Emerging microbial control issues in cooling water systems

Use these guidelines to understand and deal with biological problems

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Microbial life affects everything including many industrial processes. The nature and activity of microorganisms determines whether their presence is beneficial or destructive. In cooling towers, the destructive capability of these organisms is manifested. The microorganisms that inhabit industrial cooling water systems can adversely affect the efficiency of the operation by their sheer number and diversity, metabolic wastes or deposits and associated corrosion. Microbiologically influenced corrosion is emerging as a serious problem in cooling systems. This article brings into focus the problems created by microbial infestations in cooling water systems and the control procedures evolved to combat them. Further, the future strategies being evolved in view of environmental concerns with biocides currently used are also discussed.

Need for cooling water. Water can be called the workhorse of the industry. With minor exceptions, water is the preferred industrial medium for removing unwanted residual heat from process streams. Clean water, once in abundance, is becoming increasingly difficult to locate. In some instances, one plant's effluent is, with its chemical pollutants, the influent for another plant downstream. Also, natural pollution is being noticed in some water supplies, including groundwater with certain contaminants like phosphate, nitrates, iron, manganese and sulfides, and salinity. Advanced water treatment and conservation techniques are required to cope with the situation. This especially applies to cooling water.

Open evaporative cooling water (CW) systems provide economical heat sinks since they can handle high heat loads with minimum water loss, mainly attributable to evaporation. Thus, open evaporative cooling water provides efficient water reuse. However, this capability simultaneously is associated with a very important phenomenon—the concentration effect. Evaporation results in increased concentration of dissolved and suspended impurities in the remaining cool water. This concentration of impurities, combined with the natural action of water on system metals and temperature variations within a system, leads to myriad of water-related problems.

Table 1. Oxidants and reductants in various bacterial respirations

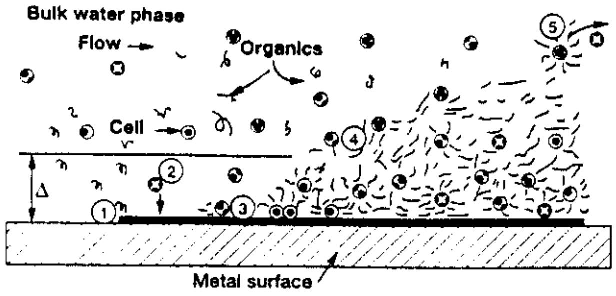
Reductant	Oxidant	Products	Organisms
H_2	O_2	H_2O	Hydrogen bacteria
N_2	SO_2^{2-}	$H_2O + S^{2-}$	Desulfovibrio
Organic compounds	O_2	$CO_2 + H_2O$	Many bacteria, all plants and animals
NH_3	O_2	$NO_2^- + H_2O$	Nitrifying bacteria
NO_2^-	O_2	$NO_3^- + H_2O$	Nitrifying bacteria
Organic compounds	NO_3^-	$N_2 + CO_2$	Denitrifying bacteria
Fe^{2+}	O_2	Fe^{3+}	Ferrobacilus
S^{2-}	O_2	$SO_4^{2-} + H_2O$	Thiobacillus

Table 2. Nutrient requirements for organisms

Sources of energy	Elements for protein		Trace elements	
Sunlight	Carbon	Hydrogen	Magnesium	Copper
S° (Elemental sulfur)	Oxygen	Nitrogen	Potassium	Cobalt
Fe^{2-}	Sulfur		Phosphates	Manganese
Organic molecules			Iron	Zinc

To offset this, a portion of the system water is "bled off" intentionally in an attempt to deconcentrate it. Even though bleeding assists in reducing many potential problems, applying various chemical treatments including those for microbial control is required to maintain efficient operation and protect the system from water-related catastrophies. In view of the high cost of these speciality chemicals, a bleed-off constitutes a recurring revenue loss. Bleed-off also leads to environmental problems due the presence of increased dissolved solids and chemicals. The nature of many chemical process plants is such that a shutdown is not permissible due to costs associated with the downtime. This imposes severe demand on the chemical treatment, since corrosion of heat exchangers can cause a shutdown as well as pollution.

Attempts are being made to reduce the heat reject from the process to cooling water using energy analysis techniques like pinch technology. The fresh water demand for cooling is optimized by using air cooling, and wet and dry cooling systems. Further attempts are being made to raise the cycles in cooling water and



Steps in biofilm formation:
Initiation when small molecules get attached to an inert surface (1).
Microbial cells are adsorbed on the surface (2).
The cells send out hair-like exopolymers (3) to feed on organic matter, adding to the coating (4).
Flowing water detaches some of the formation (5).
An equilibrium Δ layer is produced.

Fig. 1. Stages in biofilm formation.

reduce blowdown. Attempts are being made to treat the blowdown and recycle it. In water-scarce areas, even treated wastewater is being used for make up. Reducing blowdown water is the major cost reduction potential in the system.

Operating problems. Operating problems associated with open evaporative cooling systems are:

Corrosion. The destructive oxidation of system metals, primarily caused by oxygen saturated water.

Deposition. 1) Scale: the precipitation of crystalline salts,usually hardness salts, from solution and 2) Fouling: the sedimentation of suspended materials such as mud, silt, sand, clay, biomatter, etc.

Microbiological growth. Bacterial, fungal and algal growths resulting from the excellent breeding environment of an open system and the continuous entry of bacteria from the makeup water and ambient air coming in contact with the water.

To effectively and economically treat an open evaporative cooling system, it is necessary to not only recognize potential problems and to select and optimize the proper treatment chemicals, but also to realize that to a great extent these problems are interrelated and cannot be handled in isolation. For example, the corrosion process causes deposition which can accelerate corrosion by a phenomenon called "underdeposit corrosion." Microbiological growth itself is a deposit and can also accelerate corrosion. Therefore, selecting a treatment from a total system standpoint cannot be overemphasized.

MICROBIAL PROBLEMS

In the last decade, cooling water treatment programs have developed from experience in the process industry. New hydrocarbon processing plants, in view of their single stream process and high-capacity potential, are imposing high performance demands on CW treatment programs. Stringent environmental regulations are demanding increased compliance. Chromate-based chemicals are being phased out due to environmental restrictions. A good deal of success has been achieved with nonchromate-based corrosion inhibitors coupled with deposit control polymers for controlling corrosion and deposit problems. However, microbiologically influenced (induced) corrosion (MIC) continues to be an area of concern.

