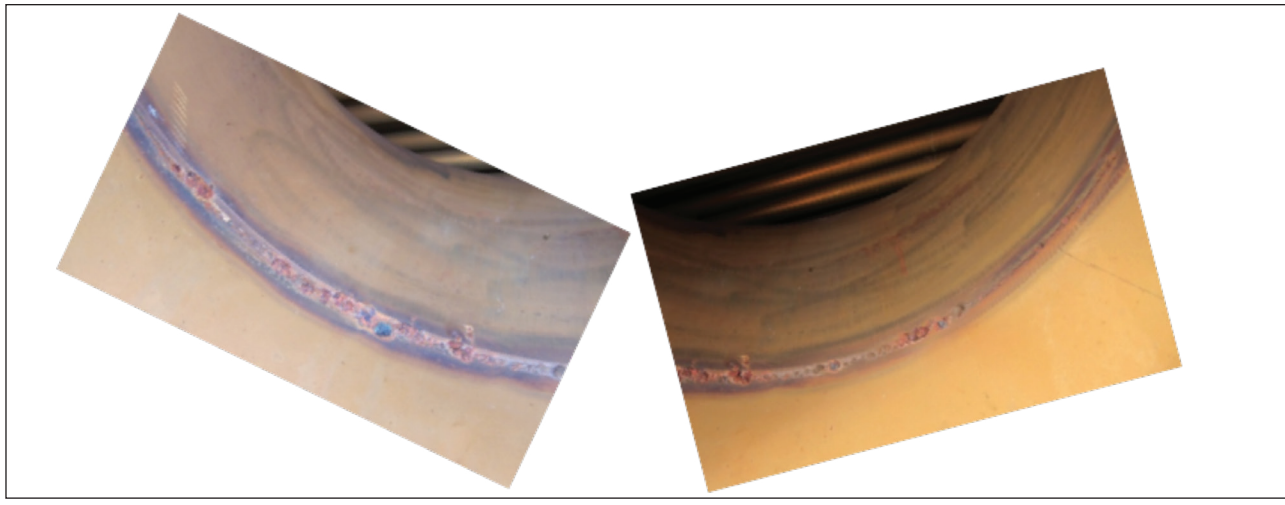


11. The water-side surface of a sample cut from the shell of heat exchanger 1.

12. Heat exchanger 2: Pass 4 tube sheet beside the cooling water discharge nozzle.

13. Heat exchanger 2: Clean surfaces of the chamber at the cooling water supply nozzle.

The localized corrosion that caused leaks in this heat exchanger had propagated under mounds of corrosion products. Transmission electron microscopy and X-ray diffraction indicated that the iron-rich outer layer of the deposits was crystalline or nanocrystalline, but that the iron-chromium-sulfur inner layer was amorphous. MIC typically produces amorphous deposits. Also, the stainless steel surfaces covered by brown-orange corrosion products were harder than the deposit-free surfaces. This is consistent with the fact that welded material, which is harder than unwelded (forged) material, is more vulnerable to MIC.



14. Heat exchanger 3: Localized corrosion in a circumferential weld seam attaching the cooling water discharge nozzle. Photographs taken facing upstream toward the heat exchanger tubes.

Heat exchanger 3

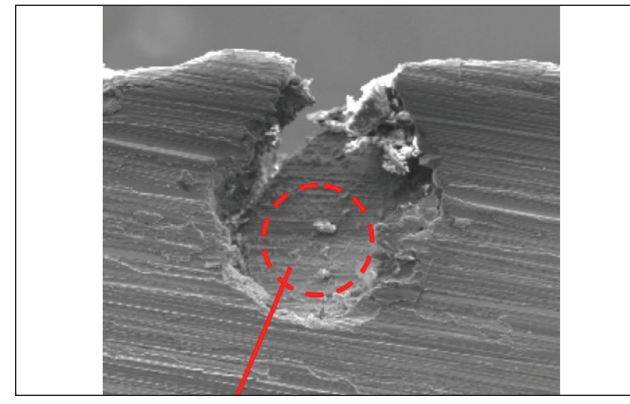
Leaks in heat exchanger 3 were all either at weld seams in the shell of the heat exchanger or in the hot water discharge piping. The cooling water discharge nozzle showed severe localized corrosion in the water-side surface of the field weld attaching the discharge pipe to a downstream nozzle. **Figure 14** shows isolated rounded corrosion pits similar to those in the other heat exchangers. Most of these pits were open and empty, but some were covered by blue deposit mounds.

