OPTIMAL SCHEDULING FOR BIOCIDE DOSING AND HEAT EXCHANGERS MAINTENANCE TOWARDS ENVIRONMENTALLY FRIENDLY SEAWATER COOLING SYSTEMS

A Dissertation

by

ABDULLAH S. O. BINMAHFOUZ

Submitted to the Office of Graduate Studies of
Texas A&M University
in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

August 2011

Major Subject: Chemical Engineering

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Approved by:

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ABSTRACT

Optimal Scheduling for Biocide and Heat Exchangers Maintenance Towards
Environmentally Friendly Seawater Cooling Systems. (August 2011)

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Using seawater in cooling systems is a common practice in many parts of the world where there is a shortage of freshwater. However, biofouling is one of the major operational problems associated with the usage of seawater in cooling systems. Microfouling is caused by the activities of microorganisms, such as bacteria and algae, producing a very thin layer that sticks to the inside surface of the tubes in heat exchangers. This thin layer has a tremendously negative impact on heat transferred across the heat exchanger tubes in the system. In some instances, even a 250 micrometer thickness of fouling film can reduce the heat exchanger's heat transfer coefficient by 50%. On the other hand, macrofouling is the blockage caused by relatively large marine organisms, such as oysters, mussels, clams, and barnacles. A biocide is typically added to eliminate, or at least reduce, biofouling. Typically, microfouling can be controlled by intermittent dosages, and macrofouling can be controlled by continuous dosages of biocide.

The aim of this research work is to develop a systematic approach to the optimal operating and design alternatives for integrated seawater cooling systems in industrial facilities. A process integration framework is used to provide a holistic approach to optimizing the design and operation of the seawater cooling system, along with the dosage and discharge systems. Optimization formulations are employed to systematize the decision-making and to reconcile the various economic, technical, and environmental aspects of the problem. Building blocks of the approach include the biocide water chemistry and kinetics, process cooling requirements, dosage scenarios and dynamic profiles, biofilm growth, seawater discharge, and environmental regulations.

Seawater chemistry is studied with emphasis on the usage of biocide for seawater cooling. A multi-period optimization formulation is developed and solved to determine.

- The optimal levels of dosing and dechlorination chemicals
- The timing of maintenance to clean the heat-exchange surfaces
- The dynamic dependence of the biofilm growth on the applied doses, the seawater-biocide chemistry, the process conditions, and seawater characteristics for each time period.

The technical, economic, and environmental considerations of the system are accounted for and discussed through case studies.

DEDICATION

I would like to devote my academic work to the spirit of my late father, Salmeen, who taught me that knowledge is the best way to raise one's qualifications, and who helped me set my essential goals for my life. I am deeply grateful to my mother, Fatimah, whose strength and faith show me how to stand with confidence through all of the ups and downs of life; she has taught me that even the largest task can be accomplished if it is done one step at a time.

Many thanks to my mother-in-law, Victoria, who has never stopped praying for my success in life and who has supported me with all means throughout my studies. Special thanks are due to my wife, Nouf, who has always been there for me and has never failed to give me encouragement and emotional support along with unconditional love. My wife believed in me before I started believing in myself and helped me to make my dreams come true.

Also, this research work is dedicated to my daughters: Mariam, who wants to be a great eye doctor, and Doha, who wants to be a famous interior designer. Both of them continuously admire my accomplishments and show that they are always proud of their father. These feelings inspire and motivate me to rise above any difficulties.

Finally, I also dedicate this work with much love to my two-year-old twins, Liane and Sultan, who are my future dreams and my joy. Having Liane and Sultan waiting for me at the end of every day charges me up and gives me the hope to overcome any challenging tasks in my work.

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First and foremost, I would like to express my deepest gratitude to God, Allah, for blessing me with the ability to gain knowledge and for helping me throughout my life with his mercy and grace to make the impossible possible.

Though only my name appears on the cover of this written research, many people have contributed to its production, without whom it might not have been completed. I cherish and owe my gratitude to all those who have helped to make this research work possible.

My deepest gratitude is to my advisor, mentor, and scientist model, Professor El - Halwagi. I am amazingly fortunate to have an advisor who has given me such thoughtful, patient guidance and support. I hope that one day I will become as good of an advisor for my students as Professor El-Halwagi has been to his students.

Dr. El-Halwagi is one of the best teachers that I have had in my life. He sets very high expectations for his students, then he encourages and guides them to meet or exceed those standards. His teaching continuously inspired me to work hard.

I am tremendously appreciative for the support and aid Professor El-Halwagi gave my family during the difficulties that I faced in the last year of my Ph.D. studies at Texas A&M University.

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I am deeply grateful to Dr. Batchelor for introducing me to the seawater chemistry world and for putting me on the right track toward fundamental resources. Dr. Batchelor has always listened to my concerns and continuously advised me in my research and publications.

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Additionally, I would like to acknowledge Dr. Abdel-Wahab and Dr. Linke from Texas A&M University at Qatar for their many valuable comments and insightful ideas that helped me understand the most complicated areas of my research. I am grateful to both Dr. Abdel-Wahab and Dr. Linke for their contribution to various domains. I would also like to acknowledge Dr. Jimenez for our numerous discussions on related topics that helped to improve my knowledge in my research area.

I would like to thank the professors at Indiana University of Pennsylvania who taught me during my MBA studies and encouraged me to continue my education in engineering through graduate school. Special thanks are due to Professor Krishnan, my academic advisor, for his kind advice and help, and to Professor Al-Bohali who introduced me to the field of optimization and made it one of the most interesting subjects to me. This interest introduced me to Process Integration, my current research area in my chemical engineering graduate studies.

I appreciate the cooperative research with Selma that resulted in my published research work. I am especially grateful to several past and current members of Dr. El-Hawlagi's group, including Nasser, Musaed, Houssein, Younas, Ian, Mohamed, Denny, Fabrecio and many others, whose support and friendship helped me to stay focused on my research and provided me with encouragement.

Finally, I appreciate the financial support from the Ministry of Higher Education (MOHE) for sponsoring my graduate studies and giving me the opportunity to study at one of the best schools in the United States, Texas A&M University. Additionally, I would like to acknowledge the funding from King Abdullah University of Science and Technology (KAUST) and the Qatar National Research Fund (QNRF).

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1. INTRODUCTION

The use of seawater in industrial cooling is a common practice in many parts of the world that have limited freshwater resources. One of the primary operational problems of using seawater in cooling is biofouling, though there are other problems such as scaling and corrosion. The formation of biofilm is caused by the biological activities of microorganisms in the seawater. Biofilms are very thin layer s that stick to the inside surface of heat exchanger tubes that use seawater. As small as a 250 micrometer biofilm thickness is enough to reduce the heat transfer coefficient by 50%. Therefore, biofouling is a serious problem (Goodman 1987).

In some cases, excessive biofouling can obstruct the heat exchangers. To prevent this, biocides are used to control the biological activities of the microorganisms and lessen the effect of fouling. Controlling microbial growth is usually achieved by using an oxidizing agent, such as chlorine, in an easy-to-disperse form, such as a hypochlorous acid or a hypochlorite ion, or in a gaseous form like chlorine gas or chlorine dioxide. An intermittent chlorine dosage of 2–5 mg/L for 10 minutes per day can control microfouling, and a continuous dosage of 0.5 mg/L during the second to fourth week of breeding season can control the blockage caused by macrofouling. Under a continuous biocide dosage, aquatic organisms like oysters and mussels tightly close their shells and often die of asphyxiation. These chlorine forms are most widely used due to cost and effectiveness factors.

This dissertation follows the style of *Chemical Engineering Science*.

Chlorine is a nonselective oxidant (it reacts with organics and inorganics), and it deactivates microbes. Also, chlorine reacts with natural organic matter (NOM), leading to the formation of numerous by-products (Ben Waren, 2006). Some of these by-products are hazardous to aquatic life and human health. While there are other means of preventing biofouling, such as periodic cleaning with sponge balls, tube heating and drying, and antifouling paint, nonetheless, chlorine dosing is the most widely-used method because of its cost-effectiveness and efficiency in controlling different organisms that cause fouling.

Because of the strong interaction between the process cooling demand, operating conditions, and biocide needs and performance, it is important to develop an integrated approach to optimizing biocide usage and discharge by understanding the key process factors and seawater chemistry aspects, then reconciling them in an effective manner. The objective of this paper is to develop a systematic approach to the optimization of biocide usage and discharge by integrating seawater chemistry and process performance issues. This includes modeling the mechanism and kinetics of the biocide, relating the biocide kinetics to process conditions, and reducing biocide usage by lowering the cooling needs of the process via heat integration. The usage and discharge of seawater is linked to the process requirements, including cooling duties. So, any reduction in cooling duties will have a direct impact on the usage and discharge of both seawater and biocide.

1.1. FOULING

Fouling refers to the process of attaching any preventable, unnecessary deposit of organics and/or inorganics onto a wetted tube surface. The unwanted consequences of fouling include directly reducing the amount of heat flowing across the surface and enhancing both the rate of corrosion on the tube and the friction resistance of fluid. There are different types of fouling:

- Crystalline fouling is the precipitation of CaCO3, CaSO4, silicates or other solids.
- Corrosion fouling is the process of oxidizing the metal of the tube surface
- Particulate fouling is the result of the adhesion of particulate matters to the surface.
- Chemical reaction fouling is the deposition caused by chemical reaction that occurs in the fluid or at the fluid/wall interface influenced by autoxidation of the fluid, thermal decomposition process and controlling chemical reaction.
- Biological fouling is the process of attachment and growth of microbial organisms on a surface.

There are three sources where biological fouling takes place:

- Microbial fouling occurs as a result of the development of microorganisms and their products.
- Macrobial fouling is a result of the deposit and growth of macroorganisms like barnacles and mussels.
- Biological fouling is a result of a collection of detritus.

Typically, the development of microbial fouling precedes any macroorganism colonization. Therefore, controlling microbial fouling has a great advantage of avoiding microbial fouling development. Biofouling usually develops over a few steps including biological, chemical, and physical processes. These processes may happen in a series and/or parallel steps. Figure 1.1. shows all of the steps of biofilm accumulation (Characklis, 1979).

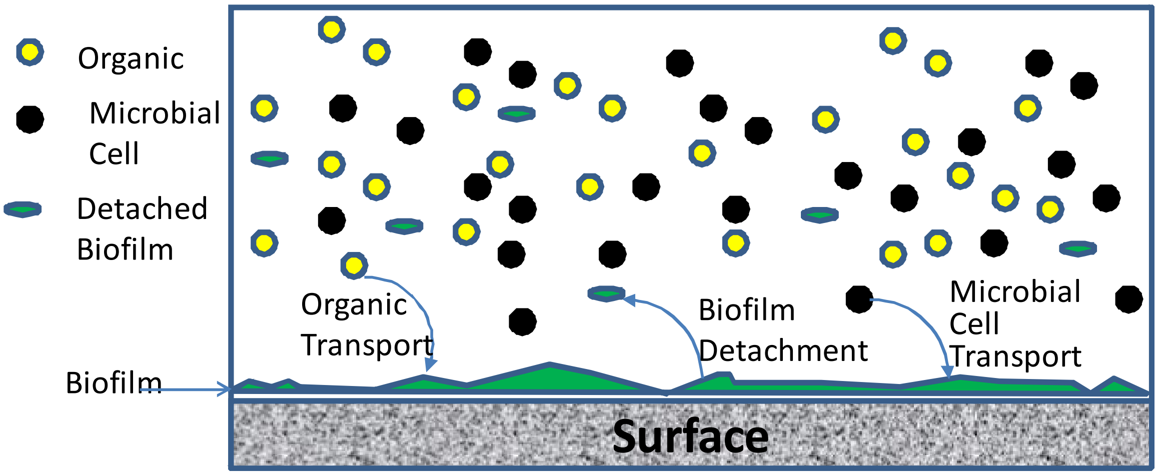

Figure 1.1. Diagram Summarizing the Biofilm Formation and Detachment Processes (Adapted from Characklis, 1979).

These steps can be described as follows:

- Transportation: the process of transporting the organic molecules and microbial cells in the fluid from bulk to the tube surface; this happens within the first minutes.
- Adsorption: mainly the process of organic molecule adsorption and sedimentation on the surface of the tube.
- Adhesion: the microbial cell adhesion to the tube surface and started with reversible followed by irreversible adhesion.

- Production: the attached microbial cells start producing, which is the major factor of biofilm development.
- Detachment: the sheer stress of the fluid plays a major role in detaching some of the developed biofilm from the beginning, but now the rates of attachment and growth of microbial cells are higher (up to a certain level of biofilm thickness which is called viscous sublayer). Then, detachment due to sheer stress will control the thickness of the biofilm.

1.2. ANTIFOULING

Antifouling agents are used in order to control the growth of biological organisms that play a great role in biofouling. Biocides are applied as disinfectants to eliminate, or at least reduce, the biological activities that contribute to biofouling and blocking of the cooling systems. Chlorine and chlorine products are among the most common biocides because of their relatively low cost and high effectiveness. Seawater may be chlorinated by diffusing chlorine gas, electrolyzing the seawater to produce chlorine, or adding a chlorinated solution such as sodium hypochlorite. Other forms of chlorinated disinfectants include chloramines (e.g., NH_2Cl, $NHCl_2$, and NCl_3) and chlorine dioxide.

Other biocides include ozone and ultraviolet radiation, but both are relatively high in cost compared to chlorine. Ozone has not been commercially utilized due to the high risk of possible leakage. A low concentration of ozone, i.e. 0.3 ppm, is considered to be harmful to workers and to the surrounding environment. Ultraviolet radiation is a n effective disinfection method; however, its applicability is limited to cases when the water has little turbidity and suspended matter. Also, there is no residual disinfection effect after the radiation.

Preventing biofouling can be alternatively achieved by hydromechanical and chemical methods. The primary chemical method is using surfactants to reduce the adhesion forces of the biofilm to the surface of heat exchangers. This method is used to reduce the development of the biofilm on the inside surface of the heat exchangers' tube. Other methods use mechanical means (e.g., rotating brushes and sponge balls) for regular scheduled cleaning, either on- or off-line (Langford, 1977). Other mechanical means include pulsating hot solutions (e.g. hot seawater) on a regular basis. The hot solution should be at a temperature hot enough to deactivate the microorganisms. But, by far, biocide dosing (primarily chlorination) is the most widely-used approach in industries. This is attributed to industrial reliability, large –scale applicability, effectiveness in disinfecting various forms of microorganisms in seawater, and cost -effectiveness.

1.3 ENVIRONMENTAL PROBLEMS OF CHLORINE

Using chlorine is not trouble-free. Discharging chlorine and its by-products back into natural bodies of waters with no treatment would definitely create some environmental problems. Chlorine is a nonselective oxidant. In seawater, chlorine and its various forms may react with organic species that exist in natural water, producing hazardous compounds. Examples of these compounds are trihalomethanes (THMs), halogenated acetic acids (HAAs), and halophenols (HPs), which are carcinogenic for human health and aquatic life. THMs are formed from a reaction of chlorine with natural organic matter. THMs are chemical compounds of methane, replacing the three hydrogen atoms with halogens like tri-chlorinated/ brominated methane demonstrated as (CHX_3):($CHCl_3$), ($CHBr_3$). THMs are environmental pollutants and they may cause damage to the liver, kidneys, and central nervous system. HAAs are acetic acids with H - atoms (fixed to a COOH-group) replaced by halogen atoms. HAAs are suspected to raise the risk of cancer. HAAs could form THMs during biological decomposition. THM and HAA concentrations are higher during the summer season than in winter. Also, THM and HAA concentrations increase in that water comes from the surface, rather than from groundwater.

1.4 DECHLORINATION

With no chlorine compound removal treatment, the effects of chlorine and its by-products will carry on disinfecting microorganisms, and they are very toxic to aquatic life when discharged back to the environment at a level higher than the safe level. Chlorine compounds are always maintained at a certain level throughout the cooling system to control biofouling. Proper treatment is required to keep a sustainable surrounding environment and to prevent the aquatic life from any damages.

Dechlorination is a process designed to remove, or at lease reduce, the concentrations of chlorine and its products at the discharged point. Chemical reduction using sulfur compounds has been used as a dechlorination agent to remove free and combined residual chlorine. Sulfur compounds like sulfur dioxide (SO_2), sodium sulphite (Na_2SO_4), bisulfite ($NaHSO_3$), or bisulphate ($NaHSO_4$) and sodium thiosulphate ($Na_2S_2O_3$), or sodium metabisulfite ($Na_2S_2O_5$), have been used to dechlorinate seawater in industrial cooling systems before discharging to the sea. Different dechlorination methods have been utilized in the industry, including activated carbon, activated carbon combined with ozonation, and photochemical reduction with ultraviolet irradiation.

Pyle (1960) and Beeton (1976) found that sodium sulfite (Na_2SO_3) was the most economically effective, the safest, and the most capable of eliminating the toxicity of residual chlorine for the aquatic life. Sodium sulfite is added at a 2:1 ratio by weight with residual chlorine in order to completely and instantaneously eliminate chloramines. However, the disadvantage of using sodium sulfite is that it requires an accurate injection system and a periodic follow-up with chlorine fluctuating in influent water.

In the industry, it was found that sulfur dioxide is the most cost-effective dechlorinating agent. Sulfur dioxide is added at a weight ratio of 0.9 of sulfur dioxide for every 1.0 of chlorine to be removed. But, practically a 10% excess amount of sulfur dioxide is always added to make sure that the dechlorination process is completed. Sulfur dioxide is the most widely used in the industry because of its high effectiveness in removing both free and combined residual chlorine in a very cost-effective way. Also, sulfur dioxide can be fed using similar equipment as is used for chlorination with a simple control scheme.

Sulfur dioxide hydrolysis happens in water rapidly and completely to form sulfuric acid, as shown in the following reaction:

$$SO_2 + H_2O \rightarrow H_2SO_3 \qquad \text{Equation 1.1}$$

The oxidation number of the aqueous sulfur (SO_3^{-2}) is four, which means it will react with free and combined chlorine rapidly and completely, as shown in the following equations:

$$SO_3^{-2} + HOCl \rightarrow SO_4^{-2} + Cl^{-} + H^{+} \qquad \text{Equation 1.2}$$

$$SO_3^{-2} + NH_2Cl + H_2O \rightarrow SO_4^{-2} + Cl^{-} + NH_4^{+} \qquad \text{Equation 1.3}$$

2. BACKGROUND AND LITERATURE REVIEW

2.1. OVERVIEW

Using seawater in cooling systems is a common practice in many parts of the world where there is a shortage of freshwater. However, biofouling is one of the major operational problems associated with the usage of seawater in cooling systems, beside other problems like corrosion and scaling. A biocide is typically added to eliminate or reduce biofouling. This work provides a critical review of the usage, chemistry, and discharge of biocides for seawater cooling systems. The following categories are covered:

- Characteristics of seawater impacting biocide chemistry
- Reaction pathways
- Factors impacting biocide performance
- Measurement of biocides
- Treatment of biocide discharges

The work focuses on information and data that are particularly useful in the modeling, design, and operation of seawater cooling systems.

2.2. INTRODUCTION

The scarcity of freshwater resources in particular industrial regions of the world leads to extensive use of seawater for industrial cooling. One of the primary operational problems of using seawater in cooling is biofouling, though there are other problems such as scaling and corrosion (Freese et al., 2007). The formation of bioflim is caused by the biological activities of microorganisms in the seawater. Biofilms are very thin layers of bacteria and algae that stick to the inside surface of heat exchanger tubes that use seawater and can cause serious operational problems (Goodman, 1987). As small as a 250 micrometer biofilm thickness is enough to reduce the heat transfer coefficient by 50% (Goodman, 1987). There are two broad categories of biofouling: macroscopic and microscopic. In macrofouling or macroinvertebrate fouling, clams, barnacles, and mussels block the seawater from properly flowing through the heat exchangers. On the other hand, microbiologic fouling or microfouling is caused by the growth of slime and algae.

Biofouling results in major operating costs for cleaning, repairing, and additional utilities (Nadine, 1984). There are several methods for preventing biofouling, such as periodic cleaning with sponge balls, tube heating and drying, and antifouling paint. Nonetheless, biocide (e.g., chlorine) dosing is the most widely-used method because of its cost-effectiveness and efficiency in disinfecting different microbial forms. Owing to the strong interaction between the process cooling demand, operating conditions, and biocide needs and performance, it is important to develop an integrated approach to optimizing biocide usage and discharge by understanding the key process factors and seawater chemistry aspects, then reconciling them in an effective manner. While much work has been done in the area of biocide usage and the associated chemistry, there is a major literature gap in a single source providing a comprehensive and an integrated view of this important topic. The objective of this work is to provide a critical and integrated review of biocide usage and discharge for industrial seawater cooling systems and the associated water chemistry and biofilm characteristics (Kim et al., 2001). This work focuses on critical data, information, and models that can be effectively used to guide the design, operation, troubleshooting, and optimization of seawater cooling systems. The review is categorized into the following sections:

- Characteristics of seawater impacting biocide chemistry
- Reaction pathways
- Factors impacting biocide performance
- Measurement of biocides
- Treatment of biocide discharges

2.3. CHARACTERISTICS OF SEAWATER IMPACTING BIOCIDE CHEMISTRY

Several seawater characteristics impact the biocide chemistry. These include concentration of ammonia, bromide, and organic carbon, pH, and salinity. Ammonia concentration in seawater typically ranges from 1.0 ppb to 1.0 ppm, and as the salinity increases, the ammonia concentration decreases (Lietzke, 1977). As the ammonia concentration decreases, it causes a shift from combined oxidants to free oxidants (e.g., HOBr) (Lietzke, 1977). Bromide concentration is very low in freshwater, but can go up to 65 ppm in high salinity seawater (Lietzke, 1977; Minear et al., 2004). As organic carbon content decreases, there is a corresponding reduction in demand for the biocide dosage. There are un-reactive chemical constituents in marine or estuarine waters from chlorination. These constituents, such as sulfur, manganese ion, and iodide, play a key part in the chlorination of seawater. Components such as (Org-C, NO_2-N, S, Mn, Fe) are oxidized to inert products like carbon dioxide and carboxylic acids, which help chlorine residuals disappear. Components such as (NH_3-N, Org-N, Br, I) react to produce oxidative products or biocide. Chlorine-produced oxidants are mainly formed from chlorinating bromide, inorganic amino-nitrogen and organic amino-nitrogen (Helz et al., 2005).

A low oxidant level means low chlorinity at the transition from chlorine to bromine dominance. At a low ratio of ammonia-nitrogen to total oxidant, the free bromine species, HOBr and OBr^-, are predominant. On the other hand, halogenation happens to the aminated compounds in a high ammonia concentration.

At low ammonia-nitrogen concentration and pH 6-8, the important oxidant species are HOBr, OBr-, and NBr_3. But at high ammonia-nitrogen levels and same pH range (6-8), the important oxidant species is first $NHBr_2$ and then NH_2Br and NH_2Cl (Helz et al., 2005). Chlorination of river water produces predominantly $CHCl_3$, while, chlorination of sea or estuarine water would produce mainly $CHBr_3$. Chlorination of seawater, with NaCl to 5 mg/liter as Cl_2, at pH 8.1 and 0.01 mg/liter of natural ammonia-nitrogen, would produce $CHBr_3$ in one hour as the only trihalomethane. This shows that chloramines do not react with organic matter during water treatments (Helz et al., 2005). Chlorination of marine water with more than 3 g/Kg and at pH range 6-8 would produce five important oxidants (HOBr, OBr-, NH_2Br, $NHBr_2$, NBr_3). At conditions where NH_4 is rich in seawater, trihalomethane yield would become less, and bromamines would replace HOBr to reach equilibrium, and NH_2Cl would become dominant (Helz et al., 2005). Residual oxidants decay slowly in high salinity water (Richardson et al., 1981).

2.4. SEAWATER SALINITY AND DENSITY

The salinity of any seawater can be calculated by the sum of salts. Conductivity of seawater, one of the important characteristics, can be used to determine its salinity. Cl has 64% and Na has 25% contribution in seawater conductivity, as shown in Table 2.1.

Table 2.1. Relative Conductivity Contribution of Seawater Salt Composition at 1 atm, 356 Salinity, and 230C (Drumeva, 1986).

Ion	Cl^-	Na^+	Mg^{2+}	SO_4^{2-}	K^+	Ca^{2+}	Br^-	HCO_4^+
Contribution %	64	29	2.7	2.3	1.1	0.77	0.12	0.06

The conductivity-density-salinity-chlorinity relationships for estuarine waters were also examined. The difference between the actual salinity and the salinity measured from conductivity was 0.047. Also, the difference between measured and calculated salinity was 35 x 10^{-6} g/cm^3. The limitation of using the Practical Salinity Scale is to determine the conductivity-density-salinity-chlorinity relationships for estuarine waters. River water has 105.7 g of salt, and the chlorinity is 0.008 g for every 1 Kg. Therefore, assuming seawater has the same composition, the total salt in grams as a function of chlorinity is represented as:

$$g_T\,(\mathrm{est}) = 0.092 + 1.80271\,\mathrm{Cl} \qquad \text{Equation 2.1}$$

where Cl is grams of chlorinity in 1 Kg of solution. Chlorinity in this mathematical expression is the mass of chlorine representing the equivalent total mass of halogen contained in one kilo of seawater.

Total salinity of estuarine water is $S_t = g_t / 1.00488$:

$$S_T = 0.092 + 1.80183\ Cl \qquad \text{Equation 2.2}$$

From the conductivity ratios (R_{24}) at 24^0C, conductivity salinity (S_{COND}) is measured as shown in this equation (Millero, 1984):

$$S_{COND} = 0.044 + 1.803898\ Cl \qquad \text{Equation 2.3}$$

Millero and Poisson (1981) developed an expression relating seawater density to salinity as shown below:

$$S_{DENS} = 0.092 + 1.80186\ Cl \qquad \text{Equation 2.4}$$

For low chlorinity (below 2.0) the result shows that the conductivity is 0.94 times lower. So the true salinity can be measured as (Millero, 1984):

$$S_T = 0.131 + 1.78982\ Cl \qquad \text{Equation 2.5}$$

Also, S_{COND} and S_{DENS} can be measured by the Practical Salinity Scale and International Equation of State (Millero, 1984):

$$S_{COND} = 0.084 + 1.8028\ Cl \qquad \text{Equation 2.6}$$

$$S_{DENS} = 0.092 + 1.7996\ Cl \qquad \text{Equation 2.7}$$

with errors of +/- 0.004 in salinity and 50 x 10^{-6} $g.cm^{-3}$.

These errors can be accepted. Therefore, the estuarine density and conductivity can be calculated without the detailed knowledge of ionic composition. Total salt concentration varies from ocean to ocean, but the composition of its constituents and the ratio of principal ions to chlorinity are constants. Salinity as a function of chlorinity is defined with this expression (Millero, 1984):

$$\text{Salinity} = \text{chlorinity} \times 1.805 + 0.03 \qquad \text{Equation 2.8}$$

2.5. PROBLEMS FROM USING SEAWATER FOR COOLING

Seawater is typically used in industry as once-through systems or by using cooling towers. If the ambient temperature drops below 10o C, the fouling problem is significantly reduced (Helz et al., 2005). The kind and number of the microorganisms that colonize on the metal surface are determined by the type and electrical potential induced by the electrochemical polarization of the metal. There are two main factors impacting microorganism adhesion to surfaces (Wagner et al., 2004):

- Surface characteristics of the cell (e.g., hydrophobicity)
- Substratumnature including composition and chemistry.
- Substratum can be defined as the material in which an organism grows and attached.

It is not clear what metal characteristics have key influence on the adhesion force of microorganisms to metal surface (Wagner et al., 2004).

Typically, the development of microbial fouling precedes any macroorganism colonization. Therefore, controlling microbial fouling has a great advantage of avoiding macrobial fouling development. Biofouling usually develops over a few steps including biological, chemical, and physical processes. These processes may happen in a series and/or parallel steps. Figure 2.1 from Characklis et al., (1979) shows all of the steps of biofilm accumulation.

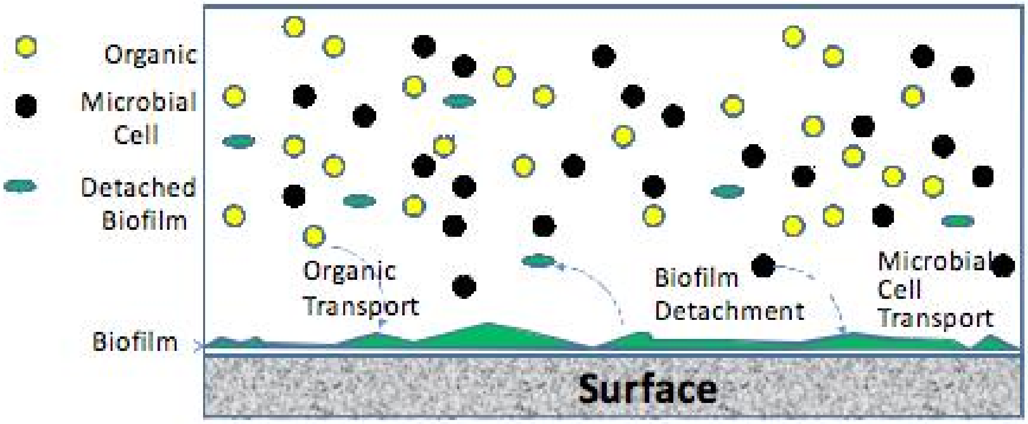

Figure 2.1. Diagram Summarizing the Biofilm Accumulation and Detachment Processes (Characklis et al., 1979).

The steps can be described as follows:

- Transportation: the process of transporting the organic molecules and microbial cells in the fluid from bulk to the tube surface; this happens within the first minutes.
- Adsorption: mainly the process of organic molecule adsorption and sedimentation on the surface of the tube.
- Adhesion: the microbial cell adhesion to the tube surface, started with reversible adhesion and followed by irreversible adhesion.
- Production: the attached microbial cells start producing, which is the major factor of biofilm development.
- Detachment: the sheer stress of the fluid plays a major role in detaching some of the developed biofilm from the beginning, but now the rates of attachment and growth of microbial cells are higher (up to a certain level of biofilm thickness which is called viscous sublayer). Then, detachment due to sheer stress will control the thickness of the biofilm.

2.6. AVOIDING SEAWATER PROBLEMS

Controlling microbial growth is usually achieved by using an oxidizing agent, such as chlorine, in an easy-to-disperse form, such as a hypochlorous acid or a hypochlorite ion, or in a gaseous form, like chlorine gas or chlorine dioxide. An intermittent chlorine dosage of 2–5 mg/L for 10 minutes per day can prevent microfouling, and a continuous dosage of 0.5 mg/L during the second to fourth week of breeding season can prevent the blockage caused by macrofouling (Characklis et al., 1979). Under a continuous biocide dosage, aquatic organisms like oysters and mussels tightly close their shells for weeks at a time, but they often die of asphyxiation (Macdonald et al., 2009). These chlorine forms are most widely used due to cost and effectiveness factors. Chlorine is a nonselective oxidant (it reacts with organics and nonorganics), and it deactivates microbes (Venkatesan et al.; Verween et al., 2009). Also, chlorine reacts with natural organic matter (NOM), leading to the formation of numerous by-products (Ben Waren et al. 2006). Some of these by-products are hazardous to aquatic life and human health.

2.7. COMMONLY USED BIOCIDES

This section provides basic information on the following commonly used biocides:

- Chlorine
- Bromine
- Ozone

2.7.1. CHLORINE

To avoid slime accumulation, corrosion, and reduction in heat transfer efficiency, chlorine is typically used in doses of 0.5-10 mg/l for 30 minutes to several hours. Chlorine and its organic and inorganic byproducts are used as antifouling control agents (Helz et al., 2005; Shiga et al., 1995).

Another way of getting chlorine into water is by electrochlorination (Lattemann et al., 2008). Producing chlorine and hypochlorite by electrolytic cells has been a commonly used method in the industry. Anodic oxidation, electrochemical disinfection, or electrochemical treatments are typically used in water treatment processes for disinfection. (Nagarajan et al., 2010) These processes produce hypochlorous acid or hypochlorite as the main disinfecting agents from the chloride ion which naturally exists in water at 10 – 250 mg dm^{-3} or more (Rennau et al., 1990).

The electrochemical disinfection process has advantages over chlorination by using chlorine gas or a hypochlorite solution. Advantages include not requiring chemicals to be added and staying away from the risk of transporting and storing chemicals. Ultraviolet radiation and ozonation treatments are very effective but do not have any disinfecting residual byproducts (Rennau et al., 1990).

In order to obtain an accurate measurement of hypochlorite production rate, it is required to consider chlorine decay or chlorine consumption due to the rapid chlorine reaction with oxidizable agents in water and the apparatus. Hypochlorite is produced in electrolytic in the following two steps and then dissociation (Rennau et al., 1990):

- Oxidizing chloride to chlorine at the anode surface:

$$2\,Cl^- \rightarrow Cl_2 + 2\,e^- \qquad \text{Equation 2.9}$$

- Solution phase reaction:

$$Cl_2(aq) + H_2O \rightarrow HClO + Cl^- + H^+ \qquad \text{Equation 2.10}$$

- Dissociation of hypochlorous acid to form hypochlorite and H^+ which depends on water pH:

$$HOCl \rightarrow ClO^- + H^+ \qquad \text{Equation 2.11}$$

2.7.2. BROMINE

Bromine is used as a disinfectant for drinking water, wastewater, swimming pools, and cooling water (Inman 1984). Bromide concentration and contact time are the main factors for bromate formation in non-photolyzed ozonation of seawater (Richardson et al., 1981). Oxidant decay and bromate production may vary according to the natural existence of organic or nitrogenous compounds (Richardson et al., 1981).

2.7.3. OZONE

Ozonation of seawater leads to oxidation of Br^- to OBr^-, which competes with hydroxide-catalyzed decay of ozone through production of free radicals:

$$O_3 + Br^- \rightarrow OBr^- + B_2 \qquad \text{Equation 2.12}$$

The half-life of O_3 is 30 seconds at 0^0C and less than 30 seconds at higher temperatures (Richardson et al., 1981). Bromide exists in nature and can be oxidized to form bromate. The free bromine ($HOBr/OBr^-$) reacts with ozone to eventually form bromate. Ammonia reacts with free bromine to form bromamines. This ammonia reaction decreases bromate concentration (Freese et al., 2009).

2.7.4. LOOP EXPERIMENTS OF TREATING SEAWATER

This experiment was conducted with four loops. One loop, the control, had no treatment; the other three were pulsed discharge, continuous NaClO injection, and pulsed NaClO injection. The pulsed discharged loop used shockwaves, UV light, the electric field, and radicals. Each loop consisted of three sections of different flow rates: 1.1, 1.8, 3.0 m/s. Each section was composed from three different pipe materials (Poly-Ethylene, FRP, and Nylon) of 50 cm length. The pulsed injection was 3 ppm for the duration of one hour, repeated three times a day. The continuous injection was made at 0.6 ppm and measured 0.2 ppm by the end of the cooling loop. The results were checked after a period of two months (Obo et al., 2000). The conclusion of this experiment was that the flow rate of water of 3.0 m/s or higher will prevent the growth of sludge and barnacles in the pipes. However, at flow rates lower than 3.0 m/s, the water has to be treated. Therefore, it is found from Obo's experiments that adding NaClO by way of continuous dosing will prevent the growth of both sludge and barnacles. The results of these experiments are summarized in Table 2.2.

Table 2.2. Experimental Results of Treating Seawater (Obo et al., 2000).

Loops	*Flow (m/s)*		
	1.1	1.8	3.0
Control	Thick sludge film & many barnacles	Same as in 1.1 m/s	No attachment
Pulsed Discharged	Thin sludge film & no barnacles		
Pulsed NaClO	No sludge film & small # of barnacles		
Continuous NaClO	No sludge & no barnacles		

2.8. HALOGEN CHEMISTRY IN SEAWATER

The next two subsections provide a description of the chemical path ways involved when chlorine and bromine are used as biocide.

2.8.1. CHLORINE REACTION

Let us first start with some of the overall reactions involved when chlorine is added as a gas to seawater. Bin Mahfouz et al. (2009) have constructed the reaction mechanism shown in Figure 2.2. On this diagram, starting species and intermediate and final byproducts are represented in boxes. Arrows correspond to reaction steps. Boxes on the arrows represent reactive species that contribute to that reaction. First, chlorine will dissolve and hydrolyze rapidly and completely to HOCl (hypochlorous) acid:

$$Cl_2 + H_2O \leftrightarrow HOCl + HCl \qquad \text{Equation 2.13}$$

Hypochlorous acid is a strong biocide, but it is a weak acid that will dissociate to hydrogen and hypochlorite ions:

$$HOCl \leftrightarrow H^{+} + OCl^{-} \qquad \text{Equation 2.14}$$

where OCl- is the hypochlorite ion. In terms of disinfection effectiveness, hypochlorous acid is much stronger (almost two orders of magnitude) than the hypochlorite ion. Since, the hydrogen ion appears on the right side, this reaction is pH-dependent. Hypochlorous acid will reach its maximum concentration at pH ranges between 4 and 6 (Hostgaard-Jensen et al. 1977). However, the effectiveness of a chemical as a disinfectant may not be the same as its effectiveness in removing biofilms. Controlling biofilm is achieved by weakening the polysaccharide matrix of microbial cells. There is experimental evidence that shows that chlorination is more effective in causing biofilm detachment at pH values greater than pH 8, where OCl^- concentration is more dominant than HOCl (Characklis et al., 1979).

