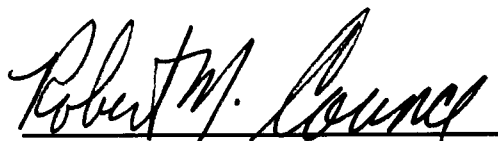
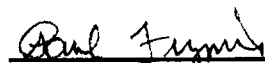


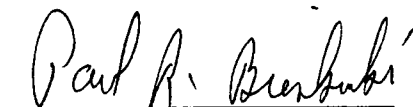
To the Graduate Council:

I am submitting herewith a thesis written by Oscar Lee Martin, Jr. entitled "Microbial Control in Industrial Water Recycle Systems." I have examined the final copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Chemical Engineering.


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MICROBIAL CONTROL IN INDUSTRIAL WATER RECYCLE SYSTEMS

A Thesis

Presented for the

Master of Science

Degree

The University of Tennessee, Knoxville

Oscar Lee Martin, Jr.

December, 1996

DEDICATION

To my mother Mrs. Margaree Colvin Martin

and

my father Mr. Oscar Lee Martin, Sr.

I dedicate this Thesis.

Their words of motivation and unlimited patience helped transform an idea into reality.

ACKNOWLEDGMENT

I would like to thank all those who have contributed in one way or another to the completion of this Thesis, but in particular I would like to express my sincere thanks to the following faculty for their special contributions: Dr. R.M. Counce (major advisor) for his guidance and intellectual stimulation, as well as for other invaluable behind-the-scenes assistance; Dr. Paul Frymier and Dr. Paul Bienkowski (Committee members) for their comments and assistance; Dr. Gary Sayler and Dr. David White for their contributions and assistance in the area of microbiology.

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ABSTRACT

Industrial water recycle systems (e.g. cooling and clarification systems) provide an ideal environment for the proliferation of microorganisms. Common microorganisms within these systems include algae, aerobic bacteria, anaerobic bacteria, and fungi. These microbes contribute to biological fouling and microbiologically influenced corrosion. These problems contribute to reduced cooling, routine cleaning, equipment replacement, and treatment. To reduce the potential for these problems, an effective microbial control program must be implemented.

An approach that considers the modification of the existing microbial control program before implementing a new program was applied to the problem. When selecting a new microbial control technology, one must consider the technical suitability (compatibility with the system's microbial problem, pH, level of solid and organic constituents, and materials of construction) and the selection criteria (investment and operating costs, environmental impact, and safety concerns) for available technologies.

Two process water systems with undesirable microbial contamination were studied at a polymer manufacturing facility (DuPont Co., Old Hickory, Tennessee). These two systems were a cooling water circulation system and a process water clarification and recycle system. An assessment of the DuPont cooling and clarification system cases was performed to determine the technical constraints for suitable microbial control technologies. Based on the cooling water recirculation system's algae and aerobic bacteria problem, basic pH (8.52 ± 0.09), relatively low level of solid and organic constituents (11 ppm) and stainless steel construction, numerous technologies were identified as potential candidates for controlling microbial contamination. Based on the clarification system's aerobic and anaerobic bacteria problem, slightly basic pH (7.56 ± 0.35), relatively high level of organic constituents (321 ± 36 ppm), and concrete construction, numerous technologies were also identified for controlling microbial contamination. Using selection criteria identified in this study to further screen the microbial control technologies, rankings and recommendations were produced.

LIST OF ABBREVIATIONS

ATP	Adenosine tri-phosphate
BNPD	Bromo-nitro-propanediol
BNS	Brominated nitrostyrenes
CC	Cycles of concentration
DNA	Dehydroxy-ribonucleic acid
DPD	N,N-dimethyl-p-phenylene-diamine
EPA	Environmental Protection Agency
FACTS	Syringaldazine free available chlorine method
MIC	Microbiologically Influenced Corrosion
ORP	Oxidation reduction potential
PAA	Peracetic acid
PHMB	Polyhexamethylene biguanide
PPM	Parts per million
PVC	Polyvinyl chloride
RNA	Ribonucleic acid
SS	Stainless steel
TOC	Total organic carbon
TSS	Total suspended solids
UV	Ultraviolet light

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CHAPTER 1

INTRODUCTION

Water recycle systems provide an ideal environment for the growth and nurturing of microorganisms. Industrial water recycle systems provide all of the essentials that are needed for biological growth including good aeration, minerals, and nutrients. In addition to the materials already present in natural waters, cycles of concentration increase the nutrient and mineral content in the water significantly.

The presence of microorganisms can be very detrimental to industrial processes that require a constant recycle of process water. In cooling towers systems, biological growth reduces the area for heat transfer, thusly reducing the heat transfer efficiency. In paper and fiber making processes, these microorganisms form biofilms or "slime" in process equipment. Over time, parts of biofilm can become dislodged and be transported and can be found in the paper or fabric product as holes, odors, or spots.

The control of microbes is critical to industries that require water reuse. The implementation of an effective microbial control system can result in both tangible and intangible savings. Operation down time, as a result of equipment cleaning to remove deposits of microorganisms, can contribute to many unnecessary costs. These costs include labor, cleaning, and material and reflect reduced process availability. Product quality, such as high grade fabric and high purity chemicals, can also suffer as a result of microbial presence.

There are two main kinds of problems that are associated with microorganisms: biological fouling and microbiological influenced corrosion. Biofilm formation induces biofouling and corrosion problems. Biofilm formation is the formation of an organic coating on the exposed surface, followed by the attachment and growth of the microorganisms, forming slime deposits. Biofouling results in the plugging of the process equipment by the slime deposits. Microbiologically influenced corrosion is the acceleration of equipment corrosion due to the chemicals secreted by microorganisms in a biofilm.

The objective of this study is to make appropriate recommendations for controlling microbial problems in two different water recycle systems. Cooling is the main

objective of the first water system. This system consists a three-cell cross-flow cooling tower used to reduce the temperature of cooling water for recycle. Clarification is the main objective of the second water system. This system consists of a clarification tank and ancillary equipment for water reuse.

Two industrial water systems, cooling and clarification, will be used as cases for this study. A general approach to the problem will be developed. This approach considers the modification of the existing treatment program before implementing a new program. Based on the system's microbial problem, water chemistry, and materials of construction, technically feasible microbial control technologies will be presented. Using a selection criteria that considers additional investment and operating costs, environmental acceptability, availability, and safety concerns, technically feasible technologies will be ranked for recommendation. The results will likely be useful for similar industrial applications.

CHAPTER 2

BACKGROUND

Cooling and clarification systems are unit operations that treat process water for recycle and reuse. Cooling systems are technologies that reduce the temperature of recycled cooling water. Clarification systems are technologies that produce a relatively low solid content effluent from an entering stream.

The maintenance of constant cooling in the cooling system and flocculation of colloidal solids in the clarification system is vital. Reduced water flow to a process and/or cooling loss can reduce functional efficiency. Microbiological growth is one cause of functional efficiency loss. Cooling and clarification systems are ideal environments for the proliferation of microorganisms. Environments for microbial growth are directly related to the system's pH and solid concentration. These water chemistry variables also play a role in the effectiveness of anti-microbial agents. Therefore, an overview of this information is necessary before proceeding with this study.

Microbial problems in water reuse systems result from algae, bacteria, and fungi growth. These microorganisms contribute to two primary problems in cooling and clarification systems: biofouling and microbial influenced corrosion. These problems are directly related to the environmental conditions within the system.

Problems associated with microorganisms are currently reduced via conventional microbial control technologies. Available technologies include industrial biocides and other chemical agents. Due to the increasing interests in environmental acceptability and safety concerns, alternative microbial control technologies have been explored.

2.1 DESCRIPTION OF COOLING SYSTEM

In cooling systems, an exchange of heat is made via air/water contact. Aerated cooling systems are subject to water loss via of evaporation. There are numerous technologies that reuse water for cooling purposes including cooling towers, evaporative condensers, and spray ponds.

Cooling towers are one of the most widely applied cooling systems for water reuse. The high temperature water is admitted at to the top of the cooling tower and

distributed via sprinkling system, trough, or other methods. Cool air contacts the warm water, in which an exchange of heat occurs. The heat can be dissipated by two mechanisms, air/water heat exchange and evaporation.

In addition to cooling process water, cooling towers are also designed to conserve cooling water for maximum reuse. As water is evaporated, the water recycled to the process is decreased, resulting in an increase in mineral concentration. Water economy is primarily based on the cycles of concentration. The cycles of concentration is defined as the ratio of the solid concentration in the effluent and make up water.

There are two primary types of cooling towers: cross flow and counter flow towers. The key difference between these two cooling systems is the method of air/water contact.

2.1.1 CROSS-FLOW COOLING TOWERS

In cross-flow cooling towers, cool air contacts the process water at a 90 degree angle. The water freely falls downward from the top of the tower to the basin. The air flows horizontally through the fill section and exchanges thermal energy via evaporation and/or air/water contact. Air enters the tower at different levels. At the top of the tower, the entering air stream contacts the warm water. Similarly, at the bottom of the tower, the entering air contacts the coldest water. As a result, the water temperature is a function of the relative vertical position along the cooling tower. A "drift eliminator", which reduces the water loss due to entrainment, is placed vertically between the center plenum and the fill section, (Burger, 1990). Figure 2.1 exhibits the components of a cross-flow cooling tower.

The cross-flow tower is subject to a higher degree of microbial growth than the counter-flow tower. The biological attack is due to the large plenum area and the open pan water distribution system. This open portion of the system is subject to sunlight, air, and aerated particles that adhere onto the pans, (Burger, 1990).

2.1.2 COUNTER-FLOW COOLING TOWERS

In counter-flow cooling towers, cool air contacts the process water at a 180 degree angle. The counter flow design disperses warm water through a low pressure spray

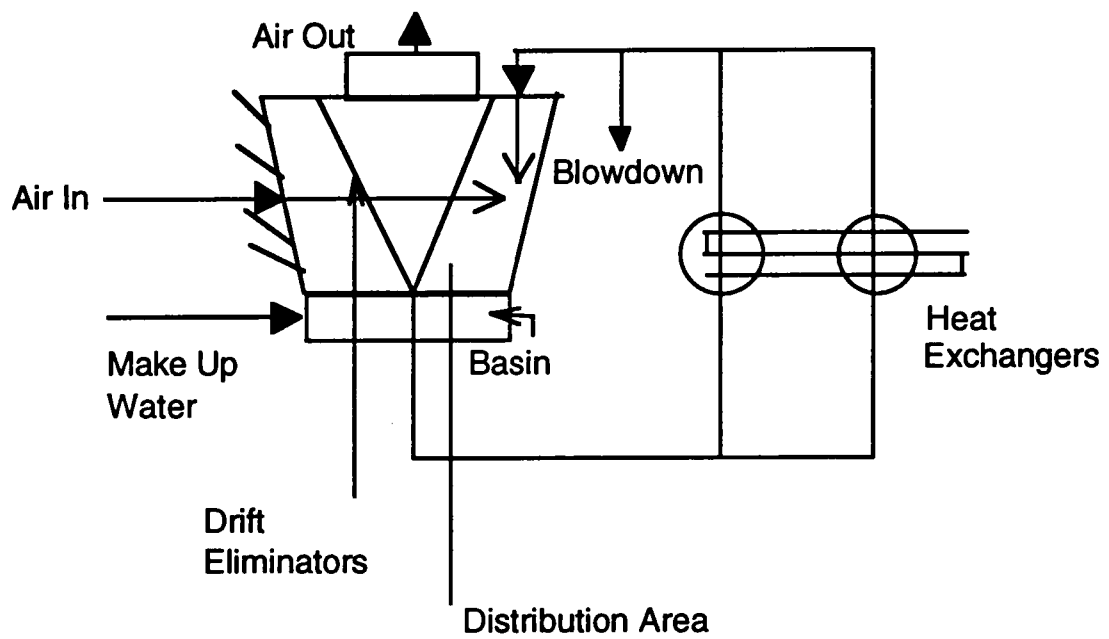


Figure 2.1: Components of a cross-flow cooling tower.

distribution system from a distributor that stretches across the cooling tower. The air enters the bottom of the tower horizontally and flows vertically upward. The cool air stream contacts the coldest water first, and travels upward through the tower. Three-fourths of the heat exchange results from evaporation, with the resulting balance from air/water contact. The drift eliminator in counter-flow towers are placed horizontally between the fan and the water distribution system, (Burger, 1990). Figure 2.2 exhibits the components of a counter flow cooling tower.

2.2 DESCRIPTION OF CLARIFICATION SYSTEM

Clarification systems produce a relatively clear effluent by removing fine suspended particulates from the entering stream. These systems require the incorporation of flocculating agents to aid in the coagulation of dilute feed streams. Flocculating agents are polymers that generate a repulsive charge between the solids. The charged solids lodge at different sites of the flocculant. For these large agglomerates, gravitational forces are dominant, making them unstable with respect to suspension. These colloidal solids aggregate into larger globules for which gravitational forces dominate, and suspension is lost, (Grayson, 1980). A high solid content sludge is drawn from the bottom, while a relatively clear effluent is taken off the top.

Paper mills are one of the most widely known applications of reused clarification water. The spunlacing process also reuses clarification water. Both processes separate wood pulp and water streams via clarification.

In the spunlacing process, two sheets of fibrous materials (for example a paper sheet and polyester batting) are impinged by high pressure water forming a single woven sheet. The water drainage from the process is rich in material content (e.g. fiber, carbon, silt, clay, color bodies, minerals, and dissolved organic matter). The water chemistry and solid content is dependent on the raw materials and process conditions used. After clarification and filtration treatment, this water stream is reused in the process. Figure 2.3 exhibits a general schematic of a clarification system.

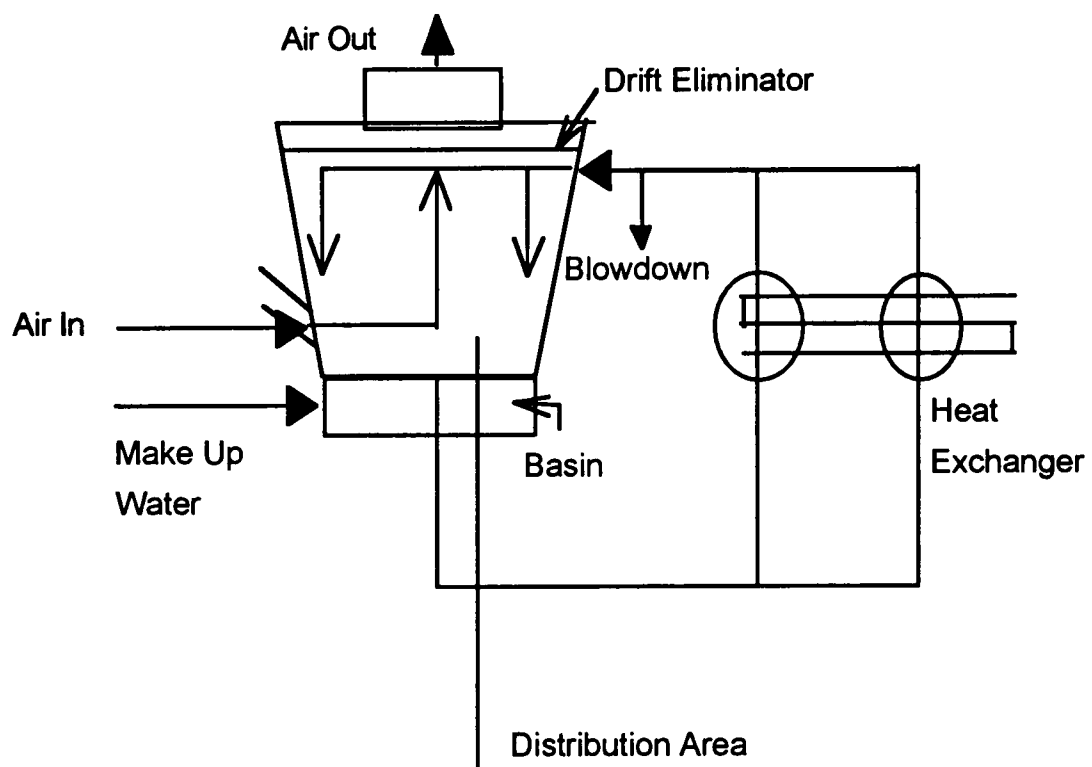


Figure 2.2: Components of a counter-flow cooling tower.

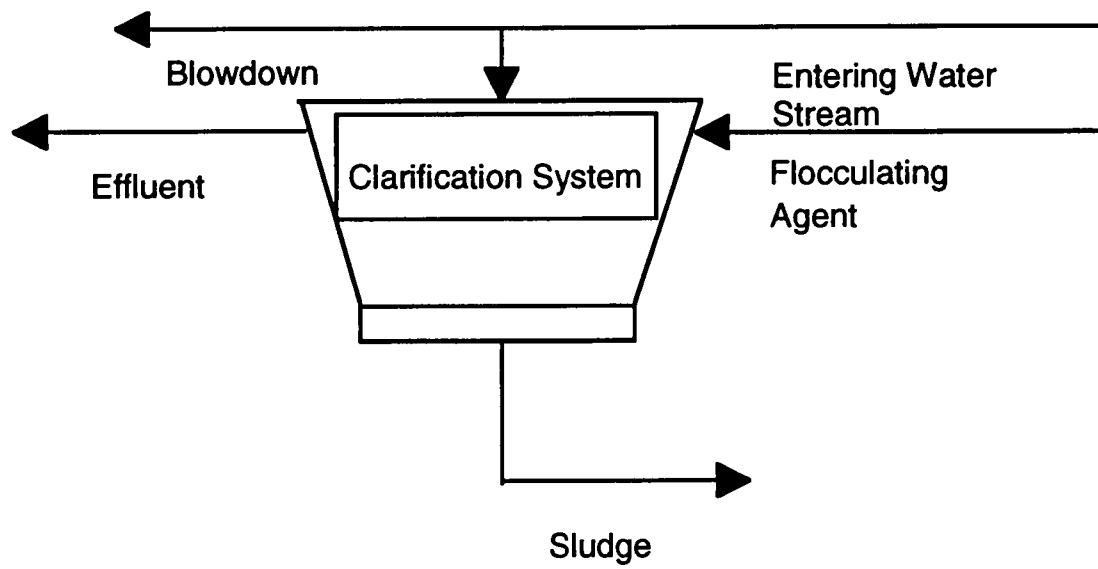


Figure 2.3: General schematic of a clarification system.

2.3 PROCESS CONDITIONS IN COOLING AND CLARIFICATION SYSTEMS

Cooling and clarification systems have two primary system conditions that induce problems associated with microorganisms: low pH and solid concentration. Acidic bulk water conditions in conjunction with relatively high solid concentrations, are often reflected by corrosion and scale problems, respectively. The system's pH and solid concentration also plays a role on the technical suitability and effectiveness of microbial control technologies. An overview of pH and solid concentration measurement and control is a necessary component of this study.

2.3.1 pH

The pH reflects the relative acid concentration within a water system. The pH scale ranges from 0 to 14, which represents acidic and basic conditions respectively. A neutral water solution exhibits a pH of 7. The pH of a solution is calculated by taking the negative logarithmic of the acid concentration (Equation 1).

$$\text{pH} = -\log [\text{H}^+] \quad (1)$$

Corrosion and scale deposition are common problems in water reuse systems. These problems are directly related to bulk water pH. In order to reduce the potential for localized corrosion and scale deposition, proper pH control is necessary. Corrosion is typically due to an uncommon decrease in bulk water pH below 7. Scale deposition is typically due a rapid increase in bulk water pH above 7. Therefore, an understanding of pH measurement and control, which aid in the reduction of corrosion and deposition, is beneficial, (NACE, 1971).

Measurement Technologies

There are two fundamental methods for determining the pH of water: glass electrode and the colorimetric procedure. The glass electrode method, which uses a pH meter, is recommended for the best accuracy. This commonly used pH measurement device is composed of a glass pH electrode, a reference cell, a temperature compensation element, a preamplifier, and a sensor body. The colorimetric procedure is based on the use of indicators which reflect pH changes by color changes, (NACE, 1971).

With the advancement in technology, industries are moving towards in-line and automated pH control techniques. This advancement is a result of previous difficulties related to variations associated with manual control techniques, (Betz, 1991). New pH controllers use micro-processor based electronics, control modes such as proportional, proportional integral, and proportional integral derivative, and computer interface systems. New sensor technology has progressed by overcoming previous obstacles related to fouling, cell depletion, and interference. For cooling tower and clarifier waters, a combination pH sensor assembly is most appropriate, (Betz, 1991).

pH Control Systems

The installation of an automated acid feeding system can be very beneficial for pH control. Overfeeding of acid results in equipment corrosion, while underfeeding results in scale formation. Figure 2.4 illustrates a typical pH control system used in water recycle systems. Conceptually, there are two measured variables that can be used for control purposes: make up water-flow and corrosion rate.

Using make-up flow as the measured variable, acid is fed proportionally with the make-up water flow. Using corrosion rate as the measured variable, an electronic device with a corrosion sensitive probe can be used to control acid feed rate. Figure 2.4 shows the conceptual feed back control design for this technology. A water sample from the process unit is sent to the transducer which convert measurements into pneumatic signals. These signals are sent to the controller, which decides on the actions that should take place. The amount of acid that should be fed is calculated by the data acquisition system. A signal from the hardware system is sent to the control valve on the acid tank, which responds by releasing acid feed, (NACE, 1971).