White water tank

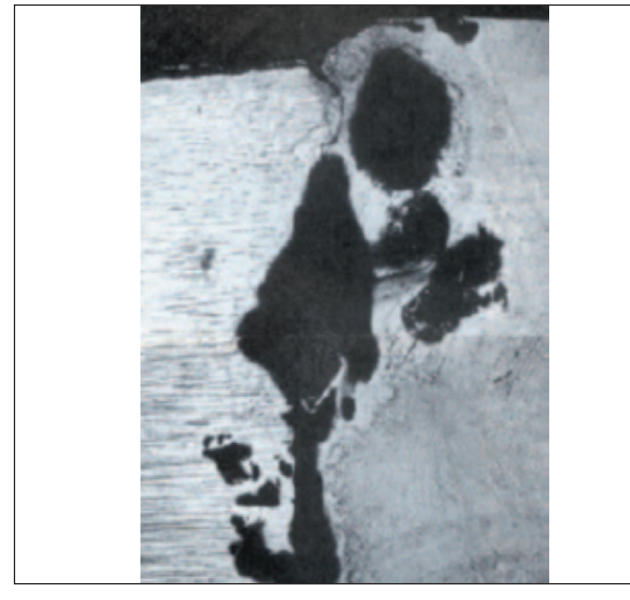
The white water tank has a carbon steel shell with an internal sheet lining of type 316L stainless steel. Corrosion first appeared as scattered pits along horizontal welds joining adjacent strips of the sheet lining. Later pits appeared at progressively higher locations.

The pits propagated under rust-brown deposits on the lining material. The rounded pit shown in **Fig. 15** had a small entrance at the waterside surface and a large rounded cavity underneath that is characteristic of MIC. Rounded subsurface pits and corrosion tunnels typical of MIC were found at several locations (**Figs. 16** and **17**).

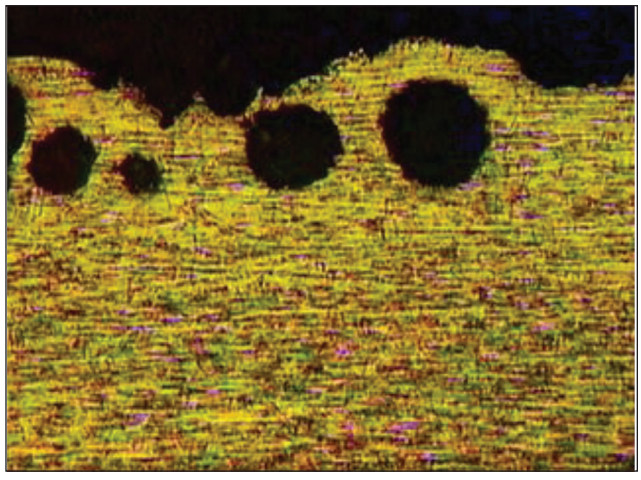
Corrosion had selectively attacked the weld metal, revealing its dendritic structure (**Fig. 18**). The first-to-freeze material would have been most vulnerable to corrosion because it would contain significantly less molybdenum than the last-to-freeze material. Molybdenum additions increase the corrosion resistance of stainless steels. Also, two samples of the sheet lining were found to contain less molybdenum (1.86% and 1.88%) than is specified for type 316L (2.00% to 3.00%). Finally, the heat-affected zone of the stainless lining was slightly sensitized, making it still more vulnerable to corrosion. In the absence of MIC, type 316L stainless steel is adequate to handle white waters that contain only a few tens of parts per million of chloride. The fact that type 316L



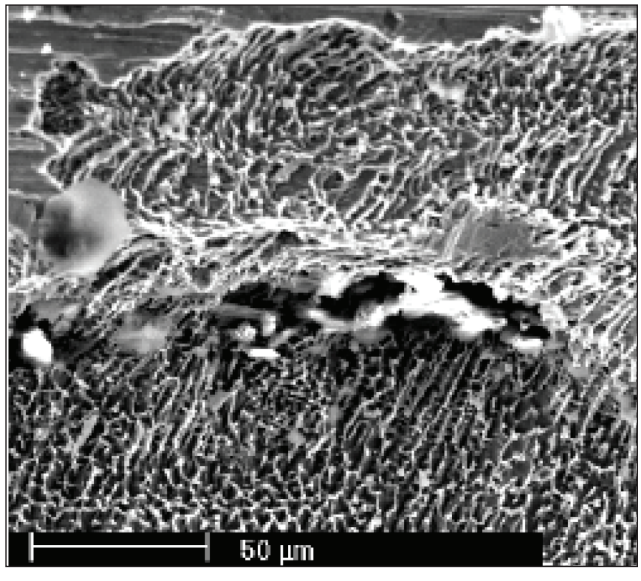
15. A spherical subsurface pit with a narrow entrance at the metal surface.