Usually, seawater contains organic and non-organic species. Of particular importance are ammonia and bromide species. Ammonia, as well as other reactive nitrogenous compounds, will be chlorinated to yield monochloramine (NH_2Cl), dichloramine ($NHCl_2$), and trichloramine (NCl_3). by replacing the hydrogen atom of the ammonia molecule with a chlorine atom while maintaining its positive charge according to the following reactions:

$$HOCl + NH_3 \rightarrow NH_2Cl \text{ (monochloramine)} + H_2O \qquad \text{Equation 2.15}$$

$$NH_2Cl + HOCl \rightarrow NHCl_2 \text{ (dichloramine)} + H_2O \qquad \text{Equation 2.16}$$

$$NHCl_2 + HOCl \rightarrow NCl_3 \text{ (trichloramine)} + H_2O \qquad \text{Equation 2.17}$$

These reactions depend on pH, temperature, contact time, but mainly on chlorine to ammonia ratio. All of the free chlorine (hypochlorous acid) will be converted to monochloramine at pH 7-8 (fastest conversion is at pH 8.3) when there is 1:1 molar ratio of chlorine to ammonia (5:1 by wt.) or less. Then, within the same range of pH, dichloramine is produced at a molar ratio of 2:1 of chlorine to ammonia (10:1 by wt.). This reaction is relatively slow, so it may take an hour. Also, within the same range of pH, trichloramine will be produced at a molar ratio of 3:1 of chlorine to ammonia (15:1 by wt.) and at equal molar ratios but at pH 5 or less. The two reactions producing di - and tri-chloramine are known as the breakpoint reactions where the chloramines are reduced suddenly to the lowest level. The significance of breakpoint reaction is that chlorine reaches its highest concentration and germicidal efficiency (at 1:1 molar ratio of chlorine to ammonia) just before reaching this point. Also, at the breakpoint monochloramine and dichloramine react together (which reduces chlorine residuals) to produce nitrogen gas, nitrate, and trichloramine.

Dichloramine decomposes to an intermediate reactive product (NOH) which consumes mono-, di-chloramine, and hypochlorous acid producing nitrogen gas and nitrate. Also, excessive chlorine will form trichloramine.

$$NHCl_2 + H_2O \rightarrow NOH + 2\ H^+ + 2\ Cl^- \qquad \text{Equation 2.18}$$

$$NOH + NH_2Cl \rightarrow N_2 + H_2O + H^+ + Cl \qquad \text{Equation 2.19}$$

$$NOH + NHCl_2 \rightarrow N_2 + HOCl + H^+ + Cl^- \qquad \text{Equation 2.20}$$

$$NOH + 2\ HOCl \rightarrow NO_3^- + 3\ H^+ + 2\ Cl^- \qquad \text{Equation 2.21}$$

$$NCl_3 + H_2O \rightarrow NHCl_2 + HOCl \qquad \text{Equation 2.22}$$

The reaction of chlorine into these forms steer it away from the disinfection function and render the biocide less effective. Consequently, it is important to understand such side reactions.

Hypochlorous acid rapidly reacts with bromide producing hypobromous acid, which also can be produced from the reaction of bromide with monochloramine as follows:

$$HOCl + Br^{-} \Leftrightarrow HOBr + Cl^{-}$$ Equation 2.23

$$NH_2Cl + Br^{-} + H_2O \rightarrow HOBr + Cl^{-} + NH_3$$ Equation 2.24

where HOBr is hypobromous acid. Additionally, the hypochlorite ion may undergo a slow reaction with the bromide ion as follows:

$$OCl^{-} + Br^{-} \Leftrightarrow OBr^{-} + Cl^{-}$$ Equation 2.25

where OBr^{-} is the hypobromite ion. Bromide in seawater may also react directly with added chlorine to give bromine and chloride:

$$Cl_2 + 2Br^{-} \Leftrightarrow Br_2 + 2Cl^{-}$$ Equation 2.26

It is worth noting that the presence of ammonia and other nitrogenous compounds in the seawater will react with HOBr to yield monobromamine (NH_2Br), dibromamine ($NHBr_2$), and tribromamine (NBr_3):

$$HOBr + NH_3 \rightarrow NH_2Br \text{ (monobromamine)} + H_2O$$ Equation 2.27

$$HOBr + NH_2Br \rightarrow NHBr_2 \text{ (dibromamine)} + H_2O$$ Equation 2.28

$$HOBr + NHBr_2 \rightarrow NBr_3 \text{ (tribromamine)} + H_2O \qquad \text{Equation 2.29}$$

The bromine breakpoint happens when the dibromamines are produced rapidly, leading to the formation of nitrogen gas:

$$NHBr_2 + H_2O \rightarrow NOH + 2\ H^+ + 2\ Br^- \qquad \text{Equation 2.30}$$

$$NOH + NHBr_2 \rightarrow N_2 + HOBr + H^+ + Br^- \qquad \text{Equation 2.31}$$

It is also important to consider the effect of bromide which naturally exists in seawater at (50 – 70 mg/l). This is in stoichiometric excess of chlorine dosage as well as ammonia concentration don't exceed 2 to 3 mg/L. The relative produced amount of bromine species to ammonia species is proportional to bromide concentration over ammonia concentration if we assume both reactions are rapid and simultaneous.

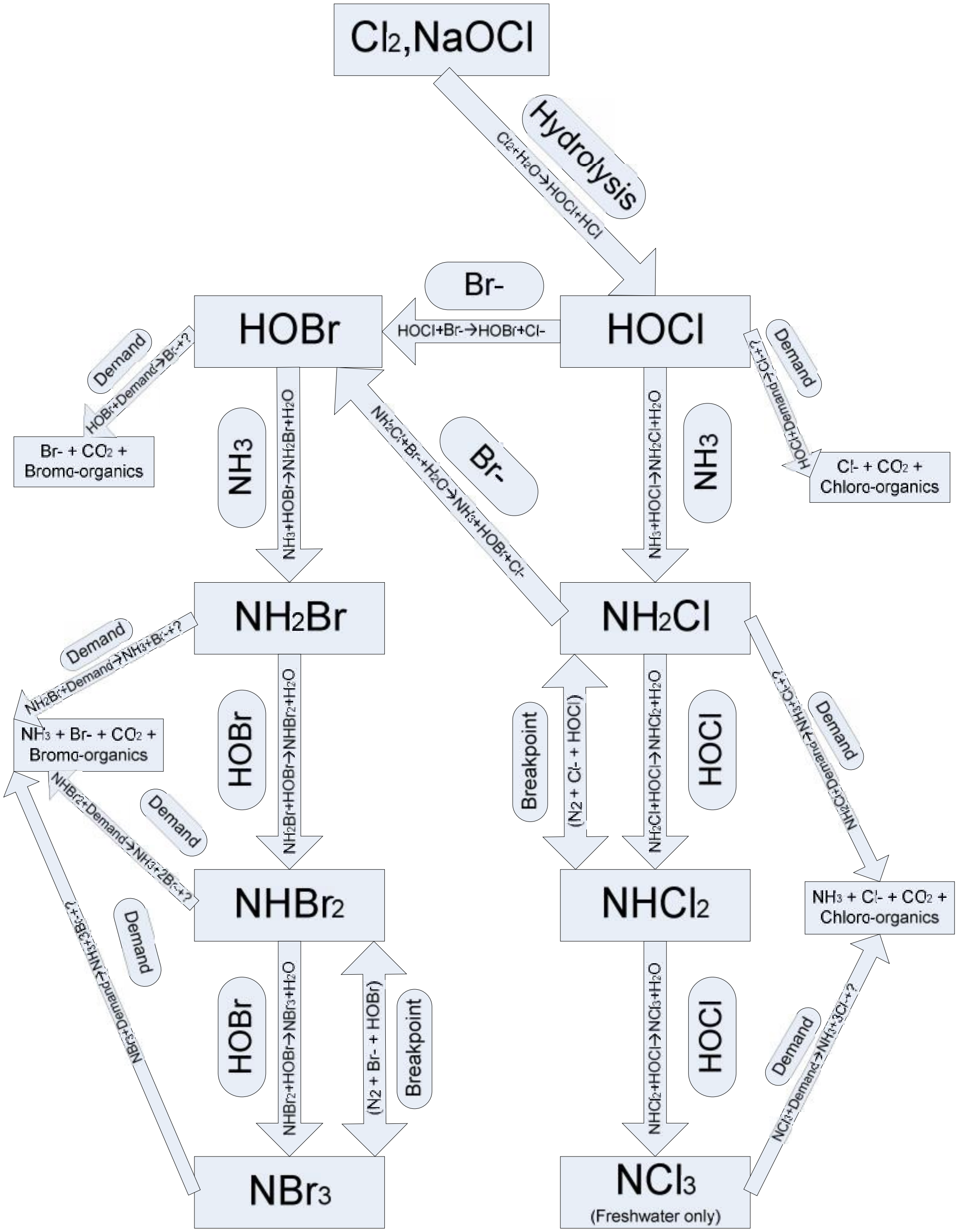

Figure 2.2. Reaction Mechanism for Seawater Reactions Upon Chlorination (Bin Mahfouz et al., 2009).

The following is a more detailed analysis of the key reaction steps which may be broken down into:

1) Hydrolysis

Chlorine as gas (Cl_2) is added to water to form hypochlorous acid (HOCl), or by adding a solution containing caustic producing hypochlorite which reacts with water to form hypochlorous acid (HOCl). This reaction is called hydrolysis of chlorine gas (White, 1999):

$$\mathrm{Cl_2 + H_2O \rightarrow HOCl + H^+ + Cl} \qquad \text{Equation 2.32}$$

Hydrolysis of chlorine gas needs a few tenths of a second at 64° F and a few seconds at 32° F.

$$\mathrm{Cl_2} + OH^- \leftrightarrow HOCl + Cl^- \qquad \text{Equation 2.33}$$

Free chlorine residual is the total chlorine residual. Available chlorines are double the amount of existing chlorine by weight, reflecting the oxidation power of the compound. Total chlorine is simply the sum of the combined and free levels (White, 1999).

2) Formation of chloramines

At ammonia nitrogen levels greater than 0.5 mg/l and with a chlorine dose less than 2.5mg/l, dibromamine and monochloramine become the predominants. At a higher ammonia concentration with a longer time, monochloramine will be the main component. However, at a lower ammonia nitrogen concentration (less than 0.4mg/l) with a high chlorine dose, tribromamine and hypobromous acid are going to be the major products (Johnson et al., 1982). The main factors determining the predominance of either chloramines or bromamines are bromide concentration or salinity, ammonia nitrogen concentration, and pH. If pH is decreased from 8.0 to 7.5, the concentration of ammonia would decrease by a factor of 3, as would the formation of monochloramine (Johnson et al., 1982). The critical ammonia nitrogen to bromide ratio is 0.008 at pH of 8.1. At higher than the critical ratio, monochloramine would be predominant after 30 minutes to one hour; at lower than the critical ratio, dibromamine would be the predominant and there would be a small amount of monochloramine remaining after the bromamine decomposes. One way to avoid forming monochloramine is to add excess chlorine because of its toxicity and low oxidant level. .In cases where there is high salinity, excess bromide exists of more than 100 fold, so only bromamine and bromine would be produced (Johnson et al., 1982).

The inorganic reaction between chlorine and ammonia nitrogen forms monochloramine, dichloramine, and trichloramine in three reactions as chlorine concentration increases up to 50 mg/L. Each reaction involves a chlorine -substituting hydrogen atom in the ammonia. The reactions are dependent of pH, temperature, time contact, initial ratio of chlorine-to-ammonia, and initial concentrations of chlorine and ammonia nitrogen (White, 1999).

$$HOCl + NH_3 \rightarrow NH_2Cl\,(monochloramine) + H_2O \qquad \text{Equation 2.34}$$

$$HOCl + NH_2Cl \rightarrow NHCl_2\,(dichloramine) + H_2O \qquad \text{Equation 2.35}$$

$$HOCl + NHCl_2 \rightarrow NCl_3\,(trichloramine) + H_2O \qquad \text{Equation 2.36}$$

The first reaction is to convert free chlorine to monochloramine at equimolar (5:1 by weight) of chlorine to ammonia or less. The highest conversion (99%) occurs at 8.3 pH at 25° C (White, 1999). The second reaction is to form dichloramine, which is slower than the first reaction at a pH of 7 to 8 with a ratio of 2 moles of chlorine to 1 mole of ammonia. This reaction takes five hours for 90% conversion at pH 8.5, and the reaction speeds up as the pH increases (White 1999). The third reaction is to form nitrogen trichloride at pH 7-8 with the chlorine to ammonia nitrogen mole ratio at 3:1 (15:1 by wt.). Nitrogen trichloride can be formed at an equimolar of chlorine to ammonia nitrogen, but only at 5 pH or less. Also, nitrogen trichloride can be formed at a high pH, such as 9 pH, when the mole ratio of chlorine to ammonia nitrogen is 5:1 (25:1 by wt.) (White, 1999).

Halamine formation reactions are rapid and completed in less than one minute, and they increase as the basicity of amine increases. The hydrolysis of the bond in N -Cl is slower compared to the bond in N-Br, which is very fast. It was assumed that the first order for calculating ammonia level NH2Br formation has to be measured for only inorganic bromamines (Lietzke, 1977). The $NHBr_2$ rate is 200 times slower than $NHCl_2$ formation, and the latter is 1.8 x 10^4, which is slower than that of NH_2Cl (Lietzke, 1977). The NBr_3 rate is 500 times slower than the NCl_3 formation, and the latter is 2.5 x 10^6 times slower than NH_2Cl (Lietzke, 1977). Unmeasured halogenation rates are based on these assumptions:

- The formation of bromamines from hydrolysis is faster than chloramines (Lietzke, 1977).
- The halogenation of organic amines and halamine is faster than inorganic ones.
- Chlorination of bromine is slower than bromination of chloramine and slower than bromination of bromine.

3) Destruction of chloramines

When the ratio of chlorine to ammonia nitrogen exceeds 1:1, monochloramine reacts to the excess free chlorine to form dichloramine, which is twice as germicidal as monochloramine. Zone 3 starts from the dip, or the breakpoint at the curve, which happens when free chlorine starts to appear. There is a lack of understanding of the breakpoint reaction behavior due to many competing reactions of high active chlorine (White, 1999). Breakpoint reactions are caused by the oxidation of ammonia by halogen to produce nitrogen, which simultaneously reduces halogen to halides. Those reactions are considered to be the most rapid reactions at a molar ratio of 1.5 halogen to ammonia because forming trihalamines are more stable. On the other hand, at a lower molar ratio, this reaction would be slower because the oxidant would be limited (Lietzke, 1977).

$$3HOX + 2NH_3 \rightarrow N_2 + 3H_2O + 3H^+ + 3X^- \qquad \text{Equation 2.37}$$

where X is bromine or chlorine.

These are the reactions representing chlorine breakpoint.

$$NHCl_2 + H_2O \rightarrow HNO + 2HCl \qquad \text{Equation 2.38}$$

$$NH_2Cl + HNO \rightarrow N_2 + H_2O + HCl \qquad \text{Equation 2.39}$$

$$NHCl_2 + HNO \rightarrow N_2 + HOCl + HCl \qquad \text{Equation 2.40}$$

$$HNO + 2HOCl \rightarrow HNN_3 + 2HCl \qquad \text{Equation 2.41}$$

An additional dosage of chlorine is needed to oxidize ammonia beyond nitrogen to a nitrate. $NHCl_2$ decomposes slowly at a ratio of Cl/N below 1.5. $NHCl_2$ rarely exists in the total oxidant residual in the case of any Br^- presence. It is very difficult to precisely predict the required dose of chlorine with other amines existent and an unstable demand (Lietzke, 1977).

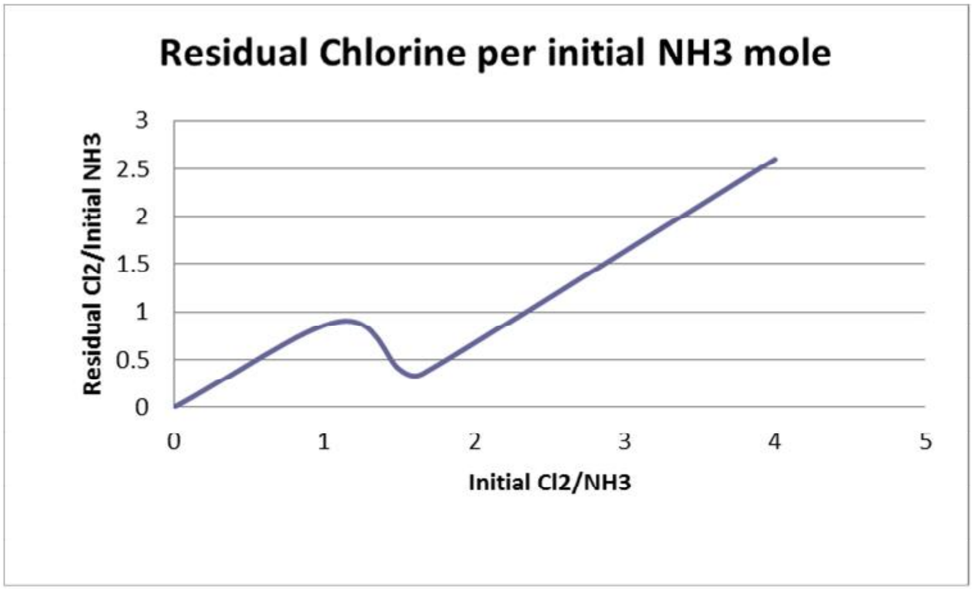

Figure 2.3. Chlorine Breakpoint Model Calculations at T = 200C, pH = 7.0, [NH3]0 = 1.01 mg/l, and Molar Ratio of Cl2/NH3 = 2.63 After One Hour (Based On Results By Lietzke, 1977).

The model shown in Figure 2.3 assumes that there is no chlorine demand and that the only nitrogenous compound that exists is ammonia. When chlorine is added at equal molar or less than ammonia, only NH_2Cl and no (or merely a trace) of $NHCl_2$ are produced. NH_2Cl is more stable with the higher ammonia molar than when chlorine is added, and after one hour, all total residual chlorine is NH_2Cl and equal to the initial chlorine added. If the chlorine dose exceeds the required amount to produce NH_2Cl, $NHCl_2$ will be produced and will decompose to react with NH_2Cl and reduce the total oxidants proportional to $NHCl_2$ formed. The breakpoint is at an equal mixture of both NH_2Cl and $NHCl_2$ and chlorine will be reduced by oxidizing ammonia to nitrogen. After passing the breakpoint, it takes only a few hours to oxidize ammonia. A chlorine dose beyond the breakpoint will remain as a hypochlorite, and the chlorine residual increases with increasing chlorine doses (Lietzke, 1977).

Monochloramine is toxic and persistent, while dibromamine is toxic and not persistent. The natural compounds that exist in seawater play a role in reducing haloamines. Monochloramine is stable in seawater for about 8 months at pH 8. On the other hand, there is a dibromamine decomposition rate of 700 L/mol/min at pH 8, 20^0 C with a half-life of four hours and a bromine concentration of 1 mg/L (Johnson et al.,1977).

4) Formation of organic byproducts

Some chlorination byproducts are carcinogenic and are formed from organic halogenated compounds like THMs, HAAs, HANs, haloketones, chlorophenols, chloral hydrate and chloropicrin (Sayato et al., 1995). Chlorination of seawater produces compounds that are toxic to aqueous life. These compounds' concentrations and lifetimes are functions of pH, temperature, salinity, dissolved organic matter and nitrogen, inorganic nitrogen and the amount of chlorine and mixing efficiency (Freese et al., 2006). The two major components that determine chlorination are bromine and ammonia . Direct toxicity of hypohalites and/or halamines from chlorination is thought to be affecting the aquatic ecosystem. Even low chlorine concentration (0.005 mg/l) would affect fish (Lietzke, 1977). Chlorination of seawater at a Kuwait desalination-power plant results in forming halomethanes, which at high concentration, measures up to 90 ug/l, near the outfalls. 95% of the total halomethanes are made up of bromoform, and the remains are mostly dibromochloromethane. Some of these volatile halogenated hydrocarbons, such as CCl_4, $CHCl_3$, $andCHBr_3$, are harmful to aquatic life (Riley et al., 1986).

Chlorine has an effect on marine life when it is dumped into costal and estuarine waters from sewage treatment plants, electric power plants, and industrial plants. Fish have to migrate to avoid the water area that is polluted with halogenated organic compounds and has ecological effects from chlorination (Helz et al., 2005).

An estimated 0.5-3.0 % of chlorine added to freshwater is transferred to chlorinated organics and mostly is chloroform. With higher salinity, chlorine is converted into more reactive bromine forming bromo-organics and brominated trihalomethanes, such as ($CHCl_2Br$, $CHClBr_2$, and $CHBr_3$). Chloroform and bromoform are carcinogen products and have direct toxicity with rapid bioaccumulation in fish and fish eggs. Peter and his colleagues found a model for trihalomethane concentration at the end of the contact period in freshwater treated with chlorine (Lietzke, 1977):

$$\text{Total haloforms (M)} = 0.01307\,(\text{CDO})\,(1 + 14[\text{Br}^-]^{0.25}) \quad \text{Equation 2.42}$$

where CDO is the molar concentration of Cl_2 that is consumed by organic demand. $[Br^-]$ is the initial molar concentration of bromide. The last term, $14[Br^-]^{0.25}$ is for rapid production of haloform at bromide presence.

The model shows that about 13 mmol of chloroform is produced for every mole of chlorine consumed in freshwater. Generally, kinetics of haloform do not apply when there is with chlorine consumption. Total haloform production does not depend on pH (Lietzke, 1977).

5) Consumption by non-organic compounds

The total chlorine demand is due to nitrogenous compounds and anything that consumes chlorine. Chlorine demand is a non-nitrogenous demand.

The objective of a chlorine demand (CD) model is to relate it to chlorine dosage (CL) at a certain temperature and for given seawater conditions. For example, the following expression is based on the work of Wong et al. at for doses from 0-30 mg/l, shown in Figure 2.4. (Wong et al., 1984):

$$CD = 0.2468 + 0.989CL - 0.02522CL^2 + 9.897 \text{ X } 10^{-4}\ CL^3 - 1.35 \text{ X } 10^{-5}\ CL^4$$

Equation 2.43

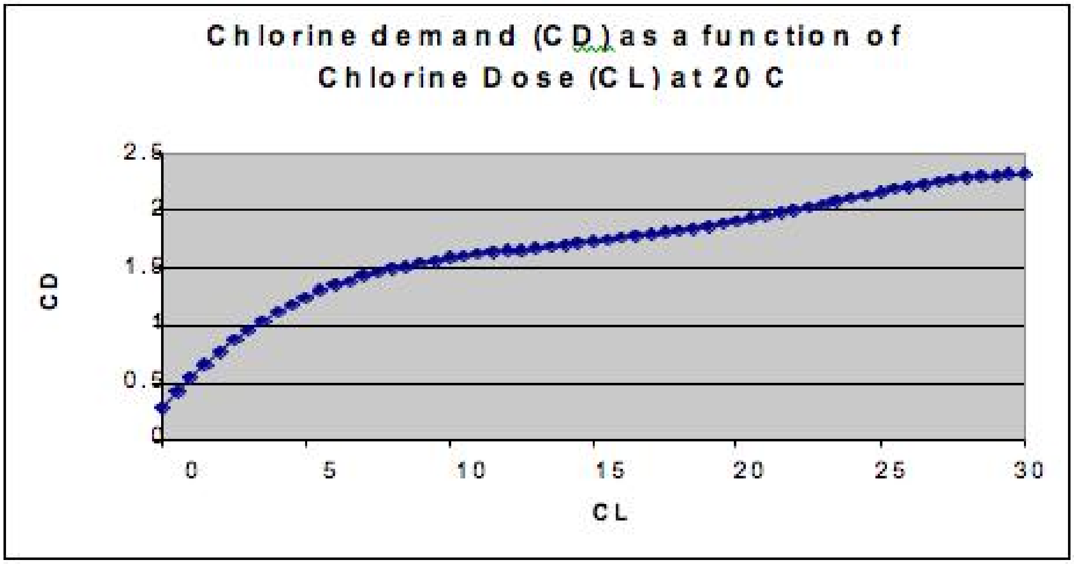

Figure 2.4. Chlorine Demand as a Function of Chlorine Dose at 200 C (Wong et al., 1984).

For freshwater there is no existence of HOBr. Figure 2.4 shows ultimate, non-nitrogenous, chlorine demand as a function of dose and temperature in seawater (Lietzke, 1977).

6) Bromide oxidation

Hypobromous acid is an active chemical constituent and is formed from oxidizing a bromine ion with chlorine in a very fast reaction. Reactions of hypochlorous acid with ammonia and a natural existence of bromide determines domination of bromine compounds or monochloramine (Johnson et al., 1982). Formation of hypobromous acid in open seawater occurs when chlorine oxidizes bromide and converts to chloride in absence of ammonia. But in estuarine or coastal sea water, ammonia concentration increases and bromide concentration decreases, so bromamine is first produced and followed by monochloramine (Johnson et al., 1982). More on the bromide reactions are given in the following subsection.

2.8.2. BROMINE REACTION

The bromine reactions typically proceed through the following steps:

- Formation of acid
- Formation of bromamines
- Destruction of bromamines
- Formation of organic products
- Consumption of non-organic byproducts

More information on these steps follows:

1) Acid-base

Bromine is used as a disinfectant and may be used with chlorine and iodine (I_2). The hydrolysis of bromine in water will produce hypobromous acid and bromide ions. Free available bromine is the concentration of both hypobromous acid and hypobromite ions. Then, hypobromous acid will dissociate into hypobromite and hydrogen ions according to the following equations (Johanneson, 1960):

$$Br_2 + H_2O \leftrightarrow HOBr + H^+ + Br^- \qquad \text{Equation 2.44}$$

$$HOBr \leftrightarrow H^+ + OBr^- \qquad \text{Equation 2.45}$$

2) Formation of bromamines

Hypobromous acid reacts with the ammonia that already exists in most treated waters to produce bromamines (Johnson et al., 1982). Bromamine formation depends on bromide ions as well as ammonia concentration, pH, natural organic content, and chlorine dosage (Minear et al.,. 2004). Inman and John found out that mixing hypobromous acid (HOBr) with ammonia at a pH range of 7.0 to 8.4 would produce monobromamine (NH_2Br). Bromamines including monobromamine, dibromamine, and tribromamine are formed by adding bromine to ammonia as shown in the following reactions (Hofmann et al., 2001):

$$HOBr + NH_3 \Leftrightarrow NH_2Br + H_2O$$
$$K_{eq} = 3.0 \times 10^{10}, \Delta G_f^\circ NH_2Br = 77.1 KJ / mol$$ Equation 2.46

$$HOBr + NH_2Br \Leftrightarrow NHBr_2 + H_2O$$
$$K_{eq} = 4.7 \times 10^{8}, \Delta G_f^\circ NHBr_2 = 181 KJ / mol$$ Equation 2.47

$$HOBr + NHBr_2 \Leftrightarrow NBr_3 + H_2O$$
$$K_{eq} = 5.3 \times 10^{6}, \Delta G_f^\circ NBr_3 = 296 KJ / mol$$ Equation 2.48

3) Destruction of bromamines

Inorganic bromamine will exchange bromine rapidly with pH dependence, while chloramines, mainly monochloramine, do the exchange of chlorine very slow at pH a range from 6 to 9. The breakpoint reaction, which is the oxidation of ammonia to nitrogen gas, of halamines occurs when the molar ratio of halogen to ammonia is 3:2. The breakpoint for chlorine is the reaction between NH_2Cl and $NHCl_2$, while for bromine it is the reaction between $NHBr_2$ and NBr_3. Organic halamines are more stable than inorganic ones. The bromine-ammonia breakpoint is the reaction between di- and tribromamine, whereas in chlorine-ammonia it was between mono- and dichloramine. The bromine-ammonia system is shown as follows (Lietzke, 1977):

$$H_2O + 2HNBr_2 \rightarrow N_2 + HOBr + 3HBr$$ Equation 2.49

$$2H_2O + HNBr_2 + NBr_3 \rightarrow N_2 + 2HOBr + 3HBr \qquad \text{Equation 2.50}$$

$$3H_2O + 2NBr_3 \rightarrow N_2 + 3HOBr + 3HBr \qquad \text{Equation 2.51}$$

The rate constant of reaction (32) is 1000 times larger than reaction (31), and reaction (33) is kinetically insignificant at a pH above 6. It is very difficult to expect which bromamine species exist initially because the breakpoint occurs very rapidly at equal concentration of di- & tri-bromamine.

The differences between all chlorine and all bromine systems are (Lietzke, 1977):

- Bromamine decomposition residuals are so rapid.
- When $NHBr_2$ and NBr_3 exist at a significant amount below breakpoint, it helps decomposition to occur at lower doses; and at a halogen/N ratio of 1.0, the peak would become flat.
- Formation and decomposition of NBr_3 above the breakpoint without evolving N_2, not like NCl_3.
- Nitrate formation is insignificant.

Dibromamine decay rate is the second order with respect to $NHBr_2$ and the half-life is 10-15 hours. There is no specific mechanism of tribromamine formation. But, tribromamine decomposition was studied by LaPoite et al. in 1975 and the result was as follows (Hofmann et al., 2001):

$$2NBr_3 + 3H_2O \rightarrow N_2 + 3HOBr + 3H^+ + 3Br^- \qquad \text{Equation 2.52}$$

At high ammonia to bromine ratios, tribromamine concentration is very low. Bromine decay occurs at the reaction between tribromamine and dibromamine, with an N:Br ratio of 2:3 according to this reaction (Hofmann et al., 2001):

$$2NH_3 + 3OBr^- \rightarrow N_2 + 3Br^- + 3H_2O \qquad \text{Equation 2.53}$$

To oxidize all chlorine, 3.2-3.6 mol of chlorine must be added to every 2 mol of ammonia to reach the breakpoint, according to White's study in 1992 (Hofmann et al., 2001):

$$4HOCl + NH_4^+ \rightarrow NH_3^- H_2O + H^+ + 4Cl^- \qquad \text{Equation 2.54}$$

Adding an excess amount of chlorine, more than the theoretical, is due to side reactions in which bromamines do not decay to form nitrate (Hofmann et al., 2001). Figure 2.5. shows $[NH_2Br]_{eq}/[NHBr_2]_{eq}$ against excess ammonia (Johnson et al., 1982).

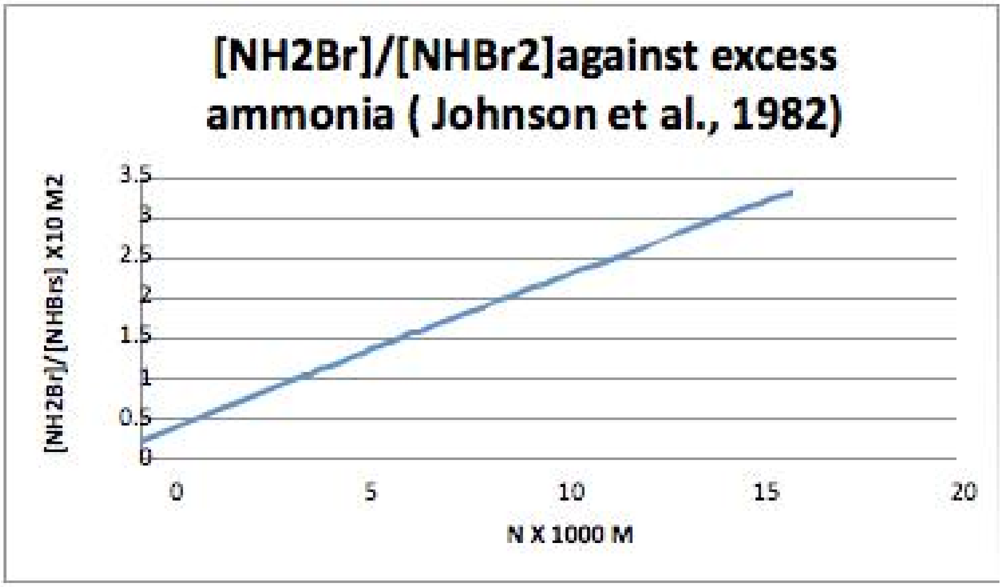

Figure 2.5. Dependence of Bromine Ratio at Equilibrium on Excess Ammonia (Johnson, 1982).

Dibromamine, $NHBr_2$, and tribromamine, NBr_3, are formed at a pH lower than 8.5 and a bromine molar concentration of at least five times the concentration of ammonia (Guy W. Inman 1984). Dibromamine decomposition occurred less than a minute after its formation. At a pH above 7, the rate of formation of monobromamine is much higher than rate of formation of dibromamine. Dibromamine formation was first order in hydrogen ion and second order in monobromamine or an initial bromine in a case with an excess amount of ammonia (Inman et al., 1984).

$d[NH_2Br]/dt = k_1[NH_3][HOBr]$ where, $k_1 = 4 \pm 1 \times 10\ Ms$ at pH 7-8 Equation 2.55

With an excess amount of ammonia, monobromamine is still present even after the dibromamine reaction reached completion. The phosphate is affecting the stability and formation of dibromamine (Inman et al., 1984). Inman and Johnson found out that the chloride ion does not affect bromamine decomposition; however, the bromide ion has no effect at pH 8.48, but at pH 6.71, the bromide ion increases the rate of the reaction of decomposition of NH_2Br to $NHBr_2$ and NH_3. The bromamine decomposition at pH 6.71 and the different initial bromide ion concentrations has been studied by Minear (Minear et al., 2004). There are similarities between bromamine decomposition and the chloramine system.

4) Formation of organic byproducts

The organic byproducts are produced by the reaction of hypobromous acid (HOBr) with natural organic matters to produce compounds with bromine attached to a carbon atom. There are many examples of bromo-organic byproducts such as bromoform, bromopicrin, dibromoacetonitrile, bromoacetone, bromoacetic acid, bromoalkanes, bromohydrins, etc. (Gunten, 2003). Then, these intermediate compounds can go further in halogenations to bond three bromine to the carbon atom forming tri - halogenated intermediates. Since the bromine atom is greater than chlorine, the bro mine compound CBr^-_3 is more stable than chlorine CCl^-_3 (Greca et al., 2008). The higher the concentration of bromite, the higher the formation of trihaloginated methane and halogenated aitic acid while they can be reduced at higher concentration of ammonia (Chang et al., 2008).

$$CX_3 - R + OH^- \leftrightarrow CX_3^- + ROH \rightarrow CHX_3 + OH^- \qquad \text{Equation 2.56}$$

5) Consumption by non-organic compounds

The N-Br bond is relatively unstable compared to the N-Cl bond. Therefore, inorganic bromamine disproportionation is rapid compared to inorganic chloramine. The latter is disregarded at a pH above 6. NH_2Cl disproportiation does not depend on pH at ranges of 6-9. $NHCl_2$ formation is negligible in organic amines' presence. $NHBr_2$ is less stable and reacts four times faster than NH_2Br and eight times faster than NH_2Cl (Lietzke et al., 1977).

2.8.3. CHLORINE/ BROMINE COMBINED

1) Competition for Chlorine

Most organic nitrogen does not react with chlorine, and its concentration is higher than free ammonia and has less correlation to salinity. Also, the organic nitrogen formation of halamines is much faster than NH_2Cl, which competes with ammonia to react with halogen. Methylamine is the simplest organic amine (Lietzke et al., 1977). Chlorine hydrolyzes rapidly and completely to produce HOCl and HCl. Then, HOCl reacts with three items: bromide, ammonia, and non-amine "demand". Non-amine consists of inorganic and organic reducing agents and autodecomposition reactions. HOCl reacts with ammonia to form monochloramine and a small amount of dichloramine. A reaction of HOCl with bromide produces HOBr. Then, HOBr would react with any available amines to form bromamines. Halamines are unstable and ultimately decay to nitrogen gas or ammonia. Halamine intermediates are part of the oxidant residual. HOCl and HOBr are the non-nitrogenous oxidants (free halogens) (Lietzke, 1977). Chlorination of polluted seawater (which contains ammonia) could form monochloramine, bromochloramine, and bromamines depending on the water's pH, temperature, salinity, ammonia concentration, and chlorine dosages (Johnson et al., 1982). In case of low halogen in seawater containing ammonia, only NH_2Br , $NHBr_2$, NH_2Cl and $NHCl_2$ are observed.