2.3.2 SOLID CONCENTRATION

The solid concentration within a water reuse system reflects the total organic constituents and other materials present. The increase in solid concentration results from water loss due to evaporation. Water loss due to evaporation results in only water transport. However, water loss due to non evaporation (e.g. process water leaks or blown away water) result in both water and solid transport. Total solids within the system are

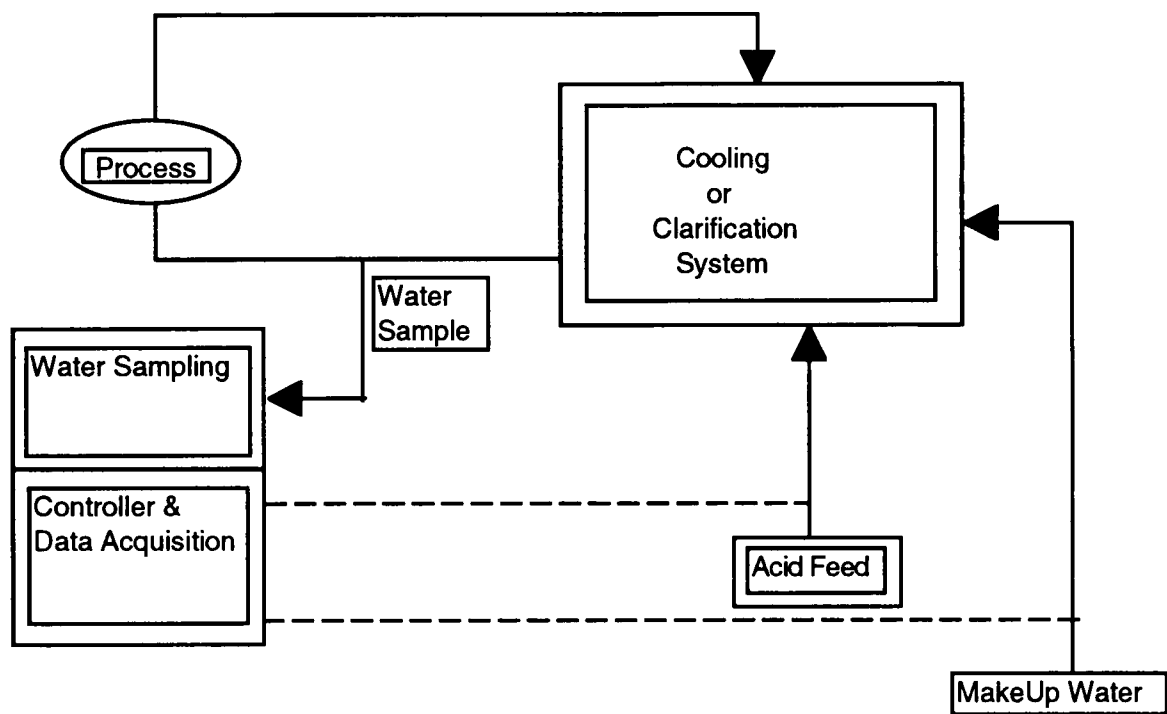


Figure 2.4: A general schematic of an automated pH control system.

reduced via water loss due to non evaporative processes. The presence of these constituents can induce problems associated with microorganisms, including scale deposition and localized corrosion. Scale deposition in water reuse systems is due to the precipitation of solid or organic constituents. Localized corrosion is induced by the proliferation of microorganisms under scale deposits. Therefore, an understanding of solid measurement and control, which aids in the reduction of corrosion and deposition, is beneficial.

Solids Measurement Technologies

The solid content within a water reuse system is quantified by the "cycles of concentration", CC. CC, as represented in Eqn 2, is a ratio of the total solids present in the recirculation water to that of the make up water.

$$\text{Cycles of Concentration} = \frac{\text{Solid concentration in recirculation water}}{\text{Solid concentration in make up water}} \quad (2)$$

There are two primary measurements of solids content: total suspended solids and soluble solids.

Total suspended solids, TSS, is the measurement of non soluble particulates. TSS quantification can be done using a fundamental filtration techniques. The water is filtered via vacuum suction through a microporous filter. Next, the retained solids are weighed. Knowing the weight of the retained solids and pre-filtered water, the suspended solids concentration can be calculated from Equation 3:

$$\text{Total Suspended Solids (TSS), ppm} = \frac{\text{Mass of retained solids}}{\text{Mass of pre-filtered water}} \times 10^6 \quad (3)$$

Soluble solids or total ions (e.g. calcium, iron, carbonates) present in water samples can be quantified by water conductivity analyses.

Solid Control Systems

Cycles of concentration can be controlled by using two methods: (1) purge a blowdown stream or (2) reduce the amount of aerated solids entering the system.

Blowdown, or bleed off, is defined as a purge stream from the water system. This stream is deliberately withdrawn to reduce the total solid content entering the system.

This method has been found to be the most economical technique for solids removal. The blowdown can be typically discharged into a sewage system feeding of conventional waste treatment plant.

There are several ways to incorporate blowdown streams into a water reuse system. One method is to install side stream filters. Usually 1 to 5% of the total recirculation water is by passed through the filter. These filters often include sand filters, granular particle filters, tubular strainers, and hydrocyclones, which reduce the suspended solids entering the system.

The blowdown may be automatically controlled using water conductivity as the measured variable. The maximum allowable conductivity value is set at the controller in one control strategy outlined in the NACE Cooling Water Treatment Manual, "when the conductivity of the water reaches the set point level, the solenoid blowdown valve is tripped open and remains open until the conductivity is reduced to approximately 90% of the set point value" (NACE, 1981). Figure 2.5 exhibits an automated solids concentration control system.

Solids can also enter the process via the air feeding the tower. Air filtration is another method of reducing the in-flow of aerated particulates. Although air filtration of influent air is usually uneconomic because of the cost of installing and cleaning air filters, and of additional power needed for blowers, in some specialized situations intake air filters have been needed, (Burger, 1990).

2.4 MICROORGANISMS FOUND IN COOLING AND CLARIFICATION SYSTEMS

Microbial problems in water reuse systems result from algae, bacteria, and fungi growth. Algae growth along the sides of cooling tower basins may cause major blockages of pump inlets, (Payne, 1988). The accumulation of bacteria growth along metal surfaces can reduce oxygen diffusion to these surfaces. This non aerated environment is suitable for the growth of anaerobic sulfate reducing bacteria. This problem rapidly induces localized corrosion, (Payne, 1988). Fungus growth can cause problems associated with the rotting of wood within a cooling system. Algae, bacteria, and fungi growth are influenced by the physical and chemical environmental factors within the water system.

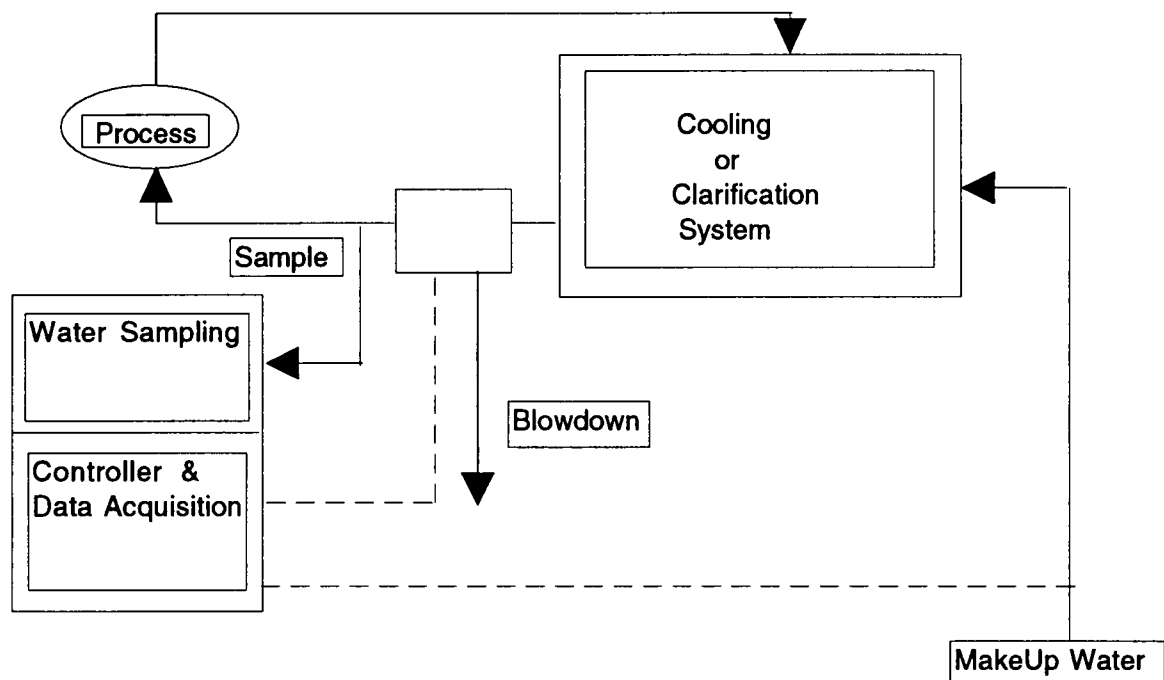


Figure 2.5: A general schematic of an automated solids control system.

A review of microorganisms is necessary before an effective control plan can be implemented.

2.4.1 TYPES OF MICROBIAL GROWTH

In industrial cooling and clarification systems, there are three primary types of microbial growth: algae, bacteria, and fungi. These microorganisms have different physical properties, survival requirements, and growth mechanisms that make them unique. Each microbe cause specific problems in water reuse systems (e.g. slime, corrosion, odors, rotting). Identification techniques have been developed for proper identification of algae, bacteria, and fungi.

2.4.1.1 ALGAE

Algae growth is the most commonly found biological fouling problem. The algae can be found in all surface water supplies, and usually appear in cooling tower basins. The organism produces its own food via photosynthesis, and grows via tip extension or cell division. Algae require air, sunlight, and water for survival. Since cooling tower

systems are subject to sunlight, they are usually plagued with more algae growth than paper manufacturing and spunlacing processes. Algae can appear red, brown, or green in damp lighted areas. Excessive algae growth can lead to the build up of large slime layers, which cause corrosion and fouling problems in recycle systems.

2.4.1.2 BACTERIA

Bacteria are life forms universally distributed in nature via air, water, and land. There are a wide variety of bacteria that colonize cooling and clarification systems. Bacteria are introduced to the water recycle system via make-up water and via air-borne from the environment. Some of the bacteria found in make up water include spherical, rod shaped, spiral, and filamentous forms, (NACE, 1971). These single-celled microorganisms have simple growth requirements, exceedingly fast growth rates, and enormous powers of adaptability, (Betz, 1981). Bacteria multiply by binary fission, in which each cell splits to form two daughter cells. There are two main categories of bacteria: aerobic and

anaerobic. Aerobic bacteria thrive in oxygenated waters, while anaerobic bacteria thrive in deoxygenated areas.

Aerobic Bacteria

Aerobes include slime forming, iron, sulfur, and spore forming bacteria. Slime forming bacteria are the most common type of bacteria found in water recycle systems. Slime forming bacteria belong to many species, but all either have a discrete, well defined capsule or sheath surrounding them, or secrete diffuse masses of polysaccharide or protein slime, (Betz, 1981). This type of bacteria forms a gelatinous matrix used to entrap other microorganisms and particulates. This matrix also provides a barrier against water treatment chemicals. Slime forming bacteria may produce yellow, green, or pink slimes, in addition to the normal brown or gray slime. Iron bacteria are filamentous fresh water microorganisms that absorb and accumulate iron when growing in iron rich environments. These microorganisms also produce relatively soft, voluminous tubercles consisting of reddish iron oxide.

There are several forms of sulfur bacteria. Some sulfur utilizing or tolerant bacteria are normally found in waters that contain dissolved hydrogen sulfide. These bacteria have a specified color, red or purple, and produce their own food via photosynthesis. Another form of sulfur bacteria is sulfur oxidizing bacteria. These microorganisms derive their energy from the oxidation of thiosulfites, hydrogen sulfides, and elemental sulfur, sometimes oxidizing sulfur forming sulfuric acid. Sulfur oxidizing bacteria also produce broad dark tubercles that trap water containing black iron oxide. Spore forming bacteria are microorganisms that add to the slime problem, and are difficult to destroy, (NACE, 1971).

Anaerobic Bacteria

Anaerobes include slime forming, spore forming, and sulfur reducing bacteria. Both slime forming and spore forming bacteria can grow either aerobically or anaerobically. These bacteria were previously discussed.

Sulfur reducing bacteria are microbes that reduce sulfate to hydrogen sulfide. This reduction reaction causes localized corrosion problems. After colonizing steel surfaces,

these types of bacteria have rusty, egg-shell like outer structures that cover a deep, step-like penetration of the underlying steel, (Becker, 1995). In addition, the bacteria produce foul odors, discolor paint, destroy plant and animal life, and corrode metals and their alloys, (NACE, 1971).

2.4.1.3 FUNGI

Fungi, in comparison to bacteria, are large, complex, and specialized microbes. There are two forms of fungi found in cooling towers and clarification tanks: molds and yeasts.

Molds are fluffy, cottony, filamentous forms of fungi. These microbes grow by forming new cells at the growing tip of the filament. In cooling towers, molds are quite disturbing, causing white or brown rot to cooling tower wood. Equipment degradation can be caused by molds that attack cellulose. This process is called cellulolytic or lignin degrading. In paper manufacturing and related processes, molds feed on sources of cellulose (e.g. wood pulp and other fibers). Unlike bacteria, molds can survive under low pH conditions, (Betz, 1981).

Yeasts are similar to molds in that they are also cellulolytic. Although some yeasts have filamentous structures, they are also similar to bacteria in their predominately single cell forms. Yeasts divide by budding; a mother cell repeatedly forms single, identical, and smaller daughter cells. Yeasts can produce slime in tremendous amounts and attach onto wood surfaces, (Betz, 1991).

2.4.1.4 IDENTIFICATION TECHNIQUES

Algae and fungi are usually identified based on their color and other physical features. Bacteria identification, on the other hand, may require extensive laboratory work, including microscopic analyses. Aerobes, including planktonic microbes, can be quantified using the standard methods plate count technique. Anaerobes, such as sulfate reducers, can be detected using two methods: precipitation and cultivation in an anaerobic glove box. The precipitation method requires incubation and growth of sulfate reducers. As the sulfate reducers grow, they convert sulfate to sulfide, which react with iron to produce a black precipitate, (Kajdasz, 1996).

More advanced and expensive identification techniques include lipid biomarker analyses and DNA identifications. The lipid biomarker analysis characterizes the total microbial community, and indicates the metabolic starvation. DNA identifications are user defined specificity techniques for microbial activity, (White, 1996). Other identification techniques include extraction of ATP (adenosine triphosphate), light transmission as a result of genetic engineering, and microscopic visualization, (Sayler, 1996). Routine water samples can also be given to a trained microbiologist for proper population count and/or identification, (Bienkowski, 1996).

These analyses can be used to quantify the volume of algae, bacteria, and fungi. From these analyses, preliminary decisions and prioritization of control technologies can be made.

2.4.2 PROBLEMS ASSOCIATED WITH MICROBIAL GROWTH

Microbes may be categorized as either planktonic or sessile. Planktonic microbes are microorganisms that are distributed randomly throughout the system. These microorganisms contribute to problems dealing with odor and health related viruses. Sessile microbes are microorganisms that attach to solid surfaces. These microorganisms contribute to the most common problems in industrial water reuse systems (e.g. deposits and corrosion), (Steelhammer et al, 1995).

Sessile microbes create a biofilm, in which a gelatinous matrix is eventually formed. The biofilms serve as a protective barrier for the microorganisms against disturbing process conditions and toxic chemicals that threaten their life cycle balance. There are five steps in the formation of a biofilm: surface conditioning, microorganism transport, adhesion, cell replication, and detachment, (Steelhammer et al, 1995)

Biofilm formation begins with the accumulation of solid particulates. In aerated cooling towers and clarification tanks, evaporation causes an increase in the mineral and organic content in the process water. The particulates settle and accumulate along the wall to create an organic conditioning film. Since natural waters contain microscopic life forms, these microbes are introduced to the system via the make up water. The combination of the organic film and the introduction of microbes result in adhesion of these life forms along the solid surface. The attached microorganisms undergo cell replication and

multiplication. In addition to replication, the microbes produce an exopolymer, extracellular polysaccharide. The exopolymer traps numerous planktonic and sessile microorganisms found in the water. Most biofilms are composed of 90% exopolymer and 10% microorganisms. After a period of time, water turbulence dislodges some of the biofilm from the surface, (Steelhammer et al, 1995).

Biofilm formation may lead to two common problems in cooling and clarification systems. The problem resulting from deposits caused by microorganisms is referred to as biological fouling. The problem resulting from corrosion influenced by microorganisms is referred to as microbiologically influenced corrosion.

2.4.2.1 BIOLOGICAL FOULING

Biological fouling, caused by slime and scale deposition, often restricts water flow in a system. There are two primary problems associated with biological fouling: biological slime and scale deposits. Biological slime consist of biological mass (e.g. algae, bacteria, fungi). The slime accumulate at high rates within cooling towers. As a result, the heat transfer and cooling efficiency is decreased. Scale deposits consist of a mixture of biological mass and material contaminants. The contaminants include clay, silt, scale, pulp, and other particulates. Biological fouling usually require several days or weeks to reach a point where operational problems are encountered, (Steelhammer et al, 1995). A case by Mann et al (1985) reported that biofouling, within a biologically active system that reuses gasification for cooling water make up, have led to replacement of heat exchangers with stainless steel units.

There are several signs and symptoms related to biological fouling present in water recycle systems:

- Loss of heat transfer
- Plugging of the process equipment
- Slime build up
- Reduced water flow
- Plugging of filter media
- Unpleasant odors

2.4.2.2 MICROBIOLOGICALLY INFLUENCED CORROSION (MIC)

Biofilms cause accelerated localized corrosion by restricting oxygen to metal surfaces. The non uniform nature of the biofilm creates an inherent differential, which is enhanced by the oxygen consumption of organisms in the biofilm, (Betz, 1991). Microbial induced corrosion of stainless steel occur beneath the biofilm. In process water containing dissolved oxygen, slime growth commences with the accumulation of aerobic microorganisms which flourish if plenty of organic compounds, such as starch, are present in the process water. The slime becomes thicker with the incorporation of paper fiber and / or minerals, and the environment beneath the slime becomes anaerobic because the aerobic microorganisms use up all the oxygen diffusing inwards, (Thorpe, 1982). As a result, anaerobic sulfate reducing bacteria accumulate.

The metabolic activity of the microorganisms include several corrosive byproducts. These corrosive byproducts include organic acids and hydrogen sulfide. The secreted chemicals accumulate in the gelatinous matrix and may contribute to localized accelerated corrosion.

Microbiologically induced corrosion commonly affects steel because steel has a basic susceptibility to corrosion and is extensively used in piping. However, copper, galvanized steel and other alloys may also undergo this type of corrosion, (Becker, 1995). Cases reported by Thorpe (1982) have been found where corrosion occurred as round bottomed pits. The associated slime deposits were more than one inch thick. The internal surface of the machine pipes were coated with 2 to 30 mm thick slime deposits. Corrosion rates as high as 24.2 mils/yr were found for carbon steel in a biologically active system that reuses gasification condensate as make up cooling water, (Mann et al, 1985).

In addition to steel corrosion, fungi accelerates the deterioration of wood in numerous cooling towers. This is a result of the hydrolysis of the wood fibers.

There are several signs and symptoms related to microbiological influenced corrosion present in water reuse systems, (Becker, 1995):

- Corrosion rates in excess of 3 mils per year
- Unusual decrease in bulk water pH
- Rusty brown staining of equipment
- Rusty discoloration of the recycle water

- Rust color turbidity in the recycle water
- Excessive usage of biocides
- Wood degradation
- Black sludge in the sump

2.4.3 PHYSICAL/CHEMICAL FACTORS THAT AFFECT MICROBIAL GROWTH

Water reuse systems often provide a favorable environment for the growth of microorganisms. There are five primary environmental factors that influence the proliferation of microorganisms, and the associated problems. These factors include ambient and system temperatures, water velocity relative to the solid surface, nutrient availability, surface roughness, pH, and particulate matter within the water, (Steelhammer et al, 1995).

2.4.3.1 AMBIENT AND SYSTEM TEMPERATURES

System temperature strongly influences microbial growth. By increasing bulk water temperature, two different results are probable. An increase in the microbial growth rate may result from chemical and enzymatic cell reactions proceeding at a faster rate. A decrease in the microbial growth rate may result from the denaturing of proteins and enzymes, (Brock, 1979). For example, hot water at 80°C has been shown by Lappin (1995) to prevent the growth of all bacteria in water systems.

Microorganisms are categorized into three groups based on their temperature survival dependencies: psychrophilic, mesophilic, and thermophilic. Psychrophiles survive -5 to 30°C temperature climates, with an optimum at 10 to 20°C. Mesophiles survive 10 to 45°C temperature climates, with an optimum at 20 to 40°C. Thermophiles survive 25 to 80°C temperature climates, with an optimum at 50 to 60°C, (Brock, 1979).

Exposure to sunlight changes plays a role in the growth of microbes. Microbial growth in aerated systems is the highest during summer months and daylight hours, due to relatively high evaporation rates. These conditions contribute to an increase in available nutrients for microbes. Winter months and night hours reflect lower cycles of concentration, corresponding to lower microbial growth rates.

concentration, corresponding to lower microbial growth rates.

Aerated systems with high sunlight exposure play a major role in the efficacy of treatment chemicals. Sunlight often breaks down and degrades oxidizing biocides.

2.4.3.2 WATER VELOCITY RELATIVE TO THE SOLID SURFACE

The water velocity relative to the solid surface is another factor that influences microbial growth. Water turbulence keeps nutrients and other suspended matter from settling along surfaces. As a result, an organic conditioning film is unable to form. High velocity water dislodges slime agglomerates along the wall, washing the matrix downstream.