Restricting specialty biocides and emerging restrictions on extensive use of chlorine, microbial control is posing new challenges for treatment programs. Microbiological control is emerging as the prime issue of concern in cooling water treatment programs in fertilizer plants. To a great extent, the problem also exists in cooling systems of other process and utility plants. In fertilizer plants the cooling water must consider:

- System metallurgy of carbon steel and stainless steel
- High heat fluxes encountered in the process cooling system
- Process temperatures up to 150°C
- Heat exchangers rated up to 20–30 Gcal/hr.

The cooling systems with large size, high hold-up volumes, associated stagnant areas, and likely ingress of nutrients due to leaks in the system, lead to proliferation of bacteria (especially the troublesome ones), that can cause corrosion of carbon steel, stainless steel and other alloys.

In a fertilizer plant recently commissioned in India, high levels of on-stream factors and production levels have been achieved. Several plants in the past experienced problems with cooling water that caused production limitations and increased downtime. The present trend of planning the plant turnaround after a gap of two or three years demands that the cooling water treatment program should give low corrosion rates (1 mpy or less) and avoid fouling due to scale or biofilm. The forced outages due to CW problems can be enormously costly.

In the recent past, a cooling tower was considered to have acceptable biological control with bacterial populations of under 100,000 colony-forming units per milliliter (cfu/ml).With planktonic bacterial populations this high, the drift of water droplets leaving a cooling tower could contain billions of potentially harmful bacteria. Often, this was the best that could be done without using dangerous chemicals or inducing excessive corrosion. However, the outbreak of Legionnaire disease due to drift from cooling towers brought into focus the harmful effects of some of the pathogenic bacteria in cooling water.

For control, the Center for Disease Control (CDC) and Cooling Tower Institute advise adherence to the policy of implementing an effective microbiological control program to reduce the risk. Emphasis should be placed on selecting the correct microbiocide. Another suggestion is to minimize the tower plume or drift into air intakes to buildings or air conditioning systems wherever possible. In some weather conditions, this is very difficult.

Another problem associated with microbial infestation is the deterioration of cooling tower lumber. This not only reduces cooling tower efficiency, but adds substantially to plant operating costs. Microorganism growths also cause other problems, such as odors and environmental pollution.

Microbial growths. Open recirculating cooling water systems are ideal incubators for promoting the growth

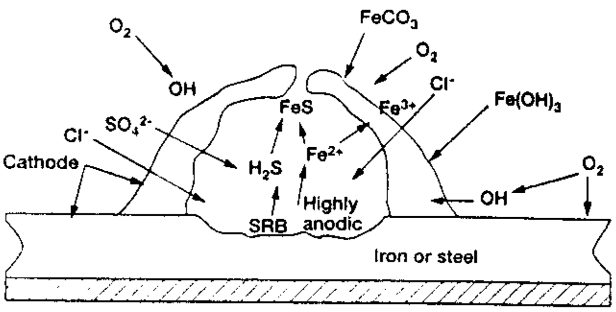


Fig. 2. Schematic diagram of the electrochemical and microbial processes involved in tuberculation.

and proliferation of microorganisms. They offer plenty of water, are exposed to sunlight, are maintained at a temperature of 30°C to 60°C, have a pH of 6 to 9, have good aeration, and provide a continuous source of bacteria from makeup water and ambient air. Additionally, there is a continuous supply of nutrients, such as inorganic or organic compounds, either from the makeup or added directly to the cooling water to control corrosion, scale or foam.

Makeup water also provides some nutrients like nitrates, potash, phosphorous, iron, manganese, etc. Air that is constantly being washed and scrubbed by the cooling tower also adds to the nutrients. Another major source of nutrient supply is leakage of the process fluids like ammonia, urea, oils, organics, etc.

Microorganisms present in cooling water can be categorized as planktonic or sessile. Planktonic microorganisms are dispersed in the cooling water, whereas sessile microorganisms attach to surfaces. Sessile organisms constitute what is known as biofilm, which accounts for the deposit and corrosion problems caused by microorganisms. Microorganisms in the biofilm are embedded in a gelatinous matrix. Nonmicrobial materials such as clay, silt and precipitated inorganic salts may also be present in the biofilm.

When deposits are primarily the result of microorganisms, the problem is referred to as biological fouling or biofouling. When corrosion is primarily the result of microorganisms, it is referred to as microbiologically induced (or influenced) corrosion (MIC).

Most microbiological problems associated with industrial process water systems are caused by a mixed group of microscopic plants or plant-like organisms referred to as the micro flora. Very rarely is a single type of microorganism completely responsible for widespread operational problems in a system. The types of microorganisms, or micro flora, responsible for creating problems in industrial water include algae, bacteria and fungi.

Structure of microorganisms. Algae are the most commonly observed biofouling problem since they are easily visible. Algae usually flourish on wetted surfaces exposed to sunlight and oxygen, such as cooling tower lumber, mist eliminators, screens, distribution systems and side louvers. All contain coloured pigments, the most important of which is chlorophyll. They can appear green, brown or red; and occur in damp areas where there is direct or diffused light. Under these conditions, algae can develop into large slime layers, causing blockages and reduced efficiency.

Table 3. The reactions involved with SRB

Electrolytic dissociation of water:	$8H_2O$	$\Rightarrow$	$8OH^- + 8H^+$
Anode reaction:	$4Fe$	$\Rightarrow$	$4Fe^{2+} + 8e^-$
Cathode reaction:	$8H^+ + 8e^-$	$\Rightarrow$	$8H^O$
Cathodic depolarization by SRB:	$SO_4^{2-} + 8H^O$	$\Rightarrow$	$S^{2-} + 4H_2O$
Corrosion product formed:	$Fe^{2+} + S^{2-}$	$\Rightarrow$	FeS
Corrosion product formed:	$3Fe^{2+} + 6(OH)^-$	$\Rightarrow$	$3Fe(OH)_2$
Summarized equation:	$4Fe + SO_4^{2-} + 4H_2O$	$\Rightarrow$	$FeS + 3Fe(OH)_2$ $+ 2(OH)^-$

Bacteria are unicellular, microscopic, plant-like organisms that are similar to algae but lack chlorophyll. They exist in three basic forms: rod-shaped (bacillus), spherical (coccus) and spiral (spirillus). In general, bacteria are the greatest biofouling problem in water systems and are most apparent on heat-transfer surfaces. In cooling towers, more than 50% of the fouling is either by Pseudomonas or Aerobactor species. Anaerobic bacteria such as sulphate-reducing bacteria (SRB) can grow under these deposits, leading to severe corrosion-related problems.

Fungi can be an important component of slime. Fungi are more likely to be found on packing inside a cooling tower, where they tend to cause rotting in wood used in the tower structure. Fungi are similar to algae, but do not contain chlorophyll. The major forms of fungi are yeast and molds. They require moisture and air, but not sunlight and exist on nutrients found in water or substances to which they are attached, like algae and bacteria.