The monochloramine formation rate is higher in low salinity-water which has more ammonia. Ammonia is competing with bromide to react with chlorine. The reaction of ammonia and chlorine is forming monochloramine not bromine or bromamine at these conditions: pH 8.1 and weight ratio of $NH_3 : Br \geq 0.008$. Morris and Weil found out that the mechanism of monochloramine formation in low ionic solution is as follows (Johnson et al., 1982):

$$HOCl \Leftrightarrow OCl^- + H^+ \qquad \text{Equation 2.57}$$

$$HOCl + NH_3 \Rightarrow NH_2Cl + H_2O \qquad \text{Equation 2.58}$$

2) Mixed Bromochloramines

Monochloramine is formed when chlorine is added to saline water, regardless of bromide presence. The two passable reactions of monochloramine with bromide are as follows:

$$2NH_2Cl + 2Br^- \rightarrow NHBr_2 + 2Cl^- + NH_3$$ Equation 2.59

$$2NH_2Cl + Br^- \rightarrow NHBrCl + Cl^- + NH_3$$ Equation 2.60

Dibromamine will be produced at stoichiometry of 1:1 (monochloramine and bromide) and bromochloramine will be produced a stoichiometry of 2:1 (monochloramine and bromide). From the plot of $\ln([Br-]/[NH_2 Cl])$ vs. time, the 2:1 stoichiometry is a better fit (Johnson et al., 1982).

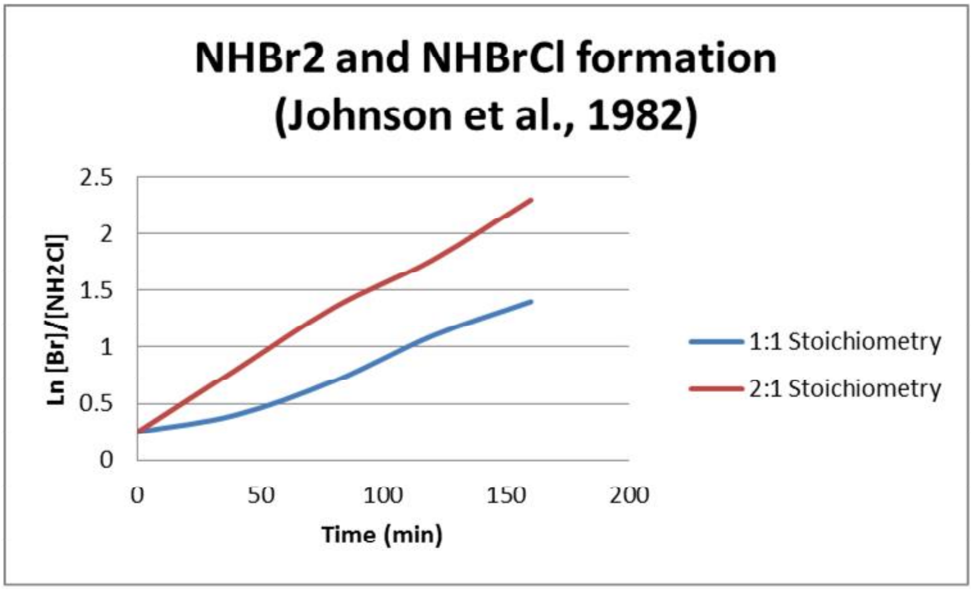

Figure 2.6. Second-Order Plots Comparing 1:1 Stoichiometry for $NHBr_2$ Formation to 2:1 Stoichiometry for NHBrCl Formation (Johnson et al., 1982).

Experiments show that the reaction is first order with respect to monochloramine, bromide ion, and hydrogen ion with stoichiometry of 2:1 between monochloramine and bromide (Johnson et al., 1982). The half-lives in hours of monochloramine at salinity between 5 to 35 % and pH between 7.00 and 8.50 would give results between 2.5 and 60 hours shown in Table 2.3 by using the following equation:

$$t_{\frac{1}{2}} = \frac{\ln 2}{3600K\left[H^{+}\right]\left[Br^{-}\right]} \qquad \text{Equation 2.61}$$

where K=2.8+0.3x10 ^{6} M^{-2} sec^{-1} at 25°C.

Table 2.3. Halflives of Monochloramine for 1.0 mg/l-1 as Cl2 Dose With Changing pH and Salinity.

	Salinity, %			
pH	35	17	10	5
8.50	25	50	90	188
8.00	8	15	29	60
7.50	2.5	5	9	20
7.00	0.75	1.5	2.8	6

For resident time of less than one hour, the oxidation of Br^- by NH_2Cl is out of consideration because it is not for generating bromamine from chloramine by bromochloramine (Lietzke et al., 1977):

$$NH_2\,Cl^- + Br^- + H_2O \rightarrow NH_3 + HOBr + Cl^- \qquad \text{Equation 2.62}$$

The HOBr can react with NH_2Cl to produce NHBrCl, and also HOBr reacts with amines, halamine, and demand to produce other products. This would show the conversion from NH_2Cl into NHBrCl (Lietzke et al., 1977).

There is not enough information about the breakpoint in systems which consist of both active chlorine and bromine. It is not clear whether chloramines react with bromamine or with bromochloramines, and there is no prediction of how bromochloramines species react as a function of pH, Br^-, or as chlorine dose. This model combines all chlorine and bromine breakpoint reactions, plus bromochloramines formation reactions. Bromochloramine interacts with the bromine breakpoint system, but not with the chlorine one, and it has a lower rate constant than bromine reactions (Lietzke et al., 1977).

Two experimental breakpoint curves are above the theoretical 1.5 Cl/N molar ratio because extra chlorine is required to satisfy the organic need (Jenner et al., 1997). An extra chlorine dose will shift the breakpoint to a higher ratio (Allonier et al., 1999 & 2000). Khalanski 1977 proved that adding an ammonia solution to seawater would give a higher breakpoint than predicted due to oxidation of NH_3 to N_2 (Lietzke et al., 1977; Rajagopal et al., 2005; Viveau et al., 1980; Shaw et al., 2006).

Demand has an effect on shifting the breakpoint. Dominant compounds below the breakpoint for NH_2Cl, are NHBrCl, and $NHBr_2$; above the breakpoint, HOBr, NBr_2Cl, and NBr_3 are dominants. At equal concentrations of dihalamines ($NHBr_2$ and NHBrCl) and trihalamines (NBr_3 and NBr_2Cl), the decomposition is rapid (Lietzke et al., 1977).

2.9. FACTORS IMPACTING THE EFFECTIVENESS OF THE BIOCIDE

This section discusses the key factors impacting the effectiveness of the biocide. Four factors are considered: free versus combined form, pH, temperature, and other factors such as ammonia concentration. The following discussion focuses on chlorine and bromine compounds because of their widespread use.

2.9.1. FACTORS IMPACTING EFFECTIVENESS OF CHLORINE COMPOUNDS

1) Free/Combined Forms

Optimization of chlorination is done to achieve disinfection efficiencies through predicting species distribution. Hypochlorous acid (HOCl) is 80 times more effective than hypochlorite OCl^-. HOCl is 80 times more effective than the hypochlorite ion (OCl^-) for reducing E Coli. A comparison between the use of bromine species and other halogens has been studied in literature (Goodenough et al., 1969 and Kristoffersen, 1958). This shows that HOX and X_2 are much more effective than X_3^-, OX^-, and chloramines. Johnson, by contrast, shows that monochloramine (NH_2Cl) and monobromamine (NH_2Br) are very effective as disinfectants (Overby, 1971).

Free chlorine is more effective in bacteria inactivation wastewater treatment than monochloramine. The study here was for inactivation of E Coli by free chlorine and monochloramine simultaneously and separately in a continuous flow system (CSTR). The highest inactivation of E Coli bacteria is when both free chlorine and monochloramine coexist at conditions close to the breakpoint. The result shows that there is a synergistic interaction between free chlorine and monochloramine in killing E Coli bacteria (Yukselen et al. 2003).

Maintaining 1-2 mg/L of chlorine residual was not enough to reduce the bacterial growth. But a 3-5 mg/L level will reduce biofilm by 2 logs. It is required to keep chlorine residual at 15-20 mg/L to control biofouling (White, 1999). Monochloramine residual at a level of 2.0 mg/L is more effective to reduce biofilming than free chlorine. Chloramine dosages are increased from 2.0 to 40 mg/L to maintain 2-3 mg/L of residual to ensure that there is no a coliform bacterium or nitrification in the distribution system. Biofilm growth can be controlled by maintaining 2-4 mg/L of chlorine residual (White, 1999).

2) Effect of pH

Free residual chlorine is twice as effective in chlorinated water at pH 7.2 as it is at 7.8 (White 1999). Free chlorine vs. combined chlorine residual: It is preferred to have combined chlorine predominantly monochloramine residual if entering a clean system. If the system is dirty, then free residual chlorine must be added to clean the system to produce nitrogen trichloride NCl_3 (White 1999).

3) Effect of temperature

It is crucial to determine the chlorine demand (chlorine consumed by inorganic and organic impurities in water) in order to measure the chlorine production rate. Chlorination Breakpoint occurs when chlorine demand is satisfied; then free chlorine can be formed. Figure 2.7. shows chlorine decay dependence on temperature with an exponential increase in decay with a temperature increase, but no dependence on pH (Rennau et al., 1990).

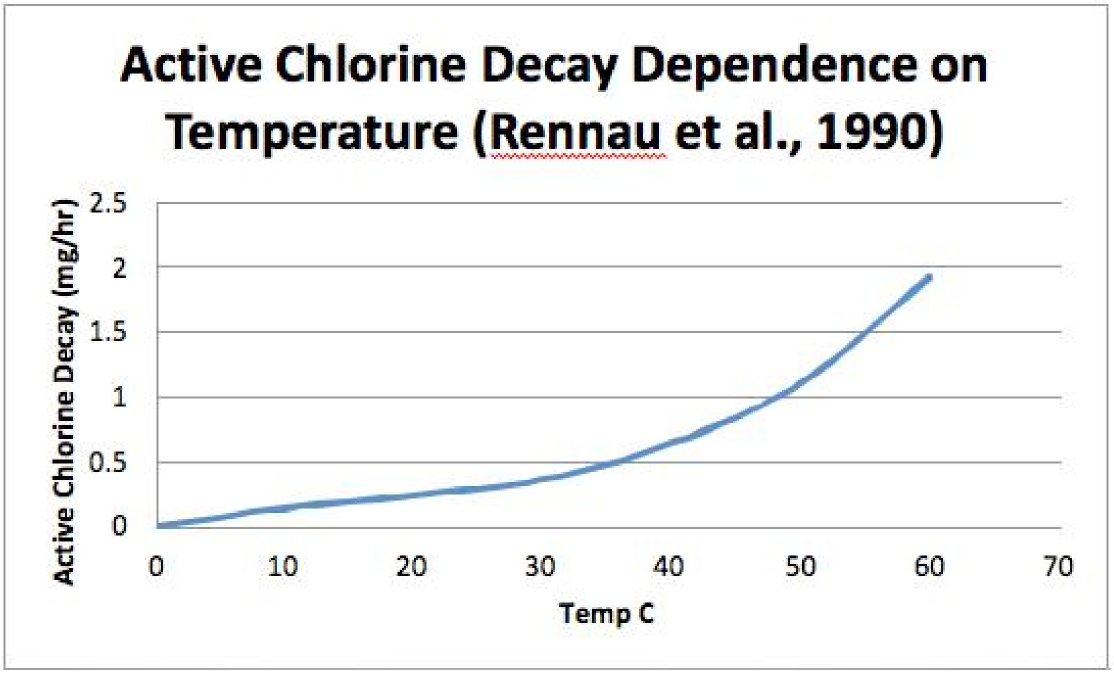

Figure 2.7. Active Chlorine Decay Rate Dependence on Temperature at pH 7 (Initial Active Chlorine Concentration 29.5mg Dm-1, Initial Chloride Concentration 134 Mg Dm-1, Electrolyte Volume 250 Cm2) (Rennau et al., 1990).

4) Calcareous deposits on the cathode surface

Electrochemical disinfection for water faces calcareous deposits on cathode surface due to pH changes. Calcium and HCO_3^- ions are responsible for deposits. pH changes come from OH^- ion according to this reaction at the cathode (Rennau et al., 1990):

$$2\ H_2O + 2\ e^- \rightarrow H_2 + 2\ OH^- \qquad \text{Equation 2.63}$$

Calcareous layers increase with temperature and reduce the current efficiency and therefore hypochlorite production. Producing chlorate from hypochlorite and hypochlorous acid with rate constant k is as follows (Rennau et al., 1990):

$$ClO^-\ 2\ HClO \rightarrow ClO_3^- + 2\ HCl \qquad \text{Equation 2.64}$$

Production of hypochlorite from much diluted chloride solution can be lower in natural water due to chlorine decay. Iridium oxide electrode showed high performance more than platinum electrode. Chlorate production is very negligible. The chlorine demand can be targeted by increasing current density which has linear relation with active chlorine production. Water disinfection can be achieved by electrolytic hypochlorite production (Rennau et al., 1990). Wong and Davidson found that decomposition of HOBr for long time is in the third decay phase (Lietzke, 1977).

$$HOBr \rightarrow \frac{1}{2} O_2 + HBr \qquad \text{Equation 2.65}$$

5) Other effects

Residual-oxidants concentration is calculated by a computer program as a function of time. In the function, time can be converted to distance in case of a constant water flow through the cooling system. Typical chlorine doses (for unpolluted water only) change from below breakpoint for freshwater to near breakpoint for estuarine water to above breakpoint for seawater. Ammonia concentration increases as pollution increases in water and may prevent breakpoint chlorination (Lietzke, 1977).

2.9.2. FACTORS IMPACTING EFFECTIVENESS OF BROMINE COMPOUNDS

1) Free/Combined Form

Monobromamine is less efficient, but bromamines are effective as HOBr and HOCl. Hypobromous acid (HOBr) is a better disinfectant than hypochlorous acid (HOCl) at the pH range of 6-9. Hypobromous acid (free available bromine) is used as a disinfectant to control biofouling. Bromamines are formed immediately by the reaction of hypobromous acid with ammonia. The disinfection capability of bromine compounds is as strong as the chlorine compounds for the toxicity of biofouling organism s (Pinkernell et al. 2000).

2) Effect of pH

From the log (NH_3/Br_2) ratio versus pH, it is known that forming tribromamine from dibromamine and reverse can be achieved by altering pH. Those reactions are assumed to occur rapidly, and the equilibrium of bromamine species is established as a result. Therefore, at equilibrium, the existence of different bromine species can be determined from the ratio of N/Br and pH. Figure 2.8. shows the equilibrium of bromamines as reported by Johnson and Overby (1979) (Hofmann et al., 2001).

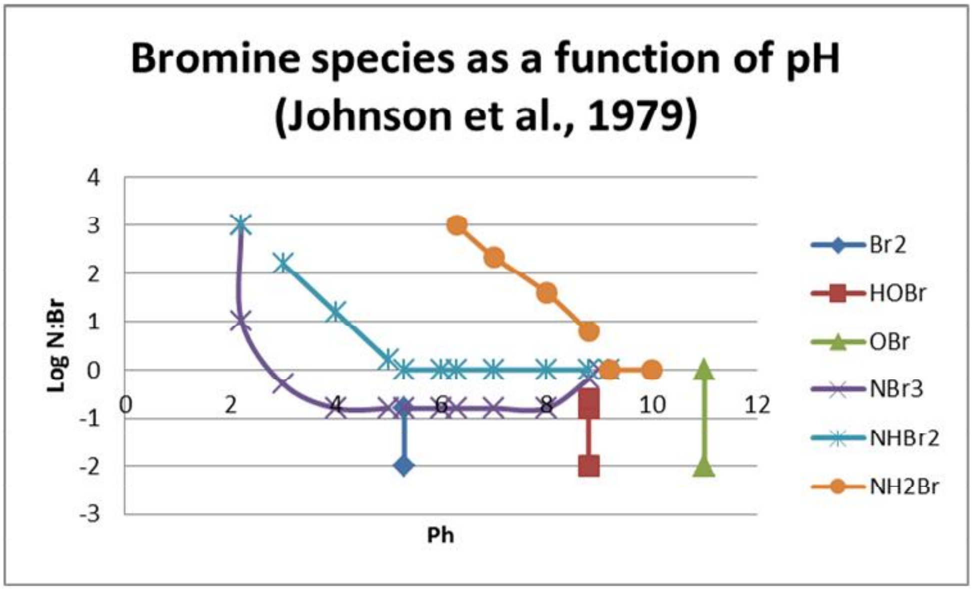

Figure 2.8. The Equilibrium Point at the Existence of Different Bromine Species Can Be Determined From the Ratio of N/Br and pH (Johnson et al., 1979).

At a high pH, such as 9, hypobromous acid is a more effective disinfectant than hypochlorous acid. Bromine is a more effective disinfectant than iodine in a case of high bromide concentration and low pH. Bromine and bromamines are more effective disinfectants than chloramines. Bromine reacts faster than chlorine with ammonia at high pH. The breakpoint is reached quickly with a 2:3 molar ratio of ammonia to bromine (Overby et al., 1971). Bromate has a high formation rate at low salinity in water, but there is no formation in darkness (Richardson et al., 1981).

Ammonia reacts with bromine to form monobromamine. This reaction happens most rapidly at pH of 9, and it takes several seconds at 6-8 pH values. Monobromamine decomposition and dibromamine formation occurs as shown in this reaction (Hofmann et al., 2001):

$$2NH_2Br + OBr^- + 2OH^- \rightarrow N_2 + 3Br^- + 3H_2O \qquad \text{Equation 2.66}$$

Monobromamine is oxidized by free bromine and becomes more unstable at high pH values (such as 12) and at a high bromine:ammonia ratio, and it may formdibromamine (Hofmann et al., 2001). Dibromamine, $NHBr_2$, is an intermediate product of chlorination of seawater containing ammonia. Dibromamine is toxic, unstable, and its formation is an optimizing disinfection and antibiofouling process.

The rate formation of dibromamine is a second order with respect to bromine and becomes faster at low pH. At a pH $\leq$ 8.5 and if the molar ratio of bromine: ammonia is equal or greater than 5, dibromamine, $NHBr_2$, and tribromamine, NBr_3, are the main products (J. D. Johnson 1982). There is an assumption that monobromamine stays in equilibrium with dibromamine and never goes completely disproportionate. Monobromamine, NH_2Br, formation rate is $4 + 1 \times 10^{7}\ M^{-1}\sec^{-1}$ where K_1 is defined based on this equation (Johnson et al., 1982):

$$\frac{d[NH_2Br]}{dt} = K_1[NH_3][HOBr]$$ Equation 2.67

It is found that the formation rate of monobromamine is much larger than the formation of dibromamine at pH 7-8.5. With a high ammonia concentration, and after dibromamine reaction completion, monobromamine can still be observed. At pH of 7.0 and excess ammonia $K_{eq} = 2.02 \times 10^{-10} M$, at 25 ^{0} C for the reaction:

$$NHBr_2 + NH_4^{+} \Leftarrow K_{eq} \Rightarrow 2NH_{2Br} + H^{+}$$ Equation 2.68

3) Other effects

Bromine is preferable as a disinfectant because it is less affected by either pH or ammonia concentration, and the decomposition of bromine oxidant species is very fast (Lietzke, 1977). As shown in Figure 2.9., Bromamines were found to be stronger and more stable disinfectants for drinking water than chloramines (1-3) (Minear et al., 2004).

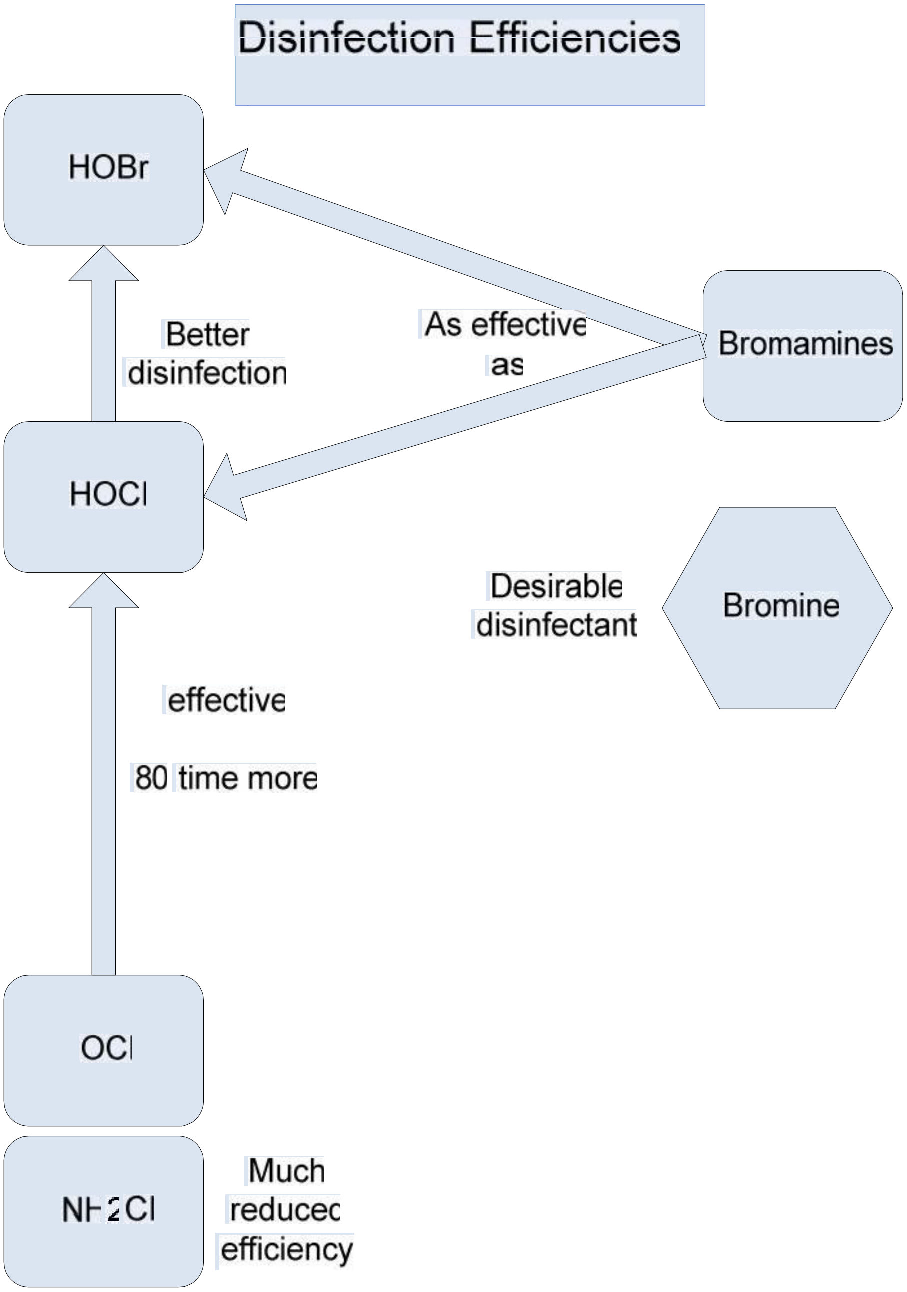

Figure 2.9. Relative Disinfection Efficiency of Some Chlorination Products.

Bromamine formation is enhanced by high salinities and high bromide concentrations. Bromide is oxidized by chlorine or hypochlorous acid, producing hypobromous acid and a hypobromite ion. Also, ammonia reacts with chlorine to produce monochloramine. Chlorination chemistry is significantly affected by a low concentration of ammonia (Johnson, et al. 1982):

1) Bromamines are produced from hypobromous acid at a low concentration of ammonia. At low ammonia concentration, tribromamine and hypobromous acid are predominant. In case of a low concentration of ammonia, the formation of dibromamine and hypobromous acid is high (Johnson et al., 1982).
2) At an intermediate level of ammonia concentration, a mixture of monochloramine and dibromamine are formed (Johnson et al., 1982).
3) At high concentrations of ammonia, forming monochloramine competes with bromide oxidation, so only monochloramine is formed. Monochloramine is undesirable because it does not assist fouling control and has a high toxicity to marine life. However, at high ammonia concentration, monobromamine and dibromamine are coexistent (Johnson et al., 1982).

Each mM of phosphate speeds dibromamine formation so that it is four times faster (Hofmann et al., 2001). Also, the presence of an acetate buffer would have the same effect as a phosphate buffer. The equilibrium would be reached in one second in the presence of either buffer; otherwise, it would take several minutes. Both phosphate and acetone do not naturally exist in sizeable amounts. On the other hand, bicarbonate exists in nature and has the same effect as phosphate and acetone (Hofmann et al., 2001).

2.10. OTHER BIOCIDES

Biocides are chemical substances used to control biofouling in heat exchangers by killing the living organisms. However, chlorine is the most widely used chemical for disinfecting in water treatment, but there is a high risk of the potential production of hazardous halogenated byproducts. There are other alternatives for treating water, like ozone, chlorine dioxide, and chloramines. On the other hand, there are some disinfectants that are less commonly used, like ultraviolet light, hydrogen peroxide, permanganate and other halogens (Fiessinger et al., 1985).

Ozonation is used in the disinfection of water and is widely used in Canad a, Europe, and the Soviet Union (Bruijs et al., 1988). Applying ozone will oxidize inorganic and organic materials. Also, ozonation is used to reduce the turbidity or to suspended solids by flocculation and microflocculation. The decomposition of ozone will form higher-oxidizing power radical intermediates. There is a high risk of using ozone when there is a leakage. Even a low concentration (3 ppm) of ozone is considered to be harmful to the workers and to the surrounding environment. The efficiency of ozone is limited because its decay rate is so high (half-life is less than one hour), and it reacts with a natural organic substance that will allow the bacteria regrowth.

Hydrogen peroxide is a disinfectant for a wide range of bacteria. It is used to disinfect the *Pseudomonas aeruginosa* bacteria, which can resist chlorine-based chemicals. Hydrogen peroxide is used widely with other disinfectants, like UV irradiation and ozone. The bactericidal is not the hydrogen peroxide, but the formed hydroxyl radical that can impinge the membrane surface by reacting with the cell component.

Ultraviolet irradiation is water disinfection without the use of chemicals. It has been developed so that it is cheaper and more reliable to be used in drinking water. The wavelength of the Ultraviolet irradiation used for this purpose is in the range of 200nm to 280 nm. The advantage of using Ultraviolet irradiation compared to other methods is that it does not produce any unwanted substances or byproducts. The efficiency of Ultraviolet irradiation method is guided by the quality of the water in terms of the turbidity, and it dissolves organic as well as inorganic substances. The transmittance of water is reduced due to the absorbance of UV irradiation by suspended matters (Freese et al., 2007).

2.11. MEASUREMENT OF HALOGEN SPECIES

Several methods are used to measure halogen species. Here, we cover the following methods:

- DPD testing
- Amperometric titration
- Iodine

1) Diethyl-P-Phenylene Diamine (DPD) Testing

Determining the amount of free available chlorine (FAC) and combined chlorine by using the Diethyl-P-Phenylene Diamine (DPD) titrimetric and colorimetric methods has been recognized as a standard method. This method quantitatively determines FAC and different forms of combined chlorine (monochloramine, dichloramine, and trichloramine). The variation of the intensity of the red color produced from the reaction of chlorine with DPD reagent determines each chlorine residual fraction. DPD reacts with FAC, and the addition of potassium iodide would react with combined chlorine (Strupler, 1985). Moore et al. found out that the interface of monochloramine on FAC by using DPD at 25^0C in one minute was 5.6% and 6.0% of 3.5 and 7.0 mg/L Cl2, respectively (Strupler, 1985). Figure 2.10. shows the determination of free chlorine by DPD as a function of time in minutes.

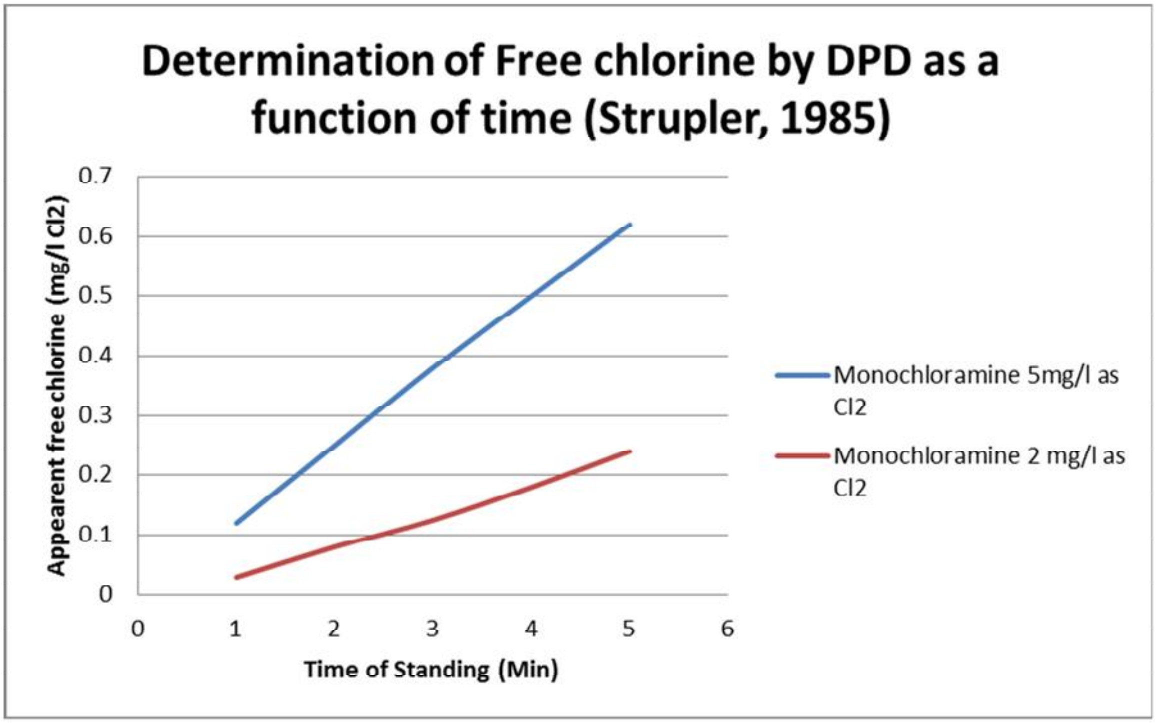

Figure 2.10. Monochloramine Interference in the Determination of Free Chlorine by DPD Colorimetric (Spectrophotometric) Method as a Function of Time (Temp 210C) (Strupler, 1985).

Apparent FAC readings as percentage of monochloramine after 1 minute at two temperatures 10^0C and 20^0C are shown in Table 2.4.

Table 2.4. Monochloramine Interference in the Determination of Free Chlorine by DPD Visual Comparator.

Monochloramine mg/l Cl_2	Apparent FAC readings as percentage of monochloramine after 1 minute	
	Temp. 10^0C	Temp. 20^0C
2	1.0	2.5
5	1.2	2.2
10	1.2	3.1
25	1.4	2.0
50	0.8	2.9

Apparent FAC readings as a percentage of monochloramine after 1 minute at different temperatures at reagents standard and non-standard are shown in Table 2.5:

Table 2.5. Comparison of the Results Obtained With Standard and Non-Standard Reagents for Monochloramine Interference in the Determination of Chlorine by DPD Colorimetric (Spectrophotometric) Method.

	Apparent FAC readings as a percentage of monochloramine after 1 minute				
	Reagents standard			Non-standard	
	10^{0}C	19^{0}C	6^{0}C	8^{0}C	18^{0}C
2	1.0	2.9	3.8	6.5	9.0
5	1.5	2.6	3.4	4.6	5.1
10	1.9	2.8	3.1	6.9	4.6
20	1.4	2.4	3.0	4.0	4.2

In any dyehouse, the consistency of water quality is an important factor in influencing the color application regardless of the quality variations of the water supply (Bowman 1998).

2) Amperometric titration

The amperometric titration method for identifying free or combined chlorine is one of the most precise methods, which needs a lot of skills and portable power in the field. This method has the ability to identify different chlorine residuals, like free chlorine, and chloramines, such as mono-, di-, and tri-chloramine. This method is lightly influenced by common oxidizing agents, temperature changes, turbidity and color (W, 2000). Measurement from both DPD and amperometric methods showed comparable results, including TRC & FRC readings, whereas ion-selective electrode results were much lower, particularly in TRC values than the other two methods (W, 2000). No major changes were found in the TRC boundary measurement during heating water or passage. The DPD method, which is EPA-approved, was found to be easy and fast for measuring both TRC and FRC in the field or at the lab (W, 2000).

3) Iodine

Disinfecting seawater would help increase the efficiency of cooling systems. Chlorine reacts with natural compounds that exist in seawater to produce residuals. Iodine cannot measure the chlorine residual accurately in seawater because it measures all oxidizing agents, such as iodine, bromine, and manganese. The toxic chlorine residuals can be found in bromine, chloro-, and bromo-amines (Johnson, 1977).

2.12. TREATMENT OF BIOCIDE DISCHARGES

2.12.1. TYPICAL REGULATIONS

An Oxidation Reduction Potential (ORP) system is used to evaluate water treatment disinfection. ORP would eliminate errors of chlorine measurements by organic compounds. ORP is a method for controlling the chlorination process in a qualitative, not quantitative, appearance of chlorine residuals. If there is any amount of combined chlorine residual alone, the response is very rapid. Whereas, in the case of the presence of combined chlorine residual with free chlorine, the response takes longer, about 30 minutes, to return back to the base potential when the reducing agent is added. White found out that the breakpoint reaction depends on the OH ion. The oxidation power of the hydroxyl radical $[OH]$, not the ion, is more important to the disinfection chemistry.

In order to have a complete chlorination, the solution should have free residual that is 85% HOCl. Unsatisfactory results with the orthotolidine method for measuring chlorine residuals guided research to the oxidation reduction potential method. ORP or "redox systems" measures the electrode potential readings for different chlorine residuals to estimate their germicidal efficiency. The main factor affecting the disinfection power of free chlorine (HOCl) is the pH of the solution.

In 1933, Schmelkes found that the germicidal efficiency is affected by pH, chlorine concentration, and the amount of chlorine relative to ammonia. The germicidal efficiency of chloramines is less than that of free chlorine (White, 1999).

The Stranco system, also called the "High Resolution Redox Control System", is a very successful automatic chlorination control system in cooling water systems. Calibrating water is important by measuring ORP before adding chlorine. Maintaining close control of pH guarantees a constant value of free chlorine (HOCl), which is the most effective disinfectant of the chlorine residual species. A higher pH would give lower ORP readings for the same free chlorine residual content. This is about 60 mV of the ORP and it shifts down for every one-point increase in pH. For a constant pH at 7.5 solution, ORP readings shift 37mV for every 0.5 mg/L in free chlorine residual (White, 1999). ORP is the only method that can precisely determine the changing in the oxidation profile throughout the distribution system while keeping the required restrictions of the ORP control system (White, 1999).Water treatment systems that use ORP control systems are saving 25-50% of chemical costs. This redox system has the ability to measure the oxidation reduction potentials for chlorine and sulfite groups (White, 1999). Considerable microbial activity in the distribution system is at $15^{\circ} C$ or higher (White, 1999).

Chlorination is widely used because it is economically feasible and efficiently disinfects microorganisms in seawater. In the chlorination process, chlorines are used in different forms such as chlorine gas, sodium hypochlorite, calcium hypochlorite, and chlorine dioxide. The residual chlorine from chlorination has to be reduced before discharging in order to protect aquatic life. This kind of process is known as dechlorinating the treated water using an agent such as SO_2 , HSO_3^- , *and* $SO^{2-}{}_3$ to consume the residual chlorine.

Traditionally, chlorine and sulfite dosages are determined by manual titration at certain scheduled intervals. But, due to dynamic characteristics of the water, the changes are continuous in this process. An insufficient chlorine dosage would allow microorganisms to survive, whereas excess chlorine would add to the operating cost for chlorination and dechlorination. Also, an excess amount of sulfite would cause consumption of dissolved oxygen in the treated water. There is a high cost for the instrumentation of frequent and rapid determination of the total residual chlorine and sulfite amounts before discharge (Kim et al., 2006).