Studies by Wolfaardt (1992) show that water velocity has a definite effect on the rate of microbial colonization on solid surfaces. The highest colonization rates were found under conditions of zero flow. A decrease in microbial colonization rates corresponded to an increase in water velocity.

2.4.3.3 NUTRIENT AVAILABILITY

Nutrient availability in water reuse systems can also influence the microbial growth. At low nutrient concentrations, the growth rate is relatively low. At moderate or higher concentrations, the growth rate begins to level off, (Brock, 1979).

There are several requirements for the survival of microorganisms: carbon, nitrogen, air, phosphorus, and sunlight. Some of these requirements are dependent on the specific microbe. For example, anaerobic microbials survive independently of oxygen.

Microorganisms differ in the way that they extract carbon, nitrogen, and energy from their surroundings. Aerobic microbes use oxygen to drive the oxidation that releases chemical energy. Anaerobes substitute nitrate and / or sulfate as an electron-accepting agent. Photosynthetic algae requires sunlight to produce the required nutrients, (Betz, 1991).

Water reuse systems provide an ideal environment for the presence and accumulation of nutrients. Cooling towers accumulate numerous organic compounds in which sources of nutrients can be found. These nutrients include organic compounds, minerals, and ions. Paper manufacturing and other related processes provide excellent

2.4.3.4 SURFACE ROUGHNESS

The surface roughness plays a key role in the adhesion of biomass. Ridges and cracks are ideal locations for biofilms to attach. Since these features furnish shelter against water turbulence and other disturbing factors, they provide a favorable habitat for microbes to grow.

2.4.3.5 pH

The water pH also affects the growth of microorganisms. For most commonly found industrial bacteria, the optimum pH is 7.2 to 7.6, (Jolik, 1992). Microbes can be classified into three categories based on their water pH survival: acidophiles, neutrophiles, and alkalophiles. Acidophiles are microorganisms that survive under acidic pH conditions. Neutrophiles are microbes that live in pH areas between 6.5 to 8.0, and alkalophiles thrive in pH areas between 8.4 to 9.0.

Aerobic sulfur bacteria are classified as acidophiles. "Most fungi and yeasts grow fairly well at low pH, and a pH of 5 is often optimal." (Brock, 1979) However, the optimum pH for most microbial cells is at neutral levels. Many cellular components are destroyed under acidic pH conditions including chlorophyll, DNA, and ATP, while RNA is destroyed under basic pH conditions, (Brock, 1979).

2.4.3.6 PARTICULATE MATTER IN THE WATER

Particulates such as fiber, silt, clay, dirt, organics, corrosion by products, and scale fragments often contribute to microbiological deposits. The actual mass of the deposit that typically causes fouling consists of a small fraction of biological mass, and a large fraction of particulate matter. The microbes entrain the non-biological suspended solids and subsequently serve as a binding agent for the deposits that cause plugging and fouling, (Steelhammer et al, 1995).

2.5 AVAILABLE MICROBIAL CONTROL TECHNOLOGIES

Problems associated with microorganisms are currently reduced via microbial control technologies. There are two categories of microbial control technologies: biocides

and biomass inhibitors. Biocides are anti microbial agents that kill and eliminate microorganisms. Biomass inhibitors are agents that prevent biofilm formation along internal surfaces. Past and present control technologies include industrial biocides and manual equipment cleaning. Oxidizing biocides reduce microbial growth by rupturing the cell wall of microorganisms. Nonoxidizing biocides reduce microbial growth by disrupting their metabolic process. Manual equipment cleaning typically involves surface scrubbing. Due to environmental and safety concerns, alternative anti-microbial agents are being explored. Emerging anti-microbial technologies include biodispersants, enzymes, bioelectric applications, surface coatings, and ultraviolet light.

2.5.1 INDUSTRIAL BIOCIDES

Microbes extract energy from their environment and transform this energy into useful activities which maintain cell integrity. The energy transfer occurs via the cell membrane. The membrane serves as a permeable barrier that facilitates osmosis, and protects the cell from environmental disturbances including system temperature and pH. Any chemical that disturbs the orderly extraction and use of nutrients, or disrupts the barrier properties of the cell membrane, can cause the microbe to die. The mechanisms by which a chemical exerts anti-microbial activity is dependent on the relative contact between the chemical and the microbe and the physical or biochemical disturbances. These disturbances may be centered around enzymes, cell membrane, cytoplasm, intracellular systems, or several combinations, (Betz, 1991).

Industrial biocides are chemicals that are used to prevent microbial contamination and deterioration of commercial products, materials, and systems by disrupting the metabolism of the microorganisms. A biocide may either destroy all of the microbial cells present, or inhibit the microbial growth (inhibitors). As discussed previously, biocides are generally categorized as oxidizing or nonoxidizing.

2.5.1.1 OXIDIZING AGENTS

Oxidizing biocides undergo oxidative reactions with organic molecules. These chemicals kill via indiscriminate oxidation of chemical species on the surface or within the cell. These agents accept electrons from other chemical compounds. The anti-microbial

properties are directly related to cell penetration, enzyme deactivation, and chemical degradation within the cell. However, system conditions can play a role in the anti-microbial properties of the oxidizing biocide. Water pH and organic content play a role in the deactivation of certain oxidizing agents. These conditions should be considered when selecting a biocide. Oxidizing agents include chlorine, bromine, ozone, chlorine dioxides, and peroxygens, (Betz, 1991).

2.5.1.1.1 CHLORINES

Chlorine is one of the most widely used oxidizing biocide. This biocide covers a wide spectrum of activity and is relatively inexpensive. The chlorinating of recycle water involves a series of reactions. Reaction 4 represents the pH dependent dissociation of hypochlorous acid to form hypochlorite and hydrogen ions. The pH of cooling water allows for HOCl and OCl⁻ mixtures, (CWI, 1991).



The most common form of chlorine that is used by industries are hypochlorites. These oxidizing agents have an oxidation/reduction potential of 1.49 volts. Sodium and calcium hypochlorites are derivatives formed by the reaction of chlorine and hydroxides. The use of hypochlorite in water systems produce the hypochlorite ion and hypochlorous acid, similar to the application of chlorine gas, (Betz, 1991).

Reactions 5 and 6 show the reaction of hypochlorites with water forming sodium hydroxide and hypochlorous acid. Since an acid and a base are formed, there is little variation in pH. However, hardness scale is sometimes formed due to minor concentrations of excess caustic found in sodium hypochlorite solutions. Dispersants are usually used to offset the scaling potential, (Betz, 1991).

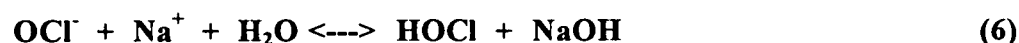


Figure 2.5 shows the indirect proportionality between percent active hypochlorous acid and bulk water pH. The percent hypochlorous acid and the consequent biocidal efficacy decreases with increasing bulk water pH. The percentage of HOCl drops from 79% at pH 7 to approximately 28% at pH 8.

Solutions of sodium hypochlorite, NaOCl, often called liquid bleach, can be

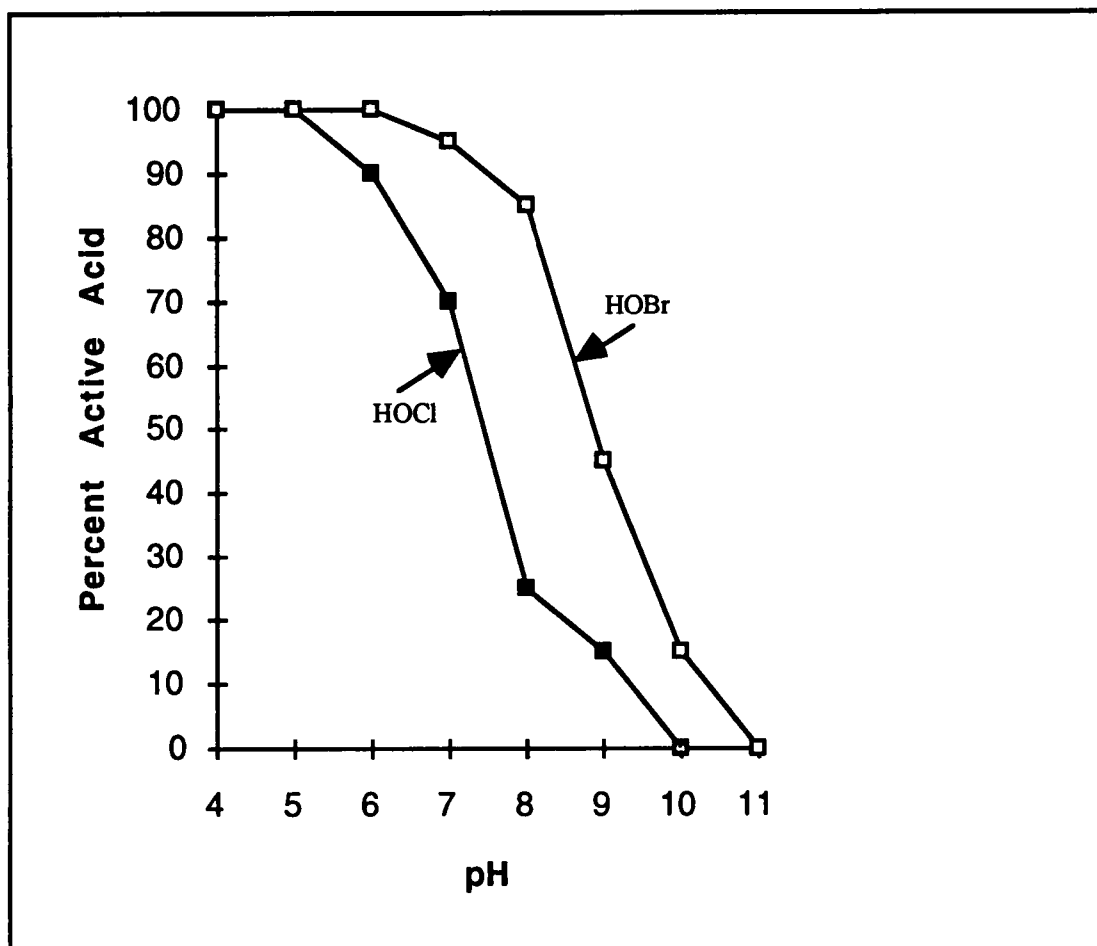


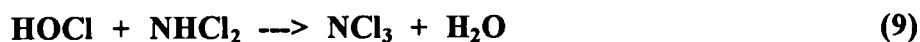
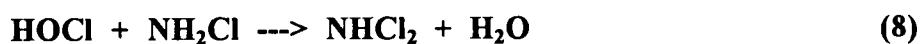
Figure 2.5: Percent active hypochlorous, HOCl, and hypobromous acid, HOBr, in solution as a function of pH.

obtained at concentrations ranging from 5.3 to 12 wt.%. Approximately one gallon of pure sodium hypochlorite is as effective as one pound of chlorine gas. Environmental conditions, such as pH, ambient temperature, light, heat, and metal contamination, often affect the stability of the sodium hypochlorite. Decomposition and degradation of NaOCl occur under the following conditions.

- 10°F temperature increase.
- Storage pH above 5.
- 0.5 ppm of iron contamination.

Calcium hypochlorite, $\text{Ca}(\text{OCl})_2$, often called HTH ("High Test" calcium hypochlorite), is the another form of chlorine biocide. HTH contains approximately 70% available chlorine. Soft (relatively low calcium content) water at 2% chlorine concentration is recommended to avoid precipitation. Decomposition occurs exothermally, releasing chlorine monoxide and oxygen, and is accelerated by water contamination.

Chlorine ions often react with various organic and inorganic constituents in water recycle streams including ammonia, ferrous ions, and sulfate. These chlorinated byproducts decrease the biocidal activity within the system. The ammonia reactions, shown by Reactions 7,8, and 9, are some of the most important chlorine consuming reactions, (CWI, 1991).



The presence of chloramine decreases the overall biocidal activity. Chloramines have approximately 1% the biocidal efficacy of hypochlorous acid. For this reason, sufficient chlorine must be fed to satisfy the chlorine demand and leave a residual that will perform the biocidal function, (Steelhammer et al, 1995).

Measurement and monitoring

The measurement and monitoring of chlorine residuals can be very complicated due to the vast amount of interfering ions. There are three main tests that are used to measure chlorine residuals: amperometric titration, DPD (N,N-diethyl-p-phenylene-

diamine), and FACTS (syringaldazine free available chlorine method), (CWI, 1991).

The amperometric method is by far the most accurate test for measuring chlorine residual. This titration method is the basis for other tests, and differentiates free and other forms of chlorine residuals, (CWI, 1991).

The DPD method is the most commonly used test for chlorine residual in cooling water. There are two possible variations of this method; titration method and the colorimetric test. Chromate, calcium, and alkalinity are all major interferences of DPD. In the titration variation, DPD, the indicator, is titrated with ferrous ammonium sulfate. This variation can also be used to differentiate between various forms of chlorine residuals. In the colorimetric method, DPD reagent(s) are added to the sample with ensuing color formation proportional to chlorine residual, (CWI, 1991).

The FACTS is a colorimetric procedure that involves the addition of the syringaldazine chemical to a water sample, in which color development is observed. (CWI, 1991)

Feed systems and requirements

Feed requirements are often based on the flow of recirculating water. According to the Cooling Water Institute (1991), 0.3 to 0.5 pounds of chlorine per million pounds of recirculating water is recommended. Slug chlorination involves chlorine addition, with maximum free residuals of 1.0-2.0 ppm, one to three times a day for one to three hour periods. Chlorine feed systems are classified as to the phase of material delivered: gas, liquid, and solid chlorine.

Chlorine is supplied as a liquefied gas under pressure in a steel container. Dispensing equipment is specifically designed to safely control and monitor gaseous chlorine to the water recycle system. This process involves the eduction of dry chlorine from the supply container, dissolving the gas in a stream of water to provide a high strength solution of chlorine and delivery of the solution to the point of application, (CWI, 1991).

Liquid chlorine derivatives often loose oxidizing power during storage. Common concentrations and factors affecting decomposition were previously discussed. There are several guidelines that should be incorporated to reduce potential problems, (CWI, 1991)

Storage tanks

- Made of high density plastic
- Placed in shaded areas
- Sized to contain no more than 1 or 2 months supply
- Diked to contain spills
- Avoid freezing temperatures
- Proper ventilation

Feed systems

- Made with CPVC schedule 80 piping
- Glue specifically for leach service
- Bleeders and flush connections for line purging during maintenance

Pumps

- Positive displacement
- PVC heads
- Check valves
- Flooded suction

Solid forms of chlorine derivatives include calcium hypochlorite, chlorobromohydantoins, chlorinated hydantoins, and chlorinated isocyanurate. The design of feed systems are chemical specific.

Environmental and safety concern

Chlorine is a poisonous, green-yellow gas at standard temperature and pressure. Moist chlorine is extremely highly corrosive. In addition, chlorine vapor causes respiratory and physiological damage, (Wentz, 1995).

There is tremendous concern regarding the toxicity of chlorine gas and the chlorinated by products. Over the past decade, the Environmental Protection Agency has taken an increasingly strong stance on regulating chlorine discharges. There are two opposing views regarding chlorinated byproducts. One view argues to treat all organochlorines as a class of chemicals. The other view regards chlorinated compounds

as diverse chemicals of various classes and structures, (Steelhammer et al, 1995).

Organic materials present in water recycle may be oxidized by chlorine including hydrocarbons, process chemicals, humics, pollen, etc. These reactions result in the production of chlorinated hydrocarbons and trihalomethanes. High priority must be given to formation of these toxic chemicals.

2.5.1.1.2 BROMINES

Bromine is another oxidizing biocide used in water recycle systems. Bromine usage in water recycle has expanded tremendously due to feeding technology advances.

In nature, bromine is found in the form of water soluble bromide salts. Elemental bromine is formed when bromide salts are reacted with gaseous chlorine and steam

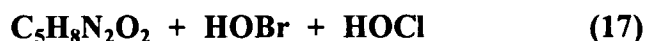
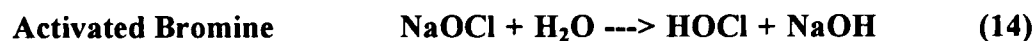


In Reaction 11, bromine undergoes hydrolysis to form hypobromous acid and hypobromic acid. In Reaction 12, hypobromide ions are formed by the dissociation of hypobromous acid under alkaline conditions.



Hypobromous acid and bromine have a strong biocidal activity due to their ability to penetrate the cell wall of the microorganism. Under basic pH conditions, bromine compounds have higher biocidal activities than chlorine compounds.

There are three main bromine compounds used for disinfection: bromine chloride (a liquid under pressure), activated bromine (liquid), and brominated hydantoin (solids). In Reaction 13, bromine chloride reacts with steam, forming hypobromous acid and salts. In Reactions 14 and 15, hypochlorous and hypobromous acid are produced from sodium hypochlorite, sodium bromide, and water. In Reactions 16 and 17, hypobromous acid is formed from brominated hydantoin and water.



Water recycle systems containing ammonia require less bromine, in comparison to chlorine, for microbial control. Under basic pH conditions, bromamines provide higher levels of biocidal activity in short contact times relative to chlorine. The ammonia reaction with bromine is similar to the reaction with chlorine, (CWI, 1991).

Measurement and monitoring

The DPD and FACTS method can be used as a form of measurement and monitoring of bromine. See Section 2.5.1.1.1 for details.

Feed systems and requirements

Brominated biocides are often dosed to water recycle systems on a continuous low level basis, with a target residual of 0.3 to 0.5 ppm of total residual halogen. Shock bromination is also an implemented application where 1.0-2.0 ppm total residual oxidant is applied one to three times a day, (CWI, 1991).

Bromine chloride is fed through a specialized liquid feeder. The feed system is made up of the storage container, nitrogen supply equipment, liquid feeder module, and control module. The steel storage container holds the compound as a liquid under pressure. The bromine chloride feed module injects BrCl directly into the water system. A check valve should be installed to prohibit water back flow. The control module houses the operating control and nitrogen supply gauges, (CWI, 1991).

Brominated hydantoins are fed using a bypass dissolution feeder or fed directly to a cooling tower's basin (at low concentrations). Brominated hydantoin dissolves as the water flows through the feeder. The dissolution rate is a function of water velocity, residence time, temperature, and surface area. Feed system specifics should be discussed with a brominated hydantoin manufacturer, (CWI, 1991).

Activated bromides are mixed with a concentrated aqueous solution of chlorine. The chemistry involved was previously discussed. The chlorine to bromine ratio is directly proportional to the order of magnitude of bacterial kill. The activated bromide feed system may be easily retrofitted to an existing chlorine treatment system with the addition of a storage tank and a standard metering pump with a corrosion resistant head, (CWI, 1991).

Environmental and safety concerns

The usage of bromine is more environmentally acceptable than chlorine, since less brominated byproducts are produced. However, similar environmental concerns are still associated, since bromine is also a halogen.

Bromine chloride should be handled similarly with respect to gaseous chlorine. Brominated hydantoins and sodium bromide are not classified as extremely toxic chemicals. Specifics on these chemicals can be found in Sections 311 and 312 of the SARA Title III regulations.

2.5.1.1.3 OZONE

Ozone, O₃, is an allotropic form of oxygen. This unstable gas is the strongest known oxidizing anti-microbial agent. Ozone must be generated at the point of use.

Ozone is produced electrically from dry air or oxygen (moisture free) sent through two high voltage electrodes, (Betz, 1991).



Ozone is partially soluble in water, which makes it very impractical to obtain relatively high levels of dissolved ozone. Ozone's concentration in water is directly related to its partial pressure above the liquid. The solubility of the gas decreases with increasing temperature, (CWI, 1991).

Measurement and monitoring

There are several instrumentation methods used to determine ozone concentration: indigo trisulfate, chemiluminescent, and ultraviolet absorption.

The indigo trisulfonate method is the recommended analysis of ozone, since there are fewer associated interferences. In this analysis, blue indigo solution is decolorized by ozone. A spectrometer is used to measure the color intensity, (CWI, 1991).

In the chemiluminescent method, a reaction between ozone and ethylene emits measurable light (excited formaldehyde). The formaldehyde returns to the neutral state through energy releases. The emitted photons are directly related to ozone concentration, (CWI, 1991).

For an ozone in air analysis, absorption of ultraviolet light at 254 nm can be

measured.

Feed systems and requirements

The ozone generator comprises of an electrical source, a discharge gap where air or oxygen is fed, a dielectric material (which prevents short circuiting), and a heat removal system. For cooling towers, ozone should be injected into the tower basin, and thoroughly mixed with the recirculating water. Up to 12 wt % ozone can be produced using a pure oxygen feed. However, only 3.5 wt % ozone can typically be produced using a dry air feed, (CWI, 1991).

It is recommended that 0.75, 3.25, and 6.50 lb./day of ozone are needed to treat 15,000, 40,000, and 100,000 gallons of recirculating water, respectively.

Environmental and safety concerns

Since ozone is a strong oxidizing agent, it is a potential safety hazard. Ozone concentrations of 50 ppm in air can cause fatalities due to oxidation of lung tissues. According to OSHA, the exposure limit is a time weighted average of 0.1 ppm, (Betz, 1991).

Ozone generating equipment must be monitored so that high ozone concentrations are not produced. Concentrations up to 20% can be very flammable. Since ozone has an extremely low respiratory threshold limit (0.02 ppm), generating equipment is considered relatively safe. Additional safety recommendations include the use of ozone compatible materials including 316 stainless steel, glass, Hypalon, and Teflon. Due to the relatively short half life of ozone, there are no specific regulations of waste water sewage disposal. As a result, ozone is an environmentally acceptable biocide.