Metabolism. Bacteria, algae and fungi are capable of synthesizing a vast number of enzymes, many of which are secreted into the surrounding environment. These enzymes can break down a variety of inorganic and organic molecules to provide the organism with the food and energy it needs to grow and multiply. Simultaneously, microorganisms excrete a large number of organic and inorganic acids and other waste materials that can create local concentrations of ions. Through respiration, microorganisms use up substantial quantities of oxygen. As a result of these normal metabolic functions, microorganisms, if left uncontrolled, lead to problems such as system deposits, loss of heat transfer, corrosion, pH depressions, depletion of dissolved oxygen and loss of applied inhibitors.

Energy and nutrient requirements. All living organisms require an energy source. Some microorganisms such as green plants and algae are capable of using light (daylight of direct sunlight) as their energy source. Some have the unique ability to use reduced inorganics such as elemental sulfur and hydrogen sulfide. Others rely on the oxidation of an element such as iron and manganese.

Respiration is an energy-yielding oxidation-reduction reaction in which the oxidant is inorganic. In the course of their evolution, bacteria have developed different kinds of respiration that can be characterized based on the nature of the reductant and oxidant. Table 1 shows the oxidants and reductants in various bacterial respirations.

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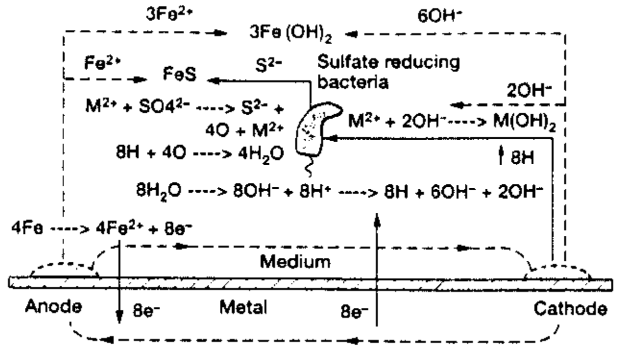

Fig. 3. Reactions involved in biofilm due to SRB-induced corrosion.

All living organisms require carbon. Some get it from carbon dioxide, some require additional complex organic carbon sources such as sugars. Green plant life converts CO_2 into carbohydrates through photosynthesis. Some organisms can use very complex carbon molecules such as cellulose, lignin and tannin as a carbon source.

All organisms require nitrogen in some form. Microorganisms vary greatly in their nitrogen requirement and their ability to use nitrogen. Some types use atmospheric nitrogen. Others use inorganic nitrogen compounds, and still others derive nitrogen from proteins and other organic sources.

All organisms require sulfur and phosphate. Some bacteria use organic sulfur compounds while others use an inorganic sulfur such as SO_4 ions. The phosphate requirement has great importance in cooling water treatment where polyphosphates or organic phosphates are present, because the microorganisms may break them down to orthophosphate. This action removes the inhibitor and usually increases the potential for tricalcium phosphate precipitation.

Trace minerals such as sodium, potassium, cadmium, magnesium, manganese, iron, zinc, copper, phosphorous and cobalt are also required for growth. These are mostly available from the makeup water, soil dust from air and treatment chemicals.

The organisms contain vitamin-like compounds. These compounds are complex molecules that are required only in minute quantities for growth. Some microorganisms (e.g., Pseudosomonas bacteria) are capable of synthesizing their entire vitamin requirement from other compounds; others must have their vitamins furnished by the environment.

The nutrient requirements are shown in Table 2.

MICROBIOLOGICAL DAMAGE

Microbiological problems are mainly biofouling and corrosion, which coexist together in an infested system.

Biofouling. The distinction between biological slime and other microbiological deposits is the fact that slime consists of almost all the biological mass itself. Very little, if any, nonmicrobiological mass is involved with the deposit formation. The build-up of biological slime can occur on heat-transfer surfaces in a short period of time, as little as 4 to 8 hours, and cause significant reduction of heat transfer. The types of microorganisms that cause slime are typically the heavily encapsulated, fast-growing bacteria such as species of Aerobacter, Arthrobactor, Proteus, Bacillus, Pseudomonas and others.

Microbiological deposits that cause plugging and fouling are perhaps the most commonly encountered problems. Fouling of cooling towers, heat exchanger surfaces, screens/filters and other parts of cooling water systems is often caused by the growth of a mixed microflora, including fungi, algae and filamentous bacteria. The actual mass of a deposit that plugs and fouls the system may consist of only a small part of the microbiological substance, with the primary component being silt, dirt, scale fragments and corrosion byproducts. The microorganisms, especially the filamentous types, entrain nonbiological suspended solids and subsequently serve as a binding agent for deposits that cause plugging and fouling. In contrast to a slime problem, plugging and fouling usually requires several days or weeks to reach a point where operational problems are encountered.

Macrofouling. Filiform organisms accumulate oil and hydrocarbons in a manner similar to that in which iron bacteria accumulate iron. Metabolism of these compounds include such harmful byproducts as carbon dioxide, hydrogen sulfide and hydrochloric acid.

In cooling water systems using fresh water as a coolant, heat exchangers have been fouled by such aquatic organisms such as spiders, ticks, mites, scorpions, river crabs, mussels and barnacles, which tend to accumulate in the low flow water box. Heat exchangers near coastal waterways have been shutdown by marine organisms such as barnacles, clams, squid, sea urchins, jellyfish, sponges, starfish and octopi. These organisms are much larger than the small unicellular types and can also form deposits in cooling systems, especially in once-through systems using surface waters. These deposits are termed macrofouling to distinguish them from those formed by the accumulation of large numbers of microorganisms.

Biofilm formation. A solid surface exposed to water in an open atmosphere can become contaminated with microorganisms and organic compounds in a relatively short period of time. The development of a biofilm is considered to be a multistage process involving the following major steps (Fig. 1):

- Formation of an organic conditioned film on the surface. It is generally believed that the first step to biofilm formation on a surface is the absorption/adsorption of organic molecules (e.g., the humic acid substances present in most natural waters). It is to this organic conditioning film that adhesion of the microorganisms occurs
- Transport of microorganisms from the water to the solid surface
- Adhesion of microorganisms at the surface water interface
- Replication of the attached cells and production of exopolymers. These polymers are referred to as extracellular polysaccharide (EPS)
- Detachment of parts of biofilm as a consequence of shear stress and reentrainment in the flowing water to repeat the process of biofilm formation elsewhere.