The new approach is to determine the dosage by monitoring oxidation-reduction potential (ORP) and/or pH. This is much cheaper compared to the old method. ORP was proposed by Kim and Hensley in 1997. Water ORP varies with the dominant specie. Water that is chlorine-free shows an ORP over 700mV, while water with monochloramine as the dominant specious has an ORP of about 450mV. Also, ORP was used by Bossard et al. in 1995 to determine the dechlorination dosages for agents such as sulfite. The ORP of water with sulfites is much lower than with chlorine specious (Kim et al., 2006). In 2005, Kim et al came up with a new pH/ORP method to determine chlorine and sulfite dosages. The bending point of ORP and pH profiles is the second derivative of ORP, $(\frac{dORP^2}{dVolNaOCl})$ during chlorination titration, and it is $(\frac{dORP^2}{dVol^2Na_2SO_3})$ during dechlorination; the first derivative of pH is $(\frac{dORP}{dVolNaOCl})$ during chlorination titration, and it is $(\frac{dORP}{dVolNa_2SO_3})$ during dechlorination (Kim et al., 2006).

As chlorine is added, ORP is increased from 300mV to 400mV, then stabilizes due to domination of the NH_2Cl which comes from N_4H^+ oxidation. Accordingly, the pH profile is increased due to the hydroxyl ion generated from NaOCl. At this point, more chlorine is added, so the ORP is going to increase due to the fact that monochloramine is oxidized to dichloramine and produces H^+, which lowers the pH and shows the “hill” on the pH profile. The second increase in ORP is from the oxidation of dichloramine and the further oxidation to trichloramine. At the second increase of ORP, you can see a drop in the pH profile (Yebra et al., 2006). The free chlorine appears after all dichloramine is oxidized (Sugita et al., 1992). The third ORP increase is when free chlorine appears and ORP is raised to an 800mV level; this is the ending point of titration. Adding more NaOCl would result in increasing pH, due to the hydroxyl ion, showing a V-shape on the pH profile. After the breakpoint there were no total coliforms, and free chlorine, which is more efficient to kill microbes, was available. The breakpoint is the third increase in the ORP profile, where $(\frac{dORP^2}{dVol^2\mathrm{NaOCl}}) = 0$, and the V-shape of the pH profile is represented by $(\frac{dORP}{dVolNaOCl}) =0$ (Kim et al., 2006).

2.12.2. SOURCE OF HALOGEN

There are three sources for halogen, depending on the size of the usage and cost effectiveness. In smaller water treatment facilities, calcium hypochlorite is commonly used in a powder form (Lee et al., 2004). This form is more expensive than using the gas or liquid form, but it is more convenient to use as a powder. The least expensive form of halogen is liquefied gas. This option is more cost effective for larger amounts of treated water. However, the gas form of chlorine requires more sophisticated equipment for dosing. It also has high risks of problems caused by uncontrolled leakages. The third option is that chlorine can be generated on-site by using electricity on brine; this is more convenient in remote areas (Freese et al., 2007).

2.12.3. DOSE CONTROL

Chlorine produces an oxidant species with small fractions of the total residual oxidant. In order to determine each species, an oxidant reduction agent is measured with an indicator dye or potassium iodide. Inorganic chloramines can be deducted by watching pH and iodide concentration in the reduction stage (Helz et al., 2005). Chlorine toxicity that affects aquatic organisms is controlled by optimizing dosing for a longer exposure (Helz et al., 2005). There are two mathematical models, kinetics and thermodynamic, to predict species distribution in water treatment. The kinetics model requires the initial species and rate of equation, and the computer calculates the changes through time. The thermodynamic model gives species distribution at a metastable equilibrium with no dependence on initial concentration (Helz et al., 2005).

Saunier's model shows that the chlorine residual vs. an initial chlorine dose at $NH_3 - N$ is 0.5 mg/L, and contact time is 2.5 minutes and also 20 minutes (White, 1999). Adding sufficient chlorine to water distributing systems to maintain enough residual throughout the system is important to insure continuous treatment. In order to meet system requirements, it is essential to develop a model for optimal chlorine dosages (Haas, 1999). It is possible to estimate the inactivation for an open system by obtaining information from batch systems used in laboratories. It is important to pay attention to avoid duplicating errors when extrapolating from the batch system in the laboratory to full scale treatment (Anmangandla et al., 1998).

The Chick-Watson relationship describes the microorganisms' inactivation process by chlorine and chloramines. Chlorine demand is available and has effect on the disinfection process by either consuming some of the chlorine residuals or reacting with free chlorine to produce organic and inorganic forms. Selleck in 1978 and White in 1972 developed this model (Karra et al., 1984):

$$\mathrm{Ln}(N/N_o) = -n \ln(1+bct) \qquad \text{Equation 2.69}$$

where N and N_o are the microorganisms survived and are represented as follows:

- C = Chlorine residuals
- t = contact time
- b and n = experimental constants.

By using the Chick-Watson relationship with the assumption that the free and combined chlorine are additives and are functions of time, the inactivation equation can be:

$$dN/dt = - N\,(k_1 C^{n1}{}_f + k_2 C^{n2}{}_c) \qquad \text{Equation 2.70}$$

where k_1, k_2, n_1, n_2 are the constants of Chick-Watson.

Assuming that the rate of chlorine demand is relatively slow and the weight ratio of chlorine dose to available ammonia is below the required amount for the breakpoint, then monochloramine is going to be the dominant form (Karra et al., 1984). The equation below describes the decay of free chlorine in the short time between adding chlorine and the conversion of free to combined chlorine (Karra et al., 1984):

$$C_f = C_o \exp(- k'' t) \qquad \text{Equation 2.71}$$

where C_o is the chlorine dose.

The decomposition of combined chlorine happens in two phases -- slow and fast (x is fraction in fast):

$$C_c = C_o\,[x \exp(- k_1' t) + (1 - x) \exp(- k_2' t) - \exp(- k'' t)] \qquad \text{Equation 2.72}$$

Solving Equation 2.71 and Equation 2.72 in Equation 2.70 would give a differential equation to disrobe the inactivation of microorganisms with existence of chlorine demand (Karra et al., 1984).

2.12.4. BIOCIDE REMOVAL

The highly chlorinated phenol derivatives, like 2,4,6-trichlorophenol (TCP) and pentachlorophenol (PCP), are highly toxic and carcinogenic. Hydrogen peroxide is commonly used as an oxidant for wastewater treatment. The optimized conditions were studied under the manipulation of pH, temperature, and concentrations of MoO_4^{2-} and H_2O_2. At 15°C the removal efficiency was 65%; at 25°C and above, the efficiency was found to be more than 95%. The highest removal efficiency was found to be in the 9 to 11 range of pH. The higher concentrations of MoO_4^{2-} and H_2O_2 have higher removal efficiency (Jiang, 2005).

Hexachlorobenxene (HCB) was taken as a model compound of polychlorinated aromatic hydrocarbons. HCB removed about 98% in about thirty minutes at 300°C in the existence of CaO and $\alpha - Fe_2O_3(CaO/\alpha - Fe_2O_3)$, which is more efficient than CaO or $\alpha - Fe_2O_3\,(CaO/\alpha - Fe_2O_3)$ by itself. Removal of HCB, by CaO only, at about 300°C, was 52% efficient after one hour. On the other hand, removal of HCB by $\alpha - Fe_2O_3$ on temperature ranges between 400 and 620°C was less efficient, about 8.4%. This is attributed to the fact that the CaO has more alkalinity than $\alpha - Fe_2O_3$ (Xiaodong et al,. 2005).

The removal efficiency (DE) was calculated by:

$$DE = 1 - \frac{\sum_{i=1}^{6} iN_1}{6N_0}$$ Equation 2.73

where N_i is the molar number of chlorinated benzene containing i chlorine atoms in the molecule. N_0 is the initial molar number of HCB (Xiaodong et al., 2005). Discharging seawater is regulated to be less than 0.02ppm of chlorine (Shiga et al., 1995).

Decomposition of residual chlorine can be achieved by three methods:

1) Adding raw seawater to water after passing a condenser.
2) Adding ozone to seawater, which has residual chlorine greater than 3 ~ 4 ppm, before discharging in order to degrade hypochlorite.
3) Exposing seawater to ultraviolet light (254 nm) to decompose residual chlorine.

The addition of seawater with UV irradiation would give better results for decomposing residual chlorine to meet regulations (Shiga et al., 1995).

In wastewater disinfection by chlorine, residual chlorine was found to be 3 M (0.2 ppm) when sulfite ($SO_{2(g)}$ or $HSO^-_{3(aq)}$) was used as a removal agent. The experiment used four other removal agents: ascorbic acid, iron, sulfite plus an iodide mediator, and thiosulfate (Helz et al., 2005). A typical chlorine dosage is 14 – 56 M (1 – 4 ppm). The study was meant to identify the removal agent to reduce the chlorine residual and remove the harm of chlorine disinfection to the aquatic life. At the lab, seawater is treated with hypochlorite; after one hour of reaction, 26 % of the dosed chlorine is found. Then sulfite is added to reduce 67 % of chlorine residual chlorine in the first two minutes, and the rest remains after 2 hours (Helz et al., 2005).

The removal agents were ranked as follows: iron metal >> sulfite plus iodide = thiosulfate > sulfite >> ascorbic acid. Thiosulfate as a reducing agent is very effective after one hour. Sulfite plus iodide is more effective and would reduce residual chlorine completely after one hour. Iron metal is highly effective for reducing residual chlorine with larger moral excess than other reducing agents. Iron reacts quickly, has low cost, and has less of an impact on the environment (Helz et al., 2005).

2.12.4.1. High Resolution Redox (HRR)

Using high resolution redox (HRR), the automated removal system, is to remove all chlorine or at least the oxidation/oxidation activities. A setpoint procedure in millivolts is used to accurately determine the dosage. The automated removal process decreases the defective products and increases efficiency (Bowman, 1998). Re-dyeing may take half of the machine time. One of the main factors that affects the performance of the dyeing process is the water chemistry. The water supply contains chlorine at different ranges, from <1.0 to 3.0 ppm, and it reaches 6.0 ppm at times. In order to avoid chlorine impairing the action of some dyes, chlorine must be removed by sodium thiosulfate ($Na_2S_2O_3$) or sodium bisulfite (Na_2HSO_4) (Bowman, 1998). The water is manually tested for residual chlorine and passes through carbon filters. Then, the water is tested once again, and a reducing agent is added as needed, like thiosulfate ($Na\ _2S_2O_3$) (Bowman, 1998).

Flow pacing is basically the process when the water passes through the flow meter and gives signals to the chemical meter pump to distribute the required amount accordingly. This method will fail if the residual chlorine is fluctuating (Bowman, 1998). Automatically analyzing residual chlorine will take several minutes, which will not accommodate the quick variation in water flow. Such analysis should be more frequent and accurate (Bowman, 1998). Using the compound loop is to combine flow pacing and chlorine analysis for more precise results (Bowman, 1998). Many dyehouses decide to overfeed the dechlorine agent to avoid chlorine residual damage in the dyeing process (Bowman, 1998).

Using a high resolution redox (HRR) removal system is to instantaneously and accurately measure the oxidation reduction potential (ORP or redox) in millivolts. downstream and send signals to the removal agent feed controller. The oxidation reduction potential (ORP) is measuring the electromotive force in millivolts of the oxidizing agent, which is transferring electrons. The electromotive force goes higher with increases in concentration of the oxidizing agent and decreases with high concentration of the reducing agent.

Chlorine activity is a function of residual chlorine, pH, load, flow, and temperature. The high resolution redox (HRR) measures the chlorine activity, represents all variables (Bowman, 1998). The system’s sensitivity is higher when the water has zero activity because the system responses are logarithmic. This system can be programmed to alert workers of pump problems or when they run out of chemicals.

A major textile plant in south Texas is processing 1500 dyebatches per month. This plant uses recycled wastewater with 0.1-0.3 ppm and may reach up to 2.0 ppm Cl2, and sometimes uses potable water with as high as 6.0 ppm Cl2. Workers will test residual chlorine manually on a regular basis, which causes overfeeding the amount of dechlorination agent or chlorine to breakthrough. At any dye defect, a worker will either use a flawed bath for a few seconds or re-bleach; both are expensive options (Bowman, 1998). After considering the HRR system with a setpoint at 450 mV, total removal without overfeeding was achieved. The amount of thiosulfate reduced by 33% and made $6,000 savings. This savings was accounted for in 16 months' payout by the initial investments in the HRR system. Also, reducing chlorine breakthrough made savings in materials, bleach, and two hours of manpower per shift (Bowman, 1998).

Jaunty Textile in Pennsylvania adopted the HRR removing strategy to avoid any variation in water flow. This system helped the company to save costs of reprocessing and dyeing with consistency and high quality (Bowman, 1998). Over a million gallons of water per day was filtered by carbon, and then sodium thiosulfate was added. The water was softened before it was used for dyeing. Conventional manual residual chlorine testing is not appropriate with water flow fluctuating from 0 to 600 gpm (Bowman, 1998). The first try was connecting a water flow meter to a dechlorination injection pump to reduce residual chlorine from 2.2 to 0.05 ppm. But this try did not help to balance with the sudden changes in water flow (Bowman, 1998). Carbon filter effectiveness is reduced in water containing high chlorine. Also, the resin in softeners is damaged by chemicals from overfeeding (Bowman, 1998).

Chlorine residual contributes in reprocessing and delays in deliveries. Customer dissatisfaction cost the company thousands of dollars in revenue loss (Bowman, 1998). The previous arrangement was that the water was filtered by carbon and then sodium thiosulfate was added based on manual residual chlorine testing (Bowman,1998).

Optimal operation was by installing an HRR system, including a dechlorination injection pump, a flow meter, an HRR sensor, and a system controller to modulate the dechlorination feed according to the redox and flow data. This setting is to insure residual chlorine is in the range of 0.02-0.08 ppm (Bowman, 1998). The HRR system reduces inefficiencies. Carbon filters remove traces of residual chlorine, whereas before, there was a 2.2 ppm of Cl2. This system helps the carbon filter to last longer—from three to ten years. Each filter replacement costs $18,500. Overfeeding the dechlorination agent helped to maintain the softening media (Bowman, 1998). The cost of installing the HRR system was recovered after a few months of operation. Other savings were in materials and an increase in both labor efficiencies and customer satisfaction (Bowman, 1998).

Operators identify variables affecting process performance, like chemistry and flow volume and others. The HRR automated removal system is used to reach optimal operation conditions including savings in chemical treatment, carbon filter replacement, and production cost (Bowman, 1998). There were three methods used to detect the chlorine residuals in standard solutions and in the Savannah River. The methods are DPD, amperometric, and ion-selective electrode. The DPD and amperometric methods showed comparable results, whereas the ion-selective method electrode presented lower values. The recommendation is assigned for DPD method for its simplicity and suitability in usage in the lab and field. Also, the DPD method has the capability to measure both total residual chlorine (TRC) and free residual chlorine (FRC) (Wilde, 1991). This study was conducted to study chlorination and removal of chlorine using Savannah River water at Aiken, South Caroline for their cooling nuclear reactor. This study should design chlorination to fight biofouling in the cooling tower and removal to meet the environmental regulation in limiting the load of discharging the residua l chlorine in the receiving water (Wilde, 1991).

2.12.4.2. U V Radiation

By using a UV sterilizer, the residual chlorine of 0.6 ug/L was reduced to 50%, then 90%, then 99% at flow rates of 4, 0.9, and 0.2 L/min respectively as shown in Figure 2.11. (Brooks et al., 1978).

Reduction of monochloramine follows first order kinetics at flow rate of 0.5-50 L/min as shown in Figure 2.11. according to the following equation:

$$K = \frac{\ln C_0 - \ln C}{t} \qquad \text{Equation 2.74}$$

where C_0 = initial chlorine concentration; C = chlorine concentration at time t; t = time in UV chamber (Brooks et al., 1978).

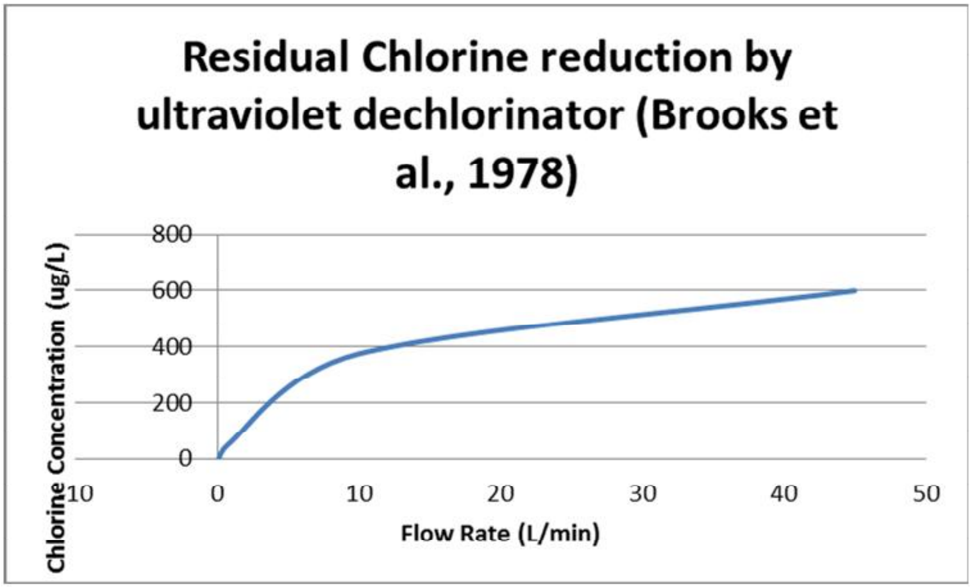

Figure 2.11. The Reduction of Residual Chlorine in Tap Water at Different Flow Rates Through an Ultraviolet Dechlorinator (Brooks et al., 1978).

Activated carbon was able to remove 100% of residual chlorine at a few hours of operation and would allow 10-20 ug/L of residual chlorine to pass through after few days. Atkins et al. 1973; Bauer and Snoeyink 1973; Snoeyink et al. 1974 showed that activated carbon is capable to remove residual carbon 100%. These findings are different from the previous result due to the fact that techniques for measuring residual chlorine were not adequate to measure residual chlorine below 0.1 mg/L. Also, activated carbon is ten times slower to remove monochloramine compared to free chlorine (Kim et al., 1978). Residual chlorine in wastewater treatment contains 1-5 mg/L with a high portion of monochloramine. Another factor is that previous work was done on short term and extrapolated into long term (Brooks et al., 1978). Free chlorine is reduced by exposure to UV radiation according to the following reaction (Brooks et al., 1978):

$$HOCl \Leftrightarrow H^{+} + Cl^{-} + \frac{1}{2}O_2$$ (Hancil et al., 1971). Equation 2.75

Chloramines and chlororganics have been reported to be reduced by UV radiation. Armstrong and Scott showed that UV is capable of 100% removal of residual chlorine as proven in this study. Most municipal treated water contains about 500 ug/L of residual chlorine. Armstrong and Scott (1974) showed that 90% of residual free chlorine was removed by two 1200-W sterilizers at a flow rate of 50 L/min, whereas in this study 99% removal was at 0.2 L/min flow rate (Brooks et al., 1978).

Two 1200-W sterilizers (Xodar XO-260) cost $14,000 and $2,000 as two lamps replacement in a year time. The electricity costs $850/year ($0.04 kW/h) (Brooks et al., 1978). Armstrong and Scott (1974) described continuation of removing after irradiation. The explanation for this phenomena is that UV lamps can produce hydrogen peroxide, which is a removal agent that reacts slowly with hypochlorous acid according to the following reaction (Brooks et al., 1978):

$$HOCl + H_2O_2 \Leftrightarrow O_2 + Cl^{-} + H_2O$$ Equation 2.76

2.12.4.3. Chemical Removal

Activated carbon, ultraviolet radiation and sodium sulfite as removal agents are evaluated. There were always from 5 to 70 ug/L of chlorine not being able to be removed due to service life of the carbon and flow rate. Ultraviolet radiation is more effective but very costly. Sodium sulfite was very effective, but requires a safety protection in case of failure (Brooks et al., 1978). Most laboratories use chlorinated wastewater for culturing aquatic organisms which provides a good disinfection environment. But removal might be needed to maintain very residual chlorine level to assure non-toxicity to aquatic life. Environmental regulations sometimes require residual chlorine to be less than 3 ug/L, but it is recommended to be less than 0.5 ug/L, which is below the deduction limit in most labs (Brooks et al., 1978).

Three methods for residual chlorine removal were considered: activated carbon, chemical reduction, and photochemical degradation. Snoeyink et al. (1974) and Atkins et al. (1973) claimed that activated carbon is most effective. Armstrong and Scott (1974) and Beeton et al. (1976) claimed that ultraviolet and chemical reductions are sufficient. The objective of this study to find out which method has the ability to completely (100%) remove all residual chlorine and to design a removal system for large quantities of culturing aquatic organisms (Brooks et al., 1978). Residual chlorine was determined by amperometric titration to as low values as 1 ug/L. Distinguishing between free chlorine and mono- and dio-chloramine was done by using the DPD method with low concentration as 20 ug/L (Brooks et al., 1978). This experiment is for Milwaukee municipal water which contains 0.3-0.6 mg/L residual chlorine and 90% of it is monochloramine. The ultraviolet radiation system was used on residual chlorine in 13.7 L and one single 91-cm lamp rated at 39 W at 2537 oA (Brooks et al., 1978).

Some sulfur compounds like $Na_2S_2O_3$, Na_2SO_3, SO_2 have been used as removal agents (Pyle, 1960; Beeton et al., 1976). It was found in 1976 that sodium sulfite, Na2SO3, was the most economically effective, safest, and capable of eliminating t oxicity of residual chlorine for the aquatic life. Sodium sulfite is added at a 2:1 ratio by weight with residual chlorine in order to eliminate chloramines completely and instantaneously (Brooks et al., 1978). The disadvantage of using sodium sulfite is that it requires an accurate injection system and periodic follow up with chlorine fluctuating in influent water (Brooks et al., 1978).

2.12.4.4. Activated Carbon

Chlorine is added to water to defeat odor and taste or to disinfect. Excess chlorine has to be removed to avoid chlorine-destroying ion exchange resins or to avoid the harm of chlorine compounds to receiving water or crops in irrigation (Young et al., 1974). Chlorine can be reduced by reacting with carbon which can also destroy NH_2Cl and $NHCl_2$. Also, organic compounds receive attention as well as chlorine (Young et al., 1974). The result of the experiment of Unit 1 with new carbon and Unit 2 with about 3 months in service at a flow rate of about 12 L/min. In Unit 1, completed removal is only for one day at a flow rate of 7 L/min, but residual chlorine increased to 23 ug/L in 23 days (Brooks et al., 1978). At the same flow rate of 4.5 L/min unit 2 in 105 days service remove all residual chlorine except 37 ug/L However, in Unit 1, after 23 days, service removed all residual chlorine except 19 ug/L residual chlorine (Brooks et al., 1978).

Two units in series at 4.5 L/min flow rate will form only 9 ug/L of residual chlorine while passing similar flow rate through unit 1 would result in only 10 ug/L of residual chlorine. A higher flow rate of about 17 L/min had little effect (Brooks et al., 1978). From observation, the same set up of units in a series at range of 4-7 L/min flow rate only 10-15 ug/L of residual chlorine would pass through at about 2 days of operation. Eight months later, at a flow rate of 2 L/min, about 20-30 ug/L of residual chlorine could pass through (Brooks et al., 1978). After a large capacity observation, it was shown that at 60 L/min of flow rate, 5, 10, 15 ug/L of residual chlorine would pass through after 1, 2, 24 hours, respectively. Six months later, 40-50 ug/L of residual chlorine would pass through at 38 L/min of flow rate. After three years, 70 ug/L of residual chlorine would pass from an original 560 ug/L (Brooks et al., 1978).

2.12.4.5. Chlorine-Active Carbon Reactions

Magee and others show that hypochlorous acid reacts with active carbon, a reducing agent, producing H^+, Cl^-, and oxidized carbon surface. But with the case of hypochlorite, OCl^-, no hydrogen ion, H^+, is produced (Young et al., 1974):

$$\mathrm{HOCl + C(activecarbon) \rightarrow H^{+} + Cl^{-} + CO(surfaceoxide)} \quad \text{Equation 2.77}$$

When gaseous chlorine is added to water, hydrolysis takes place and produces H+, Cl-, and hydrochlorous acid (Young et al., 1974):

$$\mathrm{Cl_2(g) + H_2O \leftrightarrow HOCl + Cl^- + H^+} \quad \text{Equation 2.78}$$

Magee found out that the rate of reaction occurs in two phases. First, there is a diffusion controlled step where the rate is very fast due to higher concentration of HOCl in a column more influent than effluent, and HOCl is starting to build up at the carbon site. The second phase happens near the saturation when the reaction rate is slower and the limiting step is carbon surface reduction of HOCl. At this phase, the amount of Cl^- produced is equal to the HOCl removed (Young et al., 1974).

Magee discovered that rate of reaction is slower at the second phase, when OCl^- becomes dominant. This reaction is first order with respect to the concentration of HOCl+ OCl^- and the reaction rate constant at pH 5-6 is four times the value at pH 8.5-10. The ionization constant of HOCl is 3.7×10^{-8} and reaction rate at high pH (8.5-10) is four times the value at low pH (5-6) (Young et al., 1974). These findings are summarized in Table 2.6.

Table 2.6. Free Chlorine Reaction with Activated Carbon (Young et al., 1974).

Free Chlorine (HOCl & OCl^-) reaction with Active Carbon			
pH		**Dominant Chlorine Species**	**Reaction Rate 1st order [HOCl]+[OCl^-]**
About 7.4	(8.5-10)	OCl^-	K
Below 7.4	(5-6)	HOCl	4 x K

$$NH_2Cl + H_2O + C\,(activecarbon) \rightarrow NH_3 + Cl^- + H^+ + CO(carbonoxide)$$

Equation 2.79

$$2\,NH_2Cl + CO\,(carbon\ oxide) \rightarrow N_2 + HO + 2\,H^+ + 2Cl^- + C\,(active\ carbon)$$

Equation 2.80

Dichloramine is also destroyed at active carbon to produce oxidized ammonia (Young 1974):

$$2NHCl_2 + H_2O + C\left(activecarbon\right) \rightarrow N_2 + 4H_+ + 4Cl_- + CO\left(carbonoxide\right)$$

Equation 2.81

Some of the oxides accumulate on the carbon surface, poisoning and blocking carbon sites. Boehm and Puri showed that heating carbon to 1000oC would release all fixed oxides, but at a lower temperature, like 500-700oC, the carbon removal capacity can be restored 100%. The adsorption decrease of carbon is due to surface acidity and BET-nitrogen decrease in surface area (Young et al., 1974). The experiment was conducted by adding 100 ml deionized water with a certain amount of NaOCl solution to 0.2 g carbon. The pH is decreased from 9.5-10.5 to 5-7. Chlorine was determined by the DPD Ferrous Titrimetric Method and Cl- by the Argentometric procedure (Young et al., 1974). The experiment data shows the relationship between acidic surface oxides and the extent of free chlorine treatment. At high concentration of free chlorine, more than 15 mmoles/g, a brown color is observed. This is an indication that the carbon has been oxidized completely which is in agreement to Boehm (Young et al., 1974).

The capacity of carbon decreased by about 35%, at equilibrium concentration of 3 x 10^{-4} M, when free chlorine concentration increased from 0 to 15 mmoles/g. The carbon capacity also was decreased for p-nitrophenol after each cycle. The adsorption capacity of carbon is decreased of about 75% at equilibrium concentration of 3 x 10 $^{-4}$ M (Young et al., 1974).

It is known that there is a carbon surface plateau at about 1.7 mmoles/g and this is due to surface capacity limits for oxygen (Young et al., 1974). It was found that in titration, there is about 1:1 of chlorine and $Ba(OH)_2$ and 15:0.5-1 mmoles of chlorine with NaOH. Hagar and Flentje estimated the life time of the bed is 2-3 years for free concentration of 2-4 mg/L and rate of 1 gpm/ft^3. This estimation is for 10-15 mmoles of free chlorine and reacts with every gram of carbon for complete dechlorination (Young et al., 1974).

There is a relationship between an acidic carbon surface and a carbon bed dechlorination efficiency. Most of the oxides that build up on the carbon surface are volatile, which gives the carbon a longer removal life. The brown color appearance occurs when the carbon bed goes beyond its life's usefulness (Young et al., 1974). Carbon capacity for aromatics adsorption does not vary much by oxides, which can be easily washed or volatilized by drying. But fixed oxides on the carbon surface have to be taken into account when the dissolved organic removal process is considered as well as removal of chlorine species (Young et al., 1974). The more polar compounds adsorption to acidic carbon surface can be increased by studying the interaction between dipole-dipole molecule and surface interactions. It is necessary to study the rate of oxide buildup at low free chlorine concentration. Also, it is required to investigate the effect of the removal rate and life of carbon bed by organic compounds on carbon surface. It is important to study the characteristics of acidic reaction products which can be removed by heating. It is required to study the alteration in surface area and pore size to the effect of acidic surface on organic compounds adsorption.

2.12.4.6. Carbon-Sulfite System

Each system has its own drawbacks: carbon effectiveness, UV cost, Sulfite injection system. A combination of carbon and sulfite is made to build effective reliability, and it is relatively inexpensive. A flow rate of up to 60 L/min is passed through activated carbon to remove 90-95% of chlorine and then sodium sulfite is added at 6:1 weight ratio to the remaining residual chlorine. It is assumed that the remaining residual chlorine is about 0.05 ug/L and sodium sulfite is added at 0.3 ug/L (about 6 g of sodium sulfite at 60 L/min flow rate). An excess amount of sodium sulfite has no effect on fish or on oxygen content (Brooks et al., 1978).

Any failure on the sodium sulfite injector would also have a removal result of 90%. This carbon-sulfite system is provided hassle-free, and the effectiveness in removing chlorine by-products species is high (Brooks et al., 1978).

Installing an active carbon bed and sodium sulfite pump would cost around \$2065 and \$2290 respectively. The annual operating cost is \$150 and \$21 for carbon and sulfite respectively (Brooks et al., 1978).

2.12.4.7. Combination of Removal Systems

This study was to evaluate chlorine species removal by activated carbon filtration, U.V. irradiation and sodium sulphite. Activated carbon couldn’t totally remove all residual chlorine but was not insensitive to the chlorine level and water flow rates. Activated carbon reduces organic carbon to 65 % and halogenated methane derivatives to 97-100%. By using ultraviolet irradiation, residual chlorine was reduced to 99% in municipal water with sensitivity to flow rates in the range of 10 – 271 min^{-1}. Temperature from 7.5 to 20.6 0C has no effect on the removal process by neither activated carbon nor UV. All chlorine was totally removed by using sodium sulphite at 3:1 molar ratio to chlorine in municipal water or at 6:1 molar ratio after filtered by active carbon (Danell et al., 1983).

Chlorine is often used to disinfect municipal water. Chlorine is very toxic to aquatic life except at low levels of 2 and 10 ugl^{-1}. Normally, municipal water is two to three orders of magnitude higher than the safe level (2 and 10 ugl^{-1}). Sulphur compounds in +4 oxidation state [like sulphur dioxide (SO_2), sodium sulphite (Na_2SO_4) or bisulphate ($NaHSO_4$) and sodium thiosulphate ($Na_2S_2O_3$)] have been used to remove chlorine species from municipal water and industrial wastewater (Danell et al., 1983). Different removal methods have been studied, including activated carbon, activated carbon combined with ozonation, and photochemical reduction with ultraviolet irradiation (Danell et al., 1983).

The experiments used the tap water of the city of Winnipeg, which has a residual chlorine of 81 ug/L at 19^0C in summer and 750 ug/L at 3^0C in winter (Danell et al., 1983). The removal process was examined by combining carbon filtration and with UV irradiation at two times: March –April period with 300-550 ug/L of residual chlorine and August-September of 81-124 of residual chlorine (Danell et al., 1983).

Also, the removal process was tested for municipal water by using sodium sulphite in sand-filtered and in sand followed by carbon-filtered water at 5^0C and 15^0C

(Danell et al., 1983). The water treatment consisted of a series of sand filters, plastic contact columns for ozone, and carbon filter (Danell et al., 1983). Total residual chlorine was tested by using the o-tolidine method (APHA et al., 1971). Dissolved ozone was tested by potassium iodide. Organic compounds were measured by the Stainton et al. (1977) method (Danell et al., 1983).

When the carbon filter was first, the efficiency was changed by less than 10%. When UV was first in the configuration, efficiency was decreased from 98% to 75% when the flow rate was increased from 5 L/min to 20 L/min. The second carbon filter did not do so much in chlorine removal so it was removed from any further experiments Danell et al., 1983). For municipal water containing 80-110 ug/L of total chlorine at flow rate ranges between 5 and 27 L/min, the increase of 0.8 ug/L of chlorine breaking through the filter is for every L/min increase in flow rate (Danell et al., 1983). At a low flow rate of about 1-2 L/min residual chlorine at post-carbon was 25-29 ug/L and at higher flow rate residual chlorine was as high as 40 ug/L (Danell et al., 1983).

Initial concentration variation between 40 to 500 ug/L of residual chlorine has no effect on removal process results by UV. Removal process relation with flow rate ranges between 5 to 28 L/min is a first order kinetics with rate constant of K = 2.02 /min according to K = (ln Co – ln C)/ t. For higher efficiency, more than one UV system is used in parallel rather than in series (Danell et al., 1983). As shown in Table 2.7., a water flow rate of 4L/min and chlorine residual of 306-676 ug/L that water temperature (6.2-25.5^{o}C) has negligible effect on % removal either by UV irradiation or activated carbon filters (Danell et al., 1983).

In city water the bacterial content was less than 1bacterium/ml. In chlorine species removal by activated carbon filters, the bacterium was 8000, 5000, 2000 at flow rates of 5, 10, 20 L/min respectively. Whereas, after the UV process, the bacteria was observed as 5, 60, 200 per ml, respectively. It was shown from the data that the carbon bed was a good environment for bacterial growth. On the other hand, UV kills 90-99% of bacteria but has decreased as the flow rate increases due to less exposure to the UV light (Danell et al., 1983).

Table 2.7. Bacterium Concentration at Different Flow Rates (Young et al., 1974).

City Water (Bacterium/ ml)	Flow Rate (L/min)	(Bacterium/ml)	
		After activated carbon filters	After UV irradiation
< 1/ml	5	8000	5
	10	5000	60
	20	2000	200

Dechlorination efficiency by sodium sulphite to untreated municipal water (200-450 ug/L TR-chlorine) and filtered water (40-90 ug/L TR-chlorine) with activated carbon at both 5 and 15^{o}C are shown on the below figures. The relation between dechlorination % and the molar ratio of sulphite and chlorine is hyperbolic and very similar for both temperatures (Danell et al., 1983).

The efficiency of removal for untreated water is higher than the filtered water. At 3:1 sulphite to chlorine molar ratio the removal is 100% for untreated water while only

70% for filtered water. It is required 6:1 molar ratio for 100% removal the filtered water (Danell et al., 1983).

After the diatomaceous earth filter (DE filter), 30% of the residual chlorine was removed at all incoming different chlorine concentration of range 315-750 ug/L. Since the chlorine concentration was not measured, the chlorine reduction was not determined from reducing chlorine to chloride or from adsorption to filter. Another 35% removal after passing through the ozonation system and water leaves with total residual chlorine of 110-31- ug/L. After just 30 cm of carbon filter, the total oxidant residual was reduced to 97%, and this is due to the fact that most of the oxidant residual is chlorine. No significant further removal was made by other activated carbon filters (Danell et al., 1983).

Total dissolved organic carbon (TDOC) was reduced by 5.3% by DE filters and no reduction during ozonation. 58% of TDOC was removed in the first 30 cm of carbon filter and 13 % reduction in 60 cm carbon filters (Danell et al., 1983). Halogenated methane derivatives (chloroform CHCl3, dichloromonobromomethane CHCl2Br, dibromomonochloromethane CHClBr2) were not removed in diatomaceous earth filters and ozonation. However, in the 30 cm carbon filter, 97% of CHCl3 was reduced and CHCl2Br and CHClBr2 was reduced to less than 0.2ug/L. Chloroform was reduced in 30 cm carbon filter from high 67.8 and low 33.0 to .7 ug/L. Carbon filter of 60 cm did not reduce chloroform any further.

In sand filtration, 2.0-10.08 um particulate is 45-50% reduced and low efficiency for 10.08-40.3 um particulate. At DE filters, particulates of less than 10.08 um are 87 - 95% reduced and low efficiency for larger particulate (Danell et al., 1983).

This study shows that activated carbon filters are capable of reducing total residual chlorine (TRC) from 80-530 ug/L → 40-70 ug/L at a flow rate of 5-27 L/min and also reduce TRC to 15-25 ug/L at a low flow rate of 100-200 L/min. Ozonation prior to carbon filtration would increase the efficiency of removal by AC filters, as suggested by Lacy & Rice in 1978. A second carbon filtration in the series would not have any further reduction in chlorine, as proved by Seegert & Brooks in 1978 (Danell et al., 1983).

