Water Treatment Strategies

Microorganism Control

Technical Report

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REPORT SUMMARY

This report presents an overview of the fundamental concepts of microorganism control and a discussion about how these concepts can be applied for optimizing current prevention and mitigation strategies in nuclear power plants service water systems. A database has been established to facilitate development of treatment and operation strategies that meet the requirement for preventing microbiological problems while overcoming limitations with current water treatment technologies.

Background

Electric power generating plants, pulp/paper mills, steel mills, sugar/alcohol plants, and refinery/petrochemical plants are a few of the many industries that are concerned with problems related to the uncontrolled growth of microorganisms in process cooling water. Process cooling water systems include once-through cooling water, open re-circulating cooling water, and closed loop cooling/chill water.

Most microbiological problems involving industrial process cooling water systems such as microbiologically influenced corrosion (MIC), biofilm/biomass (slime formation), or plugging and fouling are caused by a mixed group of microscopic plant-like organisms referred to as microflora.

In the past, operating conditions and procedures supported only secondary consideration of potential problems caused by microorganisms. However, under present operating requirements, considering and implementing microorganism control in process cooling water systems is a primary concern. Environmental impact, high energy costs, engineering innovations, high-technology operating conditions, and large capital investments are but a few of the circumstances that have made it imperative to consider microorganism control as a primary priority in process cooling water treatment.

Objectives

- To examine microorganism control strategies currently used by the nuclear power industry.
- To assess the level of industry satisfaction with these strategies.

Approach

The research team reviewed literature on the fundamental concepts of microorganism control, including use of biocides, non-biocide prevention and mitigation technologies, and other water treatment technologies currently available. The research team also conducted a survey of EPRI member utilities to assess the level of industry satisfaction with these technologies.

Results

A survey and other resource information confirmed that the majority of plants are satisfied with their current strategy but would be interested in optimizing some parts of their treatment program.

Although the industry uses a variety of strategies, the majority of plants use oxidizing biocides. A few plants supplement the biocide addition by applying non-oxidizing biocides and/or biodispersants and penetrants. These supplemental treatment chemicals are used, for example, when regulatory permits prevent increasing the dosage level or extending the duration of oxidizing biocide additions. Several plants indicated that mechanical/physical cleaning is a routine part of their microorganism control strategy. Only a few plants have explored the possibility of using non-traditional strategies for microorganism control.

A critical factor for performing an optimized microbiological control program is that the procedure must provide “real-time” information that confirms what is currently happening. Preventing microbiological problems is a more efficient approach than attempting to mitigate an existing microbiological problem.

EPRI Perspective

This report will be useful to power plant engineers who are responsible for operating, inspecting, maintaining, and repairing service water, circulating water, and fire protection systems and who encounter pitting-type degradation in stainless steel and copper alloy components. The report will help identify instances when microbiological problems may have played a key role in degradation and loss of performance, and it will suggest what can be done to reduce plant susceptibility to this type of degradation.

Keywords

Microbiologically influenced corrosion
MIC
Biofilm/biomass
Oxidizing biocides
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INTRODUCTION

1.1 Historical Background of Microorganism Control

Most microbiological problems associated with industrial process cooling water systems such as microbiologically influenced corrosion (MIC), biofilm/biomass (slime formation), or plugging and fouling are caused by a mixed group of microscopic plant-like organisms referred to as the microflora. The microflora is typically composed of algae, fungi, and bacteria. Very rarely is a single type of microorganism completely responsible for widespread operational problems in a system. Each of the different types of microorganisms has unique characteristics as well as many characteristics in common. An insight as to the growth requirements and characteristics of the microorganisms helps to identify and control the problems associated with process cooling water systems [1].

Process cooling water systems include once-through cooling water, open re-circulating cooling water, and closed loop cooling/chill water. Electric power generating plants, pulp/paper mills, steel mills, sugar/alcohol plants, refinery/petrochemical plants, etc. are a few of the many industries that are concerned with problems related to the uncontrolled growth of microorganisms in process cooling water.

In the past, operating conditions and procedures existed that supported only secondary consideration of potential problems caused by microorganisms. However, under present operating requirements, considering and implementing microorganism control in process cooling water systems is a primary concern. Impact on the environment, high energy costs, engineering innovations, high-technology operating conditions, and large capital investments are but a few of the circumstances that have made it imperative to consider microorganism control as a primary priority in process cooling water treatment [2].

Problems associated with the uncontrolled growth of microorganisms in cooling water systems can be placed in three categories:

1. Microbiological “slime” (formation of biofilm or biomass) resulting in loss of heat transfer
2. Plugging and fouling resulting in reduction in cooling water flow-rate
3. Microbiologically Influenced Corrosion (MIC)

Historically, the strategy used to deal with any or all of these problems was to operate the cooling process until its loss of performance was no longer acceptable. The system was shut down and mechanical/chemical cleaning was performed. Plant operators have now become more aware of the problems caused by microbiological growth. Current operation requirements no longer tolerate this strategy, and technologies have been developed to minimize problems caused by uncontrolled growth of microorganisms in the cooling systems. The new technology often involves the application of "biocides" to inhibit microbiological growth to some extent. The biocides are required to inhibit microbiological growth in many different system conditions using makeup (raw) water from rivers, wells, reservoirs, or the ocean. Unique growth characteristics and the impact of water chemistry (e.g., pH) initially were not primary considerations for selection of biocides. Presently, however, the impact of the discharge of biocides through plant effluent has also become a major consideration in the development of treatment strategies and selection of environmentally acceptable biocides.

It may be an understatement to say that the current treatment strategies for microorganism control have been "problem driven." Many comments have been made to support this observation. They include: "We don't treat unless, or treat only when, we have a problem." "Biocides are too expensive." "We cannot use biocides because of environmental regulations." "Biocides contribute to increased corrosion." "We are using chlorine just as we have since the plant started up (35 years ago)." "Our plant system design does not comply with using biocides."

The objective of this project is to examine the microorganism control strategies currently used by the nuclear power industry. A survey was made of EPRI member utilities to assess the level of industry satisfaction with these strategies. The survey also was intended to disclose current needs and future areas of concern. A database has been established, which should be useful in developing treatment and operation strategies that meet the requirement for preventing microbiological problems while overcoming the limitations associated with current water treatment technologies.

This report provides a review of the literature pertaining to the fundamental concepts of microorganism control including the use of biocides, non-biocide prevention and mitigation technologies, and other water treatment technologies currently available. Overviews of the historical and current technologies have been published in several textbooks [3, 4, 5, 6, 7].

2

FUNDAMENTAL CONCEPTS OF MICROBIOLOGICAL CONTROL

2.1 Fundamentals of Microbiological Control

The basic objective of controlling the growth of microorganisms in industrial process cooling water systems is to prevent or mitigate problems caused by microorganisms. The procedures for microorganism control are based on logic and common sense, using the basic fundamentals of microbiology, and in accordance with the requirements and limitations of the industrial process itself.

2.1.1 Preventing the Problem

The first fundamental to recognize is: *Preventing a problem is much more practical and achievable than trying to clean up or mitigate a microbiological problem that has gotten out of control.*

Most problems are due to negligence or some unpredictable circumstances. Therefore, the methods to be employed for preventing microbiological problems must provide some protection from possible negligence and must be flexible enough to account for most unpredictable events. The use of "broad spectrum" biocides/biostats is part of a sound microbiological control program used in process cooling water systems. "Broad spectrum" means having the capability of controlling the growth of a wide range of microorganisms. In addition to this, the broad-spectrum material must be effective over a wide range of environmental/operational conditions that are found within a single given process water system. Certainly, in a process cooling water system, there are many different conditions that may influence both the growth of microorganisms and the activity of biocides/biostats; thus, to be effective, the treatment must be able to function under all of these conditions.

Although an important factor, the routine use of broad-spectrum biocides is not the only tool required for preventing MIC. The greatest degree of success is obtained when broad-spectrum biocides/biostats are used in conjunction with the following:

- System design considerations
- Selection of materials of construction
- Physical and chemical maintenance cleaning
- Water source considerations

- Treatment during outages and wet layup
- Treatment during hydrostatic testing

These same factors must be considered when mitigating an existing microbiological problem. However, when dealing with an existing problem, the treatment approach is not one of prevention or routine maintenance. The action must be directed to eliminating the cause of the problem [1].

2.1.2 Mitigating the Problem

The second fundamental concept is: *Mitigation of MIC, or other microbiological problems, involves the use of physical and chemical cleaning procedures, as well as the application of biocides with specific efficacy to the microorganisms identified as the cause of the problem.*

Most mitigation efforts require that physical cleaning, chemical cleaning, or both be used as a first step in the process. The application of a biocide is usually a second step following cleaning, or in some cases a supplementary factor in conjunction with the chemical/physical cleaning. During mitigation, the environmental and operational conditions of the system are very atypical to those during actual operation. Therefore, the non-biological criteria become the most significant of those considerations [1].

2.1.3 Using the Basic Principles of Microbiology

The third fundamental concept is: *Basic principles of microbiology must be a part of the treatment strategy.*

Very often principles of microbiology are ignored when developing a strategy for controlling growth of microorganisms in cooling water systems. An understanding of basic microbiology offers significant insight to strategic issues such as when and where to apply biocides. The following discussion presents an overview of the principles of basic microbiology that have proven to be valuable in developing successful treatment programs [1, 2, 7].

2.1.4 Principles of Basic Microbiology

- **Population Dynamics**. The microflora of a process cooling water system exists as a combination of many types of microorganisms. This complex community establishes a biological equilibrium with the growth-controlling factors that exist in the environment, e.g., temperatures, pH, dissolved/entrained gases (O_2), and food sources. In a dynamic environment such as a process cooling water system, many of the growth-controlling conditions change constantly. When this occurs, some or all of the members of the microflora respond to the changes by increasing or decreasing in numbers. This creates a shift in the biological equilibrium and may result in the combined population reaching a level that contributes to operating problems in localized sites in the system. It is also possible that a previously minor member of the microflora becomes established as a dominant member of the total population. This is often referred to as population selection within a microflora (microbial community). Andrews and Harris describe this process by defining the *r and K*

Strategies. The *r* strategists rely upon high reproductive rates for survival in the community, where as the *K* strategists depend upon physiological adaptations to the availability of environmental resources [8]. The shift in dominance can contribute to the development of operational problems classified as "slime," plugging and fouling, or MIC. Numerous studies have shown that in actual operating systems, the combined population of microorganisms, as well as specific components of the microflora, follows a typical biological growth curve in response to the existing environment [9].

The growth curve consists of a "lag" phase where the reproduction rate and death rate of the microorganisms are relatively equal at a low level. Usually the population remains low for an extended period without approaching the critical population level where potential microbiological problems are likely to occur. In response to a change in the growth-limiting factors of the environment, reproduction rates may be stimulated and the population enters into the "log" phase. It is at this point when the population exceeds the critical level that problems begin to appear in the system. Once the limit of the environment for supporting an increasing population has been reached, the microflora enters into the "stationary" phase. It is the stationary phase of the growth cycle when most of the chronic or mature microbiological problems persist.

When attempting to prevent microbiological problems, it is obvious that maintaining the population in the "lag" phase should be a primary objective, and that efforts must be made to prevent the population from entering into the "log" phase. If the population is in the "stationary" phase, it usually is necessary to initiate a mitigation process to control the microbiological problem.

A thorough understanding of the concepts of population dynamics and the conditions that control the population growth curve is important in effectively controlling problems caused by microorganisms. This basic concept provides a basis for: (1) selection of the appropriate biocide; (2) whether to apply the biocide continuously, intermittently, or as a periodic shock dose; (3) location of point of addition; (4) concentration levels required; (5) frequency of addition of biocide; (6) requirements for alternation of types of biocides; and (7) adjusting or changing certain operating parameters of the process water system.

- **Colonization and Succession within Microbial Communities**. Atlas and Bartha provide an overview discussion of the initial microbial colonization and subsequent ecological succession, or "maturing," of the microbial community that can occur within an individual niche of the microbial ecosystem [9]. An interpretation and application of these processes provides an important tool for controlling the development of troublesome MIC microflora. A review of the research made on the development of sessile colonization and biofilm/biomass on system surfaces has been presented by numerous authors [9]. From these resources and several years of practical experience, it has been learned that successful microbiological growth control prevention can be achieved with the existing "tools" and application technologies.