2.5.1.1.4 CHLORINE DIOXIDE

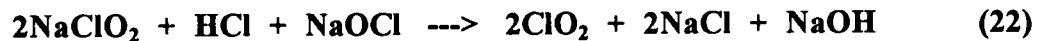
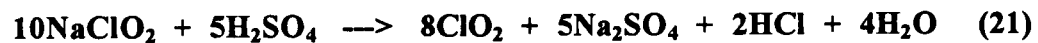
Chlorine dioxide, ClO_2 , a water soluble chlorine derivative, can be used for anti microbial purposes. This unstable, potentially explosive compound has numerous desirable characteristics that differentiates it from chlorine, including its inability to react with ammonia-nitrogen, inability to dissociate in water, and wide pH coverage (7-10).

The most common method of chlorine dioxide production is through the reaction

of sodium chlorite with gaseous chlorine (Reaction 19).



Chlorine dioxide can also be produced from several other reactions that may use hydrochloric acid, sulfuric acid, or sodium hypochlorite (Reactions 20 through 22).



Reactions 20-22 can be achieved at 90-95% conversions, and release byproducts including chlorite, chlorate, and chloride ions. In addition, the biocidal activity of chlorine dioxide has been shown to increase with increasing pH.

Measurement and monitoring

There are new techniques that have been developed for chlorine dioxide measurement. The iodometric and amperometric methods are recommended tests. The DPD method is listed as the only technique specified in EPA drinking water regulations. Chlorine residuals are suppressed by using glycine, which converts free chlorine into chloraminoacetic acid, (CWI, 1991).

Feed systems and requirements

Due to the sensitivity of gaseous chlorine dioxide, this compound cannot be shipped or transported. As a result, chlorine dioxide must be produced and used on site. Chlorine dioxide has been found to be corrosive to stainless steel piping. Compatible metallurgy includes reinforced fiberglass, CPVC, titanium.

Chlorine dioxide is more effective in the presence of organics, relative to chlorine. As a result, lower chlorine dioxide dosage rates are required to achieve comparable performance to that of chlorine. A case study by Farguhar et al (1993) shows that chlorine dioxide, at 10 ppm, was effective against test sulfate reducers.

Environmental and safety concerns

Chlorine dioxide is an anti-microbial agent used in drinking water. Here, the maximum safe limit is 0.4-0.5 mg/L, in which there is no objectionable taste or odor.

The NIOSH/OSHA Guideline for Chlorine Dioxide reports 0.1 ppm as the odor threshold and 5 ppm as irritating, (CWI, 1991).

Relative to chlorine, chlorine dioxide has desirable environmental characteristics. Some of these characteristics include chlorine dioxides inability to react with ammonia and or nitrogen compounds. Due to chlorine dioxide's low reactivity, reactivity with organic constituents typically is not a problem. As a result, the potential of producing toxic byproducts is relatively low, (CWI, 1991).

Liquid sodium chlorite, the most common precursor for off site generation, is a hazardous chemical that forms a powdered residue that can ignite or explode if contacted by oxidizable materials. In addition, use of aqueous solutions of chlorine dioxide requires extreme caution since the vapor is highly volatile, (Betz, 1991).

2.5.1.1.5 PEROXYGENS

Hydrogen peroxide, H_2O_2 , and peracetic acid, CH_3COOOH , are two major peroxygens that are used for biocidal applications. The use of these anti-microbial agents cover a wide spectrum of application and reflect to the increasing desire for environmental concern.

Hydrogen peroxide is a non-corrosive, water soluble, strong oxidizing agent, that complies with environmental protection. This agent is commonly used for odor control in sewage through selective microbial control of anaerobic sulfate reducing bacteria, a broad spectrum of filamentous bacteria, and other microorganisms, (Payne, 1988).

Peracetic acid, PAA, is a non-foaming water soluble liquid, that breaks down into environmentally acceptable decomposition products. PAA is used against a broad compass of microbes. PAA formulations are made up of peracetic acid, hydrogen peroxide, acetic acid, water, and a stabilizer to give an equilibrium mixture, (Payne, 1988).

Hydrogen peroxide is decomposed into water and oxygen in the following reaction.



Peracetic acid is decomposed in water, forming acetic acid, hydrogen peroxide, water, and oxygen, by the Reactions 24-26.





At recommended peracetic acid concentrations, the above final products are toxicological safe, (Payne, 1988).

Measurement and monitoring

There are several analytical techniques that are used to determine peroxygen content, either as hydrogen peroxide or dilute aqueous solutions of peracetic acid. The most common method relies on sample acidification with sulfuric acid solution and the addition of ferrous acid. With the addition of thiocyanate, peroxides oxidize the ferrous iron, forming a red ferric thiocyanate complex. Finally, spectrometric techniques are used to quantify peroxygen content by light absorption at 460 nm. Other techniques involve PAA reactions with chlorine ions, forming free chlorine residuals, (Payne, 1988).

Feed systems and requirements

Hydrogen peroxide concentrations as low as 25 mg/L are capable of preventing growth of a wide spectrum of bacteria. Peracetic acid concentrations as low as 10 mg/L have been shown by Payne (1988) to eliminate slime formers, e.g. pseudomonads and sulfate reducing bacteria, in several cooling towers at a major chemical manufacturing site. However, hydrogen peroxide has low biocidal activity against attached bacteria in a biofilm matrix. The dosage regime for hydrogen peroxide and PAA is 10% (v/v) and 0.02-0.05% (v/v) for 2-3 hours, respectively, (Lappin, 1995).

Commercially, an 86 wt% hydrogen peroxide concentration in water is sold. For anti-microbial applications, 35 wt% hydrogen peroxide solution is normally used. Compatible process equipment materials include PVC and/or polyethylene. Non compatible process equipment materials include rubber, mild steel, brass, bronze, and copper, (Payne, 1988).

There are several PAA formulations commercially sold. Proxitane 1507 and 4002 are typical examples of PAA. Proxitane 1507 contains 15, 14, 28, 42, and 1 wt% of peracidic acid, hydrogen peroxide, acetic acid, water, and stabilizer, respectively. Proxitane 4002 contains 38, 4, 44, 12, 1, and 1 wt% of peracidic acid, hydrogen peroxide,

acetic acid, water, sulfuric acid, and stabilizer, respectively. Compatible process equipment materials include stainless steel, polytetrafluoroethylene, or glass. Soft PVC and polyethylene are suitable only for a limited time. Positive pumps are recommended to avoid wastage through pump tube failure. Solenoid valves in conjunction with the metering pump are required to ensure back flow of liquids. A spring loaded anti syphon control valves is recommended to prevent syphoning from a head. System flushing with water is also recommended when dosing pumps are switched off, (Payne, 1988).

Unlike some biocides, peroxygens retain their biocidal activity in the presence of organic constituents in the water system. As a result, there is not a massive consumption of the biocide due to side reactions.

Environmental and safety concern

As previously stated, peroxygens produce environmentally acceptable products when decomposed in water. Hydrogen peroxides decompose to form water and oxygen. Peracetic acid decomposes to form acetic acid, hydrogen peroxide, water, and oxygen.

From a safety perspective, hand and eye protection is recommended for chemical handling. Spillage should be cleaned up using large volumes of water. Segregation from flammable and/or organic chemicals are required when storing indoor and outdoor. The greater ease and safety in handling and lower corrosivity of the less concentrated of PAA makes them particularly suitable for industrial disinfection application, (Payne, 1988).

2.5.1.2 NONOXIDIZING AGENTS

Nonoxidizing biocides kill by reaction pathway into the cell, or reactions with specific cell components. Microbes are killed or inhibited via two mechanisms: 1. cell damage or 2. biochemical machinery damage. The mode of action of a nonoxidizing biocide may be categorized as a metabolic or surface active inhibitor. Nonoxidizing biocides include quaternary ammonium compounds, organo sulfur compounds, and glutaraldehyde, (Betz, 1991).

For closed water systems, nonoxidizing agents are more economical and practical. Closed systems generally have minimal water losses, which contribute to a higher residence time of nonoxidizing agents, relative to oxidizing agents. In addition, closed

systems typically use nitrite based corrosion inhibitors. Oxidizers deactivate the inhibitors by oxidizing the nitrite, forming nitrate molecules. As a group, nonoxidizers are slow acting, and are fed periodically to achieve high concentrations, and allowed to decrease until the next dosage. This method overdoses the biocide until most of the microbes are killed, (Cleare, 1996).

There are some other differences between oxidizers and nonoxidizers that must be considered before usage. Nonoxidizers are generally more toxic than oxidizers, due to their mode of action and toxicity. In addition, nonoxidizers must meet certain toxicity thresholds for bacteria kill, which often require high dosage concentrations. In regards to the penetration and removal of microbial agglomerates, nonoxidizers are relatively ineffective, (Cleare, 1996).

2.5.1.2.1 POLYHEXAMETHYLENE BIGUANIDE (PHMB)

Polyhexamethylene biguanide, PHMB, is a biologically active synthetic polymer that is used as a wide pH range biocide. PHMB is a membrane active biocide that induces leakage of low molecular weight cytoplasm components from bacterial cells. At low PHMB concentrations, the agent has bacteriostatic properties, while at higher concentration, the agent has bactericidal properties. PHMB, at a 50 ppm concentration, has been reported by Payne (1988) to inhibit sulfate reducing bacteria in water systems.

PHMB is commercially available as a 20 weight percent aqueous solution. This agent maintain good storage stability. The non corrosive biocide does not foam or stain, and is considered non toxic. In addition, PHMB is compatible with quaternary ammonium compounds and acid compounds. It is also compatible with stainless steel, aluminum alloys, tinned steel, copper, and brass, and incompatible with rubber. In regards to safety and environmental concern, skin sensitization may occur at PHMB concentrations exceeding 5 percent. The acute toxicity of PHMB for fish is 3.0-13.0 and > 1000 mg/liter for fresh and sea water fish, respectively, (Payne, 1988).

2.5.1.2.2 QUATERNARY AMMONIUM COMPOUNDS

Quaternary ammonium compounds, "quats", are membrane active, cationic surface active quaternary nitrogen compounds, (Payne, 1988). The cationic charge forms

an electrostatic bond with the negatively charged cell wall, which results in enzyme denaturing and eventual death. Hence, quats control microbes by attaching to and rupturing the cell wall, which releases the cell material.

Quats are effective narrow spectrum agents at neutral and alkaline pH conditions, (Steelhammer et al, 1995). These agents have excellent biocidal activity in addition to their intrinsic detergency, (Lappin, 1995). These compounds are commonly used to control algae, and are ineffective against fungi. Typically, high dosages are required to control bacteria, which sometimes cause foaming. At low concentrations, the agent has bacteriostatic properties, while at high concentration, the agent has bactericidal properties, (Betz, 1991).

The dosage regime for quats range from 300-1000 ppm for 2-3 hours (Lappin, 1995) or a 30 to 120 ppm dosage once a week, (Vulcan, 1995). A case study by Farguhar et al (1993) shows that “a quaternary tributyltin oxide formulation was effective at low concentrations in the planktonic time kill test but not in the sessile time kill test.” The test summarizes by making the conclusion that the quat wasn’t able to penetrate the biofilm matrix.

Quats have several environmental constraints that affect their biocidal activity. Due to the cationic charges of quats, high levels of debris, dirt, organic constituents, and chloride residuals often reduce or inhibit the biocidal activity of quats, (Steelhammer et al, 1995). In some applications, reported by Payne (1988), quats have been known to be corrosive.

2.5.1.2.3 ORGANO BROMINE

Organobromines are effective broad spectrum biocides that are commonly used to control bacteria related problems at low biocide concentrations. Algae and fungi are controlled at higher biocide concentrations. These compounds retain their biocidal activity in the presence of organic constituents and biomass. Dibromonitrilopropionamide hydrolyzes under alkaline conditions and are normally used for “quick kill” purposes. Other organo bromines such as bromo-hydroxyacetophenone are pH independent, (Steelhammer et al, 1995).

2.5.1.2.4 GLUTARALDEHYDE

Glutaraldehyde, "glut", solutions are broad spectrum, non foaming biocides that are effective against bacteria related problems, but have limited biocidal activity against fungi and algae, (Steelhammer et al, 1995). This agent kill microbes by binding with proteins, thusly interfering with energy production. Glutaraldehyde requires a 25 to 100 ppm dosage once a week, (Vulcan, 1995). A case study by Farguhar et al (1993) shows that glutaraldehyde, at 30 ppm, was effective against test sulfate reducers.

Gluts maintain best efficacy under neutral pH conditions, and require a higher dosage under alkaline conditions. The agent is not compatible with water systems containing ammonia or amines, (Vulcan, 1995). Compatible metallurgy include stainless steel, nickel, reinforced plastic, PVC, and polyethylene. Maximum stability is found at storage and system conditions between 30-80°C, (Cleare, 1996).

Regarding safety and storage, glutaraldehyde solutions have a volatility of approximately 0.7 mg/m^3 . In addition, gluts have been cited as highly irritating, toxic, and has poor storage stability, (Payne, 1988).

2.5.1.2.5 ORGANO SULFUR COMPOUNDS

Organo sulfur compounds are nonoxidizers that control microbes by interfering with their electron transfer, which is necessary for energy production. There are three main types of organosulfur compounds: carbamates, isothiazolinones, thiocyanates, and thiones, (Vulcan, 1995).

Carbamates can be used to control algae and bacteria over a pH range between 7 and 14. These compounds are incompatible with dissolved iron and chromate. Sodium dimethyl-dithio-carbamate requires a 20 to 40 ppm dosage once a week, (Vulcan, 1995).

Isothiazolinones can be used to control bacteria, and fairly effective against algae. These compounds are effective over a pH range of 6 to 9, and are incompatible in the presence of chlorine and hydrogen sulfide. (Chloro) methyl-isothiazolinones require a 25 to 50 ppm dosage once a week, (Vulcan, 1995). Noncompatible metallurgy includes aluminum, brass, carbon steel, neoprene, nickel, and stainless steel 304.

Thiocyanates are broad spectrum biocides that may be used over a pH range of 6 to 8. These chemical agents can not tolerate dissolved iron. Methylene-bis-thiocyanate

requires a 25 to 50 ppm dosage once a week, (Vulcan, 1995).

Thiones are also broad spectrum nonoxidizers. These agents are effective over a pH range of 7 to 14, and are not compatible with chromates. Tetrahydro 3,5-dimethyl-2H-1,3,5-thiadiazine-2-thione requires a 30 to 60 ppm dosage once a week, (Vulcan, 1995).

2.5.1.2.6 DIBROMO-NITRIL-PROPIONAMIDE (DBNPA)

Dibromo-nitril-propionamide is a broad spectrum nonoxidizer that kills via interfering with material transport. This agent covers a pH range of 6 to 8, and is incompatible in the presence of organic constituents, hydrogen sulfide, or strong reducers. DBNPA requires a 6 to 15 ppm dosage once a week, (Vulcan, 1995). Noncompatible metallurgy includes aluminum, brass, carbon steel, neoprene, nickel, and stainless steel 304 and 316.

2.5.1.2.7 OTHER

Other non oxidizing biocides known to inhibit energy metabolism include organotin, brominated nitrostyrenes (BNS), dodecylguanidine salts, bromonitropropanediol (BNPD). BNS uses nitrostyrene to penetrate and accumulate within the cell. Dodecylguanidine salts have cationic surfactant properties that disrupt extracellular enzyme reactions. BNPD catalyzes the formation of disulfide bonds between sulfhydryl groups of proteins, (Betz, 1991; Steelhammer et al, 1995).

2.5.2 EQUIPMENT CLEANING

There are several mechanical operations that have been used to reduce microbial accumulation within cooling towers and other process equipment. Some of these operations require production down time and manual labor. Equipment cleaning usually consist of manual cleaning and scouring via abrasive cleaning agents.

2.5.2.1 MANUAL CLEANING

Manual cleaning of cooling towers, clarifier tanks, or any other process equipment may require production down time or cooling loss. Unless the process is non continuous,

there will be a monetary loss due to production loss or labor costs. Operators are often utilized to scrub cooling towers and clarifiers with brushes or pads. This method gets rid of biological growth, scale, debris, and organic matter from the within entire system. Once the surface is clean, the organic film that forms a biofilm, is eliminated.

2.5.2.2 ABRASIVE CLEANING AGENTS

Abrasive cleaning is another mechanical method that has been used to clean equipment. Abrasive agents (e.g. sand, silt balls, baking soda) are dispersed at specified concentrations within the cooling water and is constantly recycled throughout the fill section and pipes. The abrasive characteristics of the agent scrapes the equipment's surface, and disperses the organic particulates, biomass, and other solids. The microbes and organic constituents are prevented from adhering to the internal surface, therefore minimizing the potential for biofouling and MIC. (White, 1996) According to Carolina Equipment (1996), baking soda, NaHCO_3 , has been known to serve a dual role by removing biofilm and killing bacteria.

There are several factors that must be considered when using an abrasive agent, including the metallurgy, pumps, percent sand fed, and water velocity. Soft metallurgy (e.g. copper, brass, and aluminum) is not recommended for this form of treatment. Pumps specifically designed to handle low particulate content, are recommended. Special consideration must also be given to cases of high water velocity and high abrasive agent concentrations.

2.5.3 NEW MICROBIAL CONTROL TECHNOLOGIES

Considering the toxicity of certain biocides, an evaluation of non toxic and/or less toxic control technologies should be performed. Traditional methods involved "killing" the microorganisms. New technologies involve controlling biological fouling and MIC via dispersing the microbes and biomass, and prohibiting them from adhering to internal surfaces. These technologies include biodispersants, enzymes, bioelectric applications, surface coatings, and ultraviolet light.

2.5.3.1 BIODISPERSANTS

Most of the problems associated with microbes stem from sediment biomass that accumulates along equipment walls. Biological mass and/or sediment may be dispersed in the recirculating water so that it remains suspended, and is removed from the system as part of the blowdown, (Burger, 1990). Biodispersants are surfactants that have little or no anti-microbial activity, but prevents microbial attachment and/or remove biofilm. The biofilm removal is a result of a high electrostatic repulsion between like-charged particles, which prevents agglomeration. These dispersants reduce the amount of biocide required by reducing biofilm formation, (Betz, 1991). Commercial biodispersants include low molecular weight anionic polymers, polyacrylate, polymaleic anhydride, polymaleic anhydride copolymer, (Vulcan, 1995). Several of these commercial biodispersants are biodegradable. Recommended dosages range from 100 to 200 ppm of the bulk water, (Cleare, 1996).

Research is currently being done on biofilm formation with the intent to model the adhesion of microorganisms to the internal surface. Studies show that bacteria adhesion is more prevalent on hydrophobic surfaces. However, non ionic surfactants have been found effective on hydrophilic surfaces (e.g. glass), but not hydrophobic surfaces. The control efficacy is dependent on the microbes and the solid surface, and a blend of chemicals is typically required to effectively prohibit biofilm formation on solid surfaces. Once the biofilm formation process is fully understood, then the need for biocides will decline, (Steelhammer et al, 1995).

2.5.3.2 ENZYMES

Enzymes have received significant attention regarding their potential for controlling biofilms. Enzymes can be used to intensify the removal of a biofilm where it has been formed, prevent or inhibit biofilm formation, or improve the efficacy of biocides, (Steelhammer et al, 1995). The enzyme can be used to catalyze the hydrolysis reaction of extracellular polysaccharide to form non-polymeric substances that have no adhesive properties. The biofilm removal causes the non-polymeric substances to become dispersed within the system, therefore causing no extreme process problems, (Steelhammer et al, 1995). Enzymes can also be used to interrupt the adhesion of the

microbes to the solid surface, which also inhibits biofilm formation and other problems associated with microbes, (Steelhammer et al, 1995).

2.5.3.3 BIOELECTRIC APPLICATIONS

Future microbial control strategies will focus on the bioelectric enhancement of biocide efficacy against biofilm associated bacteria. Case studies by Lappin (1995) show that microbe killing efficacy has increased several orders of magnitude when isothiazalone or glutaraldehyde was applied in the presence of low level electric fields of approximately 100 micro amperes per cm².

2.5.3.4 SURFACE COATINGS

In cases where chemical treatment is prohibited, surface coatings of tanks, equipment, etc. is another route for controlling microbial problems. Surface modification alters the surface chemistry of the solid surface, (Lappin, 1995). These coatings are specifically designed to resist solid constituent agglomeration and corrosion. In response to regulatory demands, several coating manufacturers have been steadily rolling out a new generation of corrosion-resistant coatings, (Weismantel, 1996). Some coatings are comprised of an anti-microbial agent that assist in microbe kill. There are several silicon based surface coatings that have been used to reduce microbial adhesion to solid surfaces, (White, 1996).

2.5.3.3.5 ULTRAVIOLET LIGHT

Ultraviolet, UV, light can also be used to reduce the bacteria population in water reuse systems. UV light has been applied in the decontamination of drinking water, wastewater, and cooling water. The lamps are installed directly into a pipeline of a purged water stream (15% of recirculation flow). This environmentally acceptable technology has the possibilities of eliminating the need for chemical biocides for several reasons. From an environmental perspective, no chemicals are required for treatment purposes. From a safety perspective, chemical toxicity and volatility are non existent, (Kliwer, 1996).

The monochromatic ultraviolet light lamp emits energy that has a direct effect

on the bacteria's metabolic process, (Kliwer, 1996). UV light denature proteins necessary for microbial growth, which reduces the total bacteria population counts, (Laurens, 1942). Ultraviolet light can affect bacteria two ways: microbial death and growth rate reduction. Microbial death occurs as a result of protein and enzyme denaturing. Growth rate reduction occurs as a result of microorganisms with higher resistance to ultraviolet light. It was found that if bacteria are tested immediately after UV exposure, they will divide a few times, then go into an extended resting phase, and finally return to a more or less normal growth rate, (Hollaender, 1942). Studies performed by Hollaender (1942) show that in all cases the wavelength most effective was 2650 angstroms and energy of 452×10^2 ergs/cm².