Suidan et al. (1977) showed that the removal process was reduced by 50% when the temperature was decreased from 23 to 2^0C by using active carbon filters at 5 mg/L chlorine concentration and 758 L $min^{-1}m^{-3}$ of carbon. In the current study, the chlorine concentration and flow rate used are 10 and 30 % respectively of Suidan et al. which explains that the carbon sites were beyond thermodynamic limits over 6 – 25^0C temperature range. The size of the carbon bed does not constrain the removal rate reflected in the small increase in chlorine concentration after the carbon filter with an increase of flow rate from 5 to 27 L/min (Danell et al., 1983).

The decrease in removal rate over time by carbon filters is not directly related to the amount of chlorine contacting the carbon. There were some propositions made in 1975 by Snoeyink and Suidan, but the results are still unambiguous. A carbon filter's functional life can be increased by several times when water is ozonated before filtering by carbon (Danell et al., 1983). A carbon filter can remove 65% of total dissolved organiccarbon and 97-100% of chloroform, dichlorobromomethane and dibromochloromethane. In 1978, Seegert and Brooks recommended that adding sodium sulphite at 6:1 weight ratio for carbon-filtered water would lead to complete removal of chlorine (Danell et al., 1983).

Sulfite was added to the Winnipeg city water supply after carbon filters were at a 6:1 weight ratio and resulted in only 85% of chlorine removed and 100% at 10.7 weight ratio. Also, Sulfite was added to unfiltered water at a 5:1 weight ratio to remove all chlorine because an organochlorine complex was generated at the carbon bed which cannot be reduced by sulfite. An excess of sulphite is not desirable for aquatic organisms (Danell et al., 1983). Another alternative that is similar for chlorine species removal after carbon filtration is ultraviolet irradiation, which has the same result when chlorine concentration is at a range of 40-525 ug/L and temperature is at a range of 6-25oC (Danell et al., 1983).

A higher removal rate can be achieved by functioning two UV units in a series rather than in parallel. Chlorine concentration of 60 ug/L at 20 L/min flow rate can be reduced to 4.9 and 6.2 ug/L by series and parallel, respectively of UV units. Carbon filters are environmentally friendly to grow bacteria while the UV irradiation knocks down them (Danell et al., 1983). A system was built for treating municipal water containing 100-900 ug/L free chlorine and has a flow rate of 120 L/min. This system, which has incorporated a series sand filter, has an activated carbon filter and uses ultraviolet irradiation, was constructed at the Freshwater Institute Department of

Fisheries and Oceans in Winnipeg, Manitoba to reduce free chlorine to 4-8 ug/L. The capital and annual operating costs are shown in Table 2.8. (Danell et al., 1983).

Table 2.8. Reducing Free Chlorine in Municipal Water (Danell et al., 1983).

Municipal water containing 100-900 ug/L free chlorine and flow rate of 120 L/min Aiming to reduce free chlorine to 4-8 ug/L				
Dechlorination System Equipment (Canadian $, 1980)				
Type	**Size**	**Capital Cost**	**Annual Operating Cost**	
Sand Filter	300 L	$ 840	--	--
Activated Carbon Filter	340 L	$ 2,640	Activated Carbon Replacement	$ 400
Ultraviolet	1200-W	$ 19,700	Ultraviolet Lamps	$ 1,730
Sterilizers	12-tube			
Associated Pluming		$1,850	Electricity 2,233 KWh ($ 0.30 KWh)	$ 670
Total Capital Cost		**$ 25,030**	**Total Operating Cost**	**$ 2,800**

2.12.4.8. Mixing

The unchlorinated tempering water is mixed with a condenser discharge to meet regulations temperature discharge. The decay rate in daylight is faster than in nighttime. It is desirable to take samples at different point though the cooling system. The time (transit) for the water from intake to discharge is about 3 minutes (Helz et al., 1984).

2.13. CONCLUSIONS

This section covered the overview of the chemistry of seawater with biocide focusing on the reaction of chlorine. The reaction of chlorine is very difficult to be tracked. This is due to many organic and non-organic species that are naturally exist in seawater. Most of these reactions occur simultaneously and instantaneously. Nevertheless, the author summarized the major reaction representing the main chlorination by-products in Figure 2.2. The main by-products of chlorination of seawater are hypochlorous acid and hypobromous acid. However the production of hypobromous acid is after the consumption of most of the ammonia by the reaction with the hypochlorous acid producing the chloramine. Then, any excess production of the hypochlorous acid will react with bromide ion replacing the chlorine with bromine in the hypochlorous acid compound. The existence of bromide ion in seawater is always at much higher concentration than ammonia makes the ratio of the hypochlorous acid and its compounds to hypobromous acids compounds depending to the concentration of ammonia. Other factors that influencing the kinetic of chlorination reaction in seawater are the pH and temperature. Therefore, the chlorination kinetics of produced by-products depends on the location.

3. PROBLEM STATEMENT

Consider an industrial facility which uses seawater for cooling. The characteristics of seawater vary throughout the year leading to dynamic variations in the growth of biofilms on the surfaces of the heat exchangers. Biofilm growth is controlled through the use of biocide and regular maintenance. It is desired to identify an optimal scheduling policy for the use of biocide and heat-exchange maintenance to minimize the cost while accounting for the technical performance of the plant and the environmental discharge of the biocide and its byproducts.

The aforementioned problem statement entails several challenges to be addressed including:

- How should the biocide dosages be varied during the year?
- How does the biocide react and decay in the dosing basin and throughout the process?
- How is the biofilm growth in several exchangers related to biocide usage, reactions, and the characteristics of the process and the seawater?
- How to account for the heat-exchanger performance throughout the process as a function of the time?
- When is maintenance necessary?
- How to meet the environmental regulations on the discharge of the biocide and its byproducts throughout the year?

The following systems will be addressed in the ensuing sections:

- Industrial plants with seasonal variation in seawater temperature
- Integrated power plants and thermal desalination facilities
- Processing facilities with solar-driven biocide manufacturing

4. DEVELOPMENT OF A SHORTCUT PROCESS-INTEGRATION APPROACH TO THE OPTIMIZATION OF SEAWATER COOLING SYSTEMS WITH ECONOMIC AND ENVIRONMENTAL CONSIDERATIONS

4.1. OVERVIEW

The aim of this section is to develop a systematic approach to the optimal operating and design alternatives for integrated seawater cooling systems in industrial facilities. A shortcut process-integration framework is used to provide a holistic approach to optimizing the design and operation of the seawater cooling system, along with the dosage and discharge systems. Optimization formulations are employed to systematize the decision-making and to reconcile the various economic, technical, and environmental aspects of the problem. Building blocks of the approach include the biocide water chemistry and kinetics, process cooling requirements, dosage scenarios and dynamic profiles, biofilmgrowth, seawater discharge and environmental regulations.

4.2. PROBLEM STATEMENT

The problem is that a given process which uses seawater in a once through cooling system can experience fouling due to biofilm development in heat exchanger tubes. In order to prevent biofouling in coolers, an antifouling agent (i.e., chlorine) is added to the incoming seawater. A certain load of chemicals is added to the process intake of seawater flow, $F_{S.W.}^{Intake}$. Currently, the process discharges a flow rate, $F_{S.W.}^{Discharge}$ of used seawater and a chemical concentration of $C_{Chemical}^{Discharge}$, leading to a discharge laod of chemicals, $L_{Chemical}^{Discharge}$. Due to environmental regulations, it is desired to minimize the load of the discharged chemicals. Conventionally, the residual biocide problem in the seawater used in the cooling system before the discharge is solved by end-of-pipe treatment. This will solve the problem of excess residual chlorine, but the question can be raised whether there is a more cost-effective solution. Implementing the proposed holistic approach is one such solution. Figure 4.1 summarizes the problem statement and shows the conventional approach for biocide treatment.

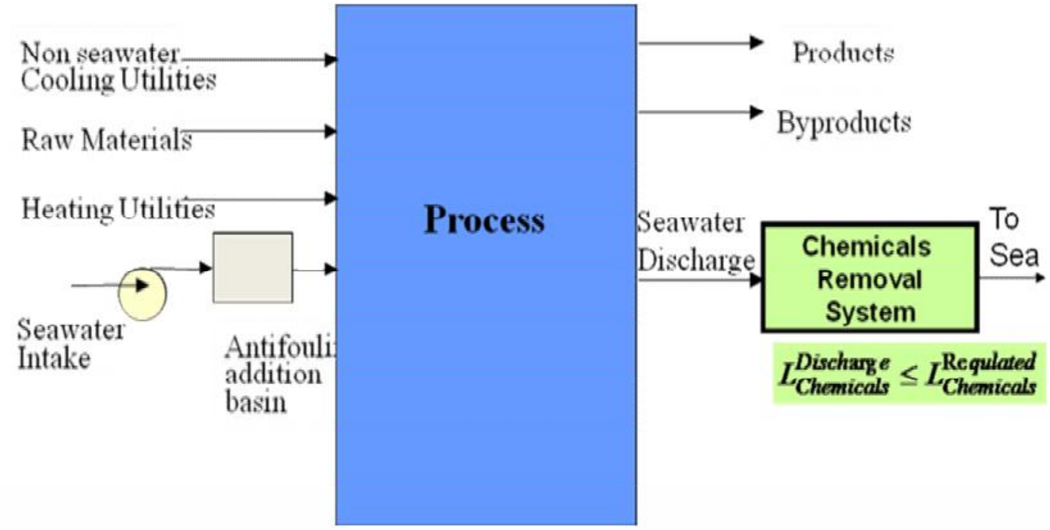

Figure 4.1. Diagram Summarizing the Problem Statement.

The objectives of this section are to:

- Develop a systematic procedure for understanding the chemical and Use shortcut input-output relations to represent the kinetics of biocide usage and their reactions with different species in seawater.

- Relate the formation of by-products to the characteristics of the seawater, the biocide, and the process.
- Identify the most effective by-product to control biofouling development.
- Develop optimal policies for process modification and biocide dosing to optimize biocide usage and discharge.

The ultimate goal is to develop a cost-effective procedure that integrates the process resources, revises the process design and/or operation, and determines the optimal scheduling of chemical dosage load and timing, along with implementing chemical removal at the minimum number of heat exchanger cleaning cycles per year. This approach might incorporate new technologies to meet the new regulations.

4.3. CHALLENGES AND SPECIFICATIONS OF THE PROPOSED DESIGN

Applying the proposed approach has some challenges. The complexity of a biocide reaction with different species that exist naturally in seawater is that it produces different by-products. It is necessary to identify the most effective by-product in controlling biofilm development. In the meantime, any hazardous compounds produced throughout the cooling system until the discharge point must be monitored. Sometimes there are regulations on the propagation of the compounds at a certain radius from the discharge point. On the other hand, the usage of seawater is linked to the process requirements, including cooling utilities. Therefore, any reduction in cooling requirements will have a direct impact on the amount of seawater used and discharged, along with the usage and discharge of biocide. In order to successfully achieve that reduction in seawater and biocide, several design and operational changes must be made. The last step is to consider new biocide removal units (e.g., dechlorination) as required to meet the environmental regulations. These units have to be screened according to techno-economic criteria. All of these challenges help to identify and allocate for the development of an applicable integrated approach deal with interactive tasks while aiming for the cost-effective solutions. The development of this approach and its application will be explained in the following sections.

The proposed approach starts with understanding the chemistry of the biocide in seawater and integrating it with the performance of the process. Also, we must try to integrate process units and streams in order to reduce seawater usage and discharge along with the usage and discharge of biocide and its by-products. Finally, if necessary, the end-of-pipe treatment must be integrated with the in-process modification. Specifically, this approach can be achieved by starting with the development of the biocide kinetic models, then using the heat integration techniques as a tool to make the most feasible possible reduction in cooling duty, and consequently on heating duties. Any optimal changes on design and operating conditions must be made to reach that approach. Then, based on the biocide kinetics and the optimal conditions for the biocide to be effectively controlling biofouling, a model for biocide dosing must be constructed. The biocide dosing amount and scheduling on different seasons must be identified. The last step is always to use the appropriate load of end-of-pipe treatment as required to meet the environmental regulations.

The foundation of the proposed approach is built on main concepts. Reducing the cooling duties of the process will influence in lowering the usage and discharge of seawater, and, consequently, the discharged biocide will be reduced. There are two advantages of reducing cooling duties: cost-savings and pollution prevention. Further reduction in the usage of seawater is achieved by a more effective heat transfer, which would lead to a reduction in the amount of biocide discharged. Optimizing the biocide dosage while complying with the process requirements for maintaining a control on biofouling will lead to minimizing the negative effect on the environment. Adding new biocide removal units (e.g., dechlorination) has to be considered and reconciled with all the approach steps, like reduction in cooling utilities and seawater flow rate, and optimizing biocide dosage. The philosophy behind this proposed design is that any reduction in cooling duties will result in lowering the usage and discharge of seawater, along with the usage and discharge of biocide. A further reduction in usage of seawater can be made by maximizing the span temperature of discharged seawater. The excess amount of biocide and its by-product before the discharge point can be treated by the conventional approach: a biocide removal unit.

4.4. SUMMARIZED PROCEDURE STEPS

The first step is to understand how the biocide would react in seawater and what different forms of by-products are going to be produced. Also, we must comprehend the kinetic reactions impacting the optimal biocide dosing in order to meet the process requirements for controlling the biofouling development. Then, we must identify the most effective biocide by-product for controlling the biofilm and utilize that piece of information in making any design and/or operational changes to satisfy the criteria.

The next step is to reduce the cooling duty of the process by using heat integration instruments. Heat integration is carried out by using a graphical thermal pinch analysis, algebraic techniques, or optimization formulations (e.g., (Smith 2005; El-Halwagi 2006; Kemp 2007)). The objective of this step is to minimize cooling and heating utilities of the process. The biocide dosage is proportional to the cooling duty. As such, reducing the cooling utility of the process leads to reducing the usage and discharge of the biocide. The rationale behind starting with heat integration is that it will generate a cost savings from the reduction of cooling utilities. Heat integration is the synthesis between process streams to feasibly exchange heat between hot process streams and cold process streams. Thus, the outsources for heat and cooling are reduced. This approach is superior to the end-of-pipe treatment because it does not start with investment in biocide removal units without considering other options for running the process at optimal design and operating conditions. Therefore, heat integration creates an economic advantage by the savings made from fewer dependents on the outside source of heating and cooling. At the same time, this is a more environmentally-friendly process. The heat integration thermal pinch analysis will define the minimum amount heating and cooling duties that can be achieved. Those amounts will be the targets that are required for feasibly implementing the heat exchangers' retrofitting using the synthesis of the heat exchanger network and the process' hot and cold streams. Using the synthesis of the heat exchanger network to perform the retrofitting for the process hot and cold streams. Normally, an inspection technique is preformed to find the best match between the process streams to meet the minimum heating and cooling duties. Then, all of the annualized cost data are calculated for the new required units to implement the heat exchanger synthesis that will meet the minimum heating and cooling utilities. How much was saved from introducing the new unit as a reduction of heating and cooling utilities out of that match can also be calculated. Then, the return on investment (ROI) of the proposed new unit can be calculated and compared with the ROI of the company. Then, the decision of installing the new unit will be made based on the ROI policy of the company. Accordingly, the reduced seawater flow rate can be calculated.

The next step is to make a further reduction in seawater flow rate by enhancing the efficiency of seawater utilization. The least complicated technique to reach that reduction is to maximize the discharged seawater temperature while complying with the environmental thermal pollution regulations. Then, the new seawater flow rate from the heat balance equation can be calculated after the reduction has been made from increasing the discharged temperature. After the reduction has been achieved in the seawater flow rate, the revised calculation can be performed by recalculating the reduced amount of biocide required for the seawater flow rate. The following step is to optimize the dosage of biocide, while meeting the requirements of the process of the minimum residual biocide remains in the cooling system to insure the control over any biofouling development. At the same time, reducing the amount of biocide and its by-products that are discharged back to the seawater saves the aquatic live. The optimal biocide dosage is chosen based on mathematical model incorporating the knowledge of biocide chemistry in seawater and utilizing the lab data of the biocide kinetics inside the used seawater because seawater characterization is based on the location. On top of that, the effect of biocide on bioflim development changes seasonally. This is one of the factors that need to be considered in modeling the biocide dosages to reach the optimal biocide -dosing scheme. In order to keep the heat exchangers effectively operating at their optimal conditions, the maintenance schedule for cleaning needs to be considered in the evaluation of biocide dosing amount and scheduling.

The previous steps generate cost savings while reducing the biocide usage and discharge. If the environmental target has not been achieved through all of the previous steps, end-of-pipe treatment can be used to reach that target. For instance, biocide removal units (e.g., dechlorination devices) are added to treat the seawater leaving the plant and to reduce the biocide load prior to environmental discharge. When there are multiple end-of-pipe alternatives, they should be screened in order to select the cheapest alternative. The economic driver for scheduling the biocide dosages should also consider the cost of removing any excess amount of biocide before discharging. Therefore, the solution should have the most effective cost, including the cost of removing the excess biocide and cleaning the heat exchangers. The proposed flowchart is shown by Figure 4.2.

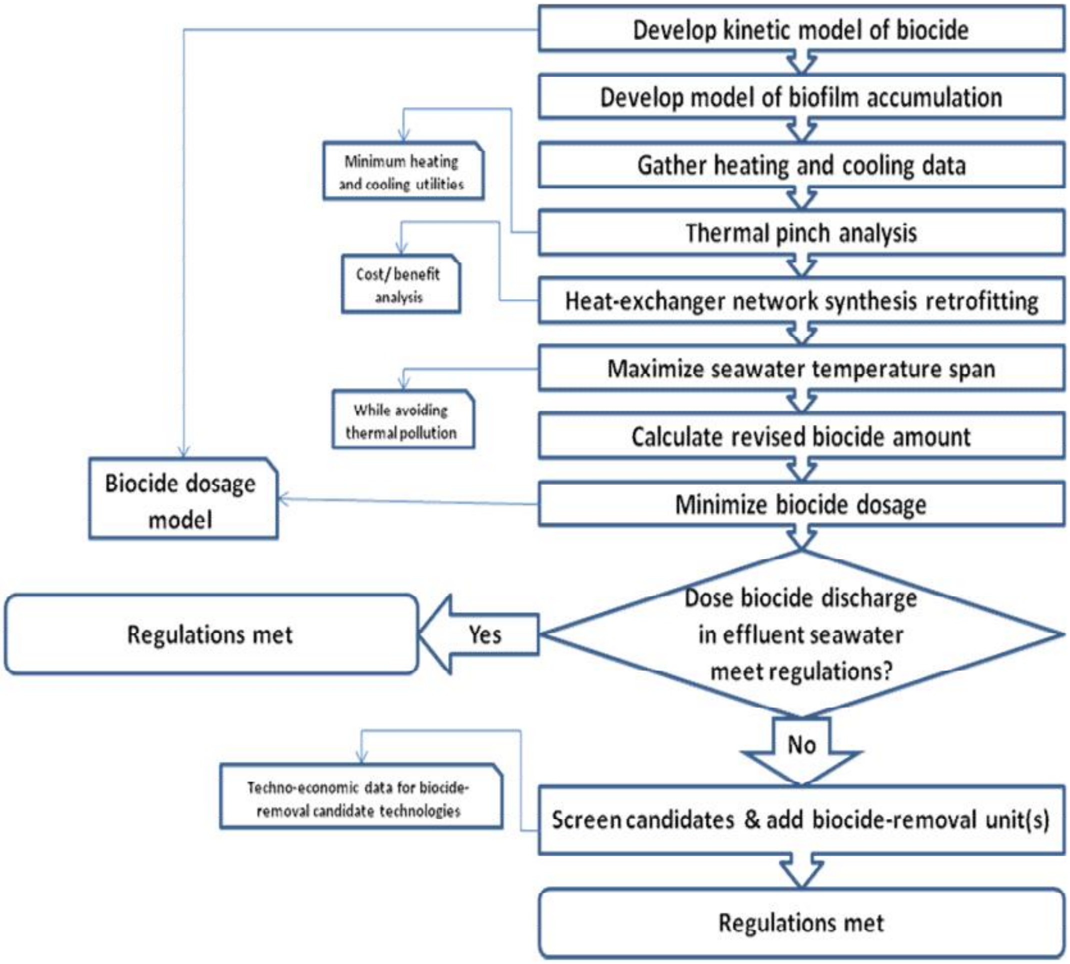

Figure 4.2. A Flowchart Summarizing the Proposed Procedure Steps.

4.5. BIOCIDE CHEMISTRY

It is necessary to develop a mechanistic model for the reaction pathways involving the biocide and the various species in the seawater. First of all, start with the reaction of chlorine when it is added to seawater as a gas or solution of a chlorine compound (e.g., sodium hypochlorite). Chlorine will dissolve and hydrolyze rapidly (almost instantaneous) and completely to HOCl (hypochlorous) acid with a reaction rate constant of $5X10^{14}$. When chlorine is added to seawater, it produces hypochlorous acid and hydrochloric acid, HCl. The latter is a relatively strong acid, and it will dissociate completely to a hydrogen ion and a chloride ion, while hydrochlorous acid, HOCl, is a relatively weaker acid, and it will dissociate slightly to a hydrogen ion and a hypochlorite OCl^-. Since the hydrogen ion appears in this reaction, this equilibrium is pH dependent. The distribution of the various species (HOCl, OCl^-) at equilibrium is a function of pH. Hypochlorous acid is the most germicidal species, but it is a weak acid that will dissociate to hydrogen and hypochlorite ions with pKa of 7.5 at 30°C, as shown in Figure 4.3:

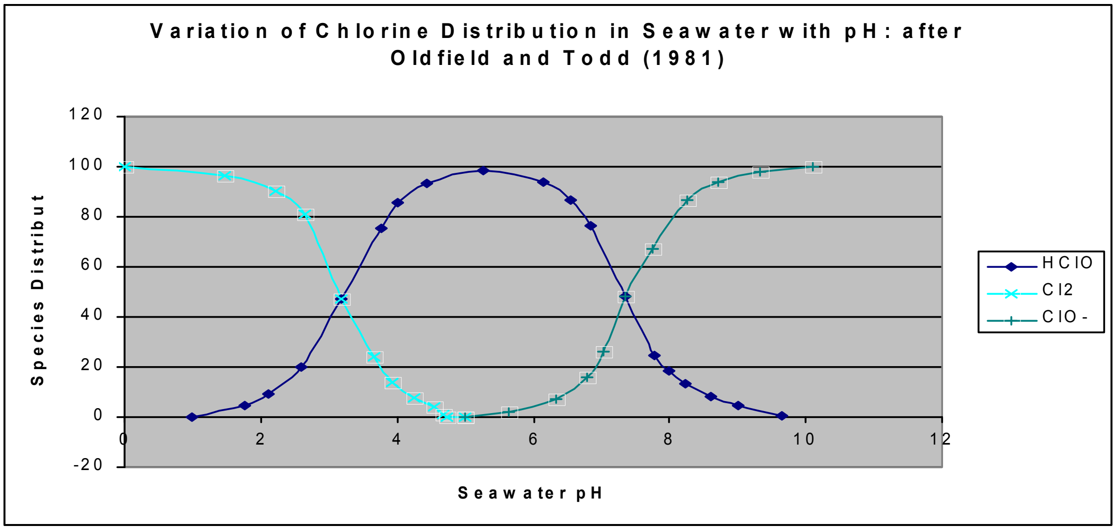

Figure 4.3. Variation of Chlorine Distribution in Seawater with pH (Based on Oldfield and Todd, 1981).

$$Cl_2+H_2O \rightarrow HOCl + HCl \qquad \text{Equation 4.1}$$

$$HOCl \leftrightarrow H^{+} + OCl^{-} \qquad \text{Equation 4.2}$$

In terms of disinfection effectiveness, hypochlorous acid is much stronger (almost two orders of magnitude) than the hypochlorite ion. Hypochlorous acid will reach its maximum concentration at pH ranges between 4 and 6 (Hostgaard-Jensen, Klitgaard et al. 1977). However, the effectiveness of a chemical species as a disinfectant does not necessary correlate with its effectiveness in removing biofilms. Weakening the polysaccharide matrix of microbial cells is one way to control the development of biofilms on the tube surface of heat exchangers. There is experimental evidence that shows that chlorination is more effective in causing biofilm detachment at pH values greater than pH 8, where OCl^- concentration is more dominant than HOCl (Characklis W. G. 1979). Naturally, seawater contains organic and nonorganic species.

Of particular importance are ammonia and bromide species. Their concentrations are varied depending on the nature of the water. For instance, seawater contains bromide with concentrations as high as 65 mg/l, but it will go as low as a negligible amount in fresh waters. Ammonia concentrations depend on pollutants of the water. In highly polluted water, ammonia concentration is as high as 15 ppm, while in unpolluted water the concentration is lower than 0.05 mg/l. At full strength salinity, seawater ammonia concentration ranges between 0.001 and 1.0 ppm. Ammonia, as well as other reactive nitrogenous compounds, will be chlorinated to yield monochloramine (NH_2Cl), and will react further to produce dichloramine ($NHCl_2$). In freshwater, and a very traceable amount in seawater, dichloramine will react further with hypochlorous acid, producing trichloramine (NCl_3). All of the reactions of ammonia and combined chlorine with hypochlorous acid are made by replacing the hydrogen atom of the ammonia molecule with a chlorine atom from a combined chlorine molecule while maintaining its positive charge according to the following reactions:

$$HOCl + NH_3 \leftrightarrow NH_2Cl\,(\text{monochloramine}) + H_2O \qquad \text{Equation 4.3}$$

$$NH_2Cl + HOCl \leftrightarrow NHCl_2\ (\text{dichloramine}) + H_2O \qquad \text{Equation 4.4}$$

$$NHCl_2 + HOCl \leftrightarrow NCl_3\ (\text{trichloramine}) + H_2O \qquad \text{Equation 4.5}$$

These aspects are summarized by Figure 4.4.

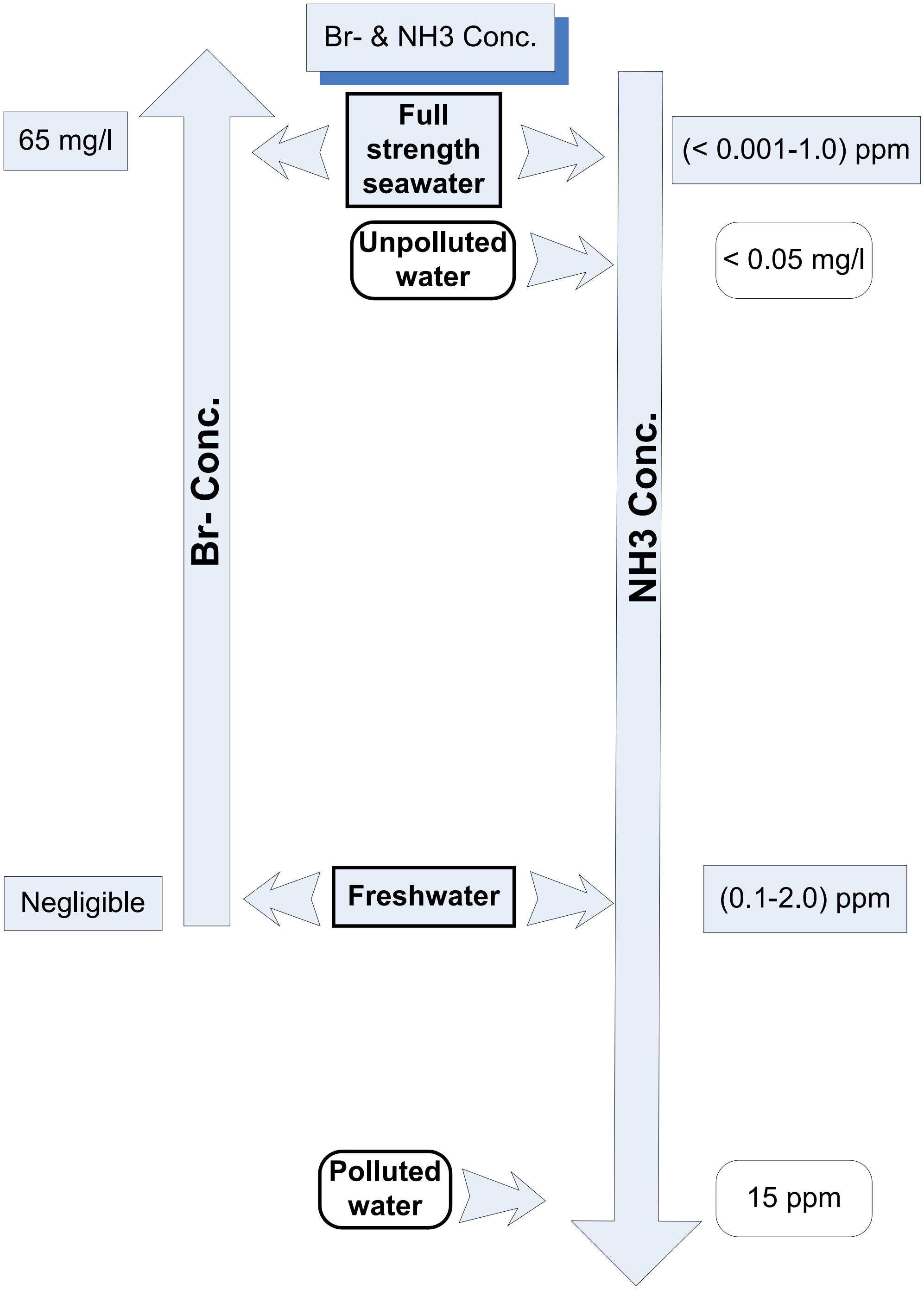

Figure 4.4. Concentrations of Bromide and Ammonia in Natural Water

These reactions depend on pH, temperature and contact time, but mainly on the chlorine to ammonia ratio. All of the free chlorine (hypochlorous acid) will be converted to monochloramine at pH 7-8 (the fastest conversion is at pH 8.3) when there is 1:1 molar ratio of chlorine to ammonia (5:1 by weight) or less. Then, within the same range of pH, dichloramine is produced at a molar ratio of 2:1 of chlorine to ammonia (10:1 by wt.). This reaction is relatively slow, so it may take up to an hour. Also, within t he same range of pH, trichloramine will be produced at a molar ratio of 3:1 of chlorine to ammonia (15:1 by wt.) and at equal molar ratios, but at pH 5 or less. The two reactions producing di- and tri-chloramine are known as the breakpoint reactions where the chloramines are reduced suddenly to the lowest level. The significance of the breakpoint reaction is that chlorine reaches its highest concentration and germicidal efficiency (at 1:1 molar ratio of chlorine to ammonia) just before reaching this point. Also, at the breakpoint, monochloramine and dichloramine react together (which reduces chlorine residuals) to produce nitrogen gas, nitrate, and trichloramine. Dichloramine decomposes to an intermediate reactive product (NOH) which consumes mono-, di-chloramine, and hypochlorous acid, producing nitrogen gas and nitrate. Also, excessive chlorine will form trichloramine. These processes are shown in the following equations:

$$\mathrm{NHCl_2} + \mathrm{H_2O} \leftrightarrow \mathrm{NOH} + 2\,\mathrm{H^+} + 2\,\mathrm{Cl^-} \qquad \text{Equation 4.6}$$

$$\mathrm{NOH} + \mathrm{NH_2Cl} \leftrightarrow \mathrm{N_2} + \mathrm{H_2O} + \mathrm{H^+} + \mathrm{Cl^-} \qquad \text{Equation 4.7}$$

$$\mathrm{NOH + NHCl2 \leftrightarrow N2 + HOCl + H + Cl^-}$$ Equation 4.8

$$\mathrm{NOH + 2\,HOCl \leftrightarrow NO_3^- + 3\,H^+ + 2\,Cl^-}$$ Equation 4.9

$$\mathrm{NCl_3 + H_2O \leftrightarrow NHCl_2 + HOCl}$$ Equation 4.10

The reaction of chlorine into these forms steers it away from the disinfection function and renders the biocide less effective. Consequently, it is important to understand such side reactions. Hypochlorous acid rapidly reacts with bromide, producing hypobromous acid, which can also be produced from the reaction of bromide with monochloramine, as follows:

$$\mathrm{HOCl + Br^- \rightarrow HOBr + Cl^-}$$ Equation 4.11

$$\mathrm{NH_2\,Cl + Br^- + H_2O \leftrightarrow HOBr + Cl^- + NH_3}$$ Equation 4.12

where HOBr is hypobromous acid. Additionally, the hypochlorite ion may undergo a slow reaction with the bromide ion, as follows:

$$\mathrm{OCl^- + Br^- \leftrightarrow OBr^- + Cl^-}$$ Equation 4.13

where OBr^- is the hypobromite ion. Bromide in seawater may also react directly with added chlorine to give bromine and chloride:

$$Cl_2 + 2Br^- \leftrightarrow Br_2 + 2Cl^- \qquad \text{Equation 4.14}$$

It is worth noting that the presence of ammonia and other nitrogenous compounds in the seawater will react with HOBr to yield monobromamine (NH2Br), dibromamine (NHBr2), and tribromamine (NBr3):

$$HOBr + NH_3 \leftrightarrow NH_2Br\,(\text{monobromamine}) + H_2O \qquad \text{Equation 4.15}$$

$$HOBr + NH_2Br \leftrightarrow NHBr_2\ (\text{dibromamine}) + H_2O \qquad \text{Equation 4.16}$$

$$HOBr + NHBr_2 \leftrightarrow NBr_3\ (\text{tribromamine}) + H_2O \qquad \text{Equation 4.17}$$

The bromine breakpoint happens when the dibromamines are produced rapidly, leading to the formation of nitrogen gas:

$$NHBr_2 + H_2O \leftrightarrow NOH + 2H^+ + 2\,Br^- \qquad \text{Equation 4.18}$$

$$NOH + NHBr_2 \leftrightarrow N_2 + HOBr + H^+ + Br^- \qquad \text{Equation 4.19}$$

It is also important to consider the effect of the bromide that naturally exists in seawater at (50–70 mg/l). Bromide is typically in stoichiometric excess over the chlorine dosage, whereas ammonia concentration doesn't exceed 2 to 3 mg/L. The relative amount of bromine species to ammonia species produced is proportional to bromide concentration over ammonia concentration if we assume both reactions are rapid and simultaneous. In order to understand the various species interactions and reaction pathways, we have constructed the reaction mechanism shown in Figure 4.5. On these diagrams, the starting species and intermediate and final by-products are represented in boxes. The arrows correspond to reaction steps, and the boxes on the arrows represent the reactive species that contribute to that reaction.

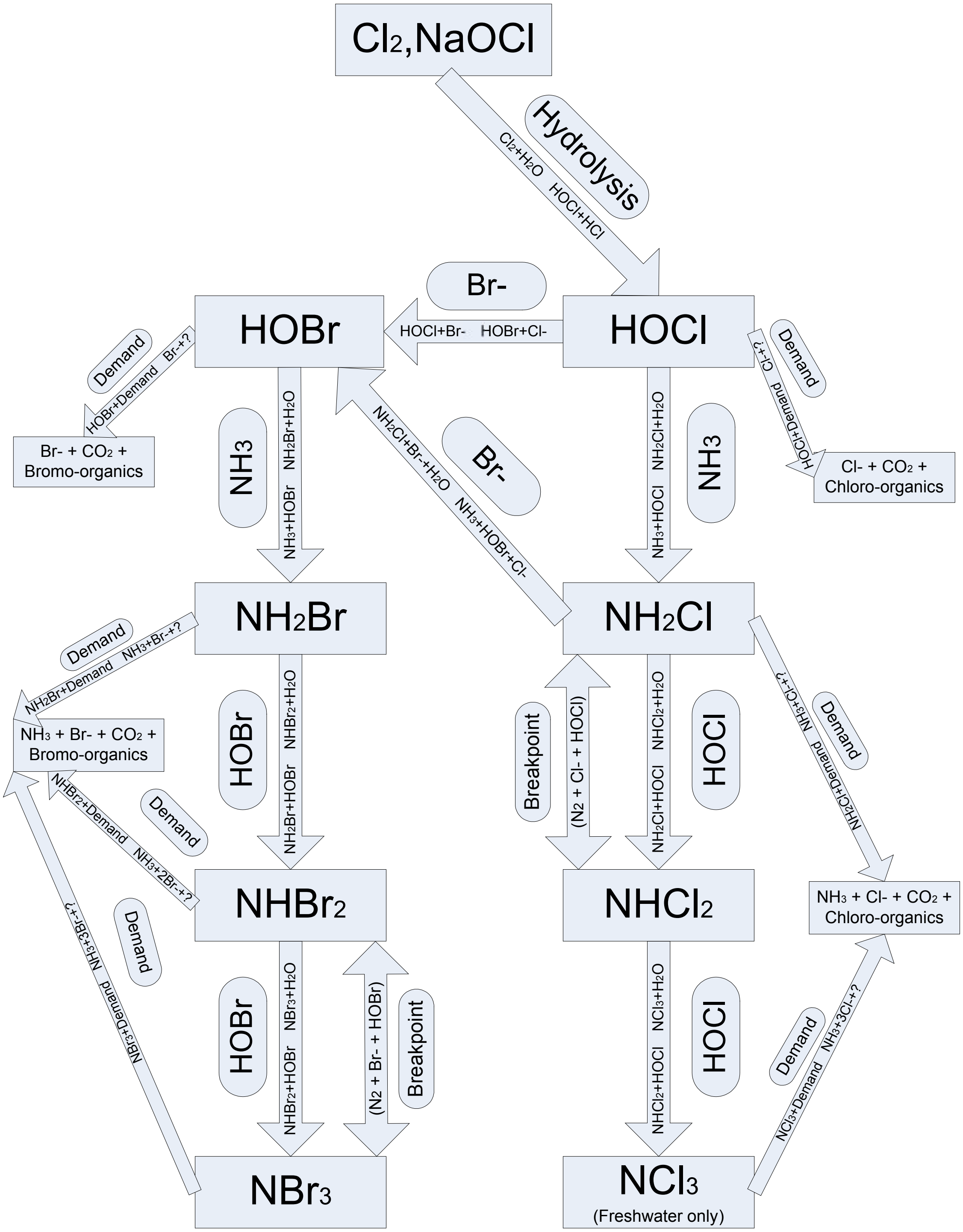

Figure 4.5. Summarizes the Reaction Mechanism of Chlorine in Seawater.