  Preemptive Colonization - Development of a more-or-less stable community of MIC-associated microorganisms usually involves a succession of sessile populations. The initial colony usually begins with an invasion of a "virgin" macro-environment by a source of inoculum, often referred to as the pioneer microorganisms. The attachment of the pioneer microorganisms on a surface in the system and subsequent development of a biofilm is known as preemptive colonization. Once the preemptive colonization is established, further succession of the population continues. The progress and direction of the succession is greatly impacted by the macro-environment (environmental characteristics of the bulk water). The dominant characteristics include pH, dissolved/dispersed gasses, temperature, and nutrient supply associated with the bulk water. Preemptive colonization continues until the impact of the macro-environment is no longer the dominant factor controlling colonization. When this point is reached, first phase succession begins.

First Phase Succession - As this phase continues, the impact of the macro-environment diminishes and the succession is impacted by the interaction of the individual types of microorganisms with each other. Refer to the *r and K strategies, Autotrophic and Heterotrophic Succession,* and *Homeostasis and Secondary Succession* discussed by Atlas and Bartha [9]. It is at this point where the impact of micro-environments begins to take effect. The micro-environment is that which is produced by the microbiological community itself within extremely localized sites in the sessile colonies. First phase succession continues to the point where further development of the community is virtually not affected by the macro-environment, but now controlled by the micro-environment produced by the dominant types of microorganisms. Once the effect of the macro-environment is minimal, second phase succession has begun.

Second Phase Succession - During second phase succession, assuming no major upset of the succession occurs, relatively regular successional population changes of microorganisms occur, leading to a relatively stable microbial community. A biological equilibrium has been established. It is when the community stabilizes, and the dominant members of the community are microorganisms associated with MIC, that operational problems and non-conformance conditions occur. At this stage, metabolic activity within the sessile community is affected very little by the ecological conditions of the macro-environment (bulk water). Bulk water pH, temperature, $O_{2,}$ and nutrient availability of the bulk water are not relevant to the activities of the microbial community.

Post Second Phase Succession - This phase may be considered the termination of ecological succession of the existing microbial community. Biological equilibrium has been lost and any number of factors led to the disestablishment of the constancy of the sessile community. It is suggested that post second phase succession is an expression of the decline or death phase of the biological growth curve. It is at this phase that control or prevention procedures for MIC are not practical and the problems are probably in an acute stage.

The significance of the process of colonization and succession of microbial communities to the technology of microorganism control (or prevention) is based on the fact that only when the community is interacting with the macro-environment is it practical to use conventional procedures to control microbiological growth. This means that use of biocides/biostats, biodispersants, and penetrants, cannot be expected to mitigate an existing problem. From preemptive colonization through first phase succession, controlling the macro-environment by adding a biocide, leads to controlling the microbial community succession. Loss of the ability of controlling the macro-environment means loss of the capability of controlling microbiological growth.

2.2 The Use of Biocides/Biostats

The chemical materials currently used to control growth of microorganisms are classified as "biocidal" or "biostatic," or in some cases both biocidal and biostatic. The biocide kills the microorganisms. The biostat inhibits their growth or reproduction.

Whether a biocide or a biostat is required depends in part at which phase of the growth cycle the microbiological population exists. Ideally, the microbiological control program should keep the population level in the lag phase at numbers well below the critical population level. It has been shown to be possible to keep the population at this level when the environment contains one or more adverse factors that limit the growth and reproduction of the microorganisms. The adverse factor must be stabilized in a consistent state so that the population does not go through a transition into the log phase. A biostat with broad-spectrum properties will create a stabilized adverse condition that effectively keeps the population in the lag phase. The frequency of addition will depend on the persistence of the biostat in the system and the residual effect that can be maintained in the environment where the microflora exists.

A broad-spectrum biocide can also be used to accomplish the same objective. The distinction, however, is that the activity of the biocide may be intermittent and does not require that the concentration of the biocide be maintained at a constant residual. Addition of the biocide to the environment is timed so that the population never achieves a reproduction rate that exceeds the death rate. Intermittent addition of an oxidizing biocide is an example. Continuous addition of an oxidizing biocide at minimum residual concentration is an example of its use as a biostat. It is necessary to maintain sufficient concentration of the biocide in the system for an adequate contact time to kill most viable segments of the microflora without upsetting the biological equilibrium. Maintaining a lag phase condition when using a true biocide can be achieved consistently only when the environmental/operating conditions of the system are relatively stable and not subjected to repeated changes. Maintaining the lag phase is controlling the ecological succession of the microbial community from progressing beyond first phase succession [1, 9].

2.3 Cleaning a Biofouled or "Dirty" System

When implementing a control program to prevent a microbiological problem, it is necessary to employ a routine cleaning (housekeeping) regimen. This usually includes physical cleaning and flushing on a routine schedule, timed to prevent the accumulation of dirt and sludge in the system. Occasionally, chemical cleaning on-line is used in conjunction with physical cleaning. Many of the chemical treatments used to control scale, scale-like deposits, and sludge deposits provide sufficient maintenance cleaning to satisfy the requirements for preventing microbiological problems.

When implementing a mitigation treatment program, it is recommended that, if at all feasible, the process cooling water system be thoroughly and physically cleaned, even chemically if necessary, prior to the initiation of the maintenance biocide treatment [2]. First, all old algal and fungal residues, slime, and other deposits should be removed by mechanical and chemical cleaning, and then the system should be drained and flushed with clean fresh water. When the system is refilled, it should be treated initially with a relatively high dosage of a biocide. The rule of thumb is to use three to five times the maintenance dosage of the biocide to be used in the subsequent maintenance program. If such cleaning is done, it will certainly simplify the prevention of residual deposits fouling the system during the mitigation process. Frequently it is not practical to shut down the process for such cleaning before starting the addition of the biocide in the mitigation program. Provisions must be made to deal with purging residual deposits from the system during the mitigation program if pre-cleaning was not done. Of course, if the system is heavily fouled, it will be necessary to do at least a certain amount of cleaning to keep the system operational.

The use of a biodispersant is recommended to assist the removal of the microbiological slime deposits and to help disperse plugging and fouling deposits [1, 11].

2.4 Factors Determining the Choice of Biocides

Selection of the proper biocide or combination of biocides depends on a number of factors. The primary considerations are: (1) types of microorganisms involved, (2) prior operating history of the system, (3) type of process cooling water system, (4) chemicals being used for scale and corrosion control, (5) chemical and physical characteristics of the water in the system, and (6) environmental limitations and restrictions and compatibility with materials of construction [7,10].

2.4.1 Type of Microorganisms

Specific target organisms are rarely considered when selecting a biocide for routine treatment of process cooling water. The reason is that in the normal operation of a cooling system, a wide variety of microorganisms enter the system and a mixed microflora is established. The dominance of a specific group of microorganisms and their relative proportions to the total microflora can vary considerably from one time to another. Specific microorganism identification procedures are usually not necessary or practical for use in the selection of one specific chemical compound instead of another. Selection is usually based on the "broad-spectrum" characteristics of the compound under the existing operating conditions. The exception to this practice is the presence of certain specific troublesome microorganisms, such as *Desulfovibrio sp.*, *Gallionella sp., Clostridium sp., Leptothrix sp.,* and other microorganisms that may be so important that a specific control program is designed to control the growth of those specific microorganisms.

Generally speaking, the most significant differentiation is made between classes of microorganisms. Thus, we may be guided in the selection of biocides by the fact that a particular cooling system has a severe algal growth problem in the distribution trays in the cooling tower. This may be associated with a buildup of a significant growth of bacteria on the fill and on the heat transfer surfaces in the heat exchanger tubes. The approach would be to select a broad-spectrum biocide that is capable of controlling the variety of microorganisms contributing to these problems, and perhaps select a supplementary material to assist in controlling the algae.

2.4.2 Prior Operating History

The prior operating history of a process cooling water system serves as a guide to biocide selection. This history may show not only the extent to which microbiological growths have occurred in the past, but also the types of biocides previously used unsuccessfully, which provides additional guidance. Process contamination such as lube oil leaks or the use of nitrite-based corrosion inhibitors may restrict the selection of the biocide to those materials that do not react chemically with the biocide. An oxidizing biocide would not be selected in these cases. If it was known that these circumstances occurred previously, it is important to know what results were obtained when other types of biocides were used. It is also important to know that the microbiological problem was a result of leakage, so that it could be stopped, preventing the problem from reoccurring in the future.

2.4.3 Type of Cooling Water System

The selection of the appropriate biocide is guided to some extent by the type of system to be treated, i.e., once-through, closed-loop, or open circulation. Systems with cooling towers and other open circulating systems can scrub a varied group of microorganisms from the air during normal operation. This requires that the biocide be effective against a broad range of microorganisms under conditions of continuous contamination. Once-through cooling systems usually involve a more limited group of microorganisms with a fairly constant level of inoculum entering the system, (subject to seasonal variations of surface water sources). Therefore, a more selective biocide may be appropriate. Cost of treatment also becomes a consideration with once-through system biocide selection because of the large amounts of water handled in such systems that require treatment. Closed-loop systems have limited makeup water requirements and are not exposed to varied or continuous contamination. The water is typically circulated in a tightly closed loop. These conditions provide the situation where a specific biocide effective against a stable microflora with minimum recontamination can be selected.

2.4.4 Characteristics of Scale and Corrosion Control Chemicals

Virtually all circulating cooling water systems are treated with additional chemicals for the prevention of scale formation, minimizing sedimentary deposits, and inhibiting corrosion. It is essential that biocides used in a particular cooling water system be compatible with these other treatments. It is also important to be aware of any changes that may be made in the scale/corrosion control treatment programs in order to be prepared to adjust the microbiological control program.

For example, if a cooling water system is being treated with a high pH scale/corrosion inhibition treatment program, pH of 8.0 or above, the use of a biocide that has low efficiency in this pH range should be avoided, e.g., chlorine or methylene bisthiocyanate. Likewise, an oxidizing biocide should not be used when the scale/corrosion treatment chemicals are readily oxidized. This limits the effectiveness of both the biocide and the scale/corrosion inhibition program. Certain non-oxidizing biocides such as the organo-sulfur compounds are not compatible with heavy metal corrosion inhibitors, especially with high levels of chromate-base and molybdate/zinc inhibitors. Cationic biocides, e.g., “quats,” are less effective under certain situations where highly anionic scale/corrosion inhibitors are used, particularly in closed loop cooling systems.

2.4.5 Chemical and Physical Characteristics of Makeup and Cooling Water

There are several characteristics of the water being treated that affect the biocide effectiveness, and therefore, affect the selection of the biocide to be used. The pH of the water is perhaps the most significant factor that affects biocide efficacy. Above pH 8.3, many copper-based compounds precipitate into non-active salts. Methylene bisthiocyanate compounds hydrolyze at a rapid rate at pH above 8.0. Phenate and chlorophenol-based biocides ionize to less active materials at pH above 8.5. Most oxidizing biocides, particularly Cl_2 or $HOCl^-$ are significantly less active and have minimal oxidizing capabilities at pH above 8.0. On the other hand, some organo-sulfur and quaternary ammonium compounds have a higher level of effectiveness at pH above 8.5.

Temperature may affect the activity of certain biocides. Quaternary ammonium compounds are sensitive to high temperatures (above 120 F). Organo-sulfur and thiocyanate compounds become less effective under most situations when the temperature increases. Ozone and peroxide materials are less effective as the temperatures increase.

Excessive dissolved solids can affect biocide effectiveness. High levels of calcium (hardness ions) will inhibit the activity of certain cationic quaternary ammonium compounds, as will high levels of chlorides. Organo-sulfur and thiocyanates form complexes with dissolved iron and biocidal effectiveness is reduced. Most chlorine/bromine oxidizing biocides are inactivated in the presence of hydrogen sulfide and ammonia.

High levels of suspended solids can have a profound effect on the activity of certain biocides such as the cationic alkyl-quaternary and polymeric quaternary ammonium compounds. Cationic biocides will complex with the anionic charged suspended particles of silt, debris, and other non-charged suspended materials in the water. This makes the active ingredients of the biocides not available for controlling the growth of microorganisms unless an excessive amount of the biocides is added to overcome the inactivation by the suspended solids.