The biofilm can cause losses in heat transfer due to

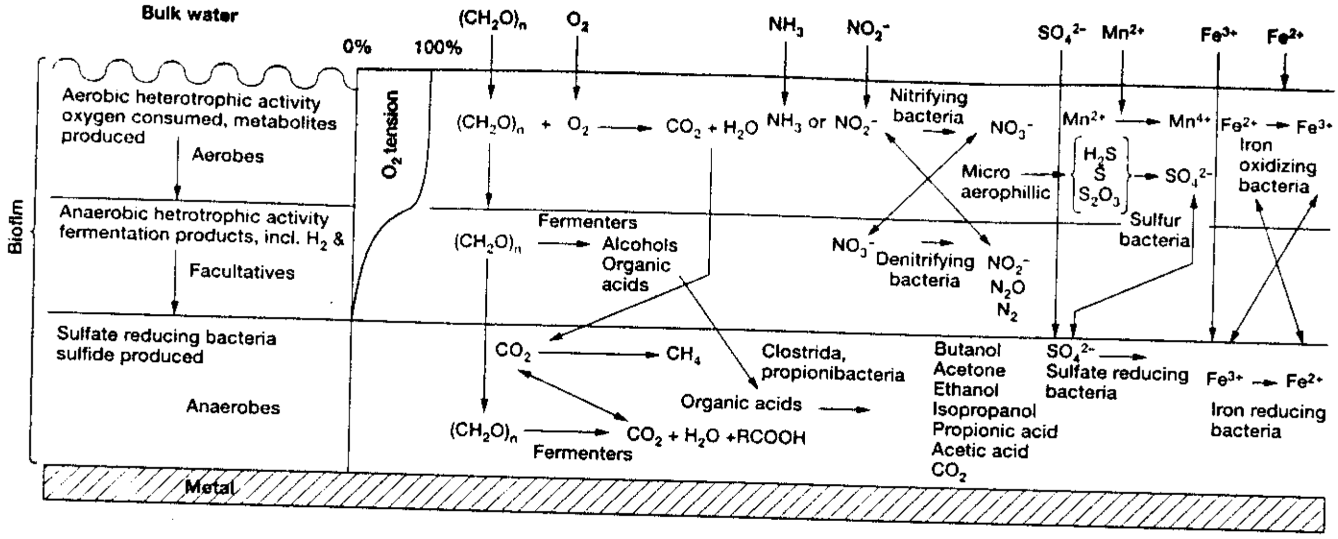

Fig. 4. Oxygen profile in a typical biofilm and possible reactions in the strata.

its insulating properties. Kinetic energy is absorbed from the flowing water. Increased pumping energy is required to overcome the frictional resistance of the biofilm. Even though the film is 95% to 98% water, the pressure decrease produced by a 500-micron thick film is greater than would be expected. If there is considerable EPS formed, such as in mature biofilm, less than 10% of its dry weight is in the form of microorganism cells. As a biofilm matures, it will have a high species diversity. Some of the physical and chemical factors that affect the biofilm's development are:

- Ambient and system temperatures
- Water flowrate (turbulence) past the solid surface
- Nutrient availability
- Roughness of the solid surface
- Water pH
- Particulate matter in the water.

Planktonic microorganisms, while not contributing to deposits or corrosion, can pose a health problem if pathogenic species are involved (e.g., Legionella), or pose odor problems if odor-producing microorganisms are present. Of course, problems associated with planktonic microorganisms can also occur in biofilms.

MIC. Corrosion related to the uncontrolled growth of microorganisms has become increasingly more frequent and more severe in all types of process cooling water systems. The reasons are numerous. Many investigators regard microbial corrosion as specialized form of electrochemical corrosion. For sake of convenience, the theories of biological corrosion are divided into aerobic and anaerobic systems. In recent nonchromate programs based on phosphate, the microbial corrosion potential is higher due to operation at higher pH which renders chlorine less effective and phosphate in the program works as nutrient.

Aerobic corrosion. Corrosion of iron and steel under oxygenated conditions generally involves the formation of acidic metabolites. The aerobic sulfur-oxidizing bacteria Thiobacillus can create an environment of up to about 10% H_2SO_4, thus encouraging rapid corrosion. Other organisms produce organic acids with similar results. This corrosion can be localized or general, depending on the distribution of organisms and metabolite products. Aerobic corrosion of iron and steel begins with the creation of oxygen concentration cells by deposits of slime-forming bacteria. Such corrosion is often accelerated by iron oxidizing bacteria in forming tubercules.

The process of tubercule formation is a complex one. A number of the reactions that can take place are illustrated in Fig. 2. The volcano-like structure often starts with a deposit of slime-forming and iron-oxidizing bacteria at a point of low flow. This creates an oxygen concentration cell, thus promoting dissolution of iron as Fe^{2+} under the deposit. As the Fe^{2+} ions move outward, they are oxidized to Fe^{3+}; this occurs electrochemically as they encounter higher oxygen concentrations and/or by the action of iron bacteria. The resulting product, $Fe(OH)_3$, mingles with the biodeposit to form a wall of the growing tubercule. When bacteria are present, the tubercule structure is usually less brittle and less easily removed from the metal surface. The outside of the tubercule becomes cathodic, while the metal surface inside becomes highly anodic.

As the tubercule matures, some of the biomass may start to decompose, providing a source of sulfates for sulfate-reducing bacteria (SRB) to use in producing H_2S in anaerobic interior solution. In some cases, the sulfur-oxidizing bacteria may assist in the formation of sulfates. Depending on the ions available in the water, the tubercule structure may contain some $FeCO_3$ and, when SRB are present, some FeS. Finally, if there is a source of chlorides and if the iron oxidizing bacteria Gallionella are present, a highly acidic, ferric chloride solution may form inside the tubercule.

Generally, not all of the above reactions will take place in any single environment. As individual tubercules on a surface grow under the influence of any combination of reactions, they will eventually combine to form a mass that severely limits the flow (or even close it off altogether), leaving a severely pitted surface underneath.

Other aerobic organisms common to cooling water systems are nitrifying, and can oxidize NH_3 to nitrate.