4.6. OBJECTIVE FUNCTION FOR OPTIMUM DOSAGE

Based on the proposed holistic approach, all scenarios from the chemical dosing of treatment and post-treatment, and all of the costs incurred from heating loss due to fouling and heat exchanger cleaning, have to be incorporated in the decision for any design or operation changes. The objective function is built on the economic criterion. It will permit the most feasible solution that would also cost the least to operate the plant. This approach might allow for biofilm growth and removal by periodic heat exchanger cleaning at the minimum overall operating cost. On top of that, there are a variety of options for chemical dosing. For each dosing course, the response of biofouling development will vary accordingly. Thus, there will be an impact on the other operating costs. Also, the nitration and the ambient temperature variations through different seasons of the year will govern the microorganisms' behavior inside the cooling system. All of the different aspects have to be integrated to make one plan that considers the impact on all of the related design and operation changes. The dynamics of the process itself will add difficulty to selecting the optimal scenario among the options.

The objective function is to minimize the annual total cost that is incurred directly and indirectly from fouling. It will include the annual operating cost of chemicals (chlorine) used to treat the cooling water against biofouling, the annual fixed and operating costs of removing chemical residuals from the effluent water, the cost of cleaning heat exchanger units, the cost of the loss incurred by biofouling, and the annual gross profit loss from shutting down the operation for cleaning the heat exchangers:

Annual Total Cost = Operating Cost of Chemicals to Treat the Water +

Annualized Fixed and Operating Costs of Chemicals for Removing Residuals +

Annual Heat Exchanger Cleaning Cost +

Cost of Heat Loss Due to Fouling +

Gross Profit Loss Due to Shutting Down the Process for Heat Exchanger Cleaning

$$AnnualTotalCost = ChemCost + Chem\,RemovCost + HxgCleaningCost + HeatLossCost + Gross\,ProfitLoss \qquad \text{Equation 4.20}$$

$\dot{V}\left(\frac{L}{day}\right)$: is the volumetric flow rate of water

$t_{Cyl}\left(\frac{cyl}{yr}\right)$: is the number of cleaning cycles per year

$t_{Opr}\left(\frac{day}{cyl}\right)$: is the number of days that the process operates per cleaning cycle

$t_{Opr}\left(\frac{day}{cyl}\right) * t_{cyl}\left(\frac{cyl}{yr}\right)$: is the number operating days per year, excluding the shutting down for cleaning heat exchangers

$ChemCost$: is the annual operating cost of chemicals for treating the water

$$ChemCost = C_{Ch}\left(\frac{mg}{L}\right) * \dot{V}\left(\frac{L}{day}\right) * Cost_{Ch}\left(\frac{\$}{mg}\right) * t_{Opr}\left(\frac{day}{cyl}\right) * t_{cyl}\left(\frac{cyl}{yr}\right)$$

Equation 4.21

$C_{Ch}\left(\frac{mg}{L}\right)$: is the chemical residual concentration

$Cost_{Ch}\left(\frac{\$}{mg}\right)$: is the cost of chemicals used

$Chem\,\mathrm{Re}\,movCost$: is the total annualized cost for removing residuals

$$Chem\,\mathrm{Re}\,movCost$$
$$= AnnualFixCost\left(\frac{\$}{Yr}\right) + C_{ChRs}\left(\frac{mg}{L}\right) * \frac{C_{ChRm}}{C_{ChRs}}\frac{(mg/L)}{(mg/L)} * \dot{V}\left(\frac{L}{day}\right) * Cost_{ChRm}\left(\frac{\$}{mg}\right) * t_{Opr}\left(\frac{day}{cyl}\right) * t_{cyl}\left(\frac{cyl}{yr}\right)$$

Equation 4.22

$AnnualFixCost\left(\frac{\$}{Yr}\right)$: is the annualized fixed cost for removing the residuals

$C_{ChRs}\left(\frac{mg}{L}\right)$: is the concentration of residuals

$\frac{C_{ChRm}}{C_{ChRs}}\frac{(mg/L)}{(mg/L)}$: is the ratio of adding chemicals for removing residuals

$Cost_{ChRm}\left(\frac{\$}{mg}\right)$: is the cost of chemicals to remove the residuals

$HxgCleaningCost$: is the cost for cleaning heat exchangers per cycle

$$HxgCleaningCost = Hxg_{C\ln}\left(\frac{\$}{cyl}\right) * t_{cyl}\left(\frac{cyl}{Yr}\right)$$

Equation 4.23

$HeatLossCost$: is the cost of the lost heating due to fouling in heat exchangers

$$HeatLossCost$$
$$= [Q_{C\ln}(KW) - Q_{Fld}(KW)] * \frac{KJ/Sec}{KW} * 86400\frac{Sec}{day} * HtCst\left(\frac{\$}{KJ}\right) * t_{Opr}\left(\frac{day}{cyl}\right) * t_{cyl}\left(\frac{cyl}{yr}\right)$$

Equation 4.24

$Q_{C\ln}(KW) \& Q_{Fld}(KW)$: is the heat transfer rate for clean and fouled heat exchangers, respectively.

The heat transfer rate would be decreasing from $Q_{C\ln}(KW)$ to $Q_{Fld}(KW)$ as the biofilm is accumulating.

$HtCst\left(\frac{\$}{KJ}\right)$: is the cost of heating

Gross profit is the revenue or sales after deducting all directed costs like manufacturing expenses, feed, labor, and selling/marketing expenses. The gross profit loss is how much of the gross profit would have been generated if the production had not been stopped for heat changer cleaning. The daily gross profit (DGPft) can be calculated by taking the revenue of a company over a period of time, with no shutdown in production, and dividing it by the number of days of that period:

$$Gross\,\mathrm{Pr}\,ofitLoss = DGPft\left(\frac{\$}{day}\right) * t_{opr}\left(\frac{day}{cyl}\right) * t_{cyl}\left(\frac{cyl}{yr}\right) \qquad \text{Equation 4.25}$$

The relationship between the chemical added to the influence on how it controls the fouling can be shown in the following model. The biofilm thickness is a function of chemical concentration and scheduled dosage:

$$X_{t_{\mathrm{Pr}d}} = X_0\left[e^{\beta * t_{\mathrm{Pr}d}} - e^{\gamma * t_{Dsg}}\right] \qquad \text{Equation 4.26}$$

where $X_{t_{\mathrm{Pr}d}}$: is the biofilm thickness at the end of the period

X_0 : is the initial biofilm thickness

β: is the biofilm growth rate constant

γ : is the biofilm destruction rate constant

t_{Dsg}: is chemical dosage schedule in hours per day

The biofilm growth rate constant, β , can be calculated on the plant itself by letting the biofilm grow for some time with no chemical added to control it. Then, a graph is generated for the biofilm thickness versus time in days. By using regression analysis, the growth rate β can be calculated from the exponential kinetic growth. This kind of experiment can be repeated at different months/seasons to generate β at each month/season.

The biofilm destruction rate constant, γ , is based on the relationship between the kinetic of biofilm destruction by chemicals and disinfection kinetics of suspended bacterial systems. Then, a graph is constructed to show different disinfection rate constants, K , for bacteria that dies off versus different chemical concentration C_{Ch} dosages. The mathematical relation, which can be linear, that represents the relationship between the rate constants with chemical concentration is:

$$\kappa = a * C_{Ch} + b \qquad \text{Equation 4.27}$$

The disinfection rate constant, K, has to be calibrated by ϕ, which can be determined by dosing the plant that is going to use this model with a certain chemical concentration for one hour per day and developing a graph from the data collected to represent the biofilm thickness versus time in days. By using a regression analysis for the curve, the destruction rate constant can be determined. From the disinfection rate constant K and destruction rate constant at the same dosage, ϕ can be calculated as follows:

$$\gamma = \phi * \kappa \qquad \text{Equation 4.28}$$

The chemical residual concentration, C_{ChRs}, at the effluent before discharge or treatment can be determined by developing a kinetic model of the process. The consumption of chemicals is due to the reaction with organic and nonorganic compounds, biofilm, and corrosion. The chemical decay in kinetics in a batch cooling system (Xin et al. 2003) may be described as follows:

$$\frac{dC_{Ch}}{dt_{Op}} = \frac{K_W * C_W}{r_h} - \frac{W}{r_h} - K_b C \qquad \text{Equation 4.29}$$

Based on examining numerous experimental results for the kinetics of seawater treated with a chemical (i.e. chlorine), decay kinetics have been correlated to several factors, including temperature, pH, and contact time, but mainly on the ratio of chlorine dosage to ammonia (Haag 1981). The reduction or decay of chlorine in seawater is due to reactions with organic and nonorganic compounds in seawater. The chlorine decay occurs in three stages, starting with a very fast rate during the first the two minutes, due to a reaction with inorganic reducing agents. The second phase is slower and usually does not last more than two hours. It mainly involves reactions with the organic compounds that started in the first phase. Then, chlorine decays continuously via a very slow rate.

Of particular importance is the dependence on residence time and temperature. Given the specific path of seawater inside the process, the following model is developed to account for chlorine decay throughout the process. The seawater goes through a number of pipes and units. The process is discretized into a number of segments. Each segment, i, represents a portion of the seawater pipeline or a heat exchanger (e.g., cooler, coil in a hot unit, cooling jacket of a unit, etc.). Consider the N key species and refer to their concentrations in segment i as: $C_{i,1}, C_{i,2}, ..., C_{i,j}, ..., C_{i,N}$.. For the jth species, in the ith segment, the following kinetic expression may be written as:

$$C_{i+1,j} = \Psi_j\left(C_{i,1}, C_{i,2}, ..., C_{i,j}, ..., C_{i,N}, T_i, pH_i\right) \qquad \text{Equation 4.30}$$

Figure 4.6. shows the typical once-through cooling using seawater and treating the influent and effluent with chemicals.

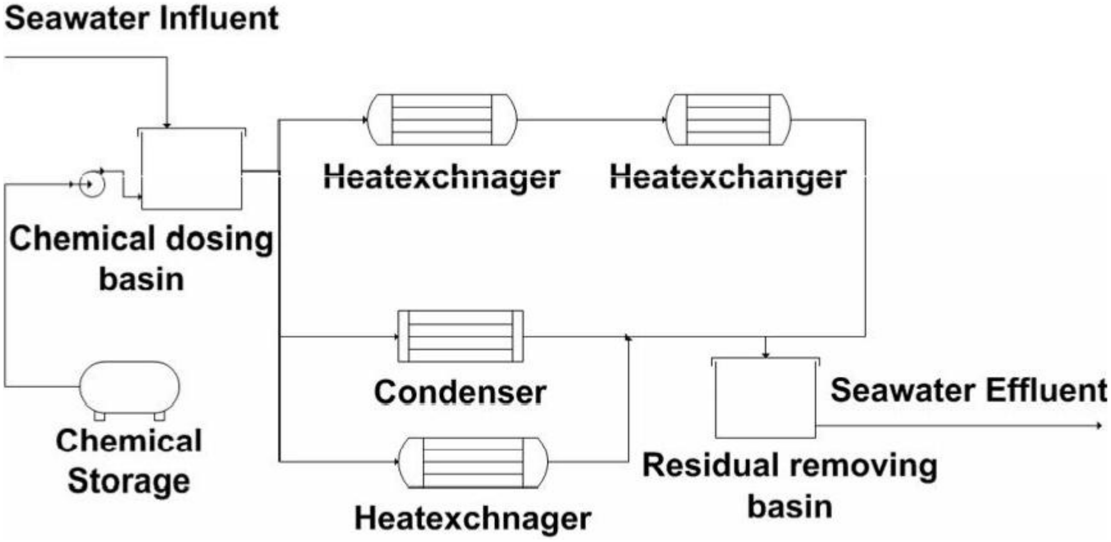

Figure 4.6. Typical Once-Through Cooling Using Seawater and Treatment.

4.7. CASE STUDY

Consider a Urea process described by Bin Mahfouz (2006). The current usage of a seawater cooling utility is 89.2 MM Btu/hr and it employs a continuous dosage of 0.75 mg/L. For maintaining the appropriate biocide effect, the residual chlorine should be kept at levels higher than 0.05 mg/L throughout the system. By carrying out heat integration, the cooling utility is reduced to 77.1 MM Btu/hr, which corresponds to about 14% reduction in the biocide usage. Next, shortcut kinetic modeling is used to track the biocide and its key reaction by-products. The experimental data of Ben Waren (2006) of residual chlorine at different chlorine dosages at 25^{o}C are used to develop the following simplified dynamic decay functions for the three continuous dosages (1.0, 5.0, and 10 mg/L, respectively) as:

$$C_1 = 0.42 * e^{-(o.0015 * t)} \qquad \text{Equation 4.31}$$

$$C_2 = 3.80 * e^{-(o.00004 * t)} \qquad \text{Equation 4.32}$$

$$C_3 = 8.55 * e^{-(o.00003 * t)} \qquad \text{Equation 4.33}$$

where C is chlorine concentration in mg/L and t is the residence time in minutes. A regression analysis was carried out with the experimental data for a residence time of 20 minutes for the case study. A linear expression was derived to relate the residual chlorine (C_{out}) to the chlorine dosage (C_{in}) through:

$$C_{ChRs} = 0.9 * C_{Ch} - 0.52 \qquad \text{Equation 4.34}$$

In order to maintain 0.05 mg/l concentration of residual chlorine at the discharge, we need a dosage concentration of no more than 0.63 mg/L, which provides 19% reduction in biocide usage from the current practice, which is 0.78 mg/L (in addition to the 14% reduction in biocide load already achieved via heat integration.

5. OPTIMAL SCHEDULING OF BIOCIDE DOSING FOR SEAWATER-COOLED POWER AND DESALINATION PLANTS

5.1. OVERVIEW

Thermal desalination systems are typically integrated with power plants to exploit the excess heat resulting from the power generation units. Using seawater in cooling the power plant and the desalination system is a common practice in many parts of the world where there is a shortage of freshwater. Biofouling is one of the major problems associated with the usage of seawater in cooling systems. Because of the dynamic variation in the power and water demands as well as the changes in the characteristics of seawater and the process, there is a need to develop an optimal policy for scheduling biocide usage and cleaning maintenance of the heat exchangers.

The objective of this paper is to introduce a systematic procedure for the optimization of scheduling the dosing of biocide and dechlorination chemicals as well as cleaning maintenance for a power production/thermal desalination plant. A multi -period optimization formulation is developed and solved to determine:

- The optimal levels of dosing and dechlorination chemicals
- The timing of maintenance to clean the heat-exchange surfaces
- The dynamic dependence of the biofilm growth on the applied doses, the seawater-biocide chemistry, the process conditions, and seawater characteristics for each time period.

The technical, economic, and environmental considerations of the system are accounted for. A case study is solved to elucidate the applicability of the developed optimization approach.

5.2. INTRODUCTION

In many regions that lack freshwater, it is common to integrate power production and desalination whereby the exhaust steam from the power-generation turbines is used to drive thermal-desalination systems (Lijesen, 2007). These cooling duties of the power-desalination processes are usually provided by seawater cooling. The cooling duties vary seasonally depending on the need for power and desalinated water. Such variations determine the various flow rates of seawater required for the cooling system at throughout the year. As a result of using seawater for cooling, biofilms grow on the heat-transfer areas of the process heat exchangers (de Beer et al., 2006). Such growth is impacted by the varying temperature of the seawater and the process and the characteristics of the seawater The biofilm negatively affects the performance of the heat exchangers as it lowers the overall heat transfer coefficient. Therefore, the incoming seawater is typically treated with a biocide to control the growth of the biofilm. The extent of biocide dosage should be tied to the seawater characteristics, the cooling tasks, and the need to maintain the level of biocide and biocide byproducts within an environmentally acceptable level prior to discharge back into the sea.

This paper is aimed at identifying optimal scheduling policies for the timing and dosing levels of biocides used for seawater cooling of power and desalination plants. The time-based variations in the characteristics of the seawater, the process, and the demands for power and desalinated water are addressed in the optimization scheme. Seasonal maintenance is also considered in the optimization framework. The technical, economic, and environmental considerations are accounted for and traded off.

Seawater stimulates the growth of aquatic species that are attached to solid surfaces by using planktonic larvae for spreading and growing films that causing fouling of heat-exchanger surfaces. Electric power plants require the usage of large amounts of water to run electric turbines by steam. Accumulating slime on condenser tubes consists of planktonic of young barnacles and mussels (Jenner et al., 1998). The large area of pipelines inside heat exchangers makes it a good environment for bacteria to attach and grow. Biofilm consists of single or multiple species of microorganisms, organic, and inorganic solids distributed heterogeneously on the attached surface (Characklis et al., 1983; Characklis et al., 1982). The development of biofilm depends on nutrients and the oxygen content of the water, as well as the cell metabolism. Fouling of heat exchangers at power plants can be referred to as trash, biological microfouling, biological macrofouling, siltation, and scaling. Other factors that influence biofilm developm ent are the physical conditions of the seawater flowing in the cooling system such as water flow and temperature, and the nature of the surface of the tube (Sriyutha Murthy et al., 2004). Some of the problems that are caused by biofouling in the cooling systems are:

1) Increased rate of corrosion of the tubes by creating a potential charge difference across the surface.
2) Increased heat transfer resistance due to fouling.

3) Increased friction resistance of the seawater flow by changing the tube surface's roughness when the biofilm thickness is higher than the monolayer and consequently the flow rate of seawater is reduced (Cloete et al., 1998).

Controlling the growth of biofilm in industrial cooling systems can be achieved by using chemical treatment that is primarily intended to:

1) Reduce the number of microbes by using biocides
2) Remove microbes by using:
    - Oxidizing biocides (e.g. chlorine) by weakening biofilms.
    - Synthetic dispersants
    - Enzymes

Biocides, also called antimicrobial agents, aim to reduce the growth of microbes. There are two types of biocides:

1) Antibiotics which are formed from the prokaryotic organisms
2) Antiseptics, disinfectants, sanitizers or biocides which do not naturally exist

Biocides are commonly used in controlling biofilm development. It is important to consider these essential aspects in treating seawater with a biocide:

1) Identify the type of organisms in the seawater
2) Use the right biocide or combination of biocides
3) Determine the required concentration of biocide and dosing scenarios
4) Observe the growth of the microorganisms and their attachment

5) Determine the contact time required for killing the bacteria

Biocides act by putting the components in the bacterial cells under stress to hinder their functionality.

Chlorine and chlorinated compounds are typically used as biocides. Chlorine is very toxic and human exposure for more than an hour to chlorine fumes with concentration as 4 ppm or higher can cause respiratory problems. Chlorine can be generated by:

- Electrolysis of saline water, typically sodium chloride, to produce chlorine gas
- Salt process which causes the reaction between sodium chloride and nitric acid

$$NaCl_{(s)}+HNO_{3(s)}\leftrightarrow NaNO_{3(S)}+HCl_{(g)}$$ Equation 5.1

- Oxidation of hydrochloric acid
- Electrolysis of hydrochloric acid solutions.

Chlorine in pure water will hydrolyze immediately and completely to form hypochlorous acid (HOCl) and hydrochloric acid (HCl) (Bin Mahfouz, 2010).

$$Cl_2+H_2O\rightarrow HOCl+HCl$$ Equation 5.2

$$HCl \Leftrightarrow H^{+} + OCl^{-}$$ Equation 5.3

The hydrochloric acid is a strong acid that will dissociate into chlorine and hydrogen ions. Whereas, hypochlorous acid is a relatively weaker acid that will dissociate slightly into hydrogen and hypochlorous ions. The concentration distribution of hypochlorite ions and hypochlorous acid at equilibrium is pH dependent. Chlorine demand is the difference between the amount of chlorine added and the available chlorine, either as free or combined chlorine. The consumed chlorine is due to the oxidation or substitution reactions with organic and inorganic species like: H_2S, Fe^{2+}, Mn^{2+}, NH_3, phenols, amino acids, proteins, and carbohydrates. After the amount of chlorine has been consumed according to the demand, the rest will be available for oxidation to treat the water. The available chlorine is computed from a half-cell reaction of reducing chlorine gas (Cl2) to a chloride ion by consuming two electrons. Only a half mole of chlorine gas will dissociate, forming one mole of chloride ion.

$$Cl_2 + 2H_2O \rightarrow 2HOCl + 2H^{+} + 2e^{-}$$ Equation 5.4

In saline waters, bromide which exists naturally at a much higher concentration (about 65 ppm) and ammonia will compete to react with hypochlorous acid. Chloramines are formed from the reaction of hypochlorous acid with ammonia, forming monochloramine (NH_2Cl), dichloramine ($NHCl_2$), and trichloramine, which is also called nitrogen trichloride (NCl_3). The formation of chloramines depends on water temperature, pH, and the relative amount of chlorine added to the amount of ammonia available prior to treatment. Typically, at higher pH (around 7 and above) there is a higher formation of monochloramine (NH_2Cl). Whereas, at lower pH (around 4 and lower) the formation of trichloramine is higher (Bin Mahfouz et al., 2006).

$$HOCl + NH_3 \rightarrow NH_2Cl + H_2O$$

Equation 5.5

$$HOCl + NH_3 \rightarrow NH_2Cl + H_2O$$

Equation 5.6

$$NHCl_2 + NH_3 \rightarrow NCl_3 + H_2O$$

Equation 5.7

The breakpoint reaction of chlorine is the reaction that satisfies the demand and eliminates all the ammonia, including nitrogen-containing organic compounds, and produces free available chlorine. The weight ratio of chlorine to be added to the available ammonia nitrogen should be 8:1 or higher to ensure formation of free available residual chlorine. These types of reactions have a higher rate at high pH (7-8) and at high temperatures. The first immediate consumption of chlorine is made by the immediate demand associated with non-nitrogenous compounds. Then, if there is enough chlorine, the reaction with ammonia will form chloramines. After consumption of all of the ammonia nitrogen, an extra amount of chlorine is added to form free available residual chlorine. Hypochlorous acid reacts with bromide, producing hypobromous acid, by replacing the chlorine atom with bromine. Hypobromous acid will react with ammonia in the same way as hypochlorous acid, producing monobromamine (NH_2Br), dibromamine ($NHBr_2$), and tribromamine, or nitrogen tribromide (NBr_3).

$$HOCl + Br^- \rightarrow HOBr + Cl^- \qquad \text{Equation 5.8}$$

$$HOBr + NH_3 \rightarrow NH_2Br + H_2O \qquad \text{Equation 5.9}$$

$$HOBr + NH_3 \rightarrow NH_2CBr + H_2O \qquad \text{Equation 5.10}$$

$$NHBr_2 + NH_3 \rightarrow NBr_3 + H_2O \qquad \text{Equation 5.11}$$

Figure 5.1. is a schematic representation of the key reaction steps in the chlorination of seawater. These reactions may happen concurrently, depending on seawater characteristics (Bin Mahfouz et al., 2009). Monochloramine (NH_2Cl) formation will dominate over HOBr formation when bromide concentration is 65 ppm and ammonia is above about 0.4 ppm. At higher concentrations of ammonia, NH_2Cl will dominate. On the other hand, in relatively uncontaminated seawater, the ammonia concentration is very low and the bromide concentration is usually higher than the chlorine dose, which results in a residual that consists mainly of HOBr. The most

important products of chlorine reaction with seawater are NH_2Cl, HOBr, and the bromamines (Lietzke et al., 1979).

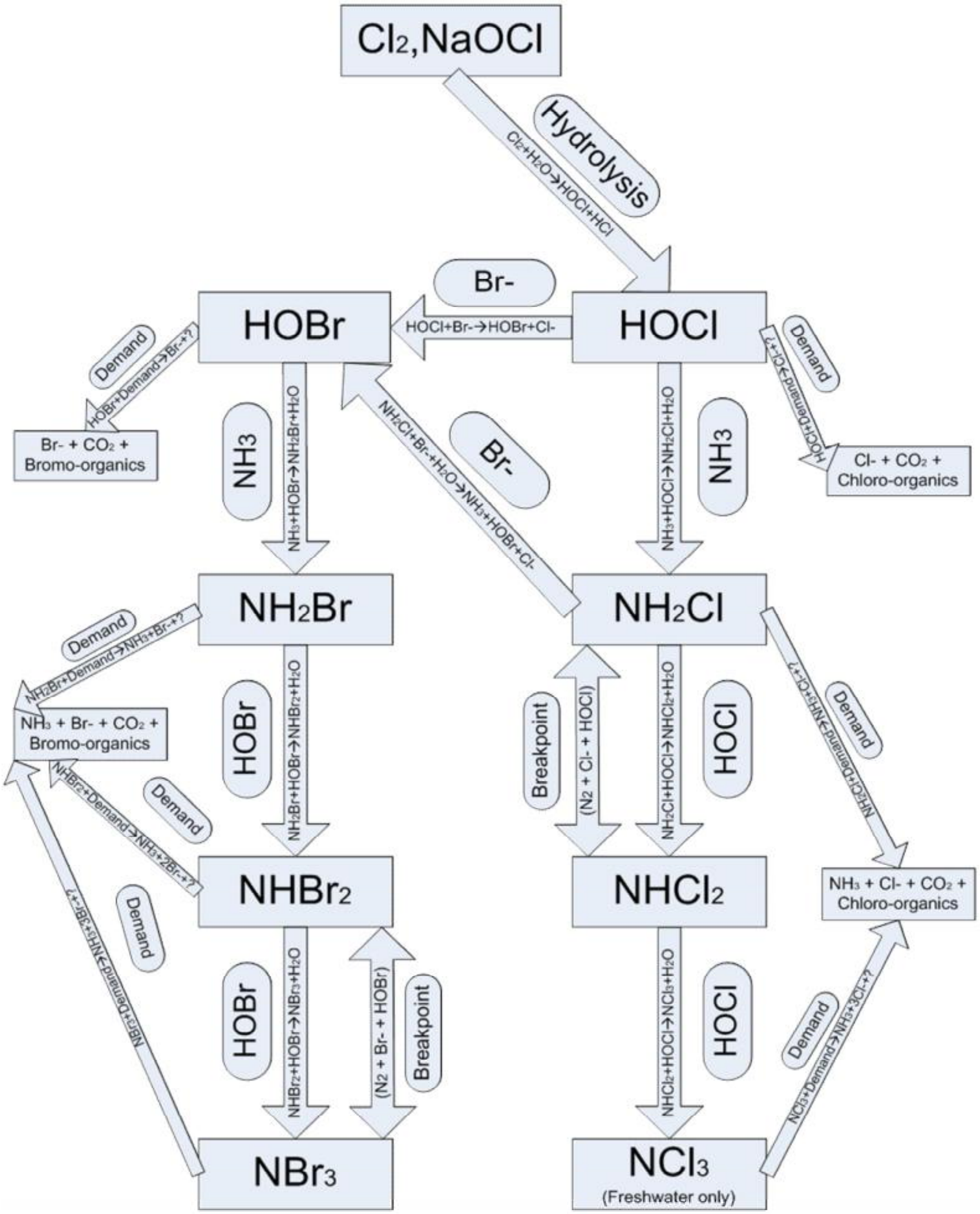

Figure 5.1. The Primary Inorganic Reaction Pathways of Chlorine in Saline Waters.

Chlorine is typically added at a concentration of 1.0 ppm to control biological growth in receiving water at the basin before entering the cooling system (Eppley et al., 1976). Chlorination is the process of adding chlorine to the treated water to kill germs. It is highly effective at pH ranges of 6.5–9.5. Using chlorine is widespread in the industry because of its high reliability, low cost, and easy application. Addition of chlorine will produce hypochlorous acid (HOCl), which has the disinfection effect on both bacteria and viruses. Hypochlorous acid will react with all types of biological molecules because it is non-selective. The existence of ammonia will reduce the effectiveness of the chlorination process because ammonia will react with hypochlorous acid, producing inorganic and organic chloramines. Hypochlorous acid aimed to control the growth of biofilm but it also will attack the cell membrane of *Escherichia coli*, causing chemical and physical changes of the porosity and leakage of macromolecules. Also, the residual chlorine can be simply measured to assess the required concentration of the dosing to avoid excessive dosing and regrowth of the bacteria. A concentration of residual chlorine is as low as 1.5 mg/l can allow bacterial regrowth. The negative aspects of chlorine are that its major byproducts (such as HOBr, chloramines and bromamines) can react with organic substances, such as humic acid and fulvine acid, that naturally exists in seawater, producing organohalogenated, hazardous, compounds such as chloroform, and trihalomethanes. Increase in seawater temperature will inhibit carbon uptake, which will consequently stimulate the development of biofilms. But if the temperature gets too high, it will decrease microbial activity and eventually kill the microbes. On the other hand, microbes can be destroyed by chlorination. The physiological activities of the algae population are increased during the summer (Morgan et al., 1969). The most accurate and sensitive method to measure the chlorine residual is the amperometric method. The potentiometric method is rapid and sensitive to be used in automated and in-line observations (Eppley et al., 1976). Intermittent chlorine dosing was used in plate heat exchangers at the Ocean Thermal Energy Conversion power plant on the east coast of India. This intermittent chlorine dosing at a residual concentration of 1.2 ppm showed a significant reduction in biofilm thickness, bacterial density, and diversity (Macdonald et al., 2008). When the primary problem of fouling is slime formation or microfouling, the intermittent dosing of chlorine has been the most commonly used technique to fix it.

But if macrofouling is the main problem, then continuous dosing of chlorine proves to be more effective (Jenner et al., 1998). Another technique of chlorine addition includes a pulsed dosing, which has proven to give better results in controlling biofouling with a 36% reduction in the mass of chlorine applied. An example of this kind of result was shown in a 10 month operation at Qatargas, the first major liquefied natural gas (LNG) company located in Doha, Qatar. The pulsing of chlorine dosing resulted in reducing the power consumption, as well as operational and maintenance costs. It also improved the discharged seawater quality by reducing chlorination by-products. In 2005, the Qatari Ministry of the Environment lowered the allowable discharge concentration of free residual halogen from 0.1 to 0.05 mg/l. The environmental agencies' regulations for the biocide residual concentration discharge will add complexity to the industrial development in reducing the environmental footprint of cooling seawater systems. End- of-pipe treatment can be used to protect the environment after optimizing the design of the cooling system and the waste heat recovery of the plant. Concentrations of residual biocide as low as 0.05 mg/l cannot assure its effectiveness in controlling biofilm development (Macdonald et al., 2008).

Chlorine used as a biocide has a negative impact on the environment not only because of its toxicity, but because of its by-products (Fayad et al., 1987). A great portion of chlorine is consumed in oxidation reactions with organic and inorganic compounds that naturally exist in seawater, but a small fraction can produce hazardous compounds like trihalomethanes, chloroform, bromodichloromethane, dibromochloromethane and bromoform. Fayad et al. (1987) conducted a study on the chlorination of Gulf seawater of the Halfmoon Bay beach off the west coast of Saudi Arabia and the results are shown in Table 5.1. The major by-product compounds were bromoform ($CHBr_3$) and chlorodibromomethane ($CHC1Br_2$).

Table 5.1. Substance of Seawater Samples Collected at Halfmoon Bay Beach in Saudi Arabia (Fayad et al., 1987).

Halfmoon Bay Beach Seawater Content		
Substance		(ppm)
Organic content		10
bromide ion	At the beach	120
	Open ocean	65
Total oxidant demand (chlorine)		0.12

5.3. PROBLEM STATEMENT

Consider a power plant which is integrated with a thermal desalination system and uses seawater for cooling. The demands for power and desalinated water vary over the year. Therefore, the process operation and the used rates of seawater change accordingly. The characteristics of seawater vary throughout the year leading to dynamic variations in the growth of biofilms on the surfaces of the heat exchangers. Biofilm growth is controlled through the use of biocide and regular maintenance. It is desired to identify an optimal scheduling policy for the use of biocide and heat-exchange maintenance to minimize the cost while accounting for the technical performance of the plant and the environmental discharge of the biocide and its byproducts.

The aforementioned problem statement entails several challenges to be addressed including:

- How should the biocide dosages be varied during the year?
- How does the biocide react and decay in the dosing basin and throughout the process?
- How is the biofilm growth in several exchangers related to biocide usage, reactions, and the characteristics of the process and the seawater?
- How to account for the heat-exchanger performance throughout the process as a function of the time?
- When is maintenance necessary?
- How to meet the environmental regulations on the discharge of the biocide and its byproducts throughout the year?

The next section introduces a systematic approach to addressing these challenges.

5.4. APPROACH

The cooling system in the plant is divided into Ni segments. Each segment (e.g., a pipeline or a heat exchanger unit) is denoted by the index i. The annual operation is discretized into N_t time intervals and t is used to designate an operational period. The coolant (seawater) average daily temperature varies depending on the time of the year. The variations in the power and water demand, the plant, and the seawater characteristics affect the required amount of biocide for treating the seawater before it enters the cooling system. Therefore, the seawater flow rate (F_t^{SW}) and biocide dosage (F_t^{B}) are to be optimized over the N_t operational periods. The biofilms growth is tracked over time for all the process segments (Ni) and is related to the biocide usage and decay throughout the process. Figure 5.2 is a schematic representation of the discretized process segments with the time-based variations in seawater flow rate and biocide usage and discharge.

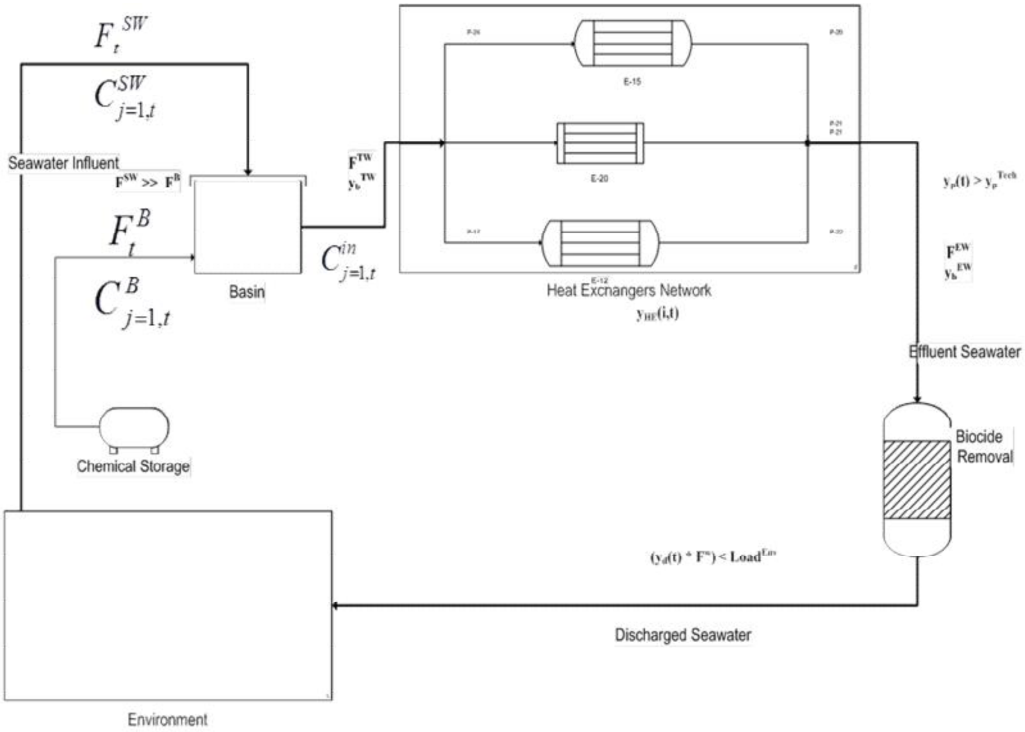

Figure 5.2. Representation of a Once-Through Cooling System.