2.4.6 Environmental Restrictions

Environmental restrictions of discharge of treated water and disposal restrictions of biocide containers constitute another factor that determines the selection of biocides. Regulatory agencies require registration of all commercial/industrial biocides, and have placed limitations on the use and application procedures of most conventional biocides. These restrictions are commonly enforced through requirements that each compound must be registered for use with appropriate agencies [10]. These requirements deal with the amount of the compound to be used (dosage/concentration level), for what purpose the compound is to be used, and the type of system in which the biocide is to be used. Once the compound has been granted a registration permit, the toxicological effects in the system effluent must comply with the environmental impact requirements, e.g., discharge permit specifications of the process or plant.

Obviously, these considerations are important when selecting a biocide for use in a specific application. Heavy metal biocide, phenolic-based compounds, formaldehyde donors and other persistent organic compounds have essentially been banned from use in many cooling water systems throughout the world. In some cases, the biocide chosen must be one that can easily be detoxified, decomposed, or biodegraded before the discharge reaches receiving water. The effect of biocide-treated water on the sludge digesting microflora in primary/secondary waste treatment plants is becoming an increasing concern.

The immediate effect of the biocide on the environment of the cooling water system should be considered. Some treatments may contribute to odor or fumes that are undesirable, or may contribute to foam and discoloration in the treated water. These factors must also be considered when selecting a biocide. Safety concerns with the storage and handling of biocides is a major factor when selecting a biocide. For example, gaseous Cl_2 is no longer permitted in most nuclear plants located in North America.

2.4.7 Compatibility With Materials of Construction

Even though biocides are used at relatively low dosage levels, e.g., parts per million range, the effect they have on corrosion of components can be significant. For this reason, elimination of a specific type of biocide is often based on this specification exclusively. Biocide chemical composition based on chlorine/chlorides, ammonia, sulfates, and heavy metals (e.g., Cu) are often eliminated as potential biocides in cooling water systems constructed of several metallurgies, including stainless steels and copper-containing alloys.

2.5 Types of Biocides

Chemicals used to control the growth of microorganisms in industrial process water systems are commonly referred to as biocides, microbicides, algicides, fungicides, bactericides, and slimicides. For purposes of clarity, the generic word "*biocides*" is used in this report.

The biocides most commonly used for cooling water treatment are usually classified into two groups: oxidizing or non-oxidizing, which relates to the mechanism of toxicity of the compound.

2.5.1 Oxidizing Biocides

Chlorine: Chlorine and chlorine-yielding materials function in essentially the same way. When added to water, a mixture of hypochlorous acid and hypochlorite ions are formed. At any given concentration of available chlorine, the oxidizing effectiveness as a biocide is dependent on the proportion of hypochlorous acid present. The pH of the treated water determines the extent of the ionization of the hypochlorous acid to the hypochlorite ion. As pH increases, less hypochlorous acid is available. A pH range of 6.0 to 7.5 is considered most practical for chlorine-based treatment programs. Chlorine becomes ineffective as an oxidizing biocide at pH above 8.3. At pH below 6.0, chlorine is not practical because of its effects on the corrosion potential in most systems.

There are a number of basic types of chlorination programs that relate to the method and point of application. In process cooling water systems, the most prevalent program is called "breakpoint" chlorination. Chlorine is dosed into the system initially to satisfy the chlorine demand and then to attain the desired free residual chlorine for a short period of time. Chlorine demand refers to the amount of chlorine that will react with organic contaminants before any free residual will exist. Organic matter, including biomass, tower lumber, and chemicals such as sulfur dioxide, hydrogen sulfide, and organic nitrogen compounds exert a chlorine demand that must first be satisfied if a free residual is to exist in the treated water.

Chlorine as an oxidizing biocide has the advantages of low cost, broad-spectrum, and a long past history of acceptable results under specific use conditions. Some limitations of chlorine when used in industrial process water treatment include ineffectiveness at high pH; inactivation by sunlight and aeration; corrosiveness to metals; adverse effect on wood; costs of feeding equipment and extensive maintenance requirements; and handling hazards. The use of chlorine oxidizing biocides has been limited within the past several decades by environmental restrictions based on the discharge of chloramines and halomethanes.

Hypochlorite salts: Hypochlorites are salts of hypochlorous acid and are formulated into several different grades and proprietary forms. Principally, they are composed of sodium hypochlorite, calcium hypochlorite, or lithium hypochlorite. They function in much the same way as other chlorine donors. Hypochlorite salts as liquid solution are easier to handle than chlorine gas, but have all the limitations of chlorine plus higher cost. Hypochlorite salts continue to increase in use, both as an activator for NaBr/hypobromous reactions and as a primary chlorine donor.

Trichloro- or dichloro-isocyanurates: These materials are more easily handled as dry products that release chlorine when added to water. The “organo-chlorine” materials are gaining increased acceptance for use in smaller systems that require an oxidizing biocide, but cannot justify the cost of gaseous or liquid chlorine feeding equipment. When the chloroisocyanurates were first used in swimming pool applications, it was observed that the cyanuric acid ions functioned as a stabilizer, reducing chlorine inactivation by ultraviolet light. The added stability, combined with the fact that the dry materials dissolve slowly, makes them satisfactory for use in small-volume recirculation cooling water systems.

Chlorine dioxide: Chlorine dioxide is an oxidizing biocide that until recently was used primarily in the textile and pulp/paper industries as a specialty bleach and dye-stripping agent. Chlorine dioxide does not produce hypochlorous acid immediately when added to water, but remains as ClO_2 in solution. Although less powerful as an oxidizing agent, it is more effective at the higher pH ranges than chlorine. Since it is an explosive gas, the compound is usually produced on-site by mixing a strong chlorine solution discharged from a chlorinator with a sodium chlorite solution and fed immediately into the system. In smaller installations, chlorine dioxide can be generated by mixing hydrochloric acid with hypochlorite/sodium chlorite solutions. Generally, chlorine dioxide is more expensive than other forms of chlorine donors. However, in cooling water systems with ammonia-nitrogen or phenolic contamination, it may warrant consideration even on a higher cost basis because it usually has a lower organic demand than other less expensive oxidizing biocides. Hazardous handling is a primary limitation on the widespread use of chlorine dioxide.

Sodium bromide/bromine chloride: These materials are becoming more widely used as an alternative to chlorination. The most common approach used is to activate bromide salt (NaBr) typically with a liquid solution of calcium or sodium hypochlorite. The activated bromide salt or bromine chloride hydrolyzes in dilute aqueous solutions to hypobromous acid and hydrochloric acid/sodium chloride. The hypobromous acid is an effective microbicide for algae and bacteria over a broader pH range than hypochlorous acid. Bromine chloride as a gas is more difficult and hazardous to handle than sodium bromide solution. The latter can be activated with sodium hypochlorite and readily handled as a liquid. Hypobromous acid biocides have the advantage of functioning over a broader pH range. Bromamines are environmentally less objectionable, and are less reactive with hydrocarbons, reducing the production of halomethane.

Solid organo-bromine/chlorine compounds: These have been developed for use in smaller process cooling water system. Because they are significantly less active as oxidizing agents, many chemists do not classify these types of compounds as oxidizing biocides. In most cases these materials have overcome the difficulties encountered with gaseous and liquid oxidizing biocides. In general they are not strong oxidizing agents, but function as a chlorine donor in a "slow release" mechanism. In this manner, inactivation by contaminating organic compounds and high pH levels are less limiting to their effectiveness. The compound most commonly used is BCDMH (1-bromo-3-chlor-5, 5-dimethylhydantoin). Other compounds in this category include BNPD (2-bromo-2-nitropropane-1, 3, diol) and DBNPA (2, 2, -dibromo-3-nitrilopionamide). Cost and controlling the dissolution rate of the solid materials continue to be the limiting factor for wide spread use of these materials.

2.5.2 Other Non-Chlorine Oxidizing Biocides

Ozone: Ozone is a strong and naturally unstable oxidizing biocide used for specific applications in process cooling water systems. In solution, it retains high oxidation potential and resembles chlorine compounds in many reactions. As with chlorine, there is an "ozone demand" that must be met before its oxidizing biocidal characteristics are exhibited. Like chlorine, ozone is affected by pH, temperature, organics, etc. Unlike chlorine, it does not contribute to the chloride content or corrosiveness of the water; it is non-polluting and harmless to aquatic organisms upon decomposition. Ozone is typically fed continuous or intermittently to the makeup water to eliminate contamination coming into a clean system. In this sense, ozone is used to treat the water rather than the system. The oxidizing effect does not persist throughout the system, and for this reason, its use has been limited to small systems or to specific sites within larger systems. Ozone must be generated on-site with ozone generators, requiring efficient use of electric power and a substantial initial investment for equipment.

The half-life of ozone in cooling water applications is typically short (5 to 20 minutes) due to its reactivity and volatility. Its very short CT (contact time for biocidal activity, e.g., concentration versus kill time) overcomes this limitation. Ozone also degrades microbial biofilm if given sufficient time. Laboratory studies have shown 0.2 to 1.0 mg/L dissolved ozone removes biofilm in about 30 minutes. These studies also demonstrated that 0.01 to 0.05 mg/L of ozone prevents biofilm formation on surfaces in relatively clean systems.

Capital expense for ozone generating equipment, pH limitation to stability of ozone, effects of contamination, hazard/storage, and safety issues are factors that still need to be resolved before ozone is widely used as an oxidizing biocide in larger systems.

Sodium/hydrogen peroxide: Hydrogen peroxide (HP) occurs as a natural component of the environment. Other per-oxygen compounds such as peracetic acid produce the same oxidant as HP. They are not routinely used for process cooling water treatment, although they have potential because there are no toxic residual byproducts. The peroxides are used primarily as sanitizing agents to batch-clean local sites or components of a cooling water system. Routine addition of peroxide has not been practical as a primary biocide treatment for once-through or open circulation system. The required high concentration levels and extensive contact time have been the limiting factors. Limited use of peroxides in closed loop systems has taken place where effluent restrictions have made use of other materials not practical. The peroxides have many of the same advantages as ozone, and when appropriate to use, are much cheaper and less hazardous than ozone. Peroxides are affected by pH and decrease in effectiveness as the pH increases. When using peroxide to sanitize a system, care must be taken not to stimulate corrosion.

2.5.3 Non-Oxidizing Biocides

Due to limitations of chlorine and other oxidizing biocides and to the increased use of alkaline scale and corrosion control programs, non-oxidizing biocides are becoming more widely used as a primary microorganism control treatment, or as a supplement to oxidizing biocides. The most widely used types are described as follows:

Quaternary ammonium salts: "Quats" as they are commonly known, are cationic surface-active quaternary nitrogen chemicals. The quaternary ammonium compounds probably represent the widest used group of non-oxidizing compounds used for process cooling water treatment. They are generally effective for controlling algae and bacteria. Their activity against specific microorganisms may vary with the structure of the compound, e.g., alkyl characteristics. Quats are generally most effective against algae and bacteria at neutral to alkaline pH. Quaternary ammonium compounds are generally not effective fungicides at any pH. Their biocidal/biostatic activity is attributed to the cationic charge, which forms an electrostatic bond with the negatively charged microorganism cell wall; and which results in distortion of the cell wall permeability, protein denaturation, and death of the cell.

The activity of most quats is reduced by high chloride concentrations, high concentrations of oil and other organic foulants, and by accumulations of sludge in the system. The "diamine-quats" are less affected by these factors. Excessive overfeed of some types of quats may contribute to foaming problems, especially in open circulating systems with organic contamination.

Polymeric quaternary ammonium compounds are effective broad-spectrum biocides produced by polymerizing quaternary nitrogen groups into low molecular weight polymers. Their activity is basically the same as the alkyl-quats, with the exception they are not surface active (do not cause foam), and have a greater degree of effectiveness against some fungal microorganisms. The polymeric quats typically require longer contact times than the alkyl-quats. High levels of suspended solids in the water inhibit the activity of these biocides due to their cationic polymeric characteristics.