2.5.4 CONTROL EFFICACY

To determine the effectiveness of a particular microbial control technology, a control efficacy must be routinely performed. The constant monitoring of the effect of microorganisms is very important for an effective microbial control program. Constant monitoring may include evaluating operating data, process flow trends, periodic equipment testing, and inspection. These early detection techniques are essential for the identification of developing problems. A vast amount of process data points must be compiled to detect a microbial problem within the recycle system. Deviations from targeted set points can be an indicator. Other profiles include available biocide within the system, laboratory analysis of microbes, surface biochemistry, and biofilm monitoring, (Wilde, 1992).

When using an oxidizing biocide, the oxidant residual should be continuously measured using the amperometric method. Usually there is a specific dosage requirement for effective microorganism kill. Therefore, it is highly recommended that there is sufficient residual for proper control. Specifics regarding residual chlorine and other chemical species methods were previously discussed, (Wilde, 1992).

A laboratory analysis (e.g. biological culturing, physical properties, and microscopic analysis) of deposits can be performed to determine the biological and chemical content. Microbial counts can also be performed to determine whether populations within the system are constant, increasing, or decreasing, (Betz, 1991).

Aerobic microorganisms can be quantified via standard plate counts and/or aerobic dip slides, (Sayler, 1996). Anaerobic microorganisms can be quantified via techniques that involve scraping material off of equipment, suspending the debris in water, and injecting the solution in sulfate reducing bottles. More reproducible techniques involve the pin extraction method. Pins made of carbon steel are inserted along the equipment walls with the intent to attract sulfate reducers. These pins are injected into a broth/water mixture for microbial count, (Kajdasz, 1996).

Constant monitoring of the surface's biochemical activity is beneficial. This approach involves the incubation of the biological growth with a substrate, in which a reaction product concentration is measured. The specific contact time is related to the microbes' health, which gives an approximate of the degree of biofouling, (Betz, 1991). Biofilms can be monitored non destructively via new analytical techniques such as microscopy, spectrochemistry, electrochemistry, and piezoelectric fields, (Nivens et al, 1995).

CHAPTER 3

APPROACH TO THE PROBLEM

A general approach was developed for making appropriate recommendations for controlling microbial problems in water reuse systems. This approach considers the modification of the existing treatment program before implementing a new program. This method is based on the evaluation of less expensive options first, before additional investments are made. The less expensive options include improved housekeeping and chemical hygiene, control feedback, water chemistry manipulation, and equipment modification. New treatment programs require a capital investment in a biocide and the corresponding feeding equipment. Table 3.1 exhibits the general approach for controlling microbial growth in water reuse systems.

3.1 MODIFICATION OF THE EXISTING TREATMENT PROGRAM

An evaluation of the existing program should be performed before implementing a new microbial control program. Improving the existing treatment program can reduce costs associated with capital investment. There are specific areas of the program in which recommendations can be made: housekeeping and chemical hygiene, modification of treatment technology, control feedback, and modification of the system's equipment and/or conditions.

Housekeeping and chemical hygiene

The first step considers housekeeping and chemical hygiene. There is a negligible capital investment cost associated with improving overall housekeeping and hygiene. This step covers simple, and sometimes overlooked items that can improve microbial control significantly. For example, injecting a partially degraded biocide is not as effective as using a fresh biocide. Housekeeping involves avoiding chemical spills, placing lids on containers, etc. Chemical hygiene involves keeping fresh batches of biocides on hand, ensuring proper storage, constant monitoring, being cognizant of chemical expiration dates, and proper chemical usage training.

Table 3.1: A general approach for controlling problems associated with microorganisms.

<u>GENERAL APPROACH</u>
<u>STEP 1</u> Ensure proper housekeeping and chemical hygiene \$
<u>STEP 2</u> Modify current treatment technology \$\$
<u>STEP 3</u> Install an automated control feedback system \$\$\$
<u>STEP 4</u> Modify current equipment and/or system conditions where possible \$\$\$\$
<u>STEP 5</u> Select and implement the best performing and most economical control technology* Total Cost = (lb.. / day * Chemical Cost / lb..) + Supplementary Equipment Cost \$\$\$\$\$

Modification of the existing microbial control technology

The second step involves the modification of the current biocide feeding system. This includes studying the microbe kill efficacy at various biocidal feeding locations within the water system. From this study, the injection point that corresponds to an optimum kill efficacy can be determined. Other modifications include increasing or decreasing the biocide feed rate.

Automated control feedback system

To determine the efficacy of a particular biocide, the installation of a control feedback system is necessary. This step involves the installation of an automated control feedback system. When using oxidizing agents, this may require the installation of an oxidation reduction potential (ORP) analyzer. This unit determines the concentration of free oxidant, and specifies the corresponding increase or decrease in biocide feed rate. To compliment ORP data, regular microorganism spot checks at various points within the water loop is also recommended. For nonoxidizing agents, laboratory bench top analyses must be routinely performed.

Equipment and/or system conditions modification

The fourth step involves process modification and/or changing process conditions were applicable. Minor adjustments in the system pH or solid concentration may aid in the reduction in the microbial population. Equipment modification may include placing sun blockage coverings over cooling tower decks, installing screen filters, installing heat exchangers, etc.

3.2 SELECTION OF A NEW MICROBIAL CONTROL TECHNOLOGY

Selection of a new microbial control program must consider a wide range of treatment technologies. Based on the physical and chemical properties of the system, technically suitable and compatible microbial control technologies can be identified. There are two categories of microbial control technologies: biocides and biomass inhibitors.

Biocides are defined as agents that kill microbes. Biomass inhibitors are defined as agents that prevent biofilm accumulation. There are five factors that can be used to evaluate the technical suitability of anti microbial agents: nature of microbes present, pH, the level of solid constituents, and materials of construction.

Microbial problem

A complete understanding of the nature of microbes present is very important for proper selection of a microbial control technology. Based on the predominant microorganism present, technologies can be selected. Appendix 2.1 ranks the available anti-microbial agents for algae, bacteria, and fungi control. Oxidizing agents are ranked according to the highest oxidation/reduction potential. Nonoxidizing agents are ranked according to previous case studies. "Other" represents emerging microbial control technologies (e.g. biodispersants, abrasive agents, surface coatings, ultraviolet light).

pH

The pH of the system is also a very important factor to consider when selecting a treatment technology. A biocide's effectiveness is dependent on the pH. The amount of available hypochlorous acid in a hypochlorite solution is indirectly related to pH. There are pH independent technologies (e.g. ozone, surface coatings, and abrasive cleaning agents, etc.) maintain their effectiveness across a broad pH range. Appendix 2.2 ranks the available anti-microbial agents for acidic and basic systems.

Solid and organic constituents

Knowledge of concentration of solid and organic constituents within the water system is also important when selecting a microbial control technology. These particulates often react with or absorb certain anti microbial agents. The resulting byproducts produced often reduces the amount of free oxidizing agent available for microbial kill. As a result, the biocidal effectiveness is reduced. In contrast, there are numerous anti microbial agents that are inert and maintain their biocidal or inhibitory activity in the presence of solid and organic constituents. Appendix 2.3 ranks the available anti-microbial agents for high solid and organic content systems.

Materials of Construction

The materials of construction of the water system (e.g. stainless steel, copper, tin, etc.) must be compatible with the proposed microbial control technology. Due to potential for corrosion problems, chlorine is not recommended for stainless steel metallurgy. Incompatible bactericides may cause pump cavitation, pipe corrosion, degradation, and staining. Special consideration must also be given to systems with soft metallurgy (e.g. aluminum, brass, copper), high water velocity, and large deviations in process variables. Appendix 2.4 summarizes the available anti microbial agents for the various materials of construction.

3.3 SELECTION CRITERIA

There are a set of criteria that can be used to further evaluate applicable microbial control technologies. These criteria include investment and operating costs, environmental impact, and safety concerns. Investment cost is the capital required for installation (e.g. biocide, pumps, pipes, etc.). Operating costs are the associated operating expenses and include depreciation. Environmental acceptability deals with the possible discharge of toxic byproducts (e.g. chlorinated hydrocarbons) as a result of biocide addition. Safety concerns deals with the risk to plant personnel due to handling and use of microbial control agents.

3.3.1 INVESTMENT AND OPERATING COST

Investment and operating cost is a key concern when selecting a microbial control technology. Investment costs typically include the cost of generators, start up chemicals, pumps, piping, and land. Operating costs typically include chemical, maintenance, depreciation, supervisory, and energy costs. This criteria is usually a heavy weighing factor selecting a microbial control technology.

3.3.2 ENVIRONMENTAL ACCEPTABILITY

Environmental impact is another concern when selecting a microbial treatment program. With the increase in environmental regulations and concern, the production of environmentally acceptable products has generated a high level of interest. The

controversy surrounding biocides stem from the chlorinated byproducts produced. Chlorine and other biocides may react with organic constituents present in the recirculating water to produce byproducts that are objectionable in taste or odor, and some, such as chloroform, may be harmful, (Wentz, 1995). The concern regarding toxicity of these byproducts has caused the Environmental Protection Agency (EPA) and other regulatory agencies to restrict chlorine usage in large effluent flows. As a result, EPA has set limits on the quantities of toxic pollutants that can be discharged into surface waters by industries.

The usage of environmentally friendly control technologies has generated considerable interest. These technologies include the use of chemicals that decompose into products that do not have an adverse effect on the environment (e.g. biodegradable). Such products may include but are not limited to water, oxygen, trace quantities of non hazardous chemicals, etc. Taking into account the water chemistry within the system, high priority should be given to an environmentally acceptable control technology.

3.3.3 SAFETY CONCERNS

Reducing risk to plant personnel in handling and storage is another desirable characteristic for microbial control technologies. Safety concern includes handling procedures, exposure limits, skin irritation, adverse effect on humans, etc. There is an extremely high liability risk when using toxic chemicals. Plant management is often resistant to the introduction of potentially dangerous chemicals onto a plant site. To reduce the potential risk of employee injury or death, it is preferred that industries move toward the implementation of non-toxic control technologies.

CHAPTER 4

DETAILS FOR THE CASE STUDIES

4.1 COOLING SYSTEM CASE STUDY

The cooling system studied is an aerated cross-flow cooling tower. The reused cooling water removes heat from process heat exchangers throughout the plant.

The cooling tower consists of three cells, six distributor valves, three fans, six hot water basins, and three 200 HP electric motors. The cooling tower circulation system consists of three Gould pumps, several supply headers, a cold water basin, filtered water supply line, and two drift eliminators.

The cooling tower has a total capacity of approximately 42,000 gpm. The water enters the tower at approximately 46°C, and exits at approximately 31°C. Depending on the ambient conditions, the wet bulb temperature can range from 0 to 38°C. Environmental conditions also play a key role in water loss due to evaporation. This tower has an evaporative water loss design specification of approximately 2.7% of water circulation flow. A blowdown stream of approximately 120 gpm is purged to achieve five cycles of concentration.

The cooling water usually contains an organic content of approximately 11 ppm. The reuse water contain residual acetic acid, debris, and insects. Water conductivity values in the summer months typically fall between 900 and 1000 mhos. Conductivities in the fall and winter months are between 800 and 900 mhos. Depending on the environmental conditions, there is a 10 - 20 mhos difference between the tower inlet and outlet. Figure 4.1 exhibits a general schematic of the cooling system.

REACTION CHEMISTRY

Reactions 27 and 28 are reactions that take place within the cooling tower.



These two reactions were previously summarized in Section 2.5.1.1.1.

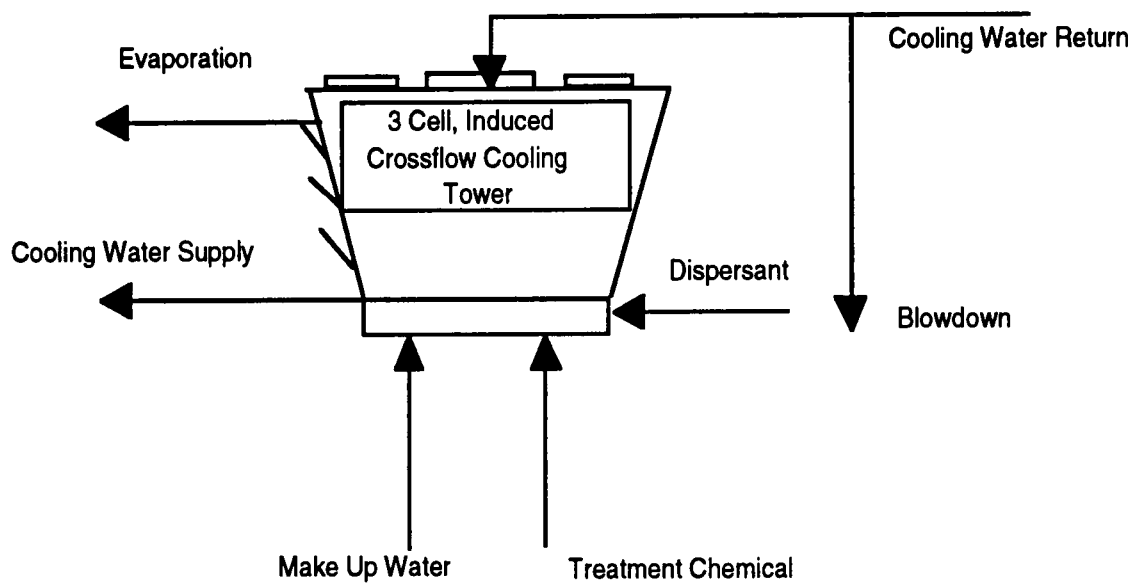


Figure 4.1: Flow diagram of cooling system case.

4.1.1 PROCESS ASSESSMENT

An assessment was performed to determine the suitability requirements for appropriate microbial control technologies. By knowing the type of microbes present, pH, solids content level, and materials of construction, the operational constraints were determined. Water chemistry and biology data were collected. The materials of construction was identified to assure that compatible microbial control technologies were selected. Appropriate technologies must maintain biocidal activity under the system's conditions, materials of construction, and the type of microbes present. Data included routine aerobic microbial counts, water conductivity, pH, hardness, iron content, and free available oxidant. Appendix 3 summarizes the water biology and chemistry throughout the testing period.

The cooling system is plagued with algae. Based on the aerobic bacteria counts and free available oxidant in the bulk water, the current treatment program (activated bromine) is effective against controlling bacteria. Using standard plate count methods, aerobic bacteria counts were negligible. Using the HACH DR/2000 Direct Reading Spectrophotometer, there was a mean 0.43 ± 0.33 ppm of free oxidant within the system.

The cooling system specifies microbial control technologies that maintain biocidal activity under basic pH conditions. Using the Orion Research Digital Ion Analyzer 501, the bulk water was found to have a mean pH of 8.52 ± 0.09 .

Due to the low relatively low level of total solids content present within the system, there are no operational constraints. Using the Nalcometer Model MLN Water Conductivity Analyzer and standard titration techniques, a moderate soluble solid content level (Ca 258 ± 46 ppm & Fe 0.188 ± 0.058 ppm) was observed, which corresponds to a mean water conductivity of 896 ± 132 mhos. The relatively high calcium content is primarily due to the calcium phosphate dispersant addition. Since the make-up water conductivity is approximately 190 mhos, there are 4.7 ± 4.0 cycles of concentration. The blowdown flow is varied in order to achieve 5.0 cycles. The total organic carbon (TOC) within the system was found to be relatively low (11 ppm).

The cooling tower is constructed of stainless steel pipes, polyethylene drift eliminators, aluminum based metals, concrete headers, and wooden pans. Chemical feeding pipes, fittings, and valves are made of PVC.

4.1.2 CURRENT TREATMENT PROGRAM

An activated bromine, which consists of 7/1 molar ratio of sodium hypochlorite and sodium bromide, is injected into the basin of the cooling tower. An activated bromine biocide is used to account for the pH dependency of sodium hypochlorite. A free oxidant residual between 0.3 and 0.5 ppm is targeted. An analyzer monitors the free oxidant residual. Based on the residual, the necessary biocide is fed. To reduce biological agglomeration, a calcium phosphate biodispersant (100 ppm) is fed. Routine aerobic spot checks, in conjunction with water chemistry analyses, are also performed.

4.2 CLARIFICATION SYSTEM CASE STUDY

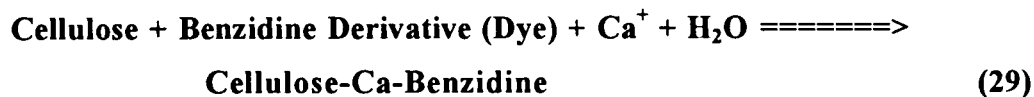
The clarification system studied is a non-aerated clarification tank. The tank holds 300,000 gallons and operates at approximately 90% capacity. The effluent water (900 gpm) is reused downstream in the spunlacing process for mechanical purposes.

The system has three entering process streams. The first stream (1000 gpm) leaves the manufacturing process and enters the clarification system. This stream is a pulp and water mixture consisting of approximately 300 ppm total suspended solids. Since the spunlacing process dissipates a high degree of energy, this stream enters the system at 50°C. The second stream is a 2.5 wt% nonionic polyacrylamide flocculating agent (1.1 gpm) that is injected to the system as a settling aid. The third stream is a 12.5 wt% sodium hypochlorite biocide (2.5 gph) that is fed to the tank for microbial control purposes.

There are two streams exiting the clarification system. A relatively clear effluent (14 ppm total suspended solids) is reused in the manufacturing process. The sludge (7000 ppm total suspended solids, 100 gpm) is recovered and landfilled. Figure 4.2 exhibits a general schematic of the clarification system.

REACTION CHEMISTRY

Reactions 29 through 32 exhibit the reaction chemistry within the clarification case system.



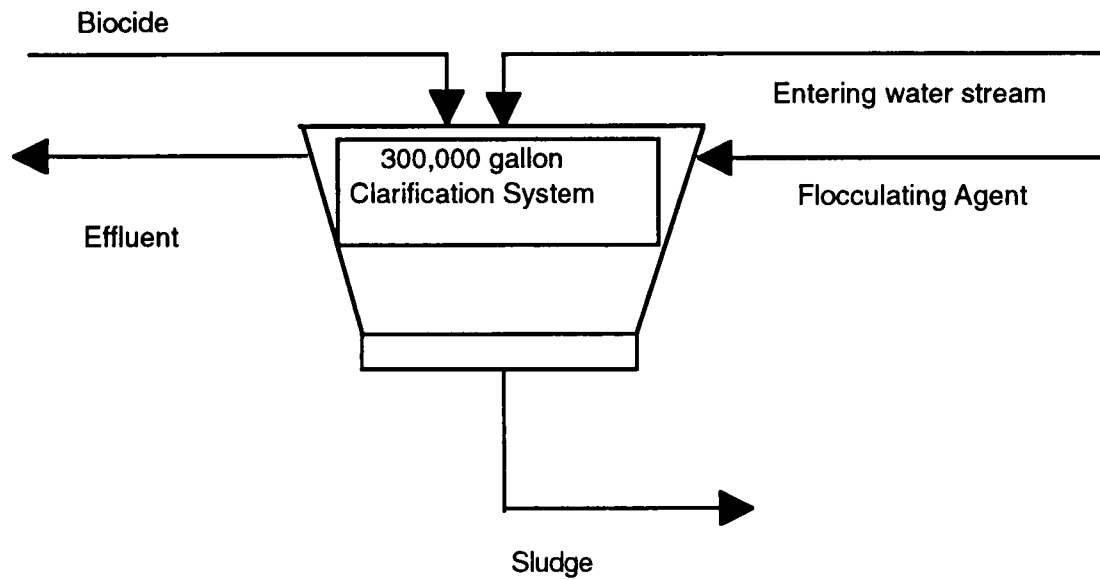


Figure 4.2: General schematic of the clarification system case.

The entering raw material is a molecular complex containing wood pulp (primarily cellulose) and a direct dye (derivatives of benzidine, toluidine, or dianisidines). Cellulose is a water insoluble polymer that is found in most wood fibers. These fibers are naturally anionic in nature. The direct dyes are color salts of color acids, and are alkaline in water. The direct dyes have a direct affinity for the hydroxyl groups of the cellulose fibers (via hydrogen bonding and cationic bridging via water hardness), forming the cellulose/calcium/dye complex, (Summers, 1996).

Cellulose/Benzidine Derivative (Dye) + Polyacrylamide ==>

Cellulose-Ca-Benzidine-Polyacrylamide (30)

A non ionic polyacrylamide flocculant is used to bond to the cellulose polymer complex via van der waal forces, hydrogen, electrostatic, and covalent bonding. The long molecule of the polyacrylamide is adsorbed onto the surface of the cellulose fibers. Loops are formed, which come into contact with, and attach to other cellulose fibers. These colloidal particles aggregate into larger entities in which gravitational forces dominate, resulting in a loss of stability suspension, (Summers, 1996).

NaOCl + H₂O =====> HOCl + NaOH (31)

Sodium hypochlorite, also called bleach, is used as the oxidizing biocide for this system. Reaction 31 exhibits the hydrolysis reaction for sodium hypochlorite.