Table 4. Some of the metal-corroding bacteria

Bacterium	Action	Problem
Aerobic		
Gallionella	Convert soluble ferrous ions to insoluble ferric ions	Produces iron oxide deposits. Increases corrosion.
Crenotrix		
Spaerotilus		
Thiobacillus ferrooxidans		
Thiobacillus thiooxidans	Sulfuric acid producer	
Anaerobic		
Desulfovibrio (D. desulfuricans)	H_2S producers (sulfate reducers)	Corrodes metals Reduces chromates Destroys chlorine Precipitates zinc
Desulfotomaculum (D. Nigrificans, Clostridium)		
Desulfomonas		

This is accompanied by decrease in pH and occurs according to the reaction:

$$NH_3 + 2O_2 = HNO_3 + H_2O \qquad (1)$$

Rapid general thinning can occur in copper-based alloys and steel. Nitrite-based corrosion inhibitors can be rendered ineffective due to their oxidation to nitrate by this species of bacteria. Several other groups of bacteria exist in cooling water environments. Iron-depositing bacteria can oxidize Fe ion to insoluble Fe_2O_3, which will subsequently deposit on the inside of the piping, reduce flow and aggravate crevice corrosion. Slime-forming bacteria form dense, sticky biomasses that impede water flow and contribute to fouling by sustaining the growth of other organisms.

Anaerobic corrosion. Acidic water produced by some forms of anaerobic bacteria will directly attack metal surfaces. One species that is quite common is SRB. These organisms are anaerobic and convert dissolved sulfur compounds, that is, sulfate ions, to hydrogen sulfide (H_2S). Carbon steel, stainless steel, and copper-based alloys can be severely corroded by H_2S. Desulfovibrio desulfuricans is the most prevalent species. It exists under deposits devoid of oxygen.

The general reactions in Table 3 occur (Fig. 3).

The formation of black iron sulfide deposits in conjunction with a rotten egg odor are also characteristic of attack by SRB. The aerobic sulfur bacteria Thiobacillus can oxidize sulfur, sulfides or sulfates to H_2SO_4. Localized pH depression as low as 1 can occur, causing severe general thinning of steels where these organisms contact the metal. Thiobacillus and desulfovibrio bacteria can both exist simultaneously in close proximity. The anaerobic SRBs can survive beneath the aerobic bacterial deposits, in symbiotic relationships. The oxygen profile and activities due to aerobic and anaerobic bacteria together in a biofilm are shown in Fig. 4.

Pitting corrosion of cooling water systems as a result of MIC has also been observed. MIC is frequently divided into two types. The first, active MIC, involves the direct participation of microbes. In other words, the microbes are intimately involved in the corrosion process. This could include an effect of microbes upon pH, dissolved oxygen, secretion of corrosive wastes, etc. Alternatively, passive MIC is observed. In this case, the biomass resulting from biological growth is an indirect contributor to MIC. The presence of biomass can, for example, lead to corrosion via an underdeposit mechanism.

The exact mechanism by which active MIC results in pitting corrosion is not fully understood. At least four types of active MIC have been identified. These include sulfate-reducing bacteria, acid-producing bacteria, metal-depositing bacteria and slime-forming organisms.

While the corrosion mechanisms associated with active MIC are complex and not completly understood, the corrosion morphology produced by MIC on selected materials has been studied rigorously and is well quantified. Microscopic examination of areas on mild steel subjected to MIC frequently display broad hemispherical pits. Smaller pits located within these pits and undercutting are another common feature of MIC. Frequently, tunneling of these pits is observed. The pits can also exhibit striated features. Finally, selective attack of specific microstructural constituents is one identifying feature of MIC.

Common SRBs include desulfovibrio, desulfobactor and desulfomaculum. Sulfide-producing (or sulfate-reducing) bacteria produce chemicals that result directly in metal corrosion. These convert water-soluble sulfur compounds to H_2S. This conversion usually starts with sulfate that either occurs naturally or comes from the addition of sulfuric acid for pH control. The bacteria metabolizes the sulfur and discharges H_2S, creating and living in an anaerobic, reducing environment. H_2S is acidic and aggressively attacks metals, principally mild steel, but also stainless steel and copper alloys. However, most metals are attacked by a combination of low pH, sulfide and reducing conditions. Nickel and nickel-based alloys are severely pitted under such conditions. This corrosion is often readily identified by concentric ridges formed in the pits. These ridges can be seen without magnification, but severe attacks can obliterate them.

In a recirculating cooling water system, corrosion due to these organisms can occur at a rapid rate. Perforations of a 16-mm mild steel corrosion coupon occurred within 60 days, a rate of approximately 100 milli-inches per year (mpy). Stainless steel, nickel and other alloys subject to this attack failed in 60 to 90 days in heat exchangers and vessels. Pitting rates vary from 50 to 200 mpy; penetration is dependent on the degree of contamination and the rate of growth. Corrosion product accumulations containing sulfate reducer counts of 10,000 or higher colony forming units per gram are usually associated with significant wastage. Counts above 100,000 are common only in severely attacked systems.

Although sulfate reducers probably are not uniformly distributed throughout the deposit and corrosion product mass (especially in aerated systems), similar counts in large amounts of material taken from corroded steel surfaces are common. Counts in fluids are almost always much lower, but any positive fluid count usually indicates large numbers of viable sessile bacteria somewhere in the system. Planktonic counts (in water samples) are usually unreliable as an indicator of active corrosion. The presence of any sulfate reducers in the water, however, indicates much higher concentrations of these organisms on surfaces somewhere in the system.

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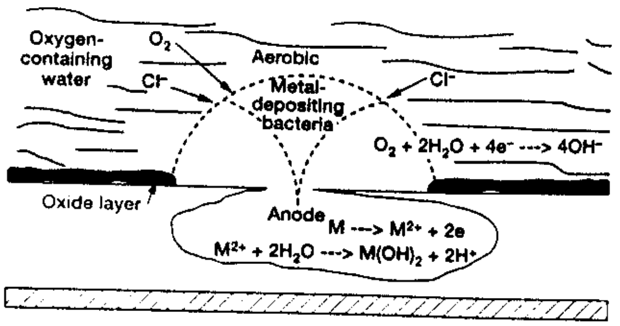


Fig. 5. Possible reactions under tubercule created by metal-depositing bacteria.

Even with chromate-zinc based corrosion inhibitors and good contol of pH in a recirculating cooling system, these organisms have the ability to penetrate metals rapidly. H_2S reacts with chromate and zinc to remove the inhibitor from solution and form a contact with the metals, resulting in reduced chromate and precipitates of zinc salts, thus causing fouling and lack of metal protection.

Using chlorine to control these organisms is not effective because: 1) the organisms are usually covered by slime masses that prevent the chlorine from reaching the sulfide producers, and 2) the H_2S surrounding these organisms reacts with chlorine to form chloride salts that negate the effect of chlorine. One part H_2S theoretically requires about 8.5 parts of chlorine for complete reaction. It has been shown by laboratory tests that a high concentration of H_2S and low pH occur around the organism colony. Thus, even large amounts of chlorine can be consumed without killing the bacteria.