Figure 5.2. sketches the cycle of the reaction of the biocide inside a once-through cooling system. It starts by adding the biocide solution to seawater in a basin before it enters the cooling system. Seawater is pumped from the body of the sea and is screened from large objects to be ready for cooling use. The biocide reacts and decays depending on many factors including residence time, temperature, initial concentration of biocide, and characterization of the seawater, including pH, salinity, and nutrients.

The annual operation is discretized into N_t time intervals (where t = 1,2, …, N_t). Within each interval (period), *t*, the operation is taken to be the overage over that period. The number of intervals is selected in a way that balances accuracy (e.g., the intervals must capture seasonal variations, action points such as changes in biocide dosage, operational variations such as increases in flow rate of product and/or seawater) versus computational effort (size of the optimization problem and computing time).

Let us use the index j to denote the key components to be tracked in the system. These include the biocide (given an index $j = 1$) as well as the biocide residuals (which impact biofouling development) and other byproducts (which also contribute to the consumption of biocide, but do not affect the biofilm). These residuals and byproducts are described by the index j (where $j = 2, 3, \ldots, N_C$). The following terms are defined:

Time Intervals:

N_t : the annual operation time is discretized into N_t time intervals.

t : is the time interval

Key Components:

j : is an index denoted to a key component, $j=1$ for the biocide.

N_C : is the number of key components tracked in the cooling system.

Process Segments:

i : is an index denoted to a process segment, $i=1$ for the basin.

N_S : is the number of the process segments (a portion of pipeline or a heat exchanger) in the cooling system.

Seawater Influent:

$C_{j,t}^{SW}$: Composition of the, j, key component of the biocide in fresh seawater as a function of, t, time interval.

F_t^{SW} : Flow rate of fresh seawater into the basin as a function of, t, time interval.

pH_t^{SW} : the pH of the seawater at the influent at time interval t.

T_t^{SW} : the temperature of the seawater at the influent at time interval t.

Biocide Storage:

$C_{j=1,t}^{B}$: Composition of biocide in the added biocide solution from the biocide storage into the basin as a function of, t, time interval.

F_t^{B} : Flow rate of the biocide solution into the basin as a function of, t, time interval.

Basin:

$C_{j,t}^{Ba\sin}$: Composition of the, j, key component of the biocide in the basin as a function of, t, time interval.

$pH_t^{Ba\sin}$: the pH of the treated seawater at the basin at time interval t.

$T_t^{Ba\sin}$: the temperature of the treated seawater at the basin at time interval t.

$\tau_t^{Ba\sin}$: is the residence time at the basin at time interval t.

$V_t^{Ba\sin}$: Volume of the water inside the basin as a function of, t, time interval.

Inlet of Cooling System:

i = 1.

Process Segment (i):

$C_{i,j,t}$: Composition of the, j, key component of biocide in the process segment, i, of the cooling system as a function of, t, time interval.

$F_{i,t}$: Flow rate of the treated seawater through the process segment, i, of the cooling system as a function of, t, time interval.

$pH_{i,t}$: the pH of the treated seawater inside the process segment, i, of the cooling system at time interval t.

$T_{i,t}$: the temperature of the treated seawater inside the process segment, i, of the cooling system at time interval t.

$\tau_{i,t}$: is the residence time inside the process segment, i, of the cooling system at time interval t.

$$\tau_{i,t} = \frac{V_{i,t}}{F_{i,t}}$$

$V_{i,t}$: Volume of the seawater inside the process segment, i, of the cooling system as a function of, t, time interval.

Outlet of Cooling System:

i = N_s-2

End Of Pipe Treatment (EOP):

$C_{N_s-1,t}^{Chem}$: Composition of the key component of chemicals at the end of pipe treatment unit as a function of, t, time interval.

i = N_s-1

Chemical Storage:

C_t^{Chem} : Composition of the chemicals out of the storage and going to the end of pipe treatment unit as a function of, t, time interval.

F_t^{Chem} : Flow rate of the chemicals to the end of pipe treatment unit as a function of, t, time interval.

Seawater Effluent:

$C_{N_s,t}^{Chem}$: Composition of the key component of chemicals out to the environment as a function of, t, time interval.

i = N_s

Typically, the flow rate of the treated seawater is significantly larger than the flow rate of the biocide solution, i.e.,

$$F_t^{SW} >> F_t^{B} \quad \forall t$$

Equation 5.12

The flow rates of the incoming seawater and of the treated seawater leaving the basin are taken to be equal to avoid any accumulation of water at the basin. Therefore, biocide flow rate can be neglected in the calculations of the residence time and of the treated seawater flow rate leaving the basin. The component material balances for any, j, key component tracked species at any process segment, i, of the cooling system at any, t, time interval are given by:

$$C_{j,t}^{Ba\sin} = B_{j,t}\begin{pmatrix} F_t^{B}, C_{j=1,t}^{B}, F_t^{SW}, C_{j=1,t}^{SW}, T_t^{SW}, pH_t^{SW}, \\ V_t^{Ba\sin}, \tau_t^{Ba\sin}, \ldots, C_{j=1,t}^{Ba\sin}, \ldots, C_{j,t}^{Ba\sin}, T_t^{Ba\sin}, pH_t^{Ba\sin}, F_{i=1,t} \end{pmatrix} \quad \forall t$$

Equation 5.13

where $\mathrm{B}_{j,t}$ is the function characterizing the reactive model of key component species j within the basin at, t, time interval. For instance, if the basin is modeled as a completely mixed system, the component material balance for the biocide is given by:

$$F_t^{B} C_{j=1,t}^{B} + F_t^{SW} C_{j=1.t}^{SW} - F_{i=1,t} C_{1,1,t} = r_{1,t}^{Basin} V_t^{Basin} \quad \forall t$$

Equation 5.14

where $r_{j=1,t}^{Ba\sin}$ is the rate of depletion of the biocide in the basin per unit volume.

Within the process, given the specific path of seawater inside the process, a "path" model is developed to account for the biocide reaction kinetics throughout the process. The seawater goes through a number of pipes and units. The process is discretized into a number of segments. Each segment, i, represents a portion of the seawater pipeline or a heat exchanger (e.g., cooler, coil in a hot unit, cooling jacket of a unit, etc.). Consider the N_c key species and refer to the concentration of key component j in segment i during period t as $C_{j,i,t}$. For the j^{th} species, in the i^{th} segment, and at t^{th} period, the following kinetic expression may be written as:

$$C_{i,j,t} = \Psi_{i,j,t}\left(F_{i,t}, C_{i-p,1,t}, \ldots, C_{i-p,j,t}, \ldots, C_{i-p,N_C,t}, V_{i,t}, \tau_{i,t}, T_{i,t}, pH_{i,t}\right) \quad \forall i, \forall t$$

Equation 5.15

where the subscript, i-p, is referring to the previous process segment of the cooling system before process segment i. The thickness of the biofilm in the i^{th} segment at the end of the t^{th} period is given by the following equation:

$$d_{i,t} = d_{i,t-1} * \left(1 - I_{i,t-1}\right) + \Delta d_{i,t}(C_{i,1,t}, \ldots, C_{i,j,t}, \ldots, C_{i,N_C,t}, T_{i,t}, pH_{i,t}, , \tau_{i,t})$$

Equation 5.16

where $I_{i,t-1}$ is a binary integer variable defined as:

$I_{i,t-1} = 1$ if maintenance/cleaning is carried out at the end of period t-1

$I_{i,t-1} = 0$ if no maintenance/cleaning is carried out at the end of period t-1

The effect of the binary in the previous equation is to set the thickness of the biofilm to zero (i.e., a clean surface) after the cleaning is carried out. The biofilm growth function $\Delta d_{i,t}$ is described in terms of the compositions of the biocide and residual byproducts, as well as the average temperature and pH of the seawater in segment i.

In addition to the economic aspects of determining when cleaning is scheduled, there is also mandatory cleaning if the biofilm thickness reaches a maximum allowable level:

$$d_{i,t} < d_{i,t}^{\max} \quad \forall i, \forall t$$ Equation 5.17

$d_{i,t}$: the biofilm thickness at process segment i and at time interval t.

$d_{i,t}^{\max}$: the maximum allowable biofilm thickness at process segment i and time interval t.

$d_{i,t}^{\infty}$: the highest level of biofilm thickness at process segment i at time interval t.

The biofilm thickness grows seasonally up to a certain level defined as d_i^{∞}, This thickness depends on the biological and process conditions. The loss in performance of the i_{th} heat exchanger resulting from the cumulative formation of the biofilm at the end of period t is given by:

$$\Delta Q_{i,t} = \Phi_{i,t}(d_{i,t}, d_{i,t-1}, d_i^{\infty}) \quad \forall i, \forall t$$ Equation 5.18

where $\Phi_{i,t}$ is the function characterizing the heat transfer reduction model in the process segment i at, t, time interval.

The objective function is to minimize the total annualized cost incurred from biofouling development. That cost includes all direct and indirect costs.

Annual Total Cost = Annual Cost of Biocide to Treat the Seawater

+ Annual Costs of Chemicals at EOP Treatment Unit for Removing the effect of Biocide Residuals

+ Annual Costs of Heat Exchanger Cleaning, Heat Loss Due to Fouling, and Gross Profit Loss Due to Shutting Down the Process for Heat Exchanger Cleaning. Mathematically, the objective function is described by:

$$Minimize\ Total\ Annualized\ Cost = \sum_{t=1}^{N_t}\left[Cost_t^{B} + Cost_t^{EOP} + \sum_{i=1}^{N_S}(Cost_t^{LP} + Cost_i^{Cleaning} * I_{i,t})\right]$$

Equation 5.19

The cost of biocide during period t is expressed as:

$$Cost_t^B = Cost\_Biocide(F_t^B, C_t^B)$$

Equation 5.20

The cost of end-of-pipe treatment during period t is given by:

$$Cost_t^{EOP} = Cost\_EOP(F_t^{Chem}, C_t^{Chem}, F_{i=N_s-2,t}, C_{N_s-2,1,t}, \ldots, C_{N_s-2,j,t}, \ldots, C_{N_s-2,N_c,t})$$

Equation 5.21

Loss of production can be defined as loss due to reduction in heat transfer in the heat exchanger units, as well as the loss of production due to shutting down the process for maintenance. The cost of loss of production is given by:

$$Cost_t^{LP} = Cost\_LP(\Delta Q_{i,t}, I_{i,t})$$

Equation 5.22

Environmental and quality constraints:

In addition to the aforementioned technical constraints, the minimization of the cost objective function is also subject to environmental and quality constraints from the process and from the environment. There is a minimum requirement from the process technical specification of the plant on the concentration of biocide residual to insure minimum biofouling development. Also, another constraint on the thickness of biofilm is to not exceed a certain thickness, $d_{i,t}^{\max}$.

$$C_{N_s-2,j,t} > y_{j,t}^{Tech}$$

Equation 5.23

$$d_{i,t} \le d_{i,t}^{\max}$$

Equation 5.24

The concentration of key component j of biocide residual must comply with the environmental regulations. Also, the concentration of chemicals added to reduce the effect of the biocide residuals is regulated by the environmental requirements. Hence,

$$C_{N_s,j,t} > y_{j,t}^{Env}$$

Equation 5.25

$$C_{N_s,j,t}^{Chem} > y_{Chem}^{Env}$$

Equation 5.26

5.5. CASE STUDY

Consider an integrated power production/desalination plant. The power plant has a maximum capacity to produce 427 MW of electricity using natural gas and turbines with steam extraction. Figures 5.3. and 5.4. provide the schematic flow diagrams of the power/desalination plant and the cooling system. The multi-stage flash (MSF) desalination plant has a maximum production capacity of 11,400 m^3/hr of desalinated water from three units, each producing 3,800 m^3/hr. The seawater ambient temperature varies from 24^{o}C to 35^{o}C. The maximum allowable temperature difference of seawater from the inlet to the outlet of the plant is 8^{o}C. The total seawater intake is designed to take a capacity of up to 67,500 m^3/hr in four pipes of 2.2 m diameter and about 1.2 km long. For maximum capacity, the flow rates of seawater used for the MSF units cooling system, the steam turbines, and the steam generators (boilers) are 36,822, 12,600, and 1,800 m^3/hr, respectively (Abdul-Wahab et al., 2009).

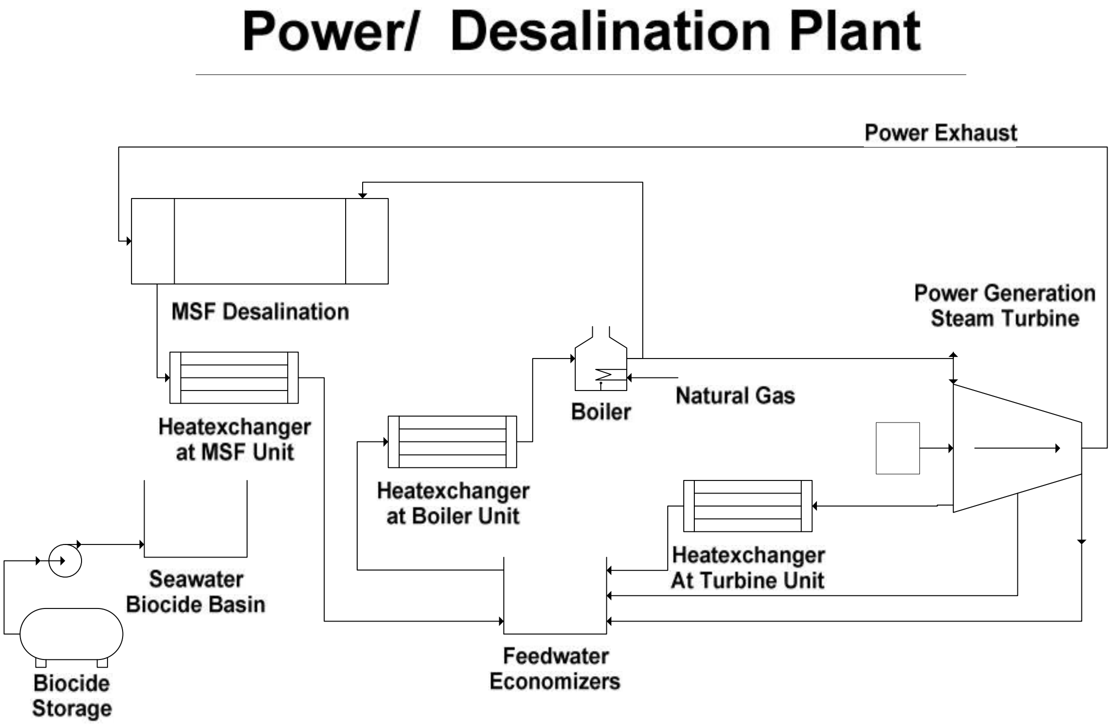

Figure 5.3. An Overall Representation of the Power/Desalination Plant.

The seawater cooling system of the power desalination plant is simplified and shown in Figure 5.4. (Abdul-Wahab et al., 2009). The production of power and the usage of seawater cooling vary monthly as shown by Table 5.2 and Table 5.3.

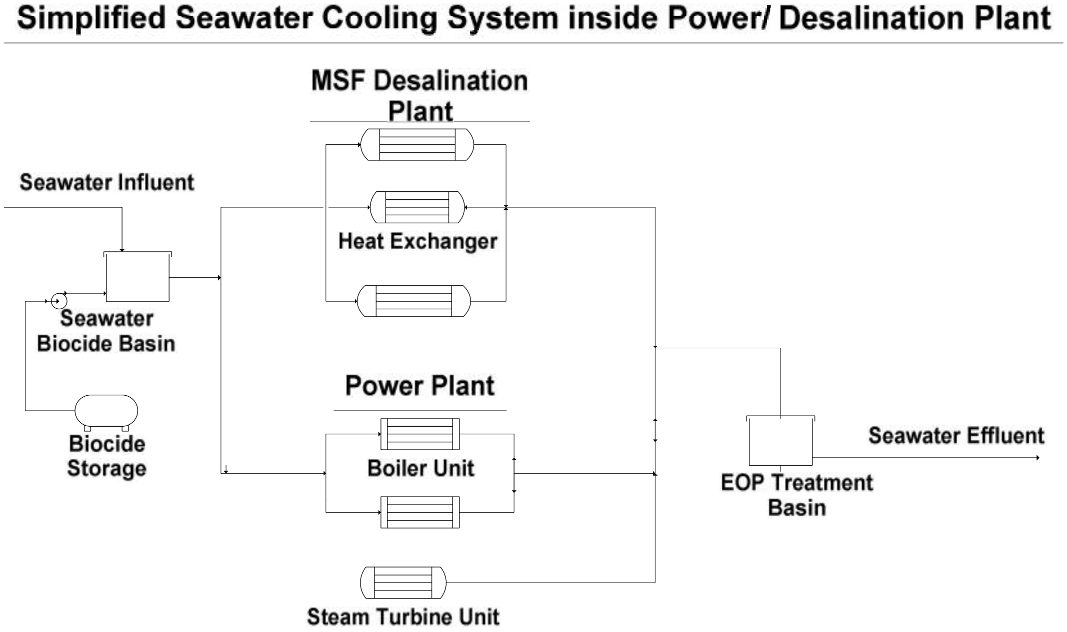

Figure 5.4. The Cooling System for the Case Study.

To meet the environmental regulations for the content of the biocide and its byproducts in the discharged seawater, there are several options for dechlorination. These include carbon adsorption and reactions with sodium dioxide, sodium metabisulfite, sodium bisulfate, or hydrogen peroxide. Sodium metabisulfite and sodium bisulfate are mostly used at smaller facilities due to the difficulty in controlling them. Hydrogen peroxide is not commonly used in the industry due to safety handling issues.

Table 5.2. The Cooling System for the Case Study.

Base-Case Amount of Seawater Used in the Cooling System of the Power/ Desalination Plant					
Plant Section	**Unit**	**Number of Units**	**Seawater used/Unit**	**Total Seawater usage**	**Heat Load**
			m^3/Hr	**m^3/Hr**	**MM Btu/hr**
Desalination	**MSF**	**3**	**12274**		**463**
			12274		**463**
			12274		**463**
				36822	
Power	**Boilers**	**2**	**900**		**34**
			900		**34**
				1800	
	Steam Turbine	**1**	**12600**	**12600**	**476**
Total				**51222**	

Table 5.3 Summary of the Solution Results of the Case Study.

Monthly Power Supply			Cooling Seawater Usage (m3/hr)			
Month	(%) of Cap.	(MW)	MSF Unit	Boiler	Steam Turbine	Total
Jan	75	322	27750	1356	9496	38602
Feb	70	297	25615	1252	8765	35632
Mar	81	347	29884	1461	10226	41571
Apr	84	359	30952	1513	10591	43056
May	93	396	34154	1669	11687	47510
Jun	93	396	34154	1669	11687	47510
Jul	99	421	36288	1774	12417	50479
Aug	100	427	36822	1800	12600	51222
Sep	94	402	34687	1695	11869	48252
Oct	93	396	34154	1669	11687	47510
Nov	90	384	33086	1617	11322	46025
Dec	81	347	29884	1461	10226	41571
Monthly Average	88	374	32286	1578	11048	44912

Based on the proposed holistic approach, all scenarios from the biocide dosing for seawater treatment and post-treatment, and all of the costs incurred from heating loss due to fouling and heat exchanger cleaning are incorporated in the optimization formulation. The objective function is the total annualized cost incurred directly and indirectly from fouling. This objective function includes the annual operating cost of the biocide (chlorine) used to treat the cooling seawater against biofouling, the annual cost of removing chemicals used for removing residuals from the effluent seawater before discharge, the cost of cleaning the heat exchanger units, the cost of the loss of production incurred by biofouling, and the annual gross profit loss from shutting down the plant operation for cleaning the heat exchangers. The objective of the optimization model here is to directly minimize the cost for treating seawater for cooling purposes and any loss occurred due to biofouling development from an untransferred heat load below the required cooling duty due to the growth of the biofilm which may affect the yield of the plant. Also, the objective function considers the cost of maintaining the cooling units on a regular basis throughout the year to clean the heat-transfer surface of the coolers.

The annual operating time is discretized into $N_t = 365$ time intervals (i.e., the optimization formulation is developed on a daily basis). The key components are tracked in the cooling system for an accumulation of biocide residuals. The cooling system is discretized into numbers of segments $i = 1, 2, \ldots, N_s$. Those segments are portions of the pipelines or heat exchanger units.

$$Minimize\ Total\ Annualized\ Cost = \sum_{t=1}^{N_t} \left[Cost_t^B + Cost_t^{EOP} + \sum_{i=1}^{N_S} (Cost_t^L * I_{i,t}) \right] \quad \text{Equation 5.27}$$

Total Annual Cost of Biocide:

$$Cost_t^B = \left[\sum_t^{N_t} F_t^B * \omega \right] * Biocide \quad \text{Equation 5.28}$$

The total annual cost of biocide is the summation of the volumetric flow rate of biocide F_t^B over all time intervals N_t, multiplied by the duration of each time interval ω. This total is multiplied by the cost of biocide (\$/m^3).

Total annual cost of end-of-pipe treatment is calculated as follows:

$$Cost_t^{EOP} = \left[\sum_t^{N_t} F_t^{Chem} * \omega \right] * Chemicals$$

Equation 5.29

Total annual cost of end of pipe treatment is equal to the summation of the volumetric flow rate of chemicals (m^3/hr) multiplied by the duration of each time interval over all time intervals, N_t. The total summation is multiplied by the cost of chemicals (\$/m^3).

Total annual cost for production loss due to heat reduction in heat exchangers caused by fouling and shutting down the process for heat exchangers cleaning is given by:

$$Cost_t^L = \left[\sum_{i=1}^{N_S} Maintenance_i \right] \quad \forall t$$

Equation 5.30

where $Maintenance_i$ is the cost for maintaining process segment I with a loss of production due to the reduction in heat transfer and being out of the process for cleaning. The total annual cost for heat exchangers' maintenance is the summation of the multiplication of binary number $I_{i,t}$ by the cost of the maintenance of a single process segment over all process segments N_i and over all time intervals N_t.

Determining the amount of residual chlorine [C_{Cl2}] after time t in minutes requires the result of the kinetic study depending on water quality and the time of the year. Also, for different temperatures, the changes in decay rate constants are considered. The models of Wang et al. (2008) and Xin et al. (2003) were used in developing the kinetic model for chlorine. The general form of chlorine decay in seawater is as follows:

$$C = A\, e^{-kt} \qquad \text{Equation 5.31}$$

It was considered that the first chlorine decay was very rapid in the first few minutes (Characklis et al., 1980). After the first five minutes, the data are fitted to the exponential form shown above (Xin et al., 2003).

The decay of biocide inside the cooling system for this case study follows this function:

$$C_{i,j,t} = C_{i-p,j,t}\, e^{-k_t * \tau_{i,t}} \qquad \text{Equation 5.32}$$

where:

$C_{j,i,t}$:is the concentration of biocide key component j at process segment, i, at time interval t in (mg/l).

$C_{j,i-p,t}$:is the concentration of biocide key component j at process segment, i-p, which precedes process segment i at time interval t.

The decay constant (1/min) has a proportional relationship with temperature (Nebot et al., 2007). As temperature increases, the decay of chlorine increases following this equation:

$$k_{i,t} = \eta * T_{i,t} \qquad \text{Equation 5.33}$$

where T is measured in Celsius

$\kappa_{j,t}$:is the disinfection kinetics rate constant for key component j at time interval t.

η: is the coefficient of the decay constant of biocide by-products $\eta = 6.8 * 10^{-4}\ (1/\min.^{o}C)$.

$T_{i,t}$ the temperature in (^{o}C) at process segment i and time interval t.

Data for the residual chlorine is in seawater at temperature range from 20 to 24C were extracted from Hostgaard-Jensen et al. (1977).

$$T_{i,t} = \frac{Q_{i,t}}{F_{i,t}\rho^{SW} C_p^{SW}} + T_{i-p,t} \qquad \text{Equation 5.34}$$

$T_{i-p,t}$:is the temperature of seawater at process segment i-p, preceding segment i at time interval t

$Q_{i,t}$: the heat transfer at process segment (in the heat exchanger) i and at time interval t.

$Q_{i,t}^{\mathrm{Re}\,q}$:is the heat transfer required for process segment i at time interval t (Btu/hr).

The heat transfer rate would decrease from $Q_{i,t}^{\mathrm{Re}\,q}$ *to* $Q_{i,t}$ as the biofilm accumulates. The required output of the plant required an operational schedule to maintain certain operational conditions. Thus, the heat load required to be transferred at each process segment (in the heat exchanger) is assigned accordingly. This amount of heat load for each process segment i at time interval t is called $Q_{i,t}^{\mathrm{Re}\,q}$. At the same time, the heat load transferred, $Q_{i,t}$, has to be within the designed margin after any reduction due to fouling according to the equation below (Nebot et al., 2007). From the percentage reduction in heat transfer in the heat exchanger, the heat transferred can be calculated from the designed value.

$$Q_{i,t} = Q_{i,t}^{\mathrm{Re}\,q} * \left(1 - \frac{\%H.T.R_{i,t}}{100}\right)$$

Equation 5.35

therefore, $Q_{i,t}$ is the actual heat load transferred at unit i and time interval t, which has to be less than or equal to the unit i is designed for. $Q_{i,t} \leq Q_{i}^{Des}$ where %HTR$_{i,t}$ is the percentage of heat transfer reduced at heat exchanger i at time interval t. The reduction in the designed heat transfer of a heat exchanger can be related to the biofilm thickness. However, biofilm thickness is not directly related to the reduced heat transfer because biofilm density changes with time. But, for simplicity in this model, it is considered that t at heat transfer reduction is calculated from biofilm thickness.

$$\%HeatTransfer\,\mathrm{Re}duction = \%HTR_{i,t} = \varepsilon * d_{i,t} \qquad \text{Equation 5.36}$$

$\%H.T.R_{i,t}$:is the percentage of heat transfer reduced for process segment i and at time interval t.

$$\varepsilon = 0.2156\left(1/\mu m\right) \qquad \text{Equation 5.37}$$

ε: is the coefficient in the heat transfer percentage equation.

The biofilm thickness increases over time by accumulating on the tubular surface of the heat exchangers (Turakhia et al., 1984). The biofilm thickness depends on the net between the rates of attachment, growth, and detachment, as well as the destruction rate of biofilm due to the biocide effect (Sriyutha Murthy et al., 2004; Morgan et al., 1969). This can be described by the following equation (Bryers et al., 1982):

$$d_{i,t} = d_i^{\infty} * \left\lfloor 1 - e^{\left(-\beta_{i,t} * \sigma i_{i,t}\right)} \right\rfloor / \; e^{\left(\gamma_{i,t} * \varpi\right)} \qquad \text{Equation 5.38}$$

$$\beta_{i,t} = \phi * T_{i,t}$$ Equation 5.39

$d_{i,t}$= net development from growth and destruction

$\beta_{i,t}$: is the biofilm growth rate constant for process segment i at time interval t (1/min)

(phi) $\phi = 2.909 * 10^{-7}\ (1/\min.^{o}C)$

ϕ: is the coefficient of biofilm growth rate constant [1/ (min.°C)].

ω : is the duration of a single time interval (day).

$$\sigma_{i,t} = \omega + \left[\left(\frac{-1}{\beta_{i,t-1}} \right) * \ln\left(1 - \frac{I_{i,t-1} * d_{i,t-1}}{d_i^{\infty}} \right) \right],$$ Equation 5.40

$\sigma_{i,t}$: is the biofilm growth rate constant considering the growth from the previous time interval for process segment i and at time interval t (min).

$$\alpha = 0.0225 \left(\frac{\mu m}{\min} \right)$$ Equation 5.41

where α is the coefficient of biofilm growth from the previous time segment.

When the biofilm thickness reaches the maximum allowable thickness, a decision for maintaining that unit has to be made. Here, this has been accounted for by multiplying the maximum allowable thickness by a binary number $I_{i,t}$. When biofilm thickness $d_{i,t-1}$ of unit i at time interval t-1 exceeds the allowable level d_i^{Max} , then $I_{i,t}$ for unit i and time interval t-1 is equal to zero. Otherwise, $I_{i,t}$ is always equal to one. The maximum allowable level of the biofilm thickness has to be less than d_i^{∞} :

$$I_{i.t-1} = \begin{bmatrix} 0 \ \ when \ \ d_{i,t-1} > d_i^{Max} \\ 1 \ \ when \ \ d_{i,t-1} \ \underline{< d_i^{Max}} \end{bmatrix}$$ Equation 5.42

$$0 - d_i^{Max} * I_{i,t} < d_{i,t} - d_i^{Max} \underset{-}{<} \left(10000 - d_i^{Max}\right) * \left(1 - I_{i,t}\right)$$ Equation 5.43

$$d_i^{Max} < d_i^{\infty}$$ Equation 5.44

$$d_i^{\infty} = 250 \mu m$$ Equation 5.45

$I_{i,t}$: is a binary number for making decisions in order to maintain process segment i at time interval t.

The destruction rate of the biofilm due to the biocide depends on the biofilm thickness of the same unit i at the pervious time interval t-1 and the concentration of biocide residual coming from the previous process segment p_i at the pervious time interval t-1 (Platon et al., 1985).

$$\gamma_{i,t} = \lambda * C_{p_i,t-1}, \quad \gamma : (1/\min)$$ Equation 4.56

$$\lambda = 2.829 * 10^{-4} \left(\frac{1}{\min.(mg/l)} \right)$$ Equation 4.57

$\gamma_{i,t}$: is the biofilm destruction rate constant for process segment i and time interval t (1/min).

λ: is the coefficient of biofilm destruction rate constant (Gamma) of biocide residual

Additional constraints used in the case study:

- The maximum allowable biofilm thickness is 70um.
- Cleaning (maintenance) of heat exchangers is only considered at the end of each month and no more than three maintenances are allowed per year.

5.6. RESULTS

The optimization formulation for the 365 daily periods was solved simultaneously using the software LINGO. The key optimization results are summarized by Figures 5.5. and 5.6. as well as Table 5.4., which show the amount of biocide and chemical dosing each month as well as the total annual cost for treating seawater before it enters the cooling system and before it is discharged back to the sea. The importance of the results emerging from this work is holistic approach with respect to the whole plant and the simultaneous consideration of the whole annual operation. The discharges conform to the environmental regulations after enforcing the new limit which reduces the allowable residual chlorine limit from 0.10 to 0.05 ppm. The biocide dosing was on a continuous dosing on monthly basis instead of semiannual basis. The focus was on an optimal biocide dosing to meet the minimum technical process requirements. The end-of-pipe treatment was used to treat the biocide residual beyond the environmental regulations. In most of the time, the average biocide residual is below 0.002 ppm at the discharge. Heat-exchanger cleaning was carried out at the end of July. All these results were achieved while the total cost of the biocide and the chemicals used for the end-of-pipe treatment were reduced from $ 4.9 MM/yr to $3.5 MM/yr.

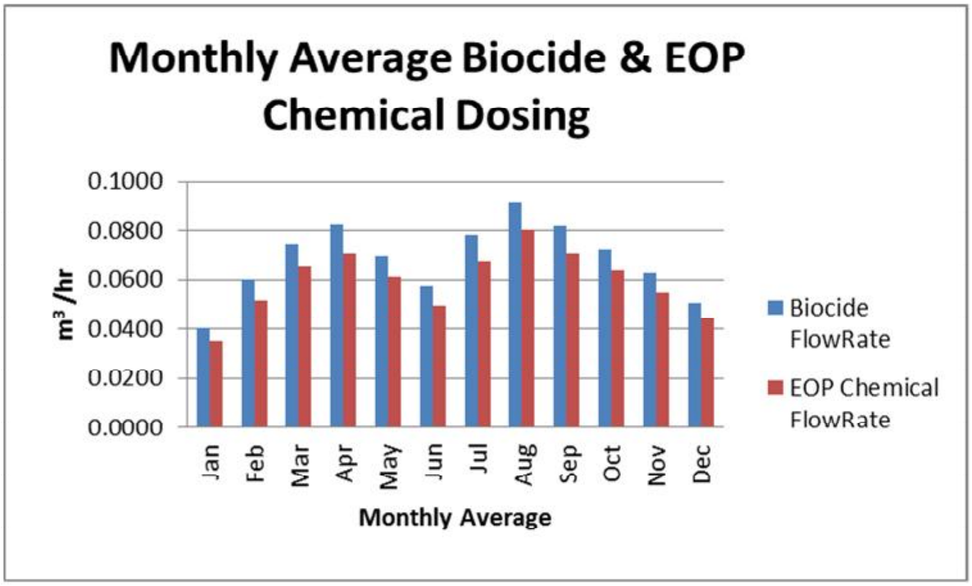

Figure 5.5. Monthly Average Biocide and EOP Chemical Dosing.

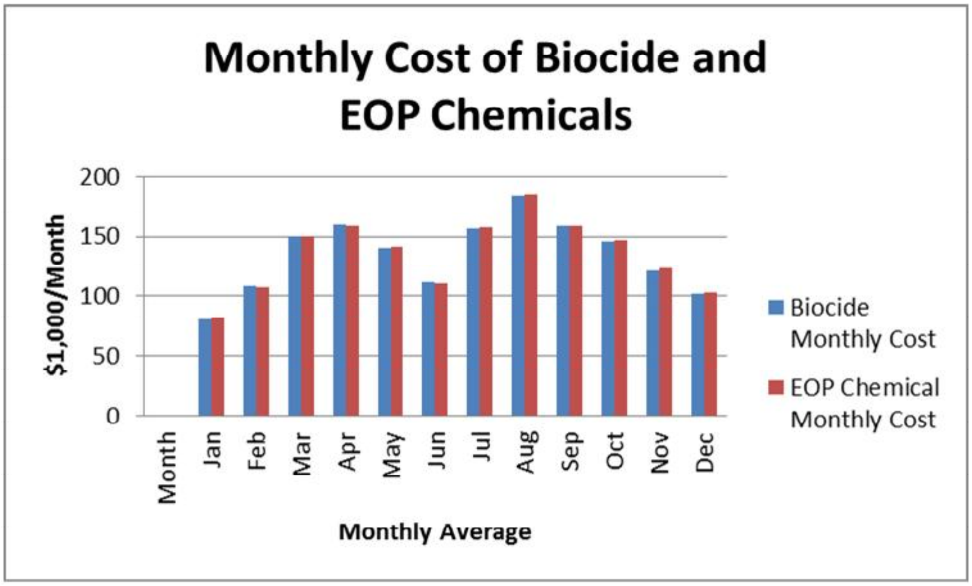

Figure 5.6. Monthly Cost of the Optimal Dosing of the Biocide and EOP Treatment Chemical.

Table 5.4. Table Showing the Summary of the Solution Results of the Case Study.

Biocide Used		Maintenance		Chemicals Used for Dechlorination		Cooling Seawater Used		Total Cost
M3/yr	MM $/yr	#/yr	MM $/yr	m3/yr	MM $/yr	m3/yr	MM $/yr	MM $/yr
600	1.620	1	0.3	523	1.621	394	0.039	3.541

There are many operating practices that impact the efficiency, performance, and cost of the plant. Adding more than the required amount of biocide would result in a higher performance of the heat exchanger units, but it would require additional treatment for seawater before it is discharged. Using less than the optimal doses of the biocide lead to reduction in heat transfer and process performance. Furthermore, there is a critical need to determine the timing of the cleaning maintenance of the heat exchangers. A systematic procedure has been developed for the optimization of scheduling the dosing of biocide and dechlorination chemicals as well as cleaning maintenance for a power production/thermal desalination plant. The annual operation is discretized into operational periods and the process is discretized into operating segment. A multi - period optimization formulation was developed to determine the optimal levels of dosing, the relationship between the applied doses, the process conditions, and seawater characteristics for each time period. The technical and environmental considerations were also accounted for and a case study has been solved to demonstrate the applicability of the devised procedure.

6. A SYSTEMS INTEGRATION APPROACH TO THE OPTIMUM OPERATION AND SCHEDULING OF BIOCIDE USAGE AND DISCHARGE FOR SEAWATER COOLING SYSTEMS

6.1. OVERVIEW

Using seawater in cooling systems is a common practice in many parts of the world where there is a shortage of freshwater. Biofouling is one of the major problems associated with the usage of seawater in cooling systems. Therefore, a biocide is typically added to seawater to control the growth of biofilms. There are numerous challenges in the design and operation of seawater cooling systems. Specifically, it is important to determine optimal strategies for the use of biocide to address the technical objectives of the process while complying with the environmental regulations for the discharge of the biocide and its byproducts. The objective of this work is to develop a systematic approach to the optimal design and integration of seawater cooling systems in industrial facilities along with the usage and discharge of biocides. The key building blocks of the approach include the chemistry and kinetics of the biocide, process cooling requirements and prospects for heat integration, dosage scenarios and dynamic profiles, biofilm growth, seawater discharge, and environmental regulations. Specifically, the paper will address the following tasks:

1) Identification of the reaction pathways for the biocide from the mixing basin to the discharge points.
2) Kinetic modeling of the biocide and byproducts throughout the process.