Organo-sulfur compounds: This group includes several different types of compounds widely used either alone, or in combination with other materials as microbicides in recirculating, once-through, and closed loop systems. Although their mechanisms of action are similar, the pH ranges of their activity differ. Their spectra of activity also differ, but are generally regarded as bactericides and fungicides. Prominent members of this group of compounds include the ethylene bisthiocarbamates, N-methyldithiocarbamates, dimethlydithiocarbamates and methylene bisthiocyanate. Organosulfones, alkylsulfonates, and thiones are also included in this group, but are generally used less widely and only for specific types of applications such as in closed-loop cooling systems

Organo-sulfur compounds are not “quick kill” biocides and generally require intermediate contact times, i.e., 4 to 9 hours at minimum required concentrations. The exception to this is methylene bisthiocyanate, which is regarded as a “quick kill” biocide, i.e., approximately two hours. For this reason, the organo-sulfur compounds are typically used in open circulation and closed-loop systems. Under certain circumstances, biocides based on methylene bisthiocyanate are used in once-through systems.

Interaction with materials of construction must be considered when using organo-sulfur compounds, especially the carbamates. These materials are not recommended for use in systems with copper/copper alloy without the appropriate corrosion inhibitor. The dithiocarbamates are less effective in systems where the water contains excessive levels of dissolved or suspended iron compounds.

Most organo-sulfur compounds hydrolyze readily at cooling-water temperatures and pH. This is an advantage from an environmental impact consideration since they hydrolyze to non-persistent materials commonly found in the environment. With the exception of methylene bisthiocyanate, the organo-sulfur compounds are readily water soluble and relatively convenient to handle and feed.

The effectiveness of most organo-sulfur compounds is pH related when used in cooling water applications. The N-methyl and dimethyldithiocarbamates function well at pH 7 and above. Most sulfones and sulfonates are most effective at pH 6.5 to 7.5 or lower, and the thiones function well at a pH of 7 to 8.5. Methylene bisthiocyanate hydrolyzes rapidly at a pH above 8 and therefore is used at that pH range only in quick kill situations.

<u>Glutaraldehyde</u>: Biocides based on aqueous solutions of glutaraldehyde are becoming more widely used where activity against troublesome bacteria, including those associated with MIC, is required. This compound has demonstrated effectiveness against both aerobic and anaerobic bacteria under conditions encountered in open circulating and closed-loop systems. It has limited effectiveness against algae and fungi associated with plugging and fouling problems, and for this reason is often used as a biocide alternating with algicides/fungicides. It is readily neutralized and offers no particular difficulty for disposal in traditional cooling water treatment situations. In once-through systems, the relatively short contact times require the material to be used at high concentrations. This introduces the need to consider cost and disposal factors. At alkaline pH, it may be necessary to potentiate glutaraldehyde with the addition of a surfactant. Since glutaraldehyde functions as a protein cross-linking agent, applications for this compound are in systems where “amino” compounds, including ammonia, from sources other than microorganisms are minimal. Glutaraldehyde is usually added as a slug/shock dose rather than continuously at a low level to optimize cost effectiveness.

Isothiazolone compounds: These biocides, usually available as a blend of two or more isothiazolone chemicals, are used as broad-spectrum biocides in circulating and closed loop cooling water systems. They are effective at low concentrations and persist over a wide range of pH found in most cooling waters. The isothiazolones effectively control most aerobic and anaerobic bacteria, including sulfate-reducing bacteria in bulk cooling water, and have activity against many fungi and algae at acidic to slightly alkaline pH. The commercial forms of these compounds are non-ionic and non-surface active, making them compatible with most of the traditional dispersants and scale/corrosion inhibitors used in cooling water systems. The activity of this compound is no more than slightly affected by chlorine, amino-nitrogen, hardness, chlorides, or suspended solids in the bulk cooling water. Although the compound is relatively persistent in water, it is used at low concentration and can be detoxified readily when necessary. It offers no specific need for consideration of materials of construction when used as recommended.

The isothiazolone compounds are less cost effective when the system contains significant amounts of sessile or adhering biomass, including plugging and fouling materials bound by algae and fungi, or in low-flow circulation/open systems. Extreme care is required when handling these compounds because of potential adverse dermal effects. Automated feeding systems are strongly recommended. In heavily fouled or "dirty" systems, the use of a penetrant/biodispersant enhances the effectiveness of the biocide, and makes the treatment more cost-effective by reducing the amount of biocide treatment required.

Heavy metal compounds: Biocides based on heavy metal chemistry, such as the organo-mercurial compounds, are effective as biocide and have a long history in the control of microorganisms. Until recent years, organic mercury compounds were used as broad-spectrum biocides. However, the discovery of the harmful environmental effects of the residues from the mercury compounds has led to a discontinuance of these compounds as biocides in cooling water systems. Other heavy metal compounds are still used in specific applications. Copper sulfate is widely used for the control of algae and mollusks in cooling system makeup sources such as lakes and reservoirs. Although algae can be controlled at quite low concentrations of copper, these salts are not widely used in cooling water treatment or cooling tower wood preservation for several reasons. Copper is readily precipitated from treated cooling water at alkaline pH making it ineffective as an algicide. The precipitated copper can also plate out on steel or aluminum surfaces in the system and contribute to galvanic corrosion.

Rosin amine salts: Aqueous solutions of the rosin amines are used at low concentrations to control algae in open circulating cooling systems and in cooling ponds/reservoirs used as an ultimate heat sink. In general, the spectrum of activity of these compounds is limited to algae and some fungi. For this reason, their application in process cooling systems is typically as an alternating biocide or blended with another material with efficacy against bacteria and fungi. The higher molecular weight rosin amines are often blended with other non-oxidizing biocides that have limited water solubility to enhance the dispersibility of the blended compound. Excess feeding can contribute to foaming, and to maximize effectiveness, the compound must be adequately dispersed into the circulating bulk water. The activity of the rosin amines appears not to be pH dependent. However, at alkaline pH, higher concentrations of the algicide are required to control the rapid-growing unicellular green algae.

Organobromine compounds (also discussed in Oxidizing Biocide Section 2.5.1): This group of compounds includes dibromonitrilopropionamide (DBNPA) and bromo-hydroxyacetophenone (BHAP). They are effective broad-spectrum biocides with particular effectiveness in controlling bacteria. They are not oxidizing agents and can thus be used in systems with relatively high levels of biomass and other organic contaminants. The DBNPA hydrolyzes rapidly at pH above 8.0, and therefore must be used under quick kill situations at alkaline pH.

The effectiveness of BHAP is not pH dependent. These materials have low solubility in water and must be adequately dispersed to insure effectiveness. Although effective against bacteria at low concentrations, higher concentrations are required to control most algae and fungi involved with plugging and fouling problems. This makes use of these materials as routine treatment chemicals less cost effective than other alternative materials. However, their use has found a need where less expensive non-oxidizing biocides have failed to adequately control microbiological problems. Misting and overfeeding must be avoided to prevent foaming and skin contact difficulties. There are no apparent difficulties related to effluent discharge with these materials when applied as recommended.

Organic thiocyano-azole compounds: These are generally specialty-type biocide that are used where traditional treatments with other biocides cannot adequately control a troublesome microflora, or are used to mitigate a severe microbiological problem (e.g., MIC, plugging and fouling). An example of these compounds is 2-(thiocyanomethlythio) benzothiazole (TCMTB). This material is used primarily as a fungicide to prevent the growth of wood-rotting fungi. However, it is frequently used in mitigating severe plugging and fouling problems caused by bacteria, filamentous fungi, and algae. It has also been effective in mitigating MIC caused by the iron oxidizing bacteria that form extensive tuberculation in process water systems. Although TCMTB is not usually used alone as a biocide for routine microorganism control in cooling water systems, combinations of these materials, particularly with methylene bisthiocyanate, are becoming more widely used for that application.

Dodecylguanidine hydrochloride: This material is one of several guanidine compounds used for broad-spectrum microorganism control in process water systems. These materials function as a cationic surfactant that disrupts extracellular enzyme reactions and the development of bacterial and algal cell walls. It provides some degree of protection to wood from fungal attack as well. The activity of these materials is not pH dependent. They can be used in systems containing relatively high levels of hydrocarbon contamination (i.e., oils and greases). However, high levels of suspended inorganic solids will limit the effectiveness of these compounds. Most commercially available products based on quanidine chemistry are used at relatively high concentrations and foam problems can occur when overfed. These compounds are most effective in keeping systems free from microbiological problems and less effective for use in attempting to mitigate severely fouled systems. The quanidine compounds offer no specific difficulties with respect to effluent discharge when applied as recommended.

Synergistic blends: In the discussion of materials listed above, references were made to the blend of certain compounds with others to expand the effectiveness of the biocide. Biocides used in industrial process waters will frequently contain two or more different types of active ingredients. In most cases, this is done because one type will be effective against a particular group of microorganisms and the other against another group. This is, in effect, to expand the spectrum of activity of a single product. Frequently, there is an overlap in the spectrum of activity, but it has been found that blending the different active ingredients produces synergism. Synergism is a condition where the effects produced by dosages of two different materials blended together are considerably higher than the sum of the effects when the materials are used individually. Because of the increasing costs to develop new active ingredients for biocides, and the increasing limitations placed on "new" compounds from a toxicological/environmental position, recent research and development in the field of microorganism control has been directed to exploiting all possible benefits obtained from the synergism effects with blended materials [7].

2.5.4 State-of-the-Art Technology

The state-of-the-art technology related to control of microorganisms in process cooling water by using biocides/biostat is a dynamic process. We are continually learning from advances in applied research and especially from practical experience. At this point in time, the author believes the most important advances are being made in the use of biodispersants as part of the treatment program for controlling microbiological problems. The effect of biodispersants on the colonization characteristics of the microflora causing the problems, the effect of biodispersants on the water-contact surfaces where sessile microflora grow, and the complimentary effect of biodispersants on the mode of action of biocide/biostat offer the greatest potential for meeting existing and future needs. Biodispersants are discussed later in this report. This approach has made, and will continue to make, great impact of the effectiveness of procedures used to control microbiological problems in process cooling water systems [7, 10].

2.6 Mitigating Microbiological Problems

2.6.1 Mitigation of Existing Problem Caused by Microbiological Growth

In most cases, the decision to initiate a program of mitigation (elimination) of the microbiological problem, or at least preventing it from becoming a contributor to taking a system out of operation, is made after preventive measures are no longer effective. It must be noted that there also are some situations where mitigation is neither practical, nor possible. Under those circumstances, the alternatives are to replace the system component and implement a program to prevent the problem from recurring [11, 12].

Dependent on the system and the degree of severity of the problem, state-of-the-art technology provides some means of mitigating many intolerable conditions. The procedures are typically site-specific, but there are certain guidelines that can be used to increase the probability of a successful mitigation program in a majority of cases [13, 14, 15, 16].