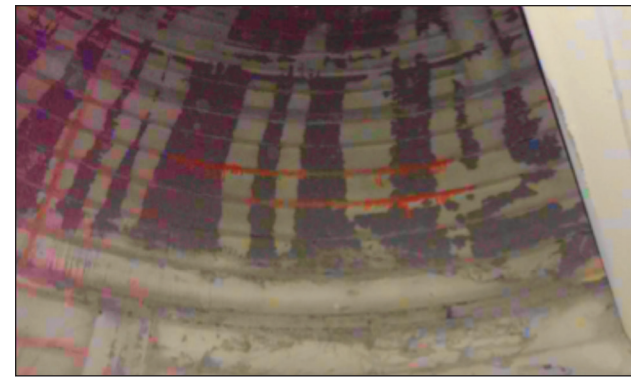
16. Rounded subsurface pits along a weld joining two adjacent lining sheets.



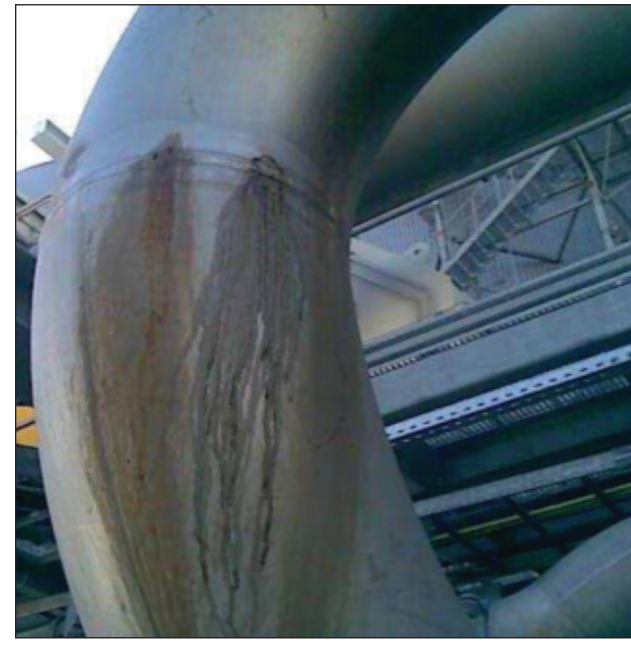
17. Rounded sub-surface corrosion tunnels in the stainless steel lining.



18. White water tank: Selective corrosion revealing the dendritic structure in the weld material.



19. White water tank: Rust-colored fluid leaking from horizontal (circumferential) welds attaching the sheet lining.



20. White water piping: External stains produced leaks at a girth weld.

suffered severe corrosion is consistent with the theory that normal (abiotic) corrosion mechanisms were augmented by MIC in this case.

Corrosion penetration, perhaps aided by cracking in the welds attaching the sheet lining, allowed warm white water to enter the cavity between the stainless steel sheet lining and the tank wall, where it corroded the carbon steel tank shell, and from which it later oozed back out of penetrations in the lining. **Figure 19** shows the remains of rust-colored fluids that flowed out of lining penetrations during a shutdown.

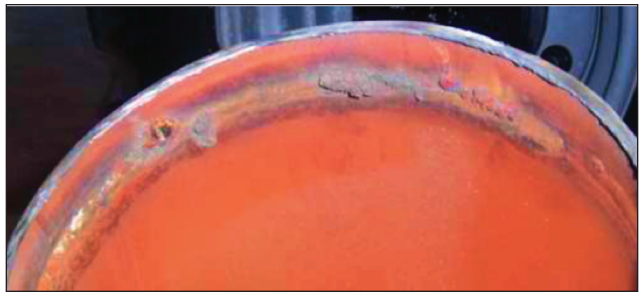
White water piping

Leaks similar to those at welds in the heat exchangers also appeared in type 316L stainless steel white water piping. **Figure 20** shows typical small leaks at girth welds between sections of pipe. Leakage rates were slow enough that the white water evaporated on the surface of the pipe rather than spraying out from it. The deposition of solids from the evaporating white water might have tended to block these leaks.

Many leaks appeared in type 304L stainless steel hot water piping operating at temperatures between 185°F and 221°F (85°C and 105°C). The water-side surface near leak sites (**Figs. 21** and **22**) showed large isolated mounds of rust-colored deposits on top of circumferential welds or on the heat-affected zones beside these welds. No further examination of these corrosion sites was performed.