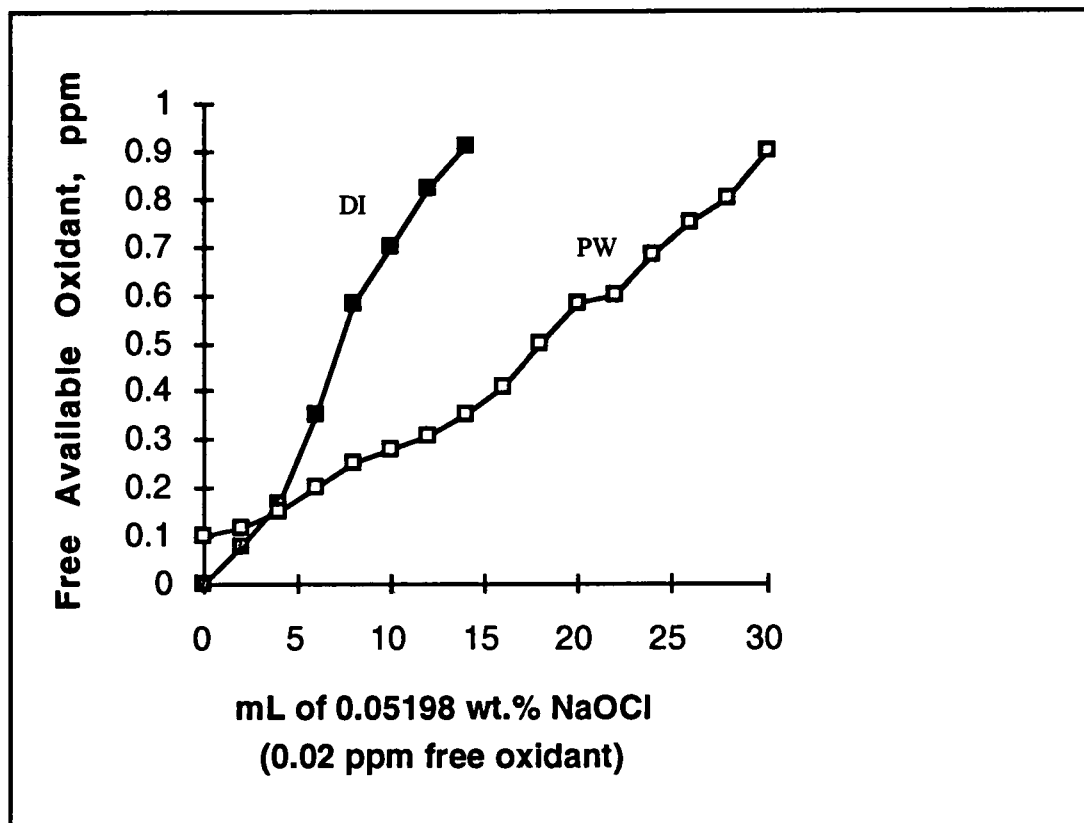
Hypochlorous acid, the desired oxidizing agent, along with sodium hydroxide is formed. The hypochlorous acid is very reactive, and oxidizes readily with the nearest molecule.

Cellulose-Benzidine-Polyacrylamide + HOCl + H₂O =====>

OCl-Cellulose-Ca-Benzidine-Acrylamide + H₂O (32)

The reactive hypochlorous acid readily oxidizes the hydroxyl groups of the cellulose/dye/polyacrylamide compound. The free oxidant is partially consumed by the cellulose fibers. The free oxidant available for microbial kill is the total hypochlorous acid fed minus the hypochlorous acid consumed by the cellulose fibers, (Crumpton, 1996). Figure 4.3 supports this hypothesis by showing the relationship between free oxidant and chlorine addition for two cases: (1) the high solid and organic stream (300 ppm total suspended solids) and (2) deionized water.

The conformation presented in Figure 4.3 supports the theory regarding organic consumption of free available oxidant. This figure shows that the presence of 350 ppm of



DI- Deionized Water

PW- Process Water @ 300 ppm TSS

Figure 4.3: Free available oxidant as a function of 0.05198 wt.% NaOCl (0.02 ppm) chlorine addition for the following: (1) Deionized Process Water @ 300 ppm TSS, and (2) Deionized water.

total suspended solids significantly decreases the amount of free available oxidant for microbial kill.

4.2.1 PROCESS ASSESSMENT

An assessment was performed to determine the suitability requirements for appropriate microbial control technologies. By knowing the nature of the system's microbial population, pH, solids content, and materials of construction, the operational constraints were determined. Water chemistry and biology data was collected. The materials of construction was identified to match compatible microbial control technologies. Appropriate technologies must maintain biocidal activity under the system's conditions, metallurgy, and type of microbes. Data included routine aerobic microbial counts, water conductivity, pH, and free available oxidant. Appendix 4 summarizes the water biology and chemistry throughout the testing period.

Previous studies by Goldey et al (1988) show higher aerobic microbial counts at 55°C, relative to 30°C. This fact indicates that the system is plagued with thermophile bacteria. These microbes are well adapted for higher temperature environments. Currently, the system is plagued with aerobic and anaerobic bacteria. Substantial biomass accumulation along the clarifier walls indicate that the treatment is ineffective in biomass penetration. This observation is consistent with the relatively low free oxidant residual. The free oxidant within the bulk water is 0.09 ± 0.05 , which is far less than the recommended 0.3 to 0.5 ppm.

The clarification system specifies microbial control technologies that maintain biocidal activity under slightly basic pH conditions. Using the Orion Research Digital Ion Analyzer 501, the bulk water was found to have a mean pH of 7.56 ± 0.35 .

Based on the system's relatively high solid organic content, microbial control technologies that maintain biocidal activity under these conditions are specified. Soluble solids are typically comprised of calcium and paper dyes. Suspended solids are typically comprised of wood pulp fibers and polyacrylamide. Using the Nalcometer Model MLN Conductivity Analyzer, low soluble solid content levels corresponding to mean water conductivities of 283 ± 11 , 275 ± 10 , 265 ± 10 mhos were observed for the sludge, entering

stream, and effluent, respectively. Using total suspended solids quantification techniques, the total suspended solids entering the clarification system were found to be relatively high (321 ± 36 ppm). The effluent and sludge had suspended solid concentrations of 18.5 ± 18.5 and 6335 ± 864 ppm, respectively.

The clarifier tank is constructed primarily of concrete. Piping is primarily constructed of stainless steel.

4.2.2 CURRENT TREATMENT PROGRAM

Due to the high organic content associated with the fibrous materials, the proliferation of microbial growth was inevitable. Past microbial control technologies included high water turbulence, water temperature, and filtration. Due to a lack of consistent microbial kill, these measures were not always effective. Therefore, other alternatives including a one-time ozonation, were investigated.

At present, a 12.5 wt% sodium hypochlorite feed is injected into the clarifier tank. Experimental studies shown in Figure 4.3 reflect the organic consumption of available oxidant. The free oxidant available for microbial kill is relatively low (total oxidant fed minus oxidant consumed by organics). Free oxidant levels within the bulk water are periodically measured.

CHAPTER 5

MAJOR RESULTS AND FINDINGS

The general approach from Table 3.1 is applied to the cooling and clarification cases. Based on the case assessment and the current treatment program, two appropriate recommendations are made. The first recommendation is based on modification of the existing treatment program. The second recommendation is based on selection of a new microbial control program.

5.1 COOLING SYSTEM

Several recommendations are made for microbial control within the cooling system case. These recommendations are based on modifications of the existing treatment program and implementation of a new treatment program. Modifications include chemical hygiene, control feedback, and equipment installations. Based on the case assessment, suitable microbial control technologies are presented and ranked. Using investment and operating costs, environmental impact, and safety concerns as a selection criteria, recommended technologies include activated bromine in conjunction with abrasive agents.

5.1.1 MODIFICATION OF THE EXISTING TREATMENT PROGRAM

The cooling system has numerous opportunities for program modification. These opportunities can be very instrumental in reducing microbial growth. Specific areas include ensuring proper biocide storage specifications, maintaining an oxidant control feedback system, and installing sun blockage on the cooling tower to prevent algae growth.

Improve chemical hygiene

Ensuring the proper biocide storage requirement is essential. Sodium hypochlorite degrades with age. As a result, the biocidal efficacy decreases with time. Therefore, it is important that a fresh batch is used at all times. Storing conditions should be within chemical specifications. See Section 2.5.1.1.1 for details regarding sodium hypochlorite

storage specifications.

Control feedback system

Control feedback is necessary in order to maintain effective microbial control. A Hach CL-17 oxidation/reduction analyzer monitors the free oxidant residual in the recirculation water. This automated control feedback system targets the recommended free oxidant level within the bulk water. Conceptually, a water sample from the basin is sent to an oxidation reduction potential (ORP), analyzer, that determines the free oxidant level. If the oxidant level is too low, then more oxidant is fed. If the oxidant level is too high, then the feed pump is shut off. As a result, the available oxidant is maintained between 0.3-0.5 ppm continuously. This technology has an associated investment cost of approximately \$2,500, (Cleare, 1996).

Equipment installation

Algae growth can be reduced by covering the cooling tower deck area. This modification prevents photosynthesis by serving as a sun blockage. This covering has an associated investment cost of approximately \$2,000, (Cleare, 1996).

5.1.2 SELECTION OF A NEW TREATMENT PROGRAM

The selection of a new program requires knowledge of the nature of microbes present, pH, solids content level, and materials of construction. This information is used to target suitable microbial control technologies. Once suitable technologies have been identified, additional criteria are used for ranking purposes. The following observations were made from the cooling system assessment. Observations in Table 5.1 will be used to determine the operational constraints of microbial control technologies.

Based on the algae and aerobic bacteria problem, basic water pH, relatively low material content, and stainless steel metallurgy, Table 5.2 presents the following technically suitable microbial control technologies are available.

Table 5.1: Observations based on cooling system assessment.

<u>Microbe Type</u>	<u>pH</u>	<u>Solids and Organic Content</u>	<u>Materials of Construction</u>
Algae Aerobic Bacteria	8.52±0.09 Basic	Relatively low level of organic constituents 11 ppm	Predominately Stainless Steel

Table 5.2: Technically feasible microbial control technologies

<u>Suitable Microbial Control Technologies</u>
Ozone
Activated Bromine
Quaternary Ammonium Salts (Phosphates and Sulfates)
Abrasive Cleaning Agents
Biodispersants

5.1.2.1 SELECTION CRITERIA

The selection criteria are used to further screen available technologies. These criteria consider additional investment and operating costs, environmental impact, and safety concerns. Based on these criteria, the following rankings were produced. Weighting factors will be assigned to each factor based on prioritization. Investment and operating costs, environmental acceptability, and safety concerns will be weighted 50, 25, and 25 percent, respectively.

Investment and Operating Costs

Table 5.3 summarizes the investment and operating costs for the available microbial control technologies. Details regarding the investment and operating costs for the cooling system can be found in Appendix 5.

Environmental Acceptability

Table 5.4 evaluates the environmental impact of each available microbial control technology by summarizing the potential byproducts produced.

Safety Concerns

Table 5.5 evaluates the safety concerns that must be considered when using available microbial control technologies.

Table 5.3: Summary of investment and operating costs for available microbial control technologies.

<u>Microbial Control Technology</u>	<u>Investment Cost</u>	<u>Operating Cost</u>
Ozone	\$303,800	\$64,533
Activated bromine	\$42,100	\$45,620
Quaternary Ammonium Salt	\$29,800	\$75,690
Sodium bicarbonate Abrasive agent	\$30,800	\$1,732,743
Calcium phosphate Biodispersant	\$30,800	\$5,763,196

Table 5.4: Potential byproducts produced via using suitable microbial control technologies

<u>Microbial Control Technology</u>	<u>Byproducts Produced</u>
Ozone	N/A
Activated Bromine	Trace quantities of chlorinated and brominated hydrocarbons
Quaternary Ammonium Salts	Possible salt precipitation
Abrasive Cleaning Agent	Possible precipitation problems
Biodispersants	Possible precipitation problems

Table 5.5: Safety concerns around the usage of suitable microbial control technologies.

<u>Microbial Control Technology</u>	<u>Safety Concerns</u>
Ozone	Flammability at high concentrations
Activated Bromine	Caution when handling
Quaternary Ammonium Salts	Moderately corrosive Chemical foaming
Abrasive Cleaning Agent	N/A
Biodispersants	N/A

5.1.2.2 FINAL RANKINGS

Microbial control technologies are divided into two categories: biocides and biomass inhibitors. Biocides are defined as agents that kill microorganisms. Biomass inhibitors are technologies that prevent slime and scale deposits from accumulating on the internal surface. Each microbial control technology was ranked (e.g. 1- best) scored based on selection criteria. Using each criteria's weighing factor, scoring was performed. The lowest total score represents the most feasible microbial control technology. Table 5.6 summarizes the rankings for each microbial control technology based on the selection criteria. Table 5.7 summarizes the final ranking of each technology based on selected weighing factors for the selection criteria.

Table 5.6: Rankings of each technology based on selection criteria.

<u>Investment and Operating Costs</u>	<u>Environmental Acceptability</u>	<u>Safety Concern</u>
<u>Biocide</u>	<u>Biocide</u>	<u>Biocide</u>
1- Activated bromine	1- Ozone	1- Activated bromine
2- Quaternary ammonium salts	2- Activated bromine	2- Ozone
3- Ozone	3- Quaternary ammonium salts	3- Quaternary ammonium salts
<u>Biomass Inhibitor</u>	<u>Biomass Inhibitor</u>	<u>Biomass Inhibitor</u>
1- Abrasive Agent	1- Abrasive Agent	1- Abrasive Agent
2- Biodispersant	1 Biodispersant	1 Biodispersant

Table 5.7: Final rankings of each microbial control technology.

<u>Microbial Control Technology</u>	<u>Final Rankings</u>
<u>Biocide</u>	
Activated bromine	1
Ozone	2
Quaternary ammonium salts	3
<u>Biomass Inhibitor</u>	
Abrasive agent	1
Biodispersant	2

Based in the technical suitability and selection criteria for the cooling system, recommended technologies for microbial control include activated bromine as a biocide, and an abrasive agent (sodium bicarbonate) as a biomass inhibitor. Table 5.8 summarizes the recommendations for the industrial cooling system case.

Table 5.8: Final recommendations for the cooling system case.

<u>Recommended Biocide</u>	<u>Recommended Biomass Inhibitor</u>
Activated bromine	Sodium bicarbonate

5.2 CLARIFICATION SYSTEM

Several recommendations are made for solving microbial problems within the clarification system case. These recommendations are based on modifications of the existing treatment program and implementation of a new treatment program. Modifications include improved chemical hygiene and new equipment installation. Based on the case assessment, suitable microbial control technologies are presented and ranked. Using investment and operating costs, environmental impact, and safety concerns as another criteria, recommended technologies include glutaraldehyde in conjunction with a polymeric surface coating within the clarification tank.

5.2.1 MODIFICATION OF THE EXISTING TREATMENT PROGRAM

The clarification system has numerous opportunities for program modification. These opportunities can be very instrumental in reducing microbial growth. Specific areas include ensuring proper biocide storage specifications, implementing a control feedback system, and incorporating a heat exchanger prior to clarification.

Improve chemical hygiene

Ensuring the proper biocide storage requirement is essential for effective microbial control. Storing conditions should be within chemical specifications.

Control feedback system

A Hach CL-17 ORP analyzer, which was discussed in Section 5.1.1, can be used to maintain the recommended free available oxidant within the clarification system.

Equipment installation

A periodic temperature shock treatment system is predicted by Summers (1996) to reduce the microbial population. This theory is based on a growth-death rate model. The death rate of one population is greater than the growth of the other population. The time required for one population to build an environmental resistance is relatively long. Therefore, the repetitious environmental change will reduce the thermophile population of microbes while increasing the mesophile population. On a long term basis, the total population of mesophiles and thermophiles will be reduced. Total investment cost is approximately \$3,000. Operating costs are negligible since recovered water will be used.

5.2.2 SELECTION OF A NEW TREATMENT PROGRAM

The following observations were made from the clarification system assessment. These observations in Table 5.9 will be used to determine the operational constraints of microbial control technologies.

Based on the aerobic and anaerobic bacteria problem, slightly basic water pH,

relatively high solid and organic content, and concrete construction, the following technically suitable microbial control technologies are available. Table 5.10 lists the available microbial control technologies for the clarification system case.

Table 5.9: Observations based on clarification system assessment.

<u>Microbe Type</u>	<u>pH</u>	<u>Solids and Organic Content</u>	<u>Materials of Construction</u>
Aerobic and Anaerobic Bacteria	7.56±0.35	Relatively high level of organic constituents (321±36 ppm)	Predominately Concrete and Stainless Steel Construction

Table 5.10: Technically feasible microbial control technologies.

<u>Suitable Microbial Control Technologies</u>
Glutaraldehyde
Organobromine
Ultraviolet Light
Surface Coatings

5.2.2.1 SELECTION CRITERIA

The selection criteria are used to further screen available technologies. These criteria consider additional investment and operating costs, environmental impact, and safety concerns. Based on these criteria, the following rankings were produced. Weighting factors will be assigned to each factor based on common prioritization. Investment and operating costs, environmental acceptability, and safety concerns will be weighted 50, 25, and 25 percent, respectively, (Summers, 1996)

Investment and Operating Costs

Table 5.11 summarizes the investment and operating costs for the available microbial control technologies. Details regarding the investment and operating costs for the cooling system can be found in Appendix 6.

Environmental Acceptability

Table 5.12 evaluates the environmental impact of each available microbial control technology by summarizing the potential byproducts produced.

Table 5.11: Summary of investment and operating costs for available microbial control technologies.

<u>Microbial Control Technology</u>	<u>Investment Cost</u>	<u>Operating Cost</u>
Glutaraldehyde	\$29,800	\$51,960
Organobromine	\$29,800	\$51,960
Ultraviolet Light	\$150,000	\$30,273
Surface Coating	\$5,337	\$1,067

Table 5.12: Potential byproducts produced via using suitable microbial control technologies

<u>Microbial Control Technology</u>	<u>Byproducts Produced</u>
Glutaraldehyde	N/A
Organobromine	N/A
Ultraviolet light	N/A
Surface coating	N/A

Safety Concerns

Table 5.13 evaluates the safety concerns that must be considered when using available microbial control technologies.

Table 5.13: Safety concerns around the usage of suitable microbial control technologies.

<u>Microbial Control Technology</u>	<u>Safety Concerns</u>
Glutaraldehyde	Low volatility concentration. 0.7 mg/m^3 May cause skin irritation
Organobromine	May cause skin irritation
Ultraviolet light	Extreme equipment temperatures
Surface coating	Caution when applying to tank

5.2.2.2 FINAL RANKINGS

Microbial control technologies are divided into two categories: biocides and biomass inhibitors. Biocides are defined as agents that kill microorganisms. These biocides include glutaraldehyde, organobromines, and ultraviolet light. Biomass inhibitors are technologies that prevent slime and scale deposits from accumulating on the internal surface. Biomass inhibitor will include only surface coatings. Each microbial control technology was ranked (e.g. 1- best) scored based on selection criteria. Using the criteria's weighing factor, scoring was performed. The lowest total score represents the most feasible microbial control technology. Table 5.14 summarizes the rankings for each microbial control technology based on the selection criteria. Table 5.15 summarizes the final ranking of each technology based on selected weighing factors for each criteria.

Table 5.14: Rankings of each technology based on selection criteria.

<u>Investment and Operating Costs</u>	<u>Environmental Acceptability</u>	<u>Safety Concern</u>
<u>Biocide</u>	<u>Biocide</u>	<u>Biocide</u>
1- Glutaraldehyde	1- Ultraviolet light	1- Ultraviolet light
1- Organobromine	2- Glutaraldehyde	2- Glutaraldehyde
2- Ultraviolet light	3- Organobromine	2- Organobromine
<u>Biomass Inhibitor</u>	<u>Biomass Inhibitor</u>	<u>Biomass Inhibitor</u>
1- Surface coating	1- Surface coating	1- Surface coating

Table 5.15: Final rankings of each microbial control technology.

<u>Microbial Control Technology</u>	<u>Final Rankings</u>
<u>Biocide</u>	
Ultraviolet light	1
Glutaraldehyde	2
Organobromine	3
<u>Biomass Inhibitor</u>	
Surface coating	1

Based in the technical suitability and selection criteria for the clarification system, recommended technologies for microbial control include ultraviolet light as a biocide, and a surface coating as a biomass inhibitor. Table 5.16 summarizes the final ranking for the industrial clarification system case.

Table 5.16: Final recommendations for the clarification system case.

<u>Recommended Biocide</u>	<u>Recommended Biomass Inhibitor</u>
Ultraviolet Light	Epoxy surface coating

CHAPTER 6

CONCLUSIONS

Problems associated with microbial growth in water reuse systems can be very detrimental. These microorganisms restrict water flow, produce unpleasant odors, induce localized corrosion, and reduce cooling. To reduce costs associated with equipment replacement, cleaning, and treatment, a sound microbial control program must be implemented.

A general approach that considers improving the existing microbial control program before implementing a new program was applied to the problem. This method considers less expensive options (e.g. equipment modification) first before investing in new treatment technologies. When selecting a new microbial control program, one must consider the technical suitability (compatibility with the system's microbial problem, pH, level of solid and organic constituents, and materials of construction) and the selection criteria (investment and operating cost, environmental impact, and safety concerns) associated with each microbial control technology.

Based on the existing microbial control program, specific areas for improvement were identified. Table 6.1 summarizes these recommendations.

Table 6.1: Recommendations for improving the existing microbial control program.

<u>Cooling System</u>	<u>Clarification System</u>
1. Improve chemical hygiene	1. Improve chemical hygiene
2. Control feedback system ORP (Oxidation/reduction potential) Analyzer	2. Control feedback system ORP (Oxidation/reduction potential) Analyzer
3. Sun blockage covering over the cooling tower to prohibit algae growth	2. Heat exchanger prior to clarification for temperature shock purposes

Based on the system's microbial problem, pH, level of solid and organic constituents, and materials of construction, available technologies were identified. Using the selection criteria to further screen the agents, biocides and biomass inhibitors were

ranked. Table 6.2 ranks the available biocide and biomass inhibitors.

Table 6.2: Rankings for available microbial control technologies.