Pre-program planning: Mitigation of microbiological problems should be considered much in the same way as a major maintenance program. It requires the same degree of planning and coordination by all operating groups involved with such activities. Before the initiation of the actual mitigation procedures, several factors must be considered to ensure the success of the program. As with most operating problems, assessing the severity of the problem is a subjective situation up to the point of component failure. Mitigating a MIC problem is used as an example in this discussion. With MIC, one must consider that as long as microorganisms are involved, the problem will continue to get more severe. Very few MIC situations are self passivating. The criteria for assessing MIC severity must include this consideration. The primary criteria used to assess severity of MIC are:

- Pitting corrosion is characteristic to several different MIC mechanisms. Pitting corrosion rates can be very high, especially when the MIC involves the growth of sulfate-reducing bacteria in anaerobic environments. Anodic pitting corrosion cells are much localized. Through-wall penetrations of heat exchanger tubes and piping represent the extreme of severity.
- General (lateral) corrosion or metal loss, as a result of corrosion involving large anodic surface areas, can be extensive with MIC. The metal loss may be significant, but the severity of the corrosion often is more related to the fouling caused by the corrosion byproducts. Reduction of water flow rates, loss of heat transfer efficiency due to deposits, and plugging of filters and strainers, represent the extreme of severity.
- Crevice corrosion is characteristic of both non-microbiological and microbiologically influenced mechanisms. Most often, the non-microbiological mechanisms are a result of differential aeration under deposits and in stagnant areas where gravitational factors are involved. This is not the case with MIC crevice corrosion since it can appear anywhere around the circumference of a component and on both vertical and horizontal surfaces. Structural strength loss, metal cracking, and through-wall penetration represent the extreme of severity.
- Stainless steel corrosion is often characterized by the formation of pits or tunneling, most commonly at weldments, crevices, and other stressed-metal sites. The metal loss often is associated with attack of the weld material near the fusion line or with sensitization in the heat-affected zone. Base metal attack is much less common. Two-phase weld metal appears to be the most susceptible area, although the relative susceptibilities of austenite and delta ferrite phases have not been clearly defined. The severity of stainless steel corrosion is difficult to assess visually until component failure has occurred. This is because the pits and metal loss are subsurface and result in cavities or tunnels within the wall of the component. The most extreme severity is represented by through-wall penetration, leaks, and loss of structural strength.
- Non-ferrous alloy corrosion: Virtually all metals are susceptible to MIC. The assessment of MIC severity on the non-ferrous materials is based on the same basic criteria already discussed. The one further criterion to be pointed out is related to erosion-corrosion and de-nickelification of copper nickel alloys, which appears to be more severe when associated with microbiological growth.
- Identification of system design limitations: When dealing with mitigation of MIC, attention is usually focused on specific components or isolated systems. Only under unusual circumstances is it necessary to deal with an entire process water system. When massive systems are involved, it is advisable to divide the system into manageable segments and deal with each separately. The site(s) where MIC exists must be precisely defined. Accessibility to the sites must be evaluated. Provisions to clean the system mechanically, the capability to chemically clean, and the ability to apply chemical treatment must be assessed with respect to system design. Most limitations imposed on mitigation procedures by system design are related to availability of access ports required to do mechanical cleaning, to the capability of circulating chemical cleaning solutions, and to the procedures required to discharge cleaning

solutions, corrosion debris, and treated water from the system. As an example, an isolated heat exchanger system and related piping were severely fouled with deposits formed by Gallionella sp. (iron oxidizing bacteria) growth. Pitting corrosion also was occurring under the tubercles. The piping consisted of several different internal diameter pipes, and there were numerous valves and elbows in the design. This made mechanical cleaning quite difficult. Also, it was not possible to circulate a cleaning solution without circulating solution and debris through the entire system. An alternative considered was to isolate the heat exchanger and associated piping, valve off the main circulation lines, and tie into a temporary circulation loop from a tanker truck equipped with a 6,000-gallon tank and a pump. In-line filters on the pipe from the tanker were used to remove the corrosion byproducts from the cleaning solution being circulated from the tanker to the heat exchanger and back to the tanker. Disposal of the cleaning solution and deposits removed from the surfaces were no longer a problem. The risk of removing deposits from one site and depositing them at another site was eliminated.

- Identification of limitations of materials of construction must be made during the pre-program planning phase. This is relevant to both on-line and shutdown programs. Materials of construction play a role in the selection of mechanical/physical or chemical cleaning procedures. It must be noted here that additional consideration must be made when dealing with mitigation of an existing MIC situation. We are dealing with materials that already are in a corroded condition, and the purpose of the mitigation program is to passivate existing corrosion. Particular attention must be paid to providing a means for passivating the various materials during the mitigation program.
- Identification of effluent discharge limitations: A defined plan for handling the effluent of a mitigation program should be in-hand before the program is initiated. With shutdown programs, highly alkaline or acidic fluid effluent should be anticipated. Very often, the effluent contains high levels of suspended solids composed of both organic (oils and greases) and inorganic materials. Most industrial waste treatment facilities are not designed to handle the effluent of a shutdown mitigation based on chemical cleaning for the short period when the system is not in operation. The effect of the shutdown on the operation of the waste treatment facility must be considered.

2.6.2 On-Line Mitigation Versus Shutdown Mitigation

On-line mitigation programs do not usually present major problems related to effluent discharge. An important factor that must be considered, however, is the handling of suspended solids, corrosion by-products, and the dirt and debris that will be removed from the system during the program. In-line or side-stream filtration is often the ideal solution, but these may not be available. Therefore, it is necessary to provide a means of purging these materials from the system on a routine basis that is compatible with the effluent discharge process. Regulatory permits and registrations for chemicals used in both on-line and shutdown programs must be reviewed as part of the pre-program planning phase.

Decision between on-line vs. shutdown mitigation: An on-line mitigation program is described as a procedure designed to immediately prevent a MIC situation from becoming more severe and to ultimately eliminate it. This is to be carried out while the system or specific component still is in operation. A shutdown program involves taking the system out of operation for the purpose of carrying out procedures to eradicate MIC within a relatively short period of time.

On-line mitigation of MIC should be considered when it has been determined that shutting the system down for the duration required to do a shutdown program is not practical, nor possible. As a general rule, it is best to initiate the mitigation program as soon as possible. Delaying mitigation most likely will lead to more difficulties later and also reduce the probability of a successful program. A properly executed on-line program can be started within a short time after the MIC problem has been identified. It is difficult to generalize how long an on-line mitigation program will take to successfully eliminate MIC. However, it appears there is a correlation between how long the MIC existed before mitigation was implemented and the length of time required for a successful on-line program. The longer MIC has existed, the longer the time required mitigating it. Past experiences have shown that some on-line programs have been completed within a six-week period [18]. In other cases where the MIC was a relatively severe chronic problem, periods up to nine months were required to mitigate it [19].

On-line mitigation may offer alternatives to system-design limitations that prohibit shutdown mitigation. In many cases, on-line mitigation solves effluent discharge problems associated with shutdown procedures. Most on-line mitigation programs involve the use of specialized water treatment chemicals, which are more adaptable to open circulating systems and closed-loop systems. Once-through systems are less suited to on-line chemical treatment mitigation programs. On-line physical and mechanical procedures discussed later have been somewhat successful in certain once-through systems.

Shutdown mitigation should be scheduled to coincide with major maintenance outages or other major shutdown events when possible. However, these events should not detract from time and personnel priorities required to do the mitigation properly.

Under certain circumstances, an on-line program can be initiated to prevent the MIC from becoming more acute and then followed by a shutdown mitigation program coordinated with other shutdown activities.

2.6.3 Mechanical/Physical Cleaning

Mechanical/physical cleaning: The first stage of a mitigation program, no matter what procedure is employed, is to remove the loose or loosely adhering debris from the system as much as possible. The debris typically consists of corrosion byproducts, deposited sludge of various chemical compositions, and biomass.

- Water flushing and draining: Most removal of loose debris associated with MIC is usually done first by water flushing and draining, repeated as many times as possible. Water flushing and draining may be supplemented with air bumping by pulsing high-pressure air through pipes or into a component body. These techniques can effectively remove loose deposits, but will not do a complete job of cleaning the metal surfaces to which the more tenacious biomass and corrosion byproducts adhere. Flushing and draining may be considered as preparation for a more thorough cleaning procedure. In cases where the MIC is not extremely severe and there is a limited amount of debris associated with it, the flushing and draining procedure is adequate pre-treatment prior to initiating an on-line mitigation program.

- Mechanical removal (pigging/brushing/hydrolazing): Once the loose materials have been removed, the piping, heat exchangers, tanks, and other components can be further cleaned by mechanical methods. Piping systems and heat exchangers may be cleaned using metal or vinyl scraper plugs (pigs), which are propelled through the pipe or heat exchanger tubes by pressurized gas or water. Straight sections and smaller internal diameter pipe are most suited to the use of pigs.

Piping runs uninterrupted by valves, diameter reductions, or many changes in direction may be cleaned in this manner, assuming there are access ports for insertion and removal of the pig. Straight tube heat exchangers also are readily cleaned by this method and by brushing when manual manipulation is required due to accessibility limitations.

Methods that utilize solids suspended in a liquid stream may be effective in situations where the deposition on pipe or vessel surfaces is not severe. With relatively thin films, the abrasive particles will flow along the filmed surface and remove the deposit. The sandblasting or jetting procedure, which involves suspending sandblast materials in an air/dry nitrogen carrier, is used primarily as a means for preparing surfaces to be coated. Only under very extreme conditions should sandblasting be considered when no coating is to be applied. The use of high pressure water sprays, such as hydrolazing, have been used extensively for removal of deposits in preparation for subsequent water treatment procedures, and for tubercle removal when accessibility was not limited. Recent improvements in the hydrolazing process primarily have been associated with allowing equipment to access smaller and more remote areas of a system.

The primary limitation to hydrolazing, sandblasting, manually brushing, and other mechanical procedures, is that they must be done off-line, and single setups are limited to sites where no changes in direction or bore exist. When abrasive particles are used, it is necessary to provide for the collection and removal of particles as well.

2.6.4 Chemical Cleaning

The mechanical cleaning discussed earlier provides means for removal of the loose or loosely adhering deposits associated with MIC. Very often, it is necessary to do further cleaning to remove the tubercles and other deposits that are tightly adhering to the metal surfaces. The use of chemical cleaning solutions has become an accepted and widely used procedure. It is generally safer and more economical than the labor-intensive methods requiring extensive dismantling to employ mechanical means. Selection of the cleaning solvent or solution and how it is applied is based on several factors. These include:

- Chemical composition of deposits: Having already done analyses to confirm detection of MIC, some of these data already should be available. It is important, however, to base cleaning chemical selection on the composition of the deposits adhering to the metal surfaces and not just on sludge or loosely adhering materials found in the system. Tube or pipe samples with intact deposits are the best samples for analysis. If these are not available, then deposits must be scraped from the metal surfaces, with care taken to scrape down to the base metal surface. Deposits usually vary in depth and often have distinct layers of different composition. Location of sampling must be carefully selected, with considerations given to collection at most trouble-prone sites such as sites of low-flow velocity and areas of known MIC. Areas of catastrophic failures should be avoided because the conditions caused by the failure often wash out much of the deposit, making the immediate area unreliable for study. When practical, simulated cleaning tests with specimens taken from the system should be done in the laboratory.

- Materials of construction: Mitigation cleaning procedures require complete consideration of the materials of construction of all wetted surfaces and parts in the system. This includes items such as O-rings, packings, gaskets, non-metallic components, and coatings. If there is any question as to the compatibility of the cleaning solvent/solution with specific materials of construction, laboratory exposure tests, under the most extreme conditions, should be made before using the cleaning chemicals.
- Temperature: The system design should be reviewed to establish the maximum safe temperature that could be applied during cleaning and to determine the maximum temperature obtainable from a practical standpoint. Often the system will tolerate a higher temperature safely than can be obtained during cleaning procedures. Most cleaning solvents and solutions have an optimum temperature range for maximum performance and corrosion protection.
- Application procedures: The ideal application procedure is to make up the cleaning chemicals in a separate tank, verify its composition, and then add it to the system or component when refilling after the final flushing. Once made up, the system should be circulated continuously or intermittently throughout the project. If circulation is not possible and a "soak" procedure is necessary, the cleaning chemicals **must** be added as the system is being refilled after draining. This ensures proper distribution of the cleaning chemicals. A repeated "bleed and makeup" procedure may be necessary if circulation is not possible. Proper velocity is an important consideration when circulation is employed. Solvent movement is necessary to prevent localized spending. Corrosion rates and erosion effects increase with velocity, and usually not at a linear rate. Cleaning solvents, based on inhibited mineral acids such as HCl and sulfuric, should not be circulated at rates exceeding 1 to 2 feet per second when circulated for extended periods or continuously. Solvents, based on chelants such as EDTA and HEDTA, NTA, and organic acids, usually are circulated continuously at velocities of 1 to 5 feet per second. Some cleaning and solvent materials interact with the deposits to release gases including CO_2 and H_2. Provisions for venting should be made prior to starting the procedure. Occasionally, foam may be generated in the system as the cleaning chemicals are being circulated.

  Some types of cleaning solvents can be foam-applied. This has proven to be particularly effective for large shell and tube exchangers or surface condensers where circulation capability is a limiting factor. Foam application has the advantage of lightweight, direct application and the ability to move insoluble or sloughed pieces of deposit large in size. The primary limiting factor for foam application is accessibility.

  Methods to propel a cleaning solvent through a system with a gas, such as air, steam, or nitrogen, are being developed. This can be an effective means for cleaning piping where large volumes are being dealt with.
- Water and time requirements: Water management should not be overlooked. The availability of water is involved in deciding the concentration of the cleaning solvents and solutions. It is necessary to have adequate quantities and delivery rates for all rinses, flushes, and passivation stages. Minimum water quality requirements should be addressed as well.