Evidence of operational changes that could enhance microbial activity

At about the time that the first heat exchangers began to leak, the mill had reduced the concentration of biocides it applied to prevent failures of polymeric components in the



21. White water piping: Rust mounds at corrosion sites at a circumferential weld in a hot water pipe.

22. White water piping: Rust mounds on and beside a circumferential weld in another hot water pipe.

recirculated cooling water system, which were thought to have been damaged by the mill's biocide. The combination of this reduction in biocide dosage, biocide losses from volatilization and decomposition, and the use of analytical methods that indicated incorrectly high biocide concentrations produced conditions where MIC-causing bacteria could grow and produce crevice corrosion on stainless steels in the cooling water and white water systems. Later investigations showed that the failures of polymer components in the water system arose from mechanical stresses rather than from chemical interactions with biocides.

Role of MIC in this case history

The following pieces of evidence collected during the investigation were consistent with MIC having initiated the leaks in the water and white water systems:

1. Quantitative analysis found microorganisms that can cause MIC in the water and at the location of corrosion.
   a. Quantitative analysis showed that the mill waters contained large concentrations of planktonic low-nutrient bacteria, which can cause MIC.
   b. DGGE analysis showed that deposits formed over confirmed corrosion pits contained slime-forming bacteria that could promote biofilm growth and MIC.
2. The corroded area contained chemical indicators consistent with MIC.
   a. The presence of sulfur in the corrosion products and yellow deposits around corrosion pits suggest that sulfate-reducing bacteria might have been involved in the corrosion process.
   b. Transmission electron microscopy and X-ray diffraction showed that the iron-rich outer layer of the corrosion product on a heat exchanger that leaked after 1 year of service was crystalline or nanocrystalline, but that the iron-chromium-sulfur inner layer was amorphous. MIC underneath a deposit typically produces amorphous deposits.
3. The corrosion damage showed several features characteristic of MIC.
   a. Rapid pitting occurred under rounded mounds of corrosion products located along weld seams in stainless steel equipment.
   b. Many corrosion pits had a large, rounded subsurface cavity with a small opening to the metal surface.
   c. Sub-surface corrosion "tunnels" were found adjacent to corrosion pits.
   d. SEM/EDX analysis showed that corrosion products contained oxygen, chromium, iron, and sulfur, but not chlorine. This is consistent with MIC. Abiotic corrosion pitting would have been expected to show greater chloride concentrations.
   e. In several locations in the system, shiny or slimy deposits were observed.
4. Evidence showed operational changes occurred that could have enhanced the activity of microorganisms.
   a. Biocide dosages had been reduced to avoid unrelated materials problems.
   b. The mill's biocide application systems allowed biocide volatilization from open water treatment facilities, particularly on hot summer days.
   c. The mill's analytical methods overestimated biocide concentrations and indicated that its biocide application was sufficient to control MIC.

The combination of these various pieces of evidence indicated that leaks and failures in heat exchangers, a white water storage tank, and hot water piping were initiated by MIC. The metal temperatures at some failure locations appear too high for some bacteria to grow, but crevice corrosion is able to propagate under deposits bound by biological material, even if those bacteria have died. Although the detailed corrosion mechanisms were not identified, the existence of so many consistent indicators of MIC provided strong justification for recommendations that the mill initiate a systematic microbiological survey of its water systems as a basis for developing improved biocide treatment programs for make-up water and recirculated mill water. Ongoing monitoring of the tendency to deposit biofilms was also recommended to provide early warning of the possibility of similar corrosion in the future.

CONCLUSIONS

The recent development by the petroleum industry of systematic approaches for identifying MIC [12,13] offers the pulp and paper industry a reliable strategy for determining the role of microorganisms in corrosion in mill water systems. Multiple diagnostic methods are essential for mills to clarify the extent and severity of MIC in their equipment. Future standardization of approaches for the identification of MIC in pulp and paper industry environments would offer increased confidence in such diagnoses. **TJ**

ACKNOWLEDGEMENTS

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Sharp

We chose this topic for review because microbiologically influenced corrosion (MIC) is not well understood in the paper industry and is one of the most difficult types of corrosion to conclusively identify.

Systematic approaches for identifying MIC in the petroleum industry, including the use of new DNA analysis techniques, although largely ignored in the paper industry literature, offer the pulp and paper industry a reliable strategy for determining the role of microorganisms in corrosion in mill water systems.

The diagnosis of MIC should be based on multiple pieces of corroborative evidence rather than on any single factor. The case history described in the paper shows how the major costs of downtime and equipment replacement could have been avoided by systematic diagnosis of MIC and implementation of more efficient disinfection in the mill waters.

Mills could use the information in the paper to determine the cause of leaks or failures in cooling water systems, heat exchangers, and white water piping. The information can help to raise awareness in the industry and enable mills to reduce their corrosion costs.

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