One of the organisms of this group is chlostridium. In addition to producing H_2S gas, chlostridium yields methane, providing a nutrient source for slime-producing bacteria that grow in the immediate vicinity.

All of these bacteria are difficult to control. Chlorine cannot get to them due to the gases they produce. However, chlorine dioxide and ozone are more effective and some of the nonoxidizing biocides like long chain (fatty acid) amine salts, glutaraldehyde and organosulfur compounds are capable of controlling these SRBs.

In cooling water systems, it is often possible to find corrosion caused by SRB despite using continuous chlorination and nonoxidizing biocides, and despite consistently negative results from testing the bulk water SRB activity. Corrosion coupons frequently show the characteristic pitting indicative of SRB activity. Apparently monitoring and controlling the planktonic bacteria (SRB) may not be sufficient. Testing for sessile bacteria (SRB) may be required.

Some types of bacteria that directly cause corrosion in metals are summarized in Table 4.

MIC and metallurgy. MIC can affect all types of metals used in CW systems. MIC generally cause an intense, localized attack. Discrete hemispherical depressions form on most alloys, including stainless steels, aluminum, carpenter 20 and carbon steels. Few cases occur on titanium. Copper alloy is not well defined. Pit interiors are characteristically smooth and distinctly hemispherical, but become rougher on less-noble alloys. Pits tend to cluster together, overlapping to form irregularly dimpled surfaces.

Frequently, a lightly etched aureole surrounds the pit clusters. These etched areas are often produced by shallow corrosion beneath deposit and slime masses that cover the sulfate reducers in service. Mechanisms for MIC are different for stainless steel (SS) and carbon steel (CS). Because of this, attempts to upgrade CS systems with types 304 SS and 316 SS to alleviate MIC problems are often ineffective and sometimes result in more problems. Failures in CS are most often attributed to SRB and APB activity. Failures in SS are often due to the formation of differential aeration cells resulting from the activities of metal-depositing bacteria.

Manganese and iron-oxidizing bacteria (MFOB) have long been recognized for their ability to deposit iron hydroxide or manganese oxide in structures outside their cells. Metal depositing organisms create environments that are conducive to corrosion, especially on metals that are prone to crevice corrosion. Dense deposits of cells and metal ions create oxygen concentration cells (Fig. 5) that effectively exclude oxygen from the deposit and initiate a series of events that are individually or collectively extremely corrosive.

MICROBIOLOGICAL CONTROL

The most practical and efficient method of controlling microbiological activity in cooling water is by using microbiocides, also commonly called biocides. Microbiocides kill microbiologicals or inhibit their growth and reproductive cycles. Biocides perform their function in various ways. Some biocides alter the permeability of the microbe cell wall, thus interfering with their vital life processes. Others damage the cell by interfering with the normal flow of nutrients and discharge of waste.

Biocides can be either oxidizing or nonoxidizing toxics. Commomly used biocides are listed in Table 5.

Oxidizing biocides. Chlorine is the most prevalent industrial oxidizing biocide. However, chlorine becomes less effective at higher pH in alkaline environments. Chlorine is both an excellent algicide and bactericide. In the presence of ammonia, as is found in fertilizer plants, the chlorine effectiveness substantially reduces due to the formation of chloramines. The most troublesome SRB bacteria, desulfovibrio, can develop a strong resistance, requiring an increase in chlorine concentration or a change to an alternate biocide. In the presence of bioslimes, chlorine penetration is impaired. To improve the effectiveness of chlorine, bromine chemistry is being developed which gives a wider pH range and is not affected by ammonia. Bromine use requires chlorine for bromine generation.

Another oxiding biocide finding wider application is chlorine dioxide (ClO_2). This gas does not form HClO in water but exists solely as ClO_2 in solution. ClO_2 can be effectively used in cooling waters contaminated with ammonia or phenols due to low demand for reaction with these species. Chlorine dioxide does not produce chlorinated organics as is the case with chlorine donors.

Another oxidizing biocide which is receiving more attention is ozone. It is environmentally the most friendly biocide and has high efficacy especially for

Table 5. Different types of biocides

Oxidizing biocide	Nonoxidizing biocides
Chlorine and chlorine donors	Amine and ammonium compounds
Bromine	Organo sulfur compounds
Chlorine dioxide	Thiocyanates
Ozone	Isothiazolones
	Organo halogen compounds
	Glutaraldehyde
	Guanidine compounds
	Organic thiocyano-azole compounds

Table 6. Regulated biocides due to environmental reasons

Biocide	Reasons
Mercury-containing compounds	Potential human health effects to nervous system, and acute poisoning; concern for potential bioaccumulation in aquatic species.
Pentachlorophenol	Potential human health effects such as cancer, effects on reproductive systems and liver; concern for aquatic toxicity and bioaccumulation.
Organotin compounds	Potential human health effects to the liver and immune system.
Simazine	Cancellation from swimming pool use because of excessive cancer risk.
Formaldehyde	Potential inhalation cancer risk.
Chlorine	Potential for formation of chlorinated organics that may be hazardous to the environment and humans.
Chromium	Potential human carcinogen.

slime control. It is a strong biocide and its use leaves no harmful residues.

Chlorine donors are chemicals that release active "chlorine" in water. Two chemicals commonly used in cooling water systems are sodium dichloro-s-triazine trione, or sodium dichloroisocyanurate and 1,3-dichloro-5,5-dimethylhydantoin. Since these two chemicals do not release "chlorine" all at once, but make it slowly available, they can be considered controlled release forms of the oxidizing agent. Their modes of action are considered to be similar to gaseous chlorine, but it is possible that they can penetrate cell membranes and carry out their oxidative reactions within the cell.

Nonoxidizing biocides. Selecting of the proper biocide depends on a number of factors. These are the primary considerations:

- Type of microorganism
- Operating history of the system
- Type of process cooling water system
- Chemicals used for scale or corrosion control
- Water characteristics
- Environmental limitations and restrictions.

Nonoxidizing biocides can be more effective than oxidizing biocides because of their overall control of algae, fungi and bacteria. They also have greater persistence and many of them are pH independent.

One organo bromine broad spectrum nonoxidizing toxicant is 2,2-dibromo-3-nitrilopropionamide (DBNPA). This molecule is an extremely potent bactericide and is only slightly effective as an algicide. It has little fungicidal activity. The toxicity of DBNPA decreases with an increase in alkaline pH.

Organic sulfur compounds include a wide variety of different biocides, of which methylene bisthiocynate (MBT) is the most common. Their mode of activity is inhibiting cell growth by preventing the transfer of energy or life-sustaining chemical reactions from occuring within the cell. MBT is effective in controlling algae, fungi and bacteria, most notably desulfovibrio. A shortcoming of MBT is its pH sensitivity and rapid hydrolysis in the alkaline pH range.