Time required to do an adequate cleaning program is perhaps the most difficult factor to predict. The question is: "How much time is available and how much time is it expected to take?" Past experiences have shown that it is prudent to allow a safety factor between the maximum available time and the expected time. This may influence the final choice of solvent, concentration of solvent, and/or application method.

- Other considerations: Some other factors to consider, no less important than those discussed herein, are:
  - Disposal of spent cleaning and solvent solutions
  - Safety practices
  - Corrosion monitoring
  - Criteria that the project has been completed to the desired degree
  - Corrosion inhibition (passivation) procedures during and following conclusion of the project

2.6.5 Selection of Chemical Cleaning Application Procedure

The use of various chemical treatment procedures to mitigate existing MIC is situation-specific and dependent on the results of procedures carried out prior to the application of the chemicals. This discussion provides information related to the application of chemicals during the chemical cleaning stage and during subsequent steps to eradicate the microorganisms, passivate active corrosion sites, and to establish a preventive treatment program. A coordinated chemical treatment approach has been shown to be essential to obtain the most effective results from chemical treatment. Anything less than a total treatment program most likely will create a potential for the continuation of MIC or perhaps the reoccurrence of MIC within a short time.

Taking into consideration what pretreatment procedures were used, there are three basic chemical treatment approaches that can be used [12, 13, 14, 15, 16]. These are:

- Short term, shutdown, aggressive chemical cleaning: This approach to mitigation has been discussed to some extent earlier. The guidelines highlighted therein must be followed. It is used when a limited amount of shutdown time is available, or when the mitigation procedure must be timed with some other maintenance activity, or to comply with a short-term outage. It is usually necessary to use aggressive chemical cleaning solvents to remove the residue deposits not removed by physical cleaning and flushing. Typically, the deposits are hard tubercles that have developed over an extended period of time. This approach often is used to mitigate a problem at an isolated site or component that has ready access to add the chemicals and to circulate the cleaning solution under controlled conditions.

  The use of a chemically stable, nonionic penetrant dispersant is recommended when using aggressive cleaning chemicals. This type of chemical expedites the penetration of the deposits by the cleaning chemical and increases the rate of removal. It should be added directly to the cleaning solution as the system is being filled. Because the cleaning chemicals can more readily penetrate the deposits, it reduces the time that the metal surfaces are exposed to the aggressive chemicals, and, in general, reduces the adverse effects that this procedure has on unprotected surfaces in the system. Certain types of the penetrants or dispersants form films on metal surfaces that provide short-term passivation to the aggressive cleaning chemicals.

It should not be assumed that the cleaning chemicals will eliminate the microorganisms responsible for MIC. It is necessary to include the addition of a biocide as part of this procedure. In severe situations, non-oxidizing biocides can be added directly to the cleaning solution, but the biocide must be stable in the cleaning solution. Oxidizing biocides are not effective as part of the cleaning solution. However, chlorine, hypochlorite, peroxide, and other oxidizing agents can be applied with the rinse water following discharge of the cleaning solution.

The system must be passivated following the rinse step. This is usually done by neutralization with an alkaline solution, or by the application of a corrosion inhibitor at 3 to 5 times the maintenance dosage level. Application of non-oxidizing biocides typically is to the rinse water, or to the fresh makeup water following passivation. If added to the rinse water, adequate contact time with the biocide in the system must be provided. In most cases, non-oxidizing biocides are the materials of choice over oxidizing agents because of the lower potential for activation of corrosion.

- Short term, shutdown, non-aggressive cleaning: This approach is distinguished from the aggressive cleaning approach only by the cleaning chemicals used. It is most appropriate when the residual deposits, following physical and mechanical cleaning, are soft and porous. The cleaning solutions are based on neutral or alkaline chemicals that have a degree of surfactant activity. Included as part of the cleaning solution are chemicals with anionic polyelectrolyte properties such as sodium salts of polyacrylate, polyacrylate-acrylamide copolymer, phosphonate, or organophosphate. Alkaline chelating agents can also be used. The use of nonionic chemically stable penetrants and dispersants is recommended with this procedure as a means for increased penetration of the deposits. The aggressive procedure described earlier functions by dissolving much of the deposited materials. The non-aggressive procedure functions by penetrating and dispersing or suspending the deposits. The penetrant or dispersant increases the probability of a complete cleaning. This approach can be used only when it is possible to circulate the cleaning solution through the system and when there are facilities to remove the suspended solids from the circulating solution. In some situations, it may be necessary to repeat the circulation stage of this procedure to get a complete mitigation. Often the time required for the non-aggressive cleaning approach will be greater than that required for the aggressive approach.

  It must not be assumed that the cleaning solution will eliminate the activity of the microorganisms contributing to the problem. A biocide or biostat treatment must be included as part of the procedure. The pH and the oxidant demand of the cleaning solution determine if an oxidizing agent can be used as the biocide. If the pH is greater than 8.0, oxidizing agents should not be considered for use in the procedure. Non-oxidizing biocides and biostats with stability in the cleaning solution and a half-life greater than the duration of circulation, and with efficacy to the MIC microflora, can be added directly to the cleaning solution. A supplemental addition of biocide should be added to either the rinse water, or to the fresh makeup water following cleaning. If it is added to the rinse water, adequate contact time must be provided when non-oxidizing biocides are used.

- <u>Long term, on-line non-aggressive chemical treatment</u>: On-line cleaning approach to mitigation is considered when it is not practical to take the system or component out of service. In some cases, the primary objective of this approach is to prevent the problem from becoming more severe, until other approaches can be implemented. The basis for the on-line treatment is the modification of a maintenance or preventive treatment program focusing on gradually eliminating the cause of the problem. On-line mitigation is a passive procedure specifically designed to reduce corrosion in a corrosive environment.

  Every step in the procedure must be directed to reducing the potential for corrosion influenced both by microorganisms and by non-microbiological factors. The greatest degree of success by on-line mitigation is obtained when the problem is in early stages of development and there is a minimum interaction with other corrosion mechanisms.

  The first step in this approach is to remove as much as possible of the sludge, corrosion byproducts, and other debris from the site. Draining and flushing the system is highly recommended when possible. This must be done as passively as possible and aeration of the flush and makeup water should be minimized. The objective is not to stimulate or accelerate corrosion by the cleaning procedure. If not already in place, good housekeeping procedures must be implemented.

  The next step is to include into the routine water treatment program a mechanism to penetrate and disperse the biomass associated with the problem. Slug dosages of biodispersant should be made at frequent intervals. Care should be taken not to break loose uncontrollable amounts of deposits in severely fouled systems. As the slug doses of biodispersant are made, the system should be operated in a bleed-and-makeup cycle. Hydrophobic biodispersants are the most effective for use in once-through systems where circulation is not possible [11].

  Following completion of the periodic slug dosages of biodispersant, a routine addition of the biodispersant should be initiated and continued throughout the duration of the mitigation program. A penetrant or dispersant should be included as part of the water treatment program at that time when the majority of the biomass has been dispersed from the system surfaces. When possible, the criteria for selection of the penetrant or dispersant should include its filming and passivating properties. The penetrant or dispersant should be applied initially at high dosage levels and then gradually reduced to maintenance dosage levels.

  Biocide addition should be initiated concurrently with the addition of the biodispersant and, subsequently, with the penetrant or dispersant. Non-oxidizing biocides are the materials of choice, at least until there is good evidence that the production of biomass has been inhibited. The penetrant or dispersant will enhance the effectiveness of the biocide by providing a mechanism for the biocide to penetrate into the deposits and contact the microorganisms at the corrosion site. The gradual removal of residual deposits and tubercles adhering to the surfaces is implemented by the application of anionic polyelectrolytes. Recent advances in water-treatment technology have provided multifunctional dispersant-corrosion inhibitor compounds that are particularly effective in on-line MIC mitigation programs. The use of these materials is limited to open-circulation and closed-loop systems, primarily because of cost. Intermittent applications of anionic polymeric dispersants are suggested for once-through systems.

Periodic inspections and monitoring procedures should be implemented at the start of the mitigation program. Visual inspection of the site where the problem existed should be made at every possible opportunity. When it appears necessary, adjustments in the on-line treatments should be made. If the on-line mitigation procedure is carried out in a passive mode, passivation is not a primary consideration. However, in those situations where the process water has corrosive properties, conventional corrosion inhibitors should be used during the mitigation program.

Inhibitors based on anodic passivation typically are less effective when used at traditional dosages because of the residual materials on the metal surfaces. Incomplete anodic passivation may lead to localized pitting corrosion. Corrosion inhibitors employing cathodic inhibition or a combination of cathodic and anodic mechanisms typically provide the most-effective results. The use of the anionic polyelectrolyte dispersants in the on-line mitigation procedure complements the effectiveness of the multifunctional corrosion inhibitors.

2.6.6 Characteristics of Chemicals Used to Mitigate Microbiological Problems

Chemicals used to mitigate MIC with each of the approaches previously listed fall into four general categories. These are:

- Biocides/biostats: Chemicals designed to kill existing microorganisms or prevent the microflora from reaching critical population levels. (Discussed earlier in Sections 2.5.1 and 2.5.2).
- Penetrant/biodispersants: Chemicals designed to penetrate into the biomass, disperse the materials deposited at or near the problem sites, and provide a mechanism for the biocide to contact the sessile microflora and biofilm
- Anionic polyelectrolyte dispersants: Chemicals designed to disperse and suspend the deposits, corrosion byproducts, and sludge. These materials also provide a mechanism for the biocide to contact the sessile microflora associated with MIC.
- Electrochemical corrosion inhibitors: Chemicals designed to inhibit the corrosion process by anodic passivation, cathodic passivation, physical barrier film passivation, oxygen scavenging, or neutralization. Many of the corrosion inhibitors currently in use employ a combination of these mechanisms.

2.6.7 Maintenance and System Design Revisions

Mitigation of a microbiological problem cannot be achieved by cleaning and chemical treatment alone. It is necessary that it go directly to the origin of the problem. As discussed earlier, this may involve certain mechanical or operational conditions that contribute to the perpetuation of the problem in spite of any preventive measures and mitigation programs. Other long-range factors to consider during the pre-program and implementation phases of the mitigation procedure follow.

Mitigation of a microbiological problem will not repair a leaking vessel or a through-wall pit. The only logical option is to replace the equipment. A thorough diagnosis of the cause of the problem should provide information needed to ensure that the problem will not recur. Replacement should be done as soon as possible, not necessarily waiting for the mitigation to be complete. The optimum situation would be to complete the repairs or replacement during a shutdown mitigation program.

System design modifications must be coordinated with long-range planning of maintenance and operational modifications. The several factors described during this discussion should be added to the list of criteria that govern system design modifications. The need to carry out a mitigation procedure has illustrated the need to consider relevant system design modifications. Such modifications include adjustment of flow rates, elimination of stagnant or dead-leg flow sites, provision of chemical addition facilities, provision of cleaning and flushing facilities, side-stream filtration capabilities, bypass designs to facilitate routine cleaning, and alternative materials of construction. The purpose of bringing this matter up is twofold. First, there is no better time to observe what design modifications are needed than during a mitigation procedure. Second, there is no better time to implement certain system modifications than during a shutdown mitigation procedure.

It is advisable to use every possible method of monitoring and inspection during both shutdown and on-line mitigation procedures. A monitoring process should be planned prior to the start of a mitigation procedure. If specific equipment is required and not available, installation should be done at the time the mitigation is begun.

2.6.8 Post-Mitigation Treatment

The last, but certainly not the least, important step in the mitigation of an existing problem is the establishment of a program to prevent the recurrence of the problem. The potential for recurrence of a problem such as MIC in a system that has experienced a mitigation procedure is much greater than in a system where MIC has not yet occurred. There are several reasons for this. However, the most important factor to consider is that preventing MIC is generally more successfully achieved than mitigating MIC. Prevention of MIC should be given top priority, especially after a successful mitigation has been accomplished. A planned treatment and operations program for the prevention of MIC should be initiated immediately upon completion of the mitigation program. Nothing should be left up to chance. All points discussed concerning prevention of MIC should be reviewed and put into operation to prevent MIC from recurring.