<u>Cooling System</u>	<u>Clarification System</u>
Biocides	Biocides
1- Activated bromine	1- Ultraviolet light
2- Ozone	2- Glutaraldehyde
3- Quaternary Ammonium Salts	3- Organobromine
Biomass Inhibitors	Biomass Inhibitor
1- Sodium bicarbonate (Abrasive agent)	1- Surface Coating
2- Calcium phosphate (Dispersant)	

Activated bromine in conjunction with sodium bicarbonate was recommended for the cooling system. The combined investment and operating costs for the microbial control program are \$72,900 and \$1,778,363, respectively. For this recycle system, it is recommended to modify the current microbial program by installing a sun blockage over the cooling tower deck, and to use the abrasive agent instead of the dispersant.

Ultraviolet light in conjunction with a polymeric epoxy surface coating was recommended for the clarification system. The combined investment and operating costs for the microbial control program are \$155,337 and \$31,340, respectively. For this recycle system, it is recommended to implement the new microbial control program.

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BIBLIOGRAPHY

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APPENDICES

APPENDIX 1

ECONOMICS FOR MICROBIAL CONTROL TECHNOLOGIES

Gaseous chlorinators range from \$1,000 - \$2000.
(Wallace and Tiernan)

Gaseous chlorine \$200 per ton.
(Wallace and Tiernan)

Calcium hypochlorite \$83.50 per 100 lb..
(Chemical Marketing Reporter)

Sodium bromide, NaBr, as of 1996 costs approximately \$0.70 per pound.
(Chemical Marketing Reporter)

Hydrogen peroxide (35 wt percent), as of 1996, costs approximately \$0.245 per pound.
(Chemical Marketing Reporter)

Chlorine dioxide: \$1,300 level transmitter, \$4,500 stainless steel pump, CPVC pipe
\$15/ft, \$25,000 storage tank.
(Vulcan Chemical Company)

Baking Soda: \$18/50 lb. bag: Portable high pressure blaster unit: \$42,000
(Carolina Equipment and Supply Company)

NaOCl pump; 2.5 gallon per hour per pump; 60 gallon per day; < 150 psi; \$9 500
(Nalco Chemical Company)

NaOCl- \$ 0.60 per gallon
(Chemical Marketing Reporter)

NaBr pump; 2.5 gallon per hour per pump; 60 gallon per day; < 150 psi; \$9 500
(Nalco Chemical Company)

Glutaraldehyde- \$7.00 per pound; Shipped in 504 lb.. per container; Bulk 25% @
\$1.28/lb.. or 50% @ \$2.26/lb.. for 44,000 lb..
(Nalco Chemical Company)

Organobromine @ approximately \$7.00 per pound

Biocide pump- \$8,800 for 15 gallons/hour
(Nalco Chemical Company)

Ultraviolet Light; Equipment Price Quote @ \$150,000; Electricity 30kWhr/day
(Los Alamos Laboratory)

Ozone; Price Quote based on the cooling tower was approximately \$300,000
(Marley Ozone/Cooling Tower)

Epoxy Surface Coating; Primer @ \$49.75/gal (223 ft²/gal) ;
Coating @ \$75.00 (45 ft²/gal)
(KCC Corrosion Control)

APPENDIX 2

AVAILABLE MICROBIAL CONTROL TECHNOLOGIES BASED ON TECHNICAL SUITABILITY

2.1: Available microbial control technologies based on the type of microbes.

<u>ALGAE</u>	<u>AEROBIC BACTERIA</u>	<u>ANAEROBIC BACTERIA</u>	<u>FUNGI</u>
<u><i>Oxidizers</i></u>	<u><i>Oxidizers</i></u>	<u><i>Oxidizers</i></u>	<u><i>Oxidizers</i></u>
1-Ozone	1-Ozone	1-Ozone	1-Ozone
2-Chlorines	2-Chlorines	2-Chlorines	2-Chlorines
3-Bromines	3-Bromines	3-Bromines	3-Bromines
<u><i>Nonoxidizers</i></u>	4-Chlorine Dioxides	4-Chlorine Dioxides	4-Chlorine Dioxides
1-DBNPA	<u><i>Nonoxidizers</i></u>	5-Peroxygens	<u><i>Nonoxidizers</i></u>
2-Glutaraldehyde	1-Isothiazolinones	<u><i>Nonoxidizers</i></u>	1-Glutaraldehyde
3-Quaternary Ammonium Salts	2-Glutaraldehyde	1-Glutaraldehyde	2-Thiones
4-Carbamates	3-Organobromines	2-Isothiazolinones	3-Thiocyanates
5-Thiones	4-Quaternary Ammonium Salts	3-Organobromines	<u><i>Other</i></u>
<u><i>Other</i></u>	5-DBNPA	4-DBNPA	1-Abrasive Cleaning Agents
1-Abrasive Cleaning Agents	6-Thiones	5-PHMB	
	<u><i>Other</i></u>	6-Thiones	
	1-Ultraviolet light	<u><i>Other</i></u>	
	2-Abrasive Cleaning Agents	1-Ultraviolet light	
	3-Biodispersant	2-Abrasive Cleaning Agents	
	4-Surface Coating	3-Biodispersant	
		4-Surface Coating	

2.2: Available microbial control technologies based on pH.

<u>Acidic Water System</u>	<u>Basic Water System</u>
<u>Oxidizers</u>	<u>Oxidizers</u>
1-Ozone	1-Ozone
2-Chlorines	2-Bromines
3-Bromines	3-Chlorine Dioxides
4-Chlorine Dioxide (5.0 - 7.0)	4-Peroxygens
5-Peroxygens	<u>Nonoxidizers</u>
<u>Nonoxidizers</u>	1-Glutaraldehyde (7.0 - 8.0)
1-Glutaraldehyde (6.0 - 7.0)	2-Isothiazolinones (7.0 - 9.0)
2-Isothiazolinones (6.0 - 7.0)	3-Quaternary Ammonium Salts
3-Organobromines	4-PHMB
4-Quaternary Ammonium Salts	5-Organobromines
5-DBNPA (6.0 - 7.0)	6-DBNPA (7.0 - 8.0)
6-Thiocyanates (6.0 - 7.0)	7-Carbamates
<u>Other</u>	8-Thiones
1-Ultraviolet Light	9-Thiocyanates (7.0 - 8.0)
2-Abrasive Cleaning	<u>Other</u>
3-Biodispersants	1-Ultraviolet Light
4-Surface Coating	2-Abrasive Cleaning
	3-Biodispersants
	4-Surface Coating

2.3: Available microbial control technologies based on the presence of solid and organic constituents.

<u>Water systems with a high level of solid and organic constituents</u>
<u>Oxidizers</u>
1-Chlorine Dioxides
2-Peroxygens
3-Bromines
<u>Nonoxidizers</u>
1-Glutaraldehydes (except ammonium compounds)*
2-Organobromines
3-Isothiazolinones (except chlorine and hydrogen sulfide)*
4-Thiones (except chromate)*
5-Thiocyanates (except dissolved iron)*
6-Carbamates (except dissolved iron and chromates)*
<u>Others</u>
1-Ultraviolet Light
2-Abrasive Cleaning Agents
3-Biodispersants
4-Surface Coating

*- May sometimes cause equipment corrosion or environmental regulations if used in excess to offset consumption by ammonium and other organic constituents.

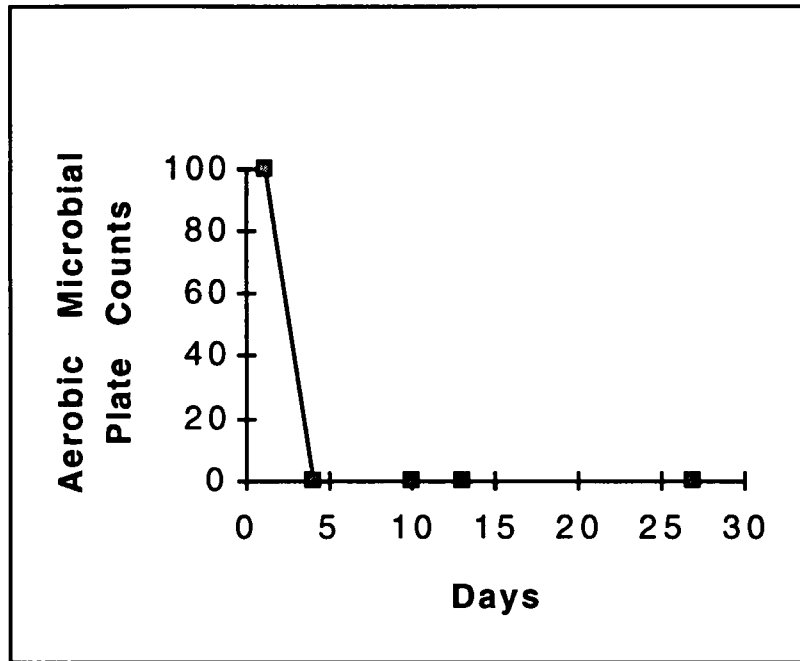
2.4: Available microbial control technologies based on materials of construction.

<u>STAINLESS STEEL</u>	<u>POLYVINYL CHLORIDE (PVC)</u>	<u>DENSE PLASTIC</u>	<u>PVDF</u>	<u>GLASS</u>
<u>Oxidizers</u>	<u>Oxidizers</u>	<u>Oxidizers</u>	<u>Oxidizers</u>	<u>Oxidizers</u>
Bromines	Chlorines	Chlorines	Bromines	Ozone
Ozone (SS 316)	Bromines	Bromines	<u>Nonoxidizers</u>	
<u>Nonoxidizers</u>	Chlorine Dioxide	Chlorine Dioxide	DBNPA	
PHMB	Peroxygens	Peroxygens	Quats	
Quaternary Ammonium Phosphates & Sulfates	<u>Nonoxidizers</u>	<u>Nonoxidizers</u>	Glutaraldehyde	
Glutaraldehyde	Quats	Quats	Isothiazolinone	
Isothiazolinone (except SS 304)	Glutaraldehyde	Glutaraldehyde	Organobromine	
Organobromine	Isothiazolinone	Isothiazolinone	DBNPA	
<u>Other</u>	DBNPA	DBNPA	<u>Other</u>	
Abrasive Cleaning	Organobromine	Organobromine	Abrasive Cleaning	
Surface Coating	<u>Other</u>	<u>Other</u>		
Biodispersant	Surface Coating	Abrasive Cleaning		
	Biodispersant	Biodispersant		
	Abrasive Cleaning			

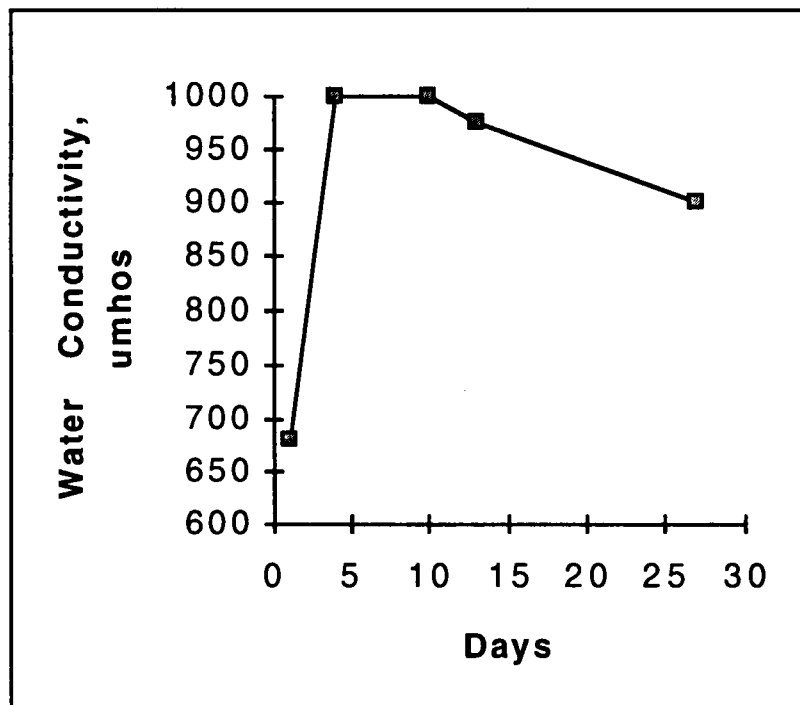
<u>HYPALON</u>	<u>TEFLON</u>	<u>COPPER</u>	<u>ALUMINUM</u>	<u>BRASS</u>
<u>Oxidizers</u>	<u>Oxidizers</u>	<u>Oxidizers</u>	<u>Nonoxidizers</u>	<u>Nonoxidizers</u>
Ozone	Bromines	Chlorines (70/30 Cu/Ni)	PHMB	PHMB
<u>Nonoxidizers</u>	Ozone	Bromines (70/30 Cu/Ni)	Quaternary Ammonium Phosphates & Sulfates	Quaternary Ammonium Phosphates & Sulfates
Quats	Chlorine Dioxide	<u>Nonoxidizers</u>	<u>Other</u>	<u>Other</u>
Isothiazolinone	<u>Nonoxidizers</u>	PHMB	Biodispersant	Biodispersant
DBNPA	Isothiazolinone	Organobromine (70/30 Cu/Zn)		
<u>Other</u>	Organobromine	Quaternary Ammonium Phosphates & Sulfates		
Biodispersant	Quats	Biodispersant		
	<u>Other</u>	Abrasive Cleaning		
	Biodispersant			

APPENDIX 3

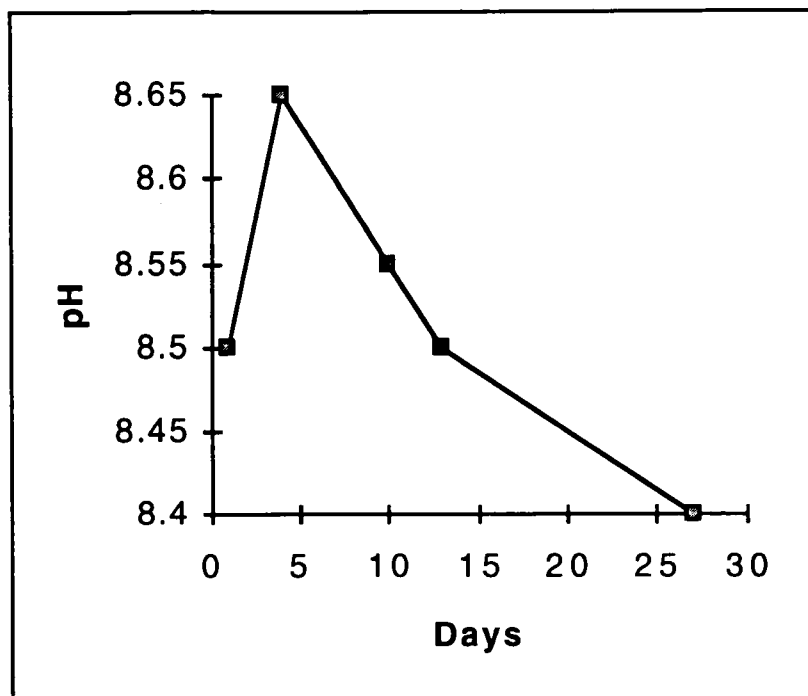
COOLING SYSTEM PROCESS DATA



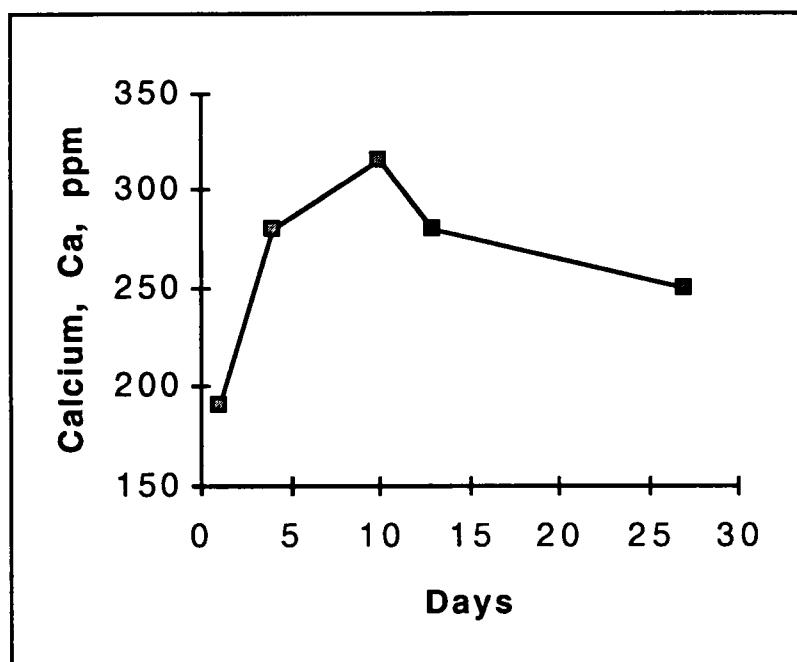
Aerobic microbiological counts as a function of days.



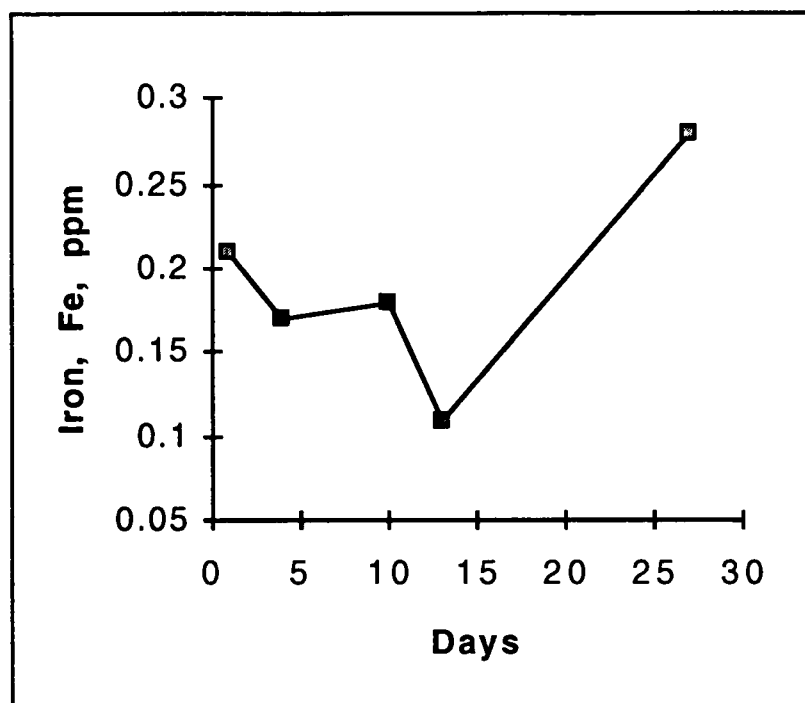
Water conductivity (soluble solids), umhos, as a function of days.



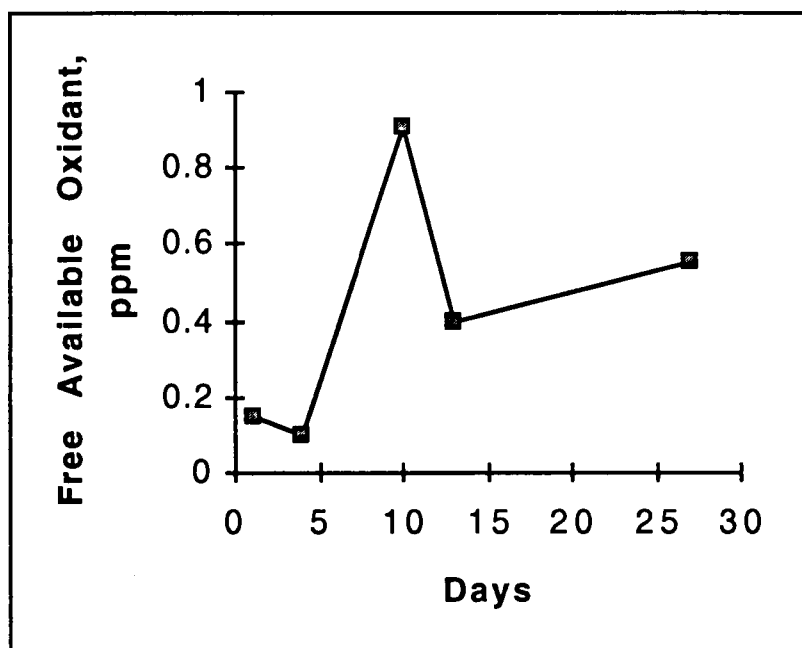
Water pH as a function of days.



Water hardness (Ca), ppm, as a function of days.