3) A process integration framework to provide a holistic approach to optimizing the design and operation of the seawater cooling systems, along with the dosage and discharge systems.

Scheduling chemical dosing to minimize the total annual cost of the system includes considering the cost of the biocide, the value of lost heat transfer resulting from the biofilm, the cost of cleaning and maintenance, and the cost of treating the biocide and byproducts in the discharged seawater. A hierarchical procedure is developed to first identify design modifications for heat integration and energy efficiency. Then, a multi-period, multi-segment optimization formulation is developed and solved to identify the optimal operation and scheduling of biocide usage and discharge. The formulation includes the biocide chemistry and kinetics, the time-based variations in seawater and process characteristics, the relationship between the biocide usage, the process conditions, and the rate of biofilm growth, and the environmental regulations for the discharge of seawater. A case study is solved to illustrate the applicability of the devised approach.

6.2. INTRODUCTION

The use of seawater in industrial cooling is a common practice in many parts of the world that have limited freshwater resources. One of the primary operational problems of using seawater in cooling is biofouling. Other problems include scaling and corrosion. The formation of bioflim is caused by the biological activities of microorganisms in the seawater. Biofilms are very thin layers that stick to the inside surface of heat exchanger tubes that use seawater. As small as a 250 micrometer biofilm thickness is enough to reduce the heat transfer coefficient by 50%. Therefore, biofouling is a serious problem (Goodman 1987). In some cases, excessive biofouling can obstruct the heat exchangers.

There are three major types of biofouling:

- Microbial fouling, which occurs as a result of the development of microorganisms and their products
- Macrobial fouling, which is a result of the deposit and growth of macroorganisms like barnacles and mussels
- Biological fouling, which is a result of a collection of detritus.

Typically, the development of microbial fouling precedes any macroorganism colonization. Therefore, controlling microbial fouling has a great advantage of avoiding macrobial fouling development. Biofouling usually develops over a few steps, including biological, chemical, and physical processes. These processes may happen in a series and/or parallel steps (Characklis, 1979). These steps include:

- Transportation of organic molecules and microbial cells from the bulk of the seawater coolant to the surface of the tubes of the heat exchangers.
- Adsorption of the organic molecule and sedimentation on the surface of the tubes of the heat exchangers.
- Adhesion of the microbial cells surface of the heat-exchange tubes.
- Growth whereby the attached microbial cells start producing more cells leading to the formation of the biofilm.

- Detachment of some cells of the formed biofilm due to sheer stress of the flowing seawater.

To prevent the harmful effects of biofouling, biocides are used to control the biological activities of the microorganisms and lessen the effect of fouling. Controlling microbial growth is usually achieved by using an oxidizing agent, such as chlorine, in an easy-to-disperse form, such as a hypochlorous acid or a hypochlorite ion, or in a gaseous form like chlorine gas or chlorine dioxide. An intermittent chlorine dosage of 2 –5 mg/L for 10 minutes per day can prevent microfouling, and a continuous dosage of 0.5 mg/L during the second to fourth week of breeding season can prevent the blockage caused by macrofouling. Under a continuous biocide dosage, aquatic organisms like oysters and mussels tightly close their shells for weeks at a time, but they often die of asphyxiation.

These chlorine forms are most widely used due to cost and effectiveness factors. Chlorine is a nonselective oxidant (it reacts with organics and nonorganics) and it deactivates microbes. Also, chlorine reacts with natural organic matter (NOM), leading to the formation of numerous by-products (Ben Waren 2006). Some of these by-products are hazardous to aquatic life and human health. While there are other means of preventing biofouling, such as periodic cleaning with sponge balls, tube heating and drying, and antifouling paint, nonetheless, chlorine dosing is the most widely-used method because of its cost-effectiveness and efficiency in slowing down or eliminating different forms of microbial growth.

Other forms of chlorinated biocides include chloramines (e.g., NH2Cl, NHCl2, and NCl3) and chlorine dioxide. Other biocides include ozone and ultraviolet radiation, but both are relatively high in cost compared to chlorine. Ozone has not been commercially utilized due to the high risk of possible leakage. A low concentration of ozone, i.e. 0.3 ppm, is considered to be harmful to workers and to the surrounding environment. Ultraviolet radiation is an effective disinfection method; however, its applicability is limited to cases when the water has little turbidity and suspended matter. Also, there is no residual disinfection effect after the radiation.

Using chlorine as a biocide is not trouble-free. Discharging chlorine and its by-products back into natural bodies of waters with no treatment would definitely create some environmental problems. Chlorine is a nonselective oxidant. In seawater, chlorine and its various forms may react with organic species that exist in natural water, producing hazardous compounds. Examples of these compounds are trihalomethanes (THMs), halogenated acetic acids (HAAs), and halophenols (HPs), which are carcinogenic for human health and aquatic life. THMs are formed from a reaction of chlorine with natural organic matter. THMs are chemical compounds of methane, replacing the three hydrogen atoms with halogens like tri-chlorinated/ brominated methane demonstrated as (CHX3):(CHCl3), (CHBr3). THMs are environmental pollutants and they may cause damage to the liver, kidneys, and central nervous system. HAAs are acetic acids with H-atoms (fixed to a COOH-group) replaced by halogen atoms. HAAs are suspected to raise the risk of cancer. HAAs could form THMs during biological decomposition. THM and HAA concentrations are higher during the summer season than in winter. Also, THM and HAA concentrations increase in that water comes from surface, rather than groundwater.

Since the seawater discharge of biocides and their reaction byproducts poses environmental and public health problems, there is a need to add end -of-pipe biocide treatment (e.g., dechlorination) units to reduce the concentrations of the biocid e and its byproducts at the discharged point. Chemical reduction using sulfur compounds has been used as a dechlorination agent to remove free and combined residual chlorine. Sulfur compounds like sulfur dioxide (SO_2), sodium sulphite (Na_2SO_4), bisulfite ($NaHSO_3$), or bisulphate ($NaHSO_4$) and sodium thiosulphate ($Na_2S_2O_3$), or sodium metabisulfite ($Na_2S_2O_5$), have been used to dechlorinate seawater in industrial cooling systems before discharging to the sea. Different dechlorination methods have been utilized in the industry, including activated carbon, activated carbon combined with ozonation, and photochemical reduction with ultraviolet irradiation.

Sodium sulfite (Na_2SO_3) was recommended for use as a dechlorinating agent by (Pyle 1960; Beeton 1976) based on economic and safety uses. It was the most economically effective, the safest, and the most capable of eliminating the toxicity of residual chlorine for the aquatic life. Sodium sulfite is added at a 2:1 ratio by weight with residual chlorine in order to completely and instantaneously eliminates chloramines. However, the disadvantage of using sodium sulfite is that it requires an accurate injection system and a periodic follow-up with chlorine fluctuating in influent water. Sulfur dioxide is another cost-effective dechlorinating agent. Sulfur dioxide is added at a weight ratio of 0.9 of sulfur dioxide for every 1.0 of chlorine to be removed. But, practically a 10% excess amount of sulfur dioxide is always added to make sure that the dechlorination process is completed. Sulfur dioxide is effective in removing both free and combined residual chlorine. Also, sulfur dioxide can be fed using similar equipment as is used for chlorination with a simple control scheme. Sulfur dioxide hydrolysis happens in water rapidly and completely to form sulfuric acid, as shown in the following reaction:

$$SO_2 + H_2O \rightarrow H_2SO_3 \qquad \text{Equation 6.1}$$

The oxidation number of the aqueous sulfur (SO_3^{-2}) is four, which means it will react with free and combined chlorine rapidly and completely, as shown in the following equations:

$$SO_3^{-2} + HOCl \rightarrow SO_4^{-2} + Cl^- + H^+ \qquad \text{Equation 6.2}$$

$$SO_3^{-2} + NH_2Cl + H_2O \rightarrow SO_4^{-2} + Cl^- + NH_4^+ \qquad \text{Equation 6.3}$$

Because of the strong interaction between the process cooling demand, operating conditions, and biocide needs and performance, it is important to develop an integrated approach to optimizing biocide usage and discharge by understanding the key process factors and seawater chemistry aspects, then reconciling them in an effective manner. The objective of this paper is to develop a systematic approach to the optimization of biocide usage and discharge by integrating seawater chemistry and process performance issues. This includes modeling the mechanism and kinetics of the biocide, relating the biocide kinetics to process conditions, and reducing biocide usage by lowering the cooling needs of the process via heat integration. The usage and discharge of seawater is linked to the process requirements, including cooling duties.

6.3. PROBLEM STATEMENT

The problem addressed in this paper can be stated as follows: given is a process which uses seawater in a once-through cooling system via a number of segments that include heat exchangers (coolers) and connecting pipelines. The heat duties of the process coolers and the temperature of the incoming seawater vary throughout the year. A typical dynamic profile for such variations is known. In order to prevent biofouling in the coolers, a biocide is added to the incoming seawater The added biocide undergoes various water chemistry reactions leading to the discharge of chemical pollutants (e.g., residual biocide, reaction byproducts). The composition and load of the pollutants as well as the temperature of the discharged seawater must meet a given set of environmental regulations. An end-of-pipe (EOP) treatment system may be added to assist in meeting the environmental regulations. Figure 6.1. is a schematic representation of the problem statement.

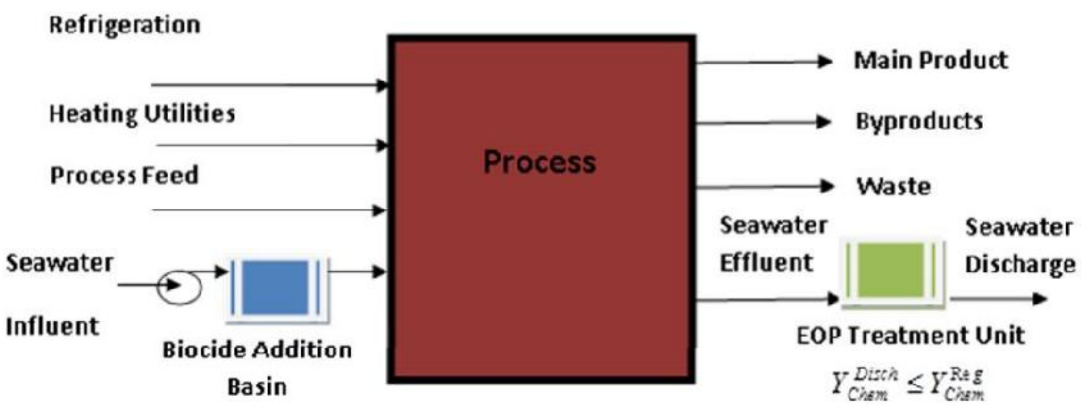

Figure 6.1. Representation of the Problem Statement.

The process resources, revises the process design and operation, and determines the optimal scheduling of chemical dosage load and timing, along with the heat - exchanger cleaning cycles per year.

6.4. APPROACH AND CHALLENGES

A systematic approach is to be developed to include the following specific tasks:

- Develop an appropriate level of modeling the chemical and kinetic aspects of biocide usage and their reactions with different species in seawater.
- Relate the usage of biocide, the generation of byproducts, the characteristics of the seawater, and the characteristics of the process to the formation of the biofilm on the heat-exchange surfaces.

- Account for the time-based variation in seawater temperature and process requirements.
- Incorporate the effect of regular maintenance activities to clean the heat-exchanger surfaces and end-of-pipe treatment to meet the environmental regulations.
- Develop optimal policies for process modification and dynamic dosing to optimize biocide usage and discharge.
- Develop an optimum scheduling strategy which determine the optimal frequency and timing of the maintenance service for cleaning the heat exchangers.

Developing the systematic approach involves several challenges. There is complexity in describing the reaction mechanism and kinetics for the biocide with the different species that exist naturally in seawater. It is necessary to identify the effective byproducts in controlling the biofilm development and to track these species. The developed models must also account for the time-based variations in the seawater characteristics (e.g., temperature) because of the impact on the reaction kinetics and the rate of biofilm growth. Additionally, any hazardous compounds produced throughout the cooling system until the discharge point must also be tracked. Appropriate levels of details should be obtained to be representative enough of the chemical behavior while avoiding too many details that will increase the size of the developed optimization formulation or complicate it mathematical nature.

Since the usage of seawater is linked to the process cooling requirements, any reduction in cooling requirements will have a direct impact on the amount of seawater used and discharged, along with the usage and discharge of the biocide. In order to successfully achieve this reduction in seawater and biocide, several design and operational changes must be made. It is also important to consider the impact of biocide-removal units (e.g., dechlorination) as required to meet the environmental regulations.

The first step in the proposed approach is to discretize the annual operation into Nt periods (e.g., days or months). For each period, the seawater characteristics are taken as the average during that period. To track the biocide chemistry and biofilm growth throughout the plant, the process is broken down into Ni segments (e.g., portion of a pipeline, heat exchanger, process unit). The next step is to reduce the cooling duty of the process by using heat integration tools such as thermal pinch analysis (e. g., (Smith 2005; El-Halwagi 2006; Kemp 2007)).

The objective of this step is to minimize cooling and heating utilities of the process. The biocide dosage is proportional to the cooling duty. As such, reducing the cooling utility of the process leads to reducing the usage and discharge of the biocide. The rationale behind starting with heat integration is that it will generate a cost savings from the reduction of cooling utilities.

The next step is to make a further reduction in seawater flow rate by enhancing the efficiency of seawater utilization. A practical technique to reach that reduction is to maximize the temperature of the discharged seawater while complying with the thermal pollution regulations. Then, the new seawater flow rate from the heat balance equation can be calculated after the reduction has been made from increasing the discharged temperature. After the reduction has been achieved in the seawater flow rate, the revised calculation can be performed by recalculating the reduced amount of biocide required for the seawater flow rate. Next, the chemical pathways and kinetics of the biocide reactions are modeled at the appropriate level of details. The following step is to optimize the dosage of biocide, while meeting the requirements of the process of the minimum residual biocide remains in the cooling system to insure the control over any biofouling development. The optimal biocide dosage is chosen based on an optimization formulation that includes the relationship between the biocide usage and the bio film growth, the impact of seawater characteristics, the effect of process conditions, the performance of the end-of-pipe biocide-removal unit, regular maintenance to clean the surfaces of the heat exchangers, and the impact of biofilm growth on the performance of the individual heat exchangers. Figure 6.2. is a schematic representation of the proposed procedure. The following sections provide more details on the key steps.

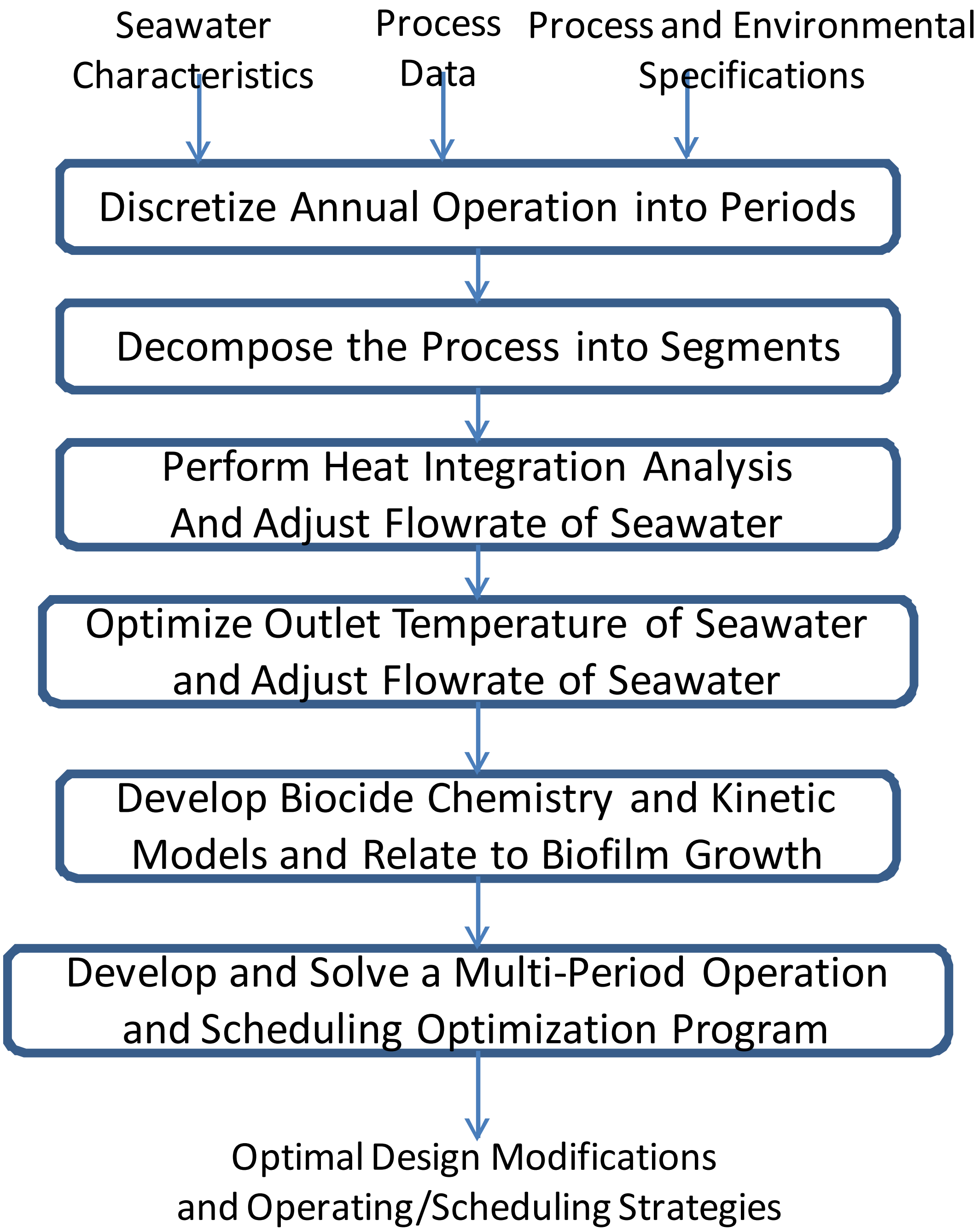

Figure 6.2. Overview of the Proposed Procedure.

6.5. BIOCIDE CHEMISTRY

It is necessary to develop a mechanistic model for the reaction pathways involving the biocide and the various species in the seawater. First of all, start with the reaction of chlorine when it is added to seawater as a gas or solution of a chlorine compound (e.g., sodium hypochlorite). Chlorine will dissolve and hydrolyze rapidly (almost instantaneous) and completely to HOCl (hypochlorous) acid with a reaction rate constant of $5X10^{14}$. When chlorine is added to seawater, it produces hypochlorous acid and hydrochloric acid, HCl. The latter is a relatively strong acid, and it will dissociate completely to a hydrogen ion and a chloride ion, while hydrochlorous acid, HOCl, is a relatively weaker acid, and it will dissociate slightly to a hydrogen ion and a hypochlorite OCl^-. Since the hydrogen ion appears in this reaction, this equilibrium is pH dependent. The distribution of the various species (HOCl, OCl^-) at equilibrium is a function of pH. Hypochlorous acid is the most germicidal species, but it is a weak acid that will dissociate to hydrogen and hypochlorite ions with pKa of 7.5 at 30 °C. Figure 6.3 shows the distribution of the species over the pH range.

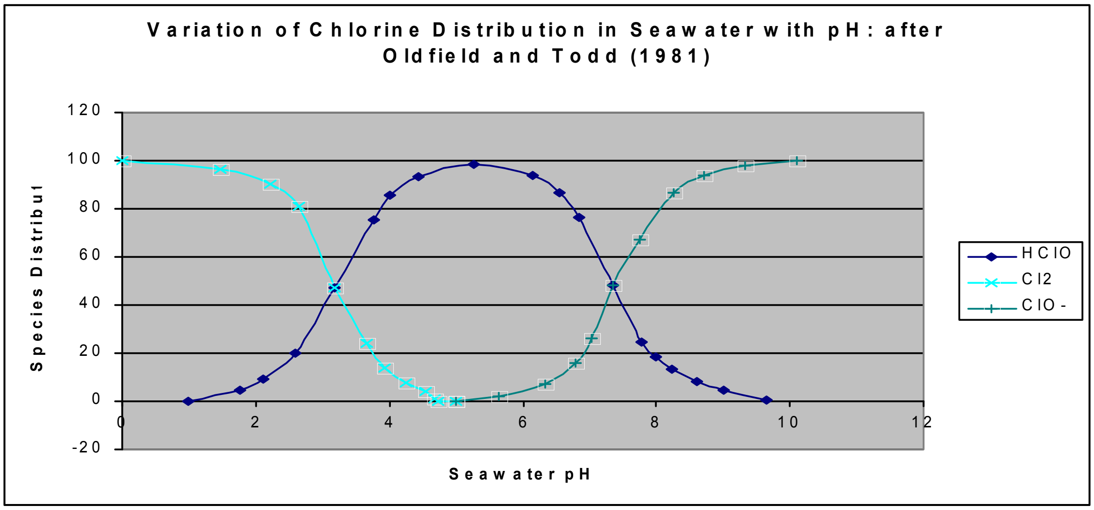

Figure 6.3. Distribution of Chlorine Species in Seawater (Based on the Data by Oldfield and Todd, 1981).

$Cl_2 + H_2O \rightarrow HOCl + HCl$ Equation 6.4

$HOCl \leftrightarrow H^+ + OCl^-$ Equation 6.5

In terms of disinfection effectiveness, hypochlorous acid is much stronger (almost two orders of magnitude) than the hypochlorite ion. Hypochlorous acid will reach its maximum concentration at pH ranges between 4 and 6 (Hostgaard-Jensen, Klitgaard et al. 1977). However, the effectiveness of a chemical species as a disinfectant does not necessary correlate with its effectiveness in removing biofilms. Weakening the polysaccharide matrix of microbial cells is one way to control the development of biofilms on the tube surface of heat exchangers. Experimental evidence shows that chlorination is more effective in causing biofilm detachment at pH values greater than pH 8, where OCl^- concentration is more dominant than HOCl (Characklis,1979).

Seawater naturally contains organic and nonorganic species, particularly ammonia and bromide species. Their concentrations vary depending on the nature of the water. For instance, seawater contains bromide with concentrations as high as 65 mg/l, but there may be a negligible amount in fresh waters. Ammonia concentrations depend on pollutants of the water. In highly polluted water, ammonia concentration is as high as 15 ppm, while in unpolluted water the concentration is lower than 0.05 mg/l. At full strength salinity, seawater ammonia concentration ranges between 0.001 and 1.0 ppm. Ammonia, as well as other reactive nitrogenous compounds, will be chlorinated to yield monochloramine (NH_2Cl), and will react further to produce dichloramine ($NHCl_2$). In freshwater, and a very traceable amount in seawater, dichloramine will react further with hypochlorous acid, producing trichloramine (NCl_3). All of the reactions of ammonia and combined chlorine with hypochlorous acid are made by replacing the hydrogen atom of the ammonia molecule with a chlorine atom from a combined chlorine molecule while maintaining its positive charge according to the following reactions:

$$HOCl + NH_3 \leftrightarrow NH_2Cl(\text{monochloramine}) + H_2O \qquad \text{Equation 6.6}$$

$$NH_2Cl + HOCl \leftrightarrow NHCl_2\ (\text{dichloramine}) + H_2O \qquad \text{Equation 6.7}$$

$$NHCl_2 + HOCl \leftrightarrow NCl_3\ (\text{trichloramine}) + H_2O \qquad \text{Equation 6.8}$$

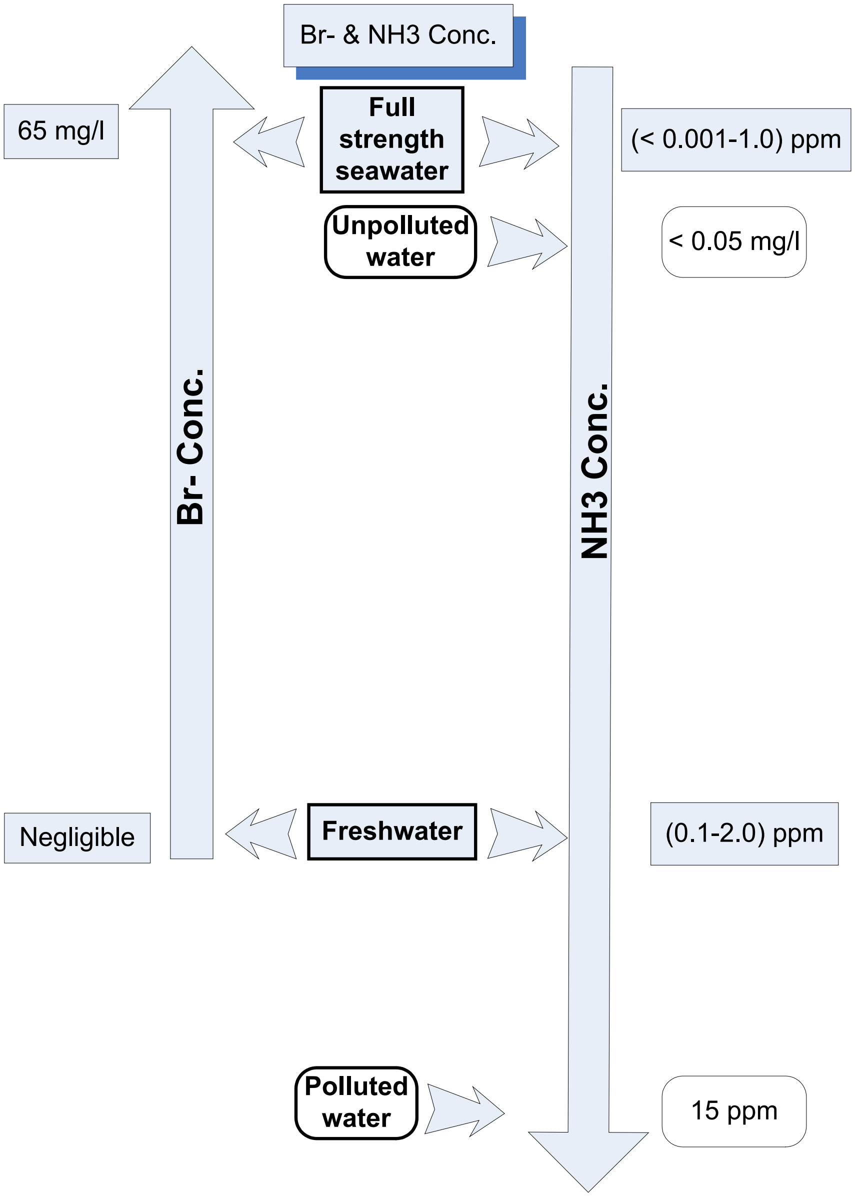

Figure 6.4. Concentration of Bromide and Ammonia in Natural Water.

These reactions depend on pH, temperature and contact time, but mainly on the chlorine to ammonia ratio. All of the free chlorine (hypochlorous acid) will be converted to monochloramine at pH 7-8 (the fastest conversion is at pH 8.3) when there is 1:1 molar ratio of chlorine to ammonia (5:1 by weight) or less. Then, within the same range of pH, dichloramine is produced at a molar ratio of 2:1 of chlorine to ammonia (10:1 by wt.). This reaction is relatively slow, so it may take up to an hour. Also, within the same range of pH, trichloramine will be produced at a molar ratio of 3:1 of chlorine to ammonia (15:1 by wt.) and at equal molar ratios, but at pH 5 or less. The two reactions producing di- and tri-chloramine are known as the breakpoint reactions where the chloramines are reduced suddenly to the lowest level. The significance of the breakpoint reaction is that chlorine reaches its highest concentration and germicidal efficiency (at 1:1 molar ratio of chlorine to ammonia) just before reaching this point. Also, at the breakpoint, monochloramine and dichloramine react together (which reduces chlorine residuals) to produce nitrogen gas, nitrate, and trichloramine. Dichloramine decomposes to an intermediate reactive product (NOH) which consumes mono-, di-chloramine, and hypochlorous acid, producing nitrogen gas and nitrate. Also, excessive chlorine will form trichloramine. These processes are shown in the following equations:

$$\mathrm{NHCl_2} + \mathrm{H_2O} \leftrightarrow \mathrm{NOH} + 2\,\mathrm{H^+} + + 2\,\mathrm{Cl^-}$$

Equation 6.9

$$\mathrm{NOH} + \mathrm{NH_2Cl} \leftrightarrow \mathrm{N_2} + \mathrm{H_2O} + \mathrm{H^+} + \mathrm{Cl^-}$$

Equation 6.10

$$NOH + NHCl2 \leftrightarrow N2 + HOCl + H + Cl^{-}$$ Equation 6.11

$$NOH + 2\,HOCl \leftrightarrow NO_3^{-} + 3\,H^{+} + 2\,Cl^{-}$$ Equation 6.12

$$NCl_3 + H_2O \leftrightarrow NHCl_2 + HOC$$ Equation 6.13

The reaction of chlorine into these forms steers it away from the disinfection function and renders the biocide less effective. Consequently, it is important to understand such side reactions. Hypochlorous acid rapidly reacts with bromide, producing hypobromous acid, which can also be produced from the reaction of bromide with monochloramine, as follows:

$$HOCl + Br^{-} \rightarrow HOBr + Cl^{-}$$ Equation 6.14

$$NH_2Cl + Br^{-} + H_2O \leftrightarrow HOBr + Cl^{-} + NH_3$$ Equation 6.15

where HOBr is hypobromous acid. Additionally, the hypochlorite ion may undergo a slow reaction with the bromide ion, as follows:

$$OCl^{-} + Br^{-} \leftrightarrow OBr^{-} + Cl^{-}$$ Equation 6.16

where OBr^- is the hypobromite ion. Bromide in seawater may also react directly with added chlorine to give bromine and chloride:

$$Cl_2 + 2Br^- \leftrightarrow Br_2 + 2Cl^- \qquad \text{Equation 6.17}$$

It is worth noting that the presence of ammonia and other nitrogenous compounds in the seawater will react with HOBr to yield monobromamine (NH2Br), dibromamine (NHBr2), and tribromamine (NBr3).

$$HOBr + NH_3 \leftrightarrow NH_2Br\,(\text{monobromamine}) + H_2O \qquad \text{Equation 6.18}$$

$$HOBr + NH_2Br \leftrightarrow NHBr_2\,(\text{dibromami ne}) + H_2O \qquad \text{Equation 6.19}$$

$$HOBr + NHBr_2 \leftrightarrow NBr_3\,(\text{tribromamine}) + H_2O \qquad \text{Equation 6.20}$$

The bromine breakpoint happens when the dibromamines are produced rapidly, leading to the formation of nitrogen gas:

$$NHBr_2 + H_2O \leftrightarrow NOH + 2H^+ + 2Br^-$$ Equation 6.21

$$NOH + NHBr_2 \leftrightarrow N_2 + HOBr + H^+ + Br^-$$ Equation 6.22

It is also important to consider the effect of the bromide that naturally exists in seawater at (50–70 mg/l). Bromide is typically in stoichiometric excess over the chlorine dosage, whereas ammonia concentration doesn't exceed 2 to 3 mg/L. The relative amount of bromine species to ammonia species produced is proportional to bromide concentration over ammonia concentration if we assume both reactions are rapid and simultaneous. In order to understand the various species interactions and reaction pathways, we have constructed the reaction mechanism shown in Figure 6.5. On these diagrams, the starting species and intermediate and final by-products are represented in boxes. The arrows correspond to reaction steps, and the boxes on the arrows represent the reactive species that contribute to that reaction.

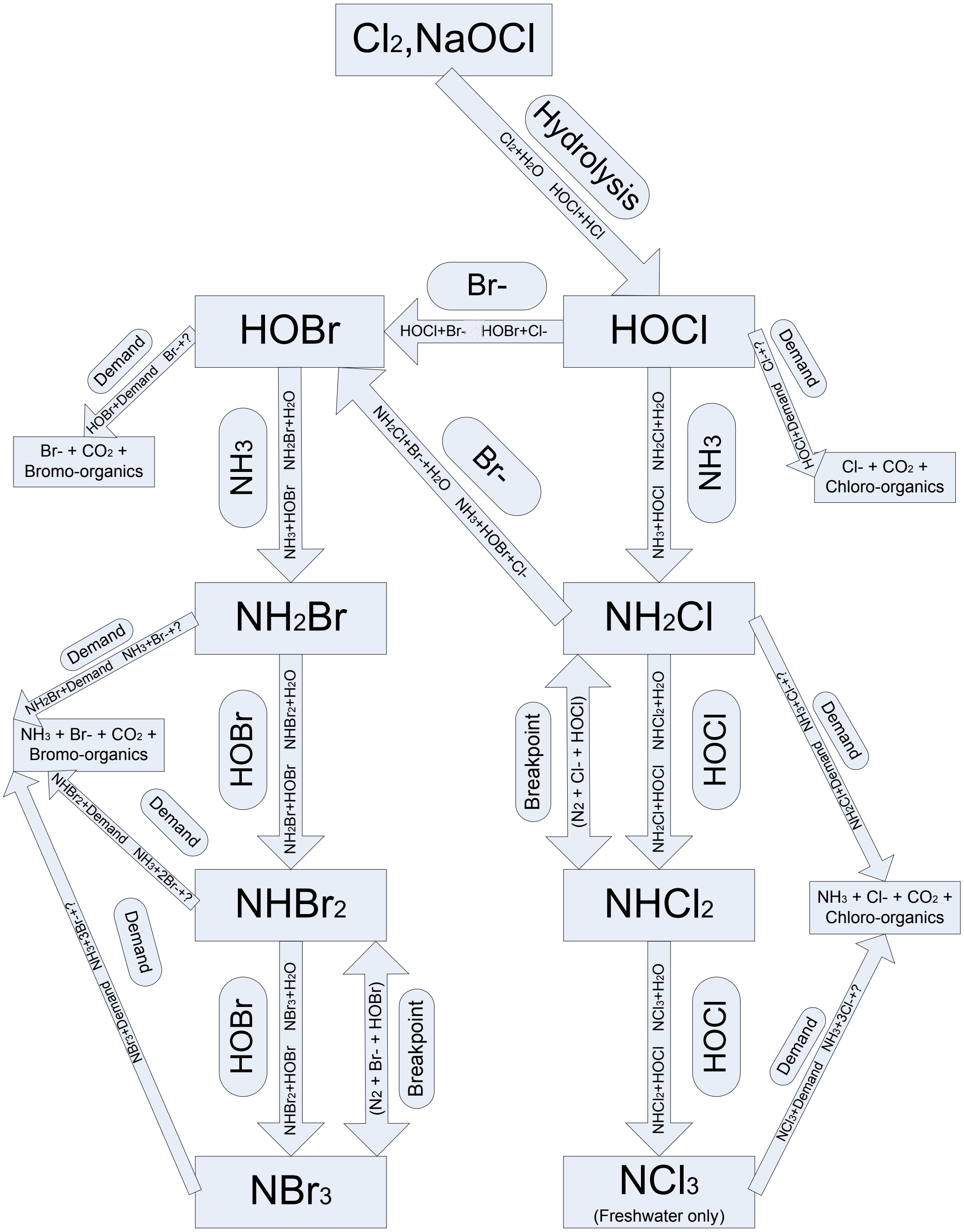

Figure 6.5. Summary of the Reaction Mechanism of Chlorine in Seawater.

6.6. MODELING OF HEAT-TRANSFER REDUCTION DUE TO BIOFILM GROWTH

The cooling system in the plant is divided into Ni segments. Each segment represents a pipe or a heat exchanger unit and is denoted by a subscript i. Figure 6.6. is a schematic representation of the segments included in the analysis. Also, for simplicity the annual operation is discretized into Nt time intervals. The values are taking as average during each time interval t. The ambient temperature of seawater (the coolant) varies depending on the time of the year. On the other hand, the scheduling changes for the operational conditions depend on the seasonal demand on the plant output. The climate changes affect the required amount of biocide because of its impact on the reaction kinetics and the rate of biofilm growth. The seasonal demand on the plant output add another variation that is making the model for optimizing the cooling system has to be more responsive to all those variations. The rate of biofilm growth depends on the temperature, nutrients, time of the year, flow rate, etc. Furthermore, the biofilm develops through a number of physical, chemical, and biological steps which happen in series and/or parallel. The biofilm begins with the attachment, then growth. Detachment is due to the sheer stress of the fluid flow and starts from early stages of the development. However, growth continues only up to a certain level where the detachment rate becomes higher than the attachment and growth rate. This limits the biofilm thickness from exceeding certain level.