3

DOCUMENTATION AND ASSESSMENT OF CURRENT TREATMENT STRATEGIES

3.1 Use of Biocides/Biostats for Microorganism Control

As discussed previously, the traditional strategy for controlling microbiological problems, including prevention and mitigation technologies, has been based on the application of biocides to the environment where the problems originate. This approach presumes that the biocide will kill the microorganisms and therefore eliminate the problem. Unfortunately, this presumption is not always true. It does not consider that biocides cannot consistently kill all the microorganisms involved with the problem and that recontamination will occur, as will the microbiological problem. This has become obvious over the past several decades and has prompted continued efforts to optimize microbiological control technology.

There have been numerous additions, revisions, and new approaches related to microorganism control in industrial process water treatment programs. Many of these are still based on the use of biocides, in many cases the use of "new" biocides. Perhaps the most significant change in the approach taken when using biocides is to use them "smarter," i.e., by applying fundamental concepts of microbiology to the application procedures of biocides and biostats. An important objective of this project has been to document what procedures are currently used for microorganism control and to assess the level of effectiveness being obtained under actual utility operating conditions. This section reports the findings of this project.

To achieve this objective, several resources were investigated and reviewed. Recently published and classic technical literature was reviewed. The available "Plant Profile" documents, and electronic databases (e.g., EPRI – CoolADD Survey) were summarized with respect to biocide strategies. These data were correlated with recent EPRI – SWAP Survey data (SWAP – 04 -09) [21, 22, 23]. The information assembled is discussed in the following.

3.2 Survey Results and Comments

Response to the EPRI – SWAP 04 – 09 survey was approximately 85% (37 replies) representing an estimated 75 nuclear operating units. Participants in the survey were both plant and corporate personnel with responsibilities related to operations, system engineering, environmental chemistry/engineering, and plant chemistry. Occasionally, more than one response was received for the same company/system. In a few cases, the responses from the same plant were contradictory. This may indicate that controlling microbiological problems at specific plants has either a low level priority, or a degree of confusion exists among plant personnel. This can be an indication of reality and not considered a criticism.

A summary of responses:

Question: Based on the last three-year plant operating experience has microbiological control been satisfactory?

Response 28 yes 4 no 5 do not know/no answer

Question: Over the past three years, have total water treatment expenditures (costs) increased more than twenty percent?

Response 6 yes 25 no 6 do not know/no answer

Question: Has the plant enlisted resources provided by EPRI or outside vendor/consultants to address water treatment issues?

Response 23 yes 11 no 3 do not know/no answer

Based on these responses and other resources mentioned earlier, it appears that current technology provides a reasonable level of satisfaction. However, there are indications that interest in optimizing strategies and reducing/maintaining costs is an issue with some of the plants. Comments provided with these responses included that interest in mollusk (zebra mussel or Asian clam) control has more priority than microorganism control. Plants indicated that the primary microbiological problem of concern is MIC with minimal concern about biofouling or loss of water flow rate. Some plants commented that they have been using the same treatment program for several years, while other plants indicated they have changed strategies or have been studying new options recently. A number of responses pointed out that the difficulties in changing an existing program is not worth the effort required in getting new NPDES and other regulatory permits. Several plants use outside expertise to oversee and evaluate their treatment strategy. Expertise is provided by vendors, consultants, company corporate personnel, and benchmarking with other nuclear plants.

Question: Does the plant have a routine monitoring procedure in place for assessing cooling water treatment performance including microorganism control?

Response 31 yes 6 no

Question: Are water treatment criteria (specifically microorganism control) considered when decisions are made related to system component modifications, major system design revisions, or materials selection for replacement of components?

Response 27 yes 5 no 6 do not know/no answer

Question: In the past three years, have there been "Action Required" projects related to cooling water treatment, including microorganism control, imposed by INPO, NRC, or regulatory agencies?

Response 6 yes 29 no 2 do not know/no answer

The majority of the plants (85%) said they have monitoring procedures in place that are used to assess the plant operating conditions and 65% are generally satisfied with the procedures. Sixty-five percent have routine monitoring procedures involving analysis of makeup/cooling water chemistry. Approximately 50% reported that some type of microbiological survey of the cooling water is made periodically. It is assumed this is a sampling of the bulk cooling water and/or sampling of the raw makeup water. In-line biofouling monitoring devices are used in approximately 25% of the plants. These are often in conjunction with corrosion monitoring devices.

These observations may indicate several things about monitoring microbiological control. First, there is interest in documenting cooling water system performance, but they are not entirely satisfied with monitoring procedures related to microbiological growth. Perhaps the survey should have asked what groups of personnel are interested in the monitoring results, and how do they use the information monitoring provides. What priority is placed on monitoring microorganism control, as compared to corrosion rates, fouling factors, and MIC? Is the monitoring program adequately performing its purpose, particularly involving detecting or predicting potential microbiological problems?

A large group of the responders indicated that results from monitoring and other observations are used when making decisions related to making changes in the system, particularly regarding materials of construction, fluid flow rates, and HX performance. Monitoring was not mentioned as a factor to consider when assessing chemical treatment costs.

Incident reports and INPO/NRC/Regulatory Institutions have resulted in the initiation of a modest number of “action plan” projects that pertained to microorganism problems. A few plants indicated “self-imposed” situations have resulted in initiating specific projects involving microbiological control issues. After reviewing all the information available, including that relating to generic letter 89-13 issues involving microorganism control, this factor may have been understated by the survey responders. When discussing practical experiences with plant personnel, many indicated that “action plan” projects involving microorganism control were included with other planned or scheduled maintenance projects and with refueling outage projects.

Question: Is an oxidizing biocide(s) used for microorganism control in cooling water systems? (Note: Database for responses to this question was expanded to include additional sources).

Response	31 yes (Expanded total 86%)	6 no (Expanded total 14%)

Question: Are different biocides used in specific CW systems? (Note: Database for responses to this question was expanded to include additional sources).

Response	27 yes (Expanded total 45%)	10 no (Expanded total 55%)

Question: Is the biocide treatment strategy supplemented with the application of a biodispersant or an anti-fouling dispersant? (Note: Database for responses to this question was expanded to include other sources).

Response	10 yes (Expanded total 33%)	27 no (Expanded total 66%)

Question: Is an oxidizing biocide added to condenser CW or SWS intermittently or continuously? (Note: Some plants reported positively to both options).

Response	6 continuous	32 intermittent to condenser CW
	0 continuous	28 intermittent to SWS

Based on data obtained from the recent SWAP survey, additional plant profile reports, and CoolADD survey data, over 85% of the plants use chlorine-based (primarily hypochlorite) oxidizing biocides. It was not possible to determine what percentage of this group used chlorine exclusively for mollusk control, but it was assumed microbiological control was achieved to some degree even when using the oxidizing biocide for mollusk control. The surveys did not include data to indicate what percentage uses hypochlorite to activate NaBr or other bromine compounds. It was assumed that this occurs at several plants (but less than 50%).

The procedure of intermittent application of oxidizing biocide is the most typical method of application. The majority applies the biocide for at least one hour per day, alternate days, or weekly. Approximately 25% of the plants using oxidizing biocide apply it to both the condenser CW and SWS. It is assumed this figure would be higher for those SWS that are circulating design rather than once-through systems (survey indicated 62% SWS were once-through). Forty-three percent of the plants have system design that includes cooling towers or cooling ponds/reservoirs as the ultimate heat sink. Two of the plants reported chlorine is used to control microbiological growth in cooling ponds. The chlorine-based treatment may be supplemented with application of a non-oxidizing biocide, especially in circulating SWS. Approximately 25% of the responders reported that a de-chlorination process is required prior to discharging treated cooling water to effluent receiving water.

Data, obtained by review of the expanded database resource, disclosed at least 33% of the plants surveyed supplement biocide addition by applying a biodispersant or sludge dispersant (anti-fouling agent). A review of published literature indicates that use of biodispersant or sludge dispersant would probably be more extensive in circulating cooling water systems. Since over 60% of the surveyed plants have a once-through SWS design, the number of plants to consider using a biodispersant or sludge dispersant as part of their microbiological control strategy is limited.

Question: Does your plant have mechanical/physical cleaning procedures included as part of the maintenance operations? Has your plant implemented a chemical cleaning of cooling water components in the past three years?

Response	26 yes mechanical cleaning	11 no (not routine maintenance)
	2 yes chemical cleaning	35 no (not routine chemical cleaning)

The responses to this question must be interpreted with consideration of what the responder understood the question asked. The intent of the question was to document what the plants considered the role of maintenance cleaning has in microbiological control. Obviously most plants perform mechanical/physical cleaning when the opportunity is available. It has to be questioned whether 70% of the plants actually perform mechanical/physical on a routine or scheduled basis as part of their microbiological control strategy.

3.3 Non-Traditional Approaches to Microorganism Control

The SWAP Survey included questions that were intended to document interest and experiences by the industry in non-traditional technologies used to prevent problems caused by microbiological growth. Unfortunately, the format of the survey did not lend itself to making a simple yes or no answer to these questions. The responders did not provide sufficient comments to adequately use the survey data as a basis for discussion of this topic. Therefore, recently published literature was reviewed in an attempt to discuss the topic in this report. The literature provides little more than research in progress reports. Several of these projects are discussed in EPRI Report TR-111830, *Nontoxic Biofouling Control Technologies,* (December 1998) [24].

At the time of preparation of this report, a limited number of research/R&D projects relevant to microbiological and macro-biological control in nuclear power generation applications were in progress. These included:

- Thermal treatment used as a raw water pre-treatment process and possibly for use in isolated sites located in the cooling water process.
- Biological pre-treatment of raw water (CW makeup) involving the use of microbiological biofilm/biomass and performed in an external bio-reactor, to remove specific nutrients from the bulk water before it gets into the cooling process.
- Development of toxic (biocidal) and non-toxic coatings for application on wetted internal surfaces of piping and heat transfer components.
- Development of coatings with surface properties designed to inhibit the ability of microorganisms to form biofilm or attach/colonize on critical surfaces in CW systems.
- “Good bugs versus bad bugs” which involves isolating naturally occurring microflora, or genetically engineered microorganisms. These microorganisms would be introduced into the environment where the “bad” bugs grow, and subsequently would proliferate and competitively prevent the growth of the microorganisms that cause problems.

- Development of natural or synthetic enzymes (or adhering protein compositions) that will function to inhibit biofilm formation or prevent the attachment of biomass on internal surfaces when added to CW systems.
- Chlorine production on the surface of a conductive film located on component surfaces.
- Ultraviolet light (UV) irradiation of raw water (including seawater) and localized surfaces within a CW system or specific component.
- Sonic or electromagnetic fields designed to prevent deposition of biofilm, (in some cases remove deposits) from component surfaces.
- Specialized filtration process designed to be installed at raw water intakes or perhaps in localized sites with cooling water systems. The filters potentially would function as full stream or side-stream components.

These projects are mentioned as matters of interest. They each raise interesting and important questions concerning potential applications in the nuclear power industry. It is not in the scope of this project to evaluate them or to discuss them in detail, since they are not accepted as microorganism control practices at the present time. When sufficient data and information are available, they may be topics for future reports.

3.4 Optimizing Microorganism Control Strategies

A number of practices and procedures are at the present time common knowledge to the industry and offer opportunities to optimize microorganism control strategies. This project has highlighted the fact that optimization is needed, and that the greatest potential for optimization in the short-term is to exploit these practices and procedures. The opportunities include:

- Use the fundamental concepts of microorganism control discussed in Section 2.1.3 as the basis for developing optimized water treatment strategy.
- Emphasize that mechanical/physical maintenance cleaning is an important part of microorganism control. Water treatment chemicals, including biocide application will not do the entire job.
- The use of biodispersants, sludge dispersants, and penetrants to augment the use of biocides/biostats has a proven role in microorganism control.
- Potential microbiological problems and strategies for microbiological control should be recognized as a high priority consideration in the operation of nuclear power generation plants.
- Establish a routine procedure for monitoring and controlling the addition of the biocide to ensure that what is actually being done complies with the specifications prescribed for the treatment strategy. Use equipment designed for automated chemical addition and monitoring biocide residual concentration. Ensure the equipment is operating properly at all times.
- Establish a routine procedure for monitoring the effectiveness of the treatment strategy (Section 4.0). Use the information provided by microbiological monitoring to make revisions or adjustments to the actual implementation treatment program. Remember the objective of the treatment strategy is to prevent problems before they occur.