Under broader alkaline conditions, sulfur-based biocides, such as bis-trichloromethylsulfone and tetrahydro-3,5-dimethyl-2H -1,3,5-thiadiazine-2-thione, are more appropriate. The former is active in the pH range of 6.5 to 8, and the latter in more alkaline cooling water systems.

Isothiazolinone is a relatively new sulfur-containing biocide. It is effective in controlling algae and bacteria and can be used over a broad pH range with no activity decrease.

Quaternary ammonium salts are generally most effective against algae and bacteria in alkaline pH range. These compounds cause cell death by reducing permeability of the cell wall, preventing the typical intake of nutrients necessary to sustain life. Because of their active surface, these compounds are easily rendered ineffective in systems heavily fouled with dirt, oil and debris.

Organic tin compounds, such as bistributyl-tin oxide are effective against algae and fungi. They function best in the alkaline pH range and provide synergistic biocidal activity when combined with quaternary ammonium salts.

Glutaraldehyde (1,5-pentanedial) is an effective broad spectrum biocide capable of controlling slime-forming and sulfate-reducing bacteria, fungi and algae. It functions over broad pH and temperature ranges and is compatible with chlorine. Glutaraldehyde is deactivated in systems containing NH_3 and other primary amines (that is, $-NH_2$ groups.)

Copper salts. Less than 1.0 ppm of copper (as Cu) dissolved in water will kill most algae and prevent future growth. The action of copper sulfate on algae appears to be one of blocking the transport of oxygen through the cell membranes, leading to death by asphyxiation. The inner cell protoplasm is released, giving a characteristic odor. Copper sulfate is not recommended for direct use in cooling water applications. Overfeed of product and plating of copper on mild steel or other noncopper surfaces can lead to severe pitting corrosion due to galvanic cells. In systems contaminated with ammonia, adding copper salts is not advisable. Additionally, because of environmental concerns, copper is not recommended.

Biocide application plans. The dynamics of microbial populations in cooling water systems are complex. In situations where one microbial group or species dominates, fouling problems can occur. In other instances, a balanced population mix can exist while no fouling is evident. One explanation for such an observation is that when balanced populations coexist, they compete with each other for the available nutrients and control each other's growth. When one group successfully displaces its competition, or has its competition removed, that group can grow unchecked.

Continued

Because of such considerations, some proprietary biocides are formulated to contain more than one active. Proper blending of actives can compensate for limitations in the kill spectrum shown by one or more of the actives. For example, if biocide A is an excellent bactericide but a weak fungicide, large amounts of A might have to be used to control potential fungal problems. Biocide B, however, is a fair bactericide and good fungicide. Combining A with B would broaden the spectrum of control without using high concentrations of A or B.

Another effect that might be noted when combining A with B is that, with no increase in the amounts of biocide used, the bactericidal power of the blend is much higher than expected. Synergistic effects can be demonstrated by combining two actives, and the outcome would be to control microorganisms at much lower combined concentration of A and B than could be achieved by A or B alone. This can result in reduced biocide concentration in an effluent as well as economic savings.

The spectrum of control can also be broadened by sequentially feeding biocides to a system. After treating the system with biocide A for a time, it is stopped and biocide B is fed. After another interval, B is stopped and A is fed again. This switching program can have the same outcome as blending the two actives for simultaneous feeding.

Another variation to be considered is the possible proliferation of biocide-resistant microbes in the system. The resistant forms may arise by mutation in the cooling system, but it is much more likely that their origin is outside the system. The biocide simply functions then to reduce its competition, and allows uncontrolled growth. This is more likely to occur during treatment with a single biocide active, because the probability of a microbe being resistant to more than one biocide active is extremely small if the actives are not similar. Switching programs or synergistically blended biocides would probably be equally effective in eradicating biocide-resistant microbes from a cooling system.

The intelligent choice of a biocide program can thus be helped by understanding the mode of action of the biocide products. This, combined with knowledge of the system and the influence the environment has on microbial ecology in cooling systems, permit proper and economical biological control.

Environmental concerns. Until now, the industry's most significant requirement for a biocide was that it be effective against a broad spectrum of microorganisms, is cost-effective, and be compatible with the product application environment (including no interference with the scale/corrosion inhibitors). However, with the current interest in environmental responsibility (i.e., greener chemicals), microbiocides must meet new demands:

- Broad spectrum of activity consistent with the application
- Very low toxicity
- Environmental acceptability
- Safety and ease of use in handling and storage
- Cost-effectiveness.

Table 6 lists a number of microbiocides that have become restricted or regulated due to environmental or human concerns in several countries.

New environmental legislation intiatives are forcing manufacturers and users of microbiocides to realize that efficacy of an active substance is only one aspect in the future assessment of acceptability of a microbiocide. Comparisons will be driven by risk assessment of the toxicology and ecotoxicology of each substance in question.

Because of the high costs and intense scrutiny associated with new biocides, active research is looking at combining two or more existing biocides as a means of reducing the amount of biocide needed for a given application or developing a more effective product for a specific application, and thus reducing the potential environmental impact. Along these lines, the use of nonbiocidal chemicals (such as surfactants, chelants and dispersants) to improve the performance of existing biocides is actively pursued.

NEW STRATEGIES

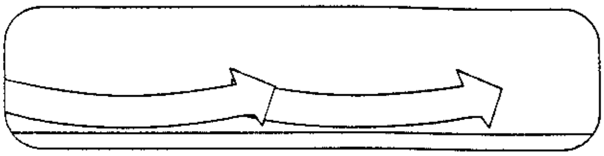
New approaches in controlling biofouling and MIC are based on what is believed to be the mechanism for biofilm formation outlined earlier. These new approaches focus on chemical treatment programs that do not function by killing the microorganisms, but by keeping the microorganisms from attaching to surfaces, or by dispersing them from surfaces if they do become attached. The dispersed microorganisms then can be killed with an oxidizing biocide such as chlorine or the more environmentally acceptable bromine, chlorine dioxide or ozone. Such chemical treatment programs are commonly referred to as biodispersants. Considering the complexity of the problem, completely replacing traditional biocides is not a possibility in the foreseeable future, but today's thinking is changing on how new biocides are developed.