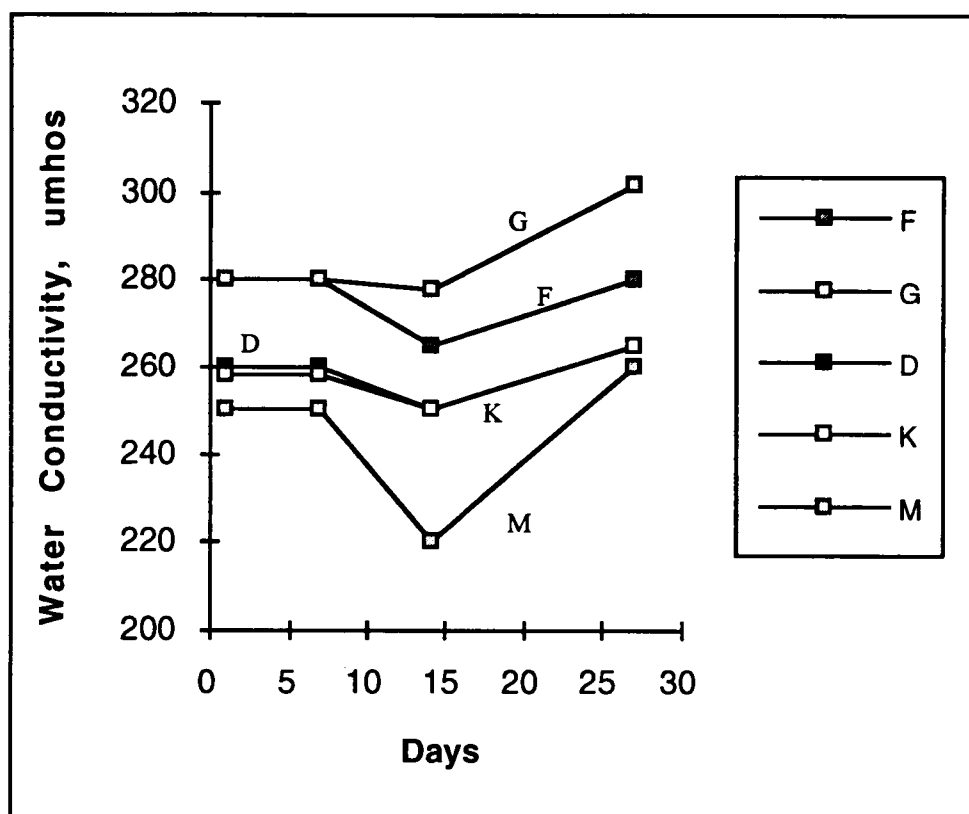
Iron (Fe) concentration, ppm, as a function of days.



Free available oxidant, ppm, as a function of days

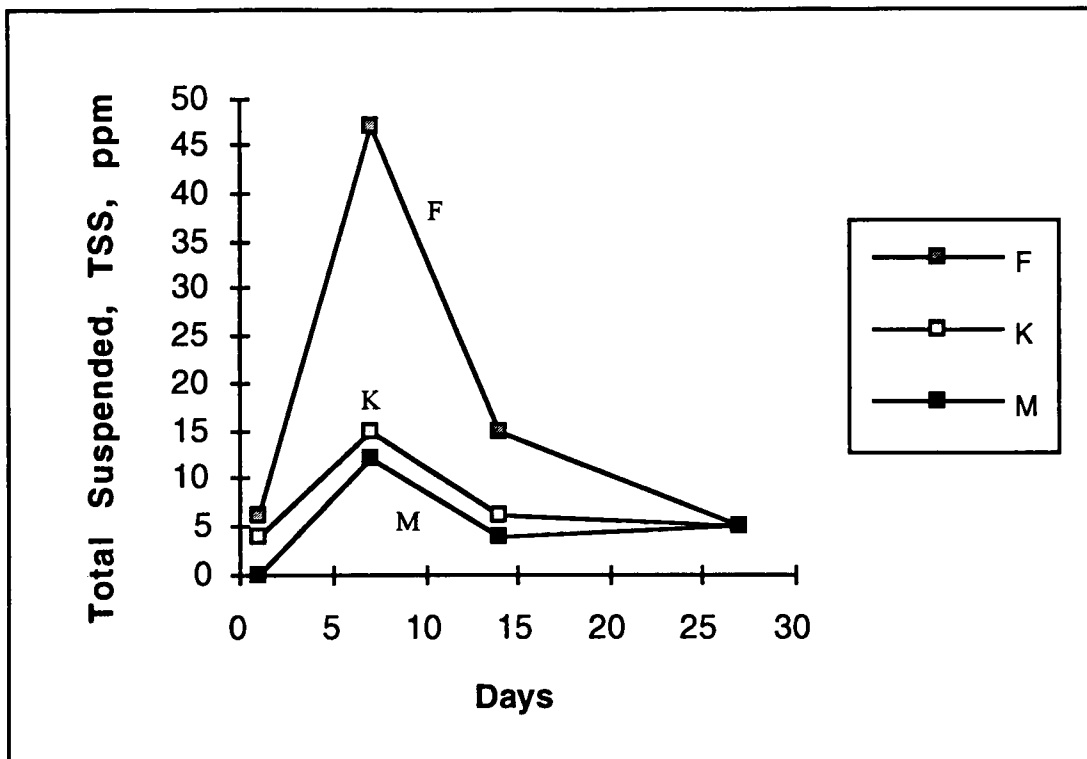
APPENDIX 4

CLARIFICATION SYSTEM DATA

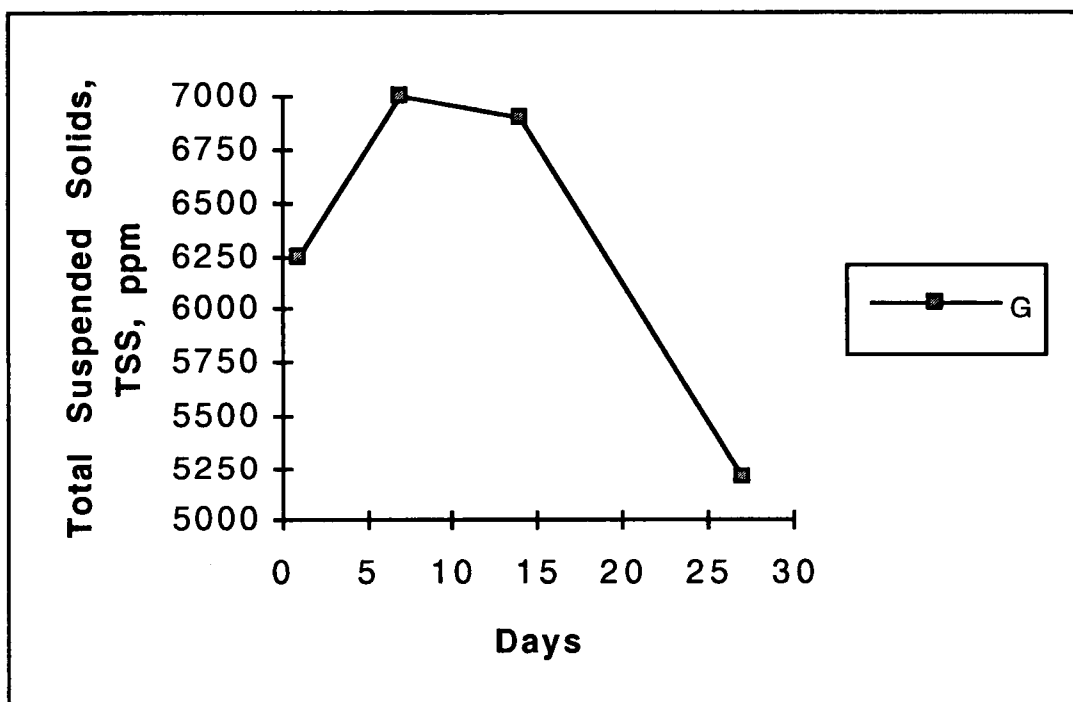


Water conductivity (soluble solids), umhos, as a function of days of various process streams

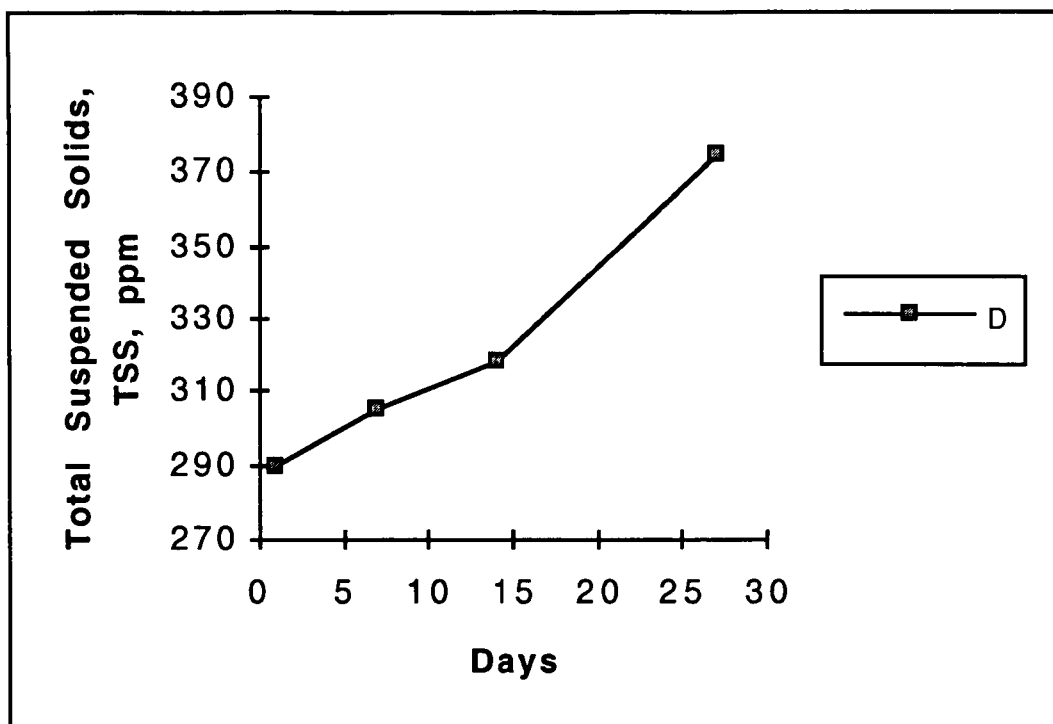
<u>Process Stream</u>	<u>Water Conductivity, umhos</u>
F-Water exiting clarifier	265±10
G-Sludge exiting clarifier	283±11
D-Water entering clarifier	275±10
K-Water exiting pre-coat filter	258±6
M-Water exiting cartridge filter	246±18



Total suspended solids, ppm, as a function of days of process streams F, K, and M

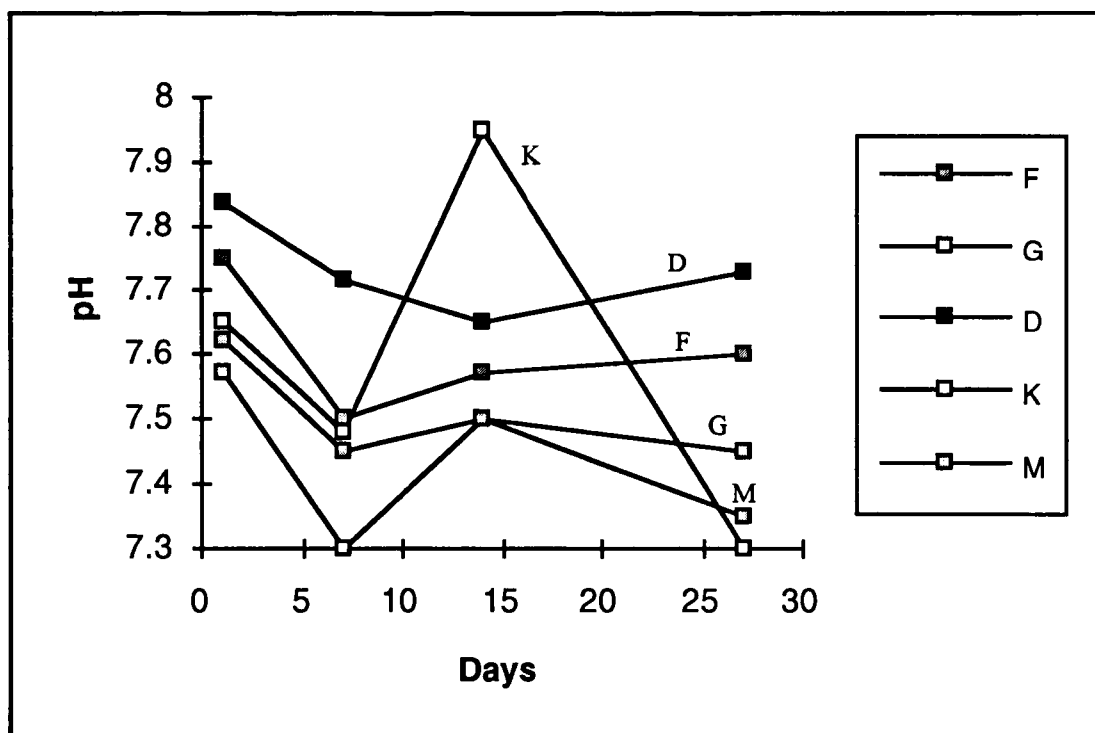


Total suspended solids, ppm, as a function of days of process stream G



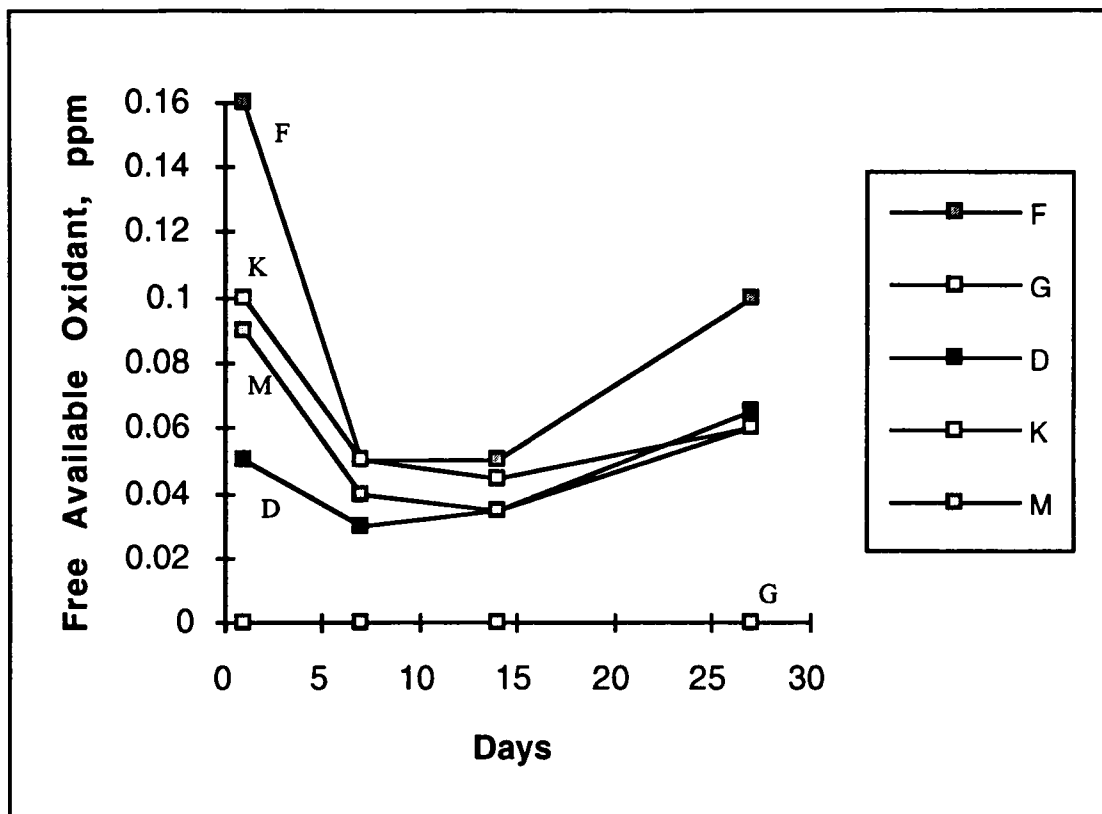
Total suspended solids, ppm, as a function of days of process stream D

<u>Process Stream</u>	<u>Total Suspended Solids, ppm</u>
F-Water exiting clarifier	18.5±18.5
G-Sludge exiting clarifier	6335±864
D-Water entering clarifier	321±36
K-Water exiting pre-coat filter	7.5±5.7
M-Water exiting cartridge filter	5.5±5.5



Water pH as a function of days of various process streams.

Process Stream	pH
F-Water exiting clarifier	7.58±0.11
G-Sludge exiting clarifier	7.45±0.11
D-Water entering clarifier	7.71±0.09
K-Water exiting pre-coat filter	7.58±0.27
M-Water exiting cartridge filter	7.47±0.12



Free available oxidant, ppm, as a function of days of various process streams

Process Stream	Free Available Oxidant, ppm
F- Water exiting clarifier	0.09±0.05
G- Water exiting sludge	0±0
D- Water entering clarifier	0.045±0.019
K- Water exiting pre-coat filter	0.062±0.026
M- Water exiting cartridge filter	0.055±0.026

APPENDIX 5

INVESTMENT AND OPERATING COSTS FOR THE COOLING SYSTEM

5.1: Investment and operating costs for ozone treatment.

Ozone	
<u>Investment Cost</u>	\$303,800
Ozone generator (\$250,000)	
Booster pump (\$ 300)	
Air compressor (\$50,000)	
Oxidation Reduction Potential Analyzer (\$2,500)	
Piping \$1,000	
<u>Annual Operating Cost</u>	\$64,533
Electricity @ 300 kWhr/day	
Air @ 120 cfm	
Supervisory and maintenance @ 10% of capital investment	
Depreciation @ 10 years	

5.2: Investment and operating costs for activated bromine treatment.

Activated Bromine	
<u>Investment Cost</u>	\$42,100
Two(2) Biofeeder pumps @ \$8,800/pump	
Oxidation Reduction Analyzer (\$2,500)	
Tank @ \$20,000	
Piping @ \$2,000	

<u>Annual Operating Cost</u>	\$45,620
Sodium hypochlorite @ \$0.60/lb. (\$29,000)	
Sodium bromide @ \$0.70/lb. (\$8,200)	
Supervisory and maintenance @ 10% of capital investment	
Depreciation @ 10 years	

5.3: Investment and operating costs for quaternary ammonium salt treatment.

Quaternary Ammonium Salt	
<u>Investment Cost</u>	\$29,800
One Biofeeder pump @ \$8,800/pump Tank @ \$20,000 Piping @ \$1,000	
<u>Annual Operating Cost</u>	\$75,960
Quaternary ammonium salt @ \$7.00/lb. (\$70,000)	
Supervisory and maintenance @ 10% of capital investment	
Depreciation @ 10 years	

5.4: Investment and operating costs for sodium bicarbonate (abrasive agent) treatment.

Abrasive Cleaning Agent	
<u>Investment Cost</u>	\$30,800
Dispersant pump @ \$8,800 Tank @ \$20,000 Piping @ \$1,000	
<u>Annual Operating Cost</u>	\$1,732,743
Sodium bicarbonate @ \$0.36/lb. (\$1,726,583) Supervisory and maintenance @ 10% of capital investment Depreciation @ 10 years	

5.5: Investment and operating costs for calcium phosphate (biodispersant) treatment.

Biodispersant	
<u>Investment Cost</u>	\$30,800
Dispersant pump @ \$8,800 Tank @ \$20,000 Piping @ \$2,000	
<u>Annual Operating Cost</u>	\$5,763,196
Calcium phosphate @ \$1.20/lb. (\$5,755,276) Supervisory and maintenance @ 10% of capital investment Depreciation @ 10 years	

APPENDIX 6

INVESTMENT AND OPERATING COSTS FOR THE CLARIFICATION SYSTEM

6.1: Investment and operating costs for glutaraldehyde treatment.

Glutaraldehyde	
<u>Investment Cost</u> Biofeeder pump @ \$8,800 Tank @ \$20,000 Piping @ \$1,000	\$29,800
<u>Annual Operating Cost</u> Glutaraldehyde @ \$7.00/lb. (\$46,000) Supervisory and maintenance @ 10% of capital investment Depreciation @ 10 years	\$51,960

6.2: Investment and operating costs for organobromine treatment.

Activated Bromine	
<u>Investment Cost</u> Biofeeder pump @ \$8,800 Tank @ \$20,000 Piping @ \$1,000	\$29,800
<u>Annual Operating Cost</u> Organobromine @ \$7.00/lb. (\$46,000) Supervisory and maintenance @ 10% of capital investment Depreciation @ 10 years	\$51,960

6.3: Investment and operating costs for ultraviolet light treatment.

Ultraviolet Light	
<u>Investment Cost</u> Ultraviolet lamp	\$150,000

<u>Annual Operating Cost</u>	\$30,273
Electricity @ 30 kWhr/day	
Supervisory and maintenance @ 10% of capital investment	
Depreciation @ 10 years	

6.4: Investment and operating costs for surface coating treatment.

Surface Coating	
<u>Investment Cost</u>	\$5,337
Primer @ \$49.75/gal (\$627)	
Coating @ \$75.00/gal (\$4,710)	
<u>Annual Operating Cost</u>	\$1,067
Supervisory and maintenance @ 10% of capital investment	
Depreciation @ 10 yrs	

VITA

Oscar Lee Martin, Jr. was born in Birmingham, Alabama, on August 21, 1974. After completing Ramsay Alternative High School in Birmingham in 1991, he enrolled into college at the University of Alabama, Tuscaloosa.

Martin was very active on campus and held many leadership positions including President and District Secretary (Tau Beta Pi National Engineering Honor Society), Vice President (National Society of Black Engineers), Vice President (Phi Eta Sigma Honor Society), and Student Body Representative (Engineering Dean Search Committee), just to name a few. He also won numerous academic and leadership awards including the Coordinating Council of Student Organizations Outstanding Leadership Award, Student Alumni Association Outstanding Leadership Award, Who's Who Among Students in American Colleges and Universities, National Society of Black Engineers' Fellow, and was inducted into nine national collegiate academic honor societies.

Martin completed three co-op terms and two summer internships at DuPont (Old Hickory, Tennessee) where he filed three notice of inventions for patent pending development work in the area of liquid filtration and process design.

In 1995, Martin was named a National Consortium for Graduate Degrees for Minorities in Science and Engineering, Inc. (GEM) Fellow sponsored by DuPont. In December of 1995, Martin received a Bachelor of Science degree in Chemical Engineering from the University of Alabama, Tuscaloosa. In January 1996, he entered graduate school at the University of Tennessee, Knoxville, and in December 1996 received a Master of Science degree in Chemical Engineering.