4

MONITORING EFFECTIVENESS OF TREATMENT STRATEGY

4.1 Monitoring the Implementation of the Treatment Program

It is important to confirm that the specifications of the treatment strategy are actually being performed. This involves verifying that the biocide is added at the dosage rate prescribed and for the duration of time intended. Monitoring is required to insure this is being done. The monitoring procedure must provide "real-time" information that confirms what is currently happening, not just "historical" information about what has happened in the past over an extended period of time. When efforts to prevent microbiological problems depends only on historical information, it may be too late to use it in a prevention effort. When real-time data are available, steps to prevent problems can be implemented.

It is not in the scope of this report to provide a comprehensive discussion of the techniques used to implement specific monitoring programs. However, information related to these techniques can be obtained by reviewing the literature cited in this document [20, 25, 26, 27, 28].

4.1.1 Chemical Addition

Biocide addition can be done by manually adding the chemical(s) to the system batch-wise or as a "slug/shock" addition. Typically, this is a less-effective, or less reliable, means to treat the system. It involves handling potentially hazardous materials and introduces the risk of human error. Effectiveness of the treatment chemicals can be limited by restrictions due to non-accessibility of the best site to add the chemicals. Addition of biodispersants, corrosion inhibitors, sludge dispersants, pH adjustment materials, and other chemicals important to prevention of microbiological problems are also affected by these limitations.

Chemical addition by means of feeding pumps, injectors/eductors, or other mechanical equipment has become a "standard practice" in the nuclear power industry. However, this practice requires two essential procedures related to monitoring to be carried out. The first requires that the equipment be maintained in the proper functioning status, i.e., it must be checked to verify (monitor) if it is working as required. Secondly, the inventory of the chemical to be added must be verified (monitored) to insure the chemical addition takes place as specified [25].

4.1.2 Monitoring Conditions Existing in the System

The overall strategy of the microbiological treatment program was based on specific information available when the procedure was developed. System water chemistry, cooling water flow-rates, system volume/retention time, etc. were considered when the specification for chemical addition was established. It is necessary to routinely monitor the system to verify that these conditions have not changed since the treatment program was initiated.

When using oxidizing biocides such as those based on chlorine, it is important to verify that the addition procedure is providing the desired oxidant residual. For example, changes in oxidant demand in the bulk water being treated, due to seasonal effects on the raw water, must be monitored and adjustment must be made to the addition procedure. Routine chemical analysis of the treated water, i.e., monitoring done on a “real-time” basis, can be used to detect these changes and make necessary adjustments to chemical addition. Chemical analysis is often done by manually sampling makeup water or system bulk water on a pre-determined schedule. However, newly available automated on-line monitoring equipment is recommended for more optimized microbiological control. On-line monitors for measuring pH, total-residual-oxidant-(TRO), oxidation-reduction-potential (ORP), total-organic-carbon (TOC), and total-dissolved-solids (TDS) are now available to provide reliable “real-time” data. In many cases, these types of on-line monitors, e.g., ORP or TRO meters, are used to control electronically operated chemical feeding systems [27, 28].

4.2 Monitoring the Results of the Treatment Program

Monitoring the impact of the presence of microorganisms in a system treated to control their growth can lead to difficulties in the monitoring process. This is due to the fact that not only is the presence of the microorganisms important, but also due to the fact that the basic objective of treatment is to prevent the problems they potentially cause. Monitoring procedures may indicate microorganisms are present in the system, but there may be no problems detected. Conversely, problems such as biofouling, loss of heat transfer, or MIC may be detected, but it may be uncertain that the problems are caused by microbiological growth.

Therefore when attempting to monitor the effectiveness of a treatment strategy, it is necessary to establish a system performance baseline. This baseline is used to make relative comparisons with current data, i.e., microbiological population trends. Very often monitoring is based on attempting to measure the amount of microbiological growth occurring in the system. Most sampling is of the bulk water and very little of sessile growth on system surfaces. It is very difficult to do this in a manner that produces information useful to preventing problems. The difficulty is seated in the lack of ability to consistently determine the amount of microbiological growth, and in the lack of knowing how much microbiological growth must occur to result in a specific level of problem(s). These gaps in monitoring technology are inherent to virtually all of the monitoring procedures currently in use. Gaps must be recognized as realities when monitoring procedures are used to assess results or effectiveness of treatment strategies.

4.2.1 MIC Indices (Models)

Indices or models have been developed recently to assess effectiveness of treatment programs or to predict the level of risk that exists for potential microbiological problems including MIC. Details are discussed in the literature. Those being used currently by several nuclear power plants are [20, 28, 29]:

- EPRI CHECWORKS™
- Lutey/Stein MIC Index
- UE Callaway MIC Index

4.2.2 Microbiological Survey Programs

Microbiological surveys involve routinely scheduled sampling and selectively culturing in an attempt to identify the presence and amount of specific types of microorganisms known to cause problems such as MIC. The survey is focused on alerting the plant of potential problems caused by:

- Sulfate reducing bacteria (SRB)
- Metal-oxidizing bacteria (*Sphaerotilus sp., Gallionella sp., Leptothrix sp.)*
- Acid-producing bacteria (*Closridium sp., Vibrio sp.)*
- Slime-forming bacteria (*Bacillus sp., Pseudomonas sp., Siderocapsa sp.)*

Microbiological survey scheduling should be coordinated with maintenance and outage scheduling so that anytime a component or cooling water system is not in operation, sampling and visual inspections can be made [20].

4.2.3 On-Line Monitoring Programs

Monitoring treatment effectiveness is done ideally on-line while the system is in operation. To achieve this, reliable sampling sites must be available for both water sample analysis and possibly for gathering deposit samples for culturing and microscopic examination. Procedures for obtaining representative samples must be developed and followed consistently if the test data are to be used for monitoring treatment effectiveness. Very often, on-line microbiological monitoring is done in conjunction with chemical analysis of cooling and other process waters.

On-line biofouling monitoring devices provide a “real-time” source of data related to assessing microbiological control. As mentioned earlier, gaps exist in microbiological monitoring, but several newly developed on-line biofouling monitors have helped close these gaps. Several publications in the literature provide use-experiences and data pertaining to the different types of biofouling monitors currently available. An early EPRI document – CS-3914, Project 2300-1, March 1985 - can be referred to for a more extensive discussion on *Biofouling Detection Monitoring Devices: Status Assessment.* Recent developments not discussed in that document include the following:

- Annular Reactor Tests measuring formation of biofilm on rotating metal surfaces [28].
- SmartCM™ device using multi-technique electrochemical (LPR, HAD, and EN) technology to monitor biofilm growth, MIC, and biocide efficacy [30].
- CORRDATA™ RDC device that has been developed from linear polarization (LPR) technology to do remote corrosion/fouling monitoring [31].
- CorrDATS™ equipment to measure on-line fouling, corrosion, and heat transfer data in side-stream installations at heat exchanger components [32].
- BioGeorge™ Monitor System designed to measure biofilm formation on in-line surfaces of process water and cooling water systems [33].
- SAM Unit (Slime Accumulation Monitor) designed to monitor on-line rates of slime accumulation on side-stream installations at heat exchanger components [34].
- Southwest Research Institute Localized Corrosion Probe (multi-array sensor) device designed to detect/measure pitting corrosion possibly due to microbiological growth (SRB) [35].
- Reports of other devices based on optical measurement of real-time on-line biofilm development by visual spectrum light/laser or “fluorescent bio-sensors” have been cited in the literature, but they have presented only experimental data so far [36].

A summary discussion of monitoring microbiological control is presented in Sections 15, 16, and 17 in the EPRI *Microbiologically Influenced Corrosion Training Course*, EPRI PSE 08/02 edition, EPRI NDE Center, Charlotte, NC [20].

5
CONCLUSIONS AND SUGGESTIONS FOR FURTHER WORK

The objective of this project was to examine the microorganism control strategies currently used by the nuclear power industry. An attempt was also made to investigate and identify other treatment options, either non-biocidal or other biocidal options. A utility survey was conducted to (i) assess the level of industry satisfaction, and (ii) flush out any significant concerns the nuclear power industry of North America might have regarding the effectiveness of currently available strategies for preventing problems caused by growth of microorganisms. The survey indicated that additional efforts to satisfy or resolve industry concerns were needed, specifically for optimizing microbiological control strategies.

5.1 Conclusions

1. Results of the survey, personal interviews, and a review of the literature have established that the industry has concerns related to microbiological control. Most of these concerns are based on specific technical problems such as: "What are the options available?" and "Is the current strategy the most efficient and economical option?"

2. An overview of the fundamental concepts of microorganism control and a discussion about how these concepts can be applied for optimizing current strategies was presented. In particular, preventing microbiological problems is a more efficient approach than attempting to mitigate an existing microbiological problem.

3. Available options for mitigating existing microbiological problems were presented. These options included mitigation of microbiologically influenced corrosion (MIC), mitigating biofilm or biofouling, and mitigating loss of flow rate or heat transfer efficiency.

4. Information was presented about the currently available biocides that represent possible options to use in refining treatment strategies. Factors that determine selection of biocides and what is pertinent to the application of specific biocides were discussed. A survey and other resource information confirmed that the majority of the plants are satisfied with their current strategy, but would be interested in optimizing some parts of their treatment program.

5. Although a variety of strategies are used by the industry, the majority of the plants use oxidizing biocides. A few plants supplement the biocide addition with application of non-oxidizing biocides and/or biodispersants and penetrants. The supplemental treatment chemicals are used when it is necessary to optimize the oxidizing biocide application, e.g., when regulatory permits prevent increasing the dosage level or extend the duration of oxidizing biocide addition. The majority of plants uses intermittent chlorine addition for at

least one hour on either a daily schedule, or 1-3 times per week. This is defined as a "break-point" treatment strategy providing a free chlorine residual for short periods (less than one hour) ranging from 0.1-0.3 ppm TRO during the feeding period. Fewer than 25% feed an oxidizing biocide on a continuous basis. Compliance with regulated effluent specifications is the primary factor that limits the amounts of biocide added. De-chlorination is required at approximately 25% of the plants responding to the survey.

Several plants indicated that mechanical/physical cleaning is a routine part of their microorganism control strategy.

6. Only a few plants have explored the possibility of using non-traditional strategies for microorganism control. A list and related references of some of the non-traditional strategy options was provided.

7. A discussion of monitoring treatment procedure highlighted critical factors for performing an optimized microbiological control program. Monitoring the results of the treatment strategy was also discussed. Many of the monitoring tools currently available were listed and referenced. A list was also provided of monitoring equipment that have recently become available, or are still in research and development stages.

5.2 Suggestions for Further Work

When working with problems caused by microorganisms, there always are numerous areas where further work is required. It is important to focus on immediate needs and to recognize there are also many long-term needs. Priorities are necessary, and immediate needs typically receive a higher priority. This project uncovered several suggestions for immediate projects and also several that may be considered long term.

5.2.1 Immediate Needs

- More effective and less complicated methods for on-line monitoring to assess potential pitting corrosion and measure rate of pitting corrosion.
- More accurate and less complicated methods for monitoring effectiveness of microorganism control and predicting potential problems.
- Plant trial data to demonstrate effectiveness of using biodispersants, biofilm penetrants, sludge dispersants, and other non-traditional technologies.
- Improved equipment for addition of biocides, increasing efficiency and reducing maintenance of application equipment.
- Automated analytical equipment to make chemical tests that are important to optimize biocide effectiveness.
- Greater understanding, supported by actual plant data, for accurately defining the cost/economic ramifications of uncontrolled microbiological growth and subsequent microbiological problems.

5.2.2 Long-Term Needs

- Innovative options for non-traditional approaches for microbiological control, and development of the most promising approaches.
- Development of additional biocides/biostats that provide greater effectiveness, lower costs, with no adverse impact on the environment.
- Continued research on equipment and technology for use in monitoring real-time system conditions and in monitoring the effectiveness of alternate treatment strategies.
- Research on biofilm development and its relationship to MIC mechanisms and biofouling.

6
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