Biodispersants. These are typically nonionic surfactants. Among the most effective are formulations consisting of ethylene and propylene copolymers. Biodispersants have no biocidal characteristics of their own; they are usually used in conjunction with oxidizing and nonoxidizing biocides to enhance their effectiveness. Biodispersants lower the water's surface tension, allowing the slime mass to disperse into the bulk water. This action makes a larger area of the biomass available for reaction with the agents. The action of biodispersants is shown in Fig. 6. By removing more of the slime mass, the biodispersant also accomplishes:

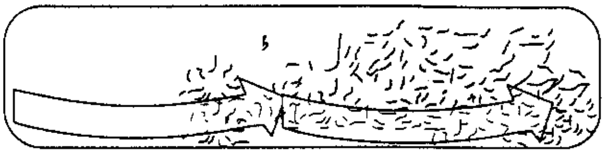
- Improved heat transfer of the metal surface by removing the biofilm
- Reduced potential for scale or fouling because less of the matrix is available for buildup
- Reduced possibility for the existence of anaerobic corrosive bacteria.

Biodispersants do not interfere with chemical treatment. They can be used with all open recirculating and once-through system treatments, corrosion inhibitors, scale inhibitors, biocides and dispersants. Being nonionic, they are effective over a wide pH range. They are also thermally stable over the typical range of cooling water temperatures. As with any surfactant, overfeed of a biodispersant can result in foaming.

While there are chemicals currently sold as biodispersants, success to date has not been such that they



Before biodispersant added



After biodispersant added

The function of biodispersant is mainly to break up slime masses, disperse them in the bulk water, and make them more accessible to biocides.

Fig. 6. The function of biodispersants.

pose a threat to eliminating the use of traditional biocides. However, this should change in the future as more research is put into understanding how bacterial attachment to a surface can be eliminated. Research into the use of chemicals 'to prevent bacterial adhesion has shown the critical nature of the substrate to which the bacteria attach. For example, the current theory is that bacteria tend to more readily attach to hydrophobic surfaces rather than to hydrophilic surfaces. While numerous nonionic surfactants are effective in preventing bacterial adhesion to hydrophilic substances such as glass, they have not been effective for hydrophobic surfaces. Whether a surface is hydrophobic or hydrophilic once submerged in water depends in part on water contaminants present.

Research indicates that it is feasible to have one chemical effective for controlling a variety of organisms and surfaces. However, performance is dependent on the surface and the microorganisms, and a blend of chemicals will usually be required to effectively prevent biofilm formation on surfaces.

Enzymes. Another approach receiving considerable attention is the use of enzymes to control biofilms. An enzyme is a protein molecule having both catalytic activity and specificity for the substrate. There are three approaches being investigated:

- Enhance the removal of biofilm
- Prevent the formation of biofilm
- Improve the efficacy of biocides.

One approach to controlling microorganism deposits is with enzymes, which can catalyze the hydrolysis reaction of extracellular polysaccharides produced by the microorganisms after they attach to surfaces. Another approach is the use of enzymes to disrupt the microorganisms' attachment to surfaces, thus preventing biofilm formation.

FUTURE OPTIONS

Ozone, the green biocide. For microbial control, there is considerable pressure on the industry to develop chemical treatment programs that are safer, more effective and have less environmental impact than currently used microbiocides. There are approaches being pursued (e.g., enzymes and biodispersants) that may possibly eliminate the need for currently used biocides. These techniques may provide some immediate benefit, however, in that they will make currently used biocides more effective against biofilms, thus abating the environmental impact by reduction of the amount of biocide needed.

Interestingly, tests of ozone with bromine and chlorine dioxide are showing encouraging results and may emerge as a greener alternative to speciality microbiocides. From previous uses of ozone in drinking water and wastewater treatment, it is known that ozone acts as a powerful oxidizer and a strong disinfectant. In addition, the short half life of ozone in aqueous solution results in minimal discharge of toxic biocide to the environment. Thus, the advantage of ozone with respect to other biocides are: minimal onsite chemical inventory, nontoxic discharge, and potential for water conservation. As a cooling tower treatment, ozone has only recently become a viable option. Well-controlled ozone systems have bacteria populations well under 1,000 cfu/ml, often less than in the makeup water to the cooling tower. The unique combination of high toxicity during treatment with nontoxic discharge could make ozone the biocide of choice in the future.

Cooling tower design and operation. Another area that must be addressed is the general layout and operation of the cooling tower system. These are some considerations:

- Instead of a single large cooling tower, the system could be split into separate towers on the basis of metallurgy so that different corrosion and microbial treatment programs can be followed. The complexity of piping layouts and large hold-up volumes can be avoided. The velocity can be uniformly maintained in all the heat exchangers in a smaller system.
- Reduce the basin and sump hold-up volume and depths to the minimum required. The depth should be such that scrubbing and cleaning of the bottom is possible, especially the basins. The sump depth will be dictated by the pump considerations.
- Side stream filters should have minimum hold-up volumes and dead spaces because they can become breeding grounds for bacteria. The filters remove all the dead biomass and suspended solids along with bacteria. The organic mass can provide food for all types of bacteria. The side stream filters should be regularly disinfected. Open self-cleaning gravity filters are better than the closed pressure sand filters because clean up is simple and biocide can be dosed any time after visual inspection.
- More use of plastic materials in the tower construction since lumber supports growth of algae, fungi and bacteria. Use FRP for side louvers and enclosures instead of asbestos sheets. Cover the water distribution decks of cross-flow cooling towers to cut off sunlight required for algae formation. Counter-current cooling towers avoid sunlight compared to cross-flow towers, and hence less algae formation.
- Use cooling water on the tube side instead of shell side as stagnant areas are more on shell side. When CW is on the tube side the channel covers should be provided with blow off ports to remove water from dead zones. Online addition of biocide in the dead zones in channels of large heat exchangers can help.
- Preclean and passivate the new system before putting into service.
- Do not keep any CW circuit idle with stagnant water. Keep circulation or keep them drained if required to be idle, biocide should be dosed periodically. Wet shutdown, coupled with stagnant water, creates an ideal environment for the growth of bacteria.
- In the cooling tower basin and sump, provide an effective distribution system for dosing of oxidizing biocide, such that the same can be used for aeration of the bottom layers which can harbor the anaerobic bacteria due to oxygen depletion.
- The critical heat exchangers should be provided an with self-cleaning filters at the inlet so that entry of foreign matter like tower material, insects, etc., is avoided which can lead to blockage and growth of bacteria in the blocked tubes.
- Locate the cooling towers to ensure that process emissions do not enter the towers.
- Maximize the use of direct air cooled heat exchangers especially for condensers. The combined wet and dry cooling towers can also be adopted depending on site conditions and locations and water availability. Use plate heat exchangers wherever possible as they have good flow turbulence to reduce biofouling. Another way is to use secondary cooling for large and critical heat exchangers using plate heat exchangers to cool closed loop coolant with secondary cooling water from the towers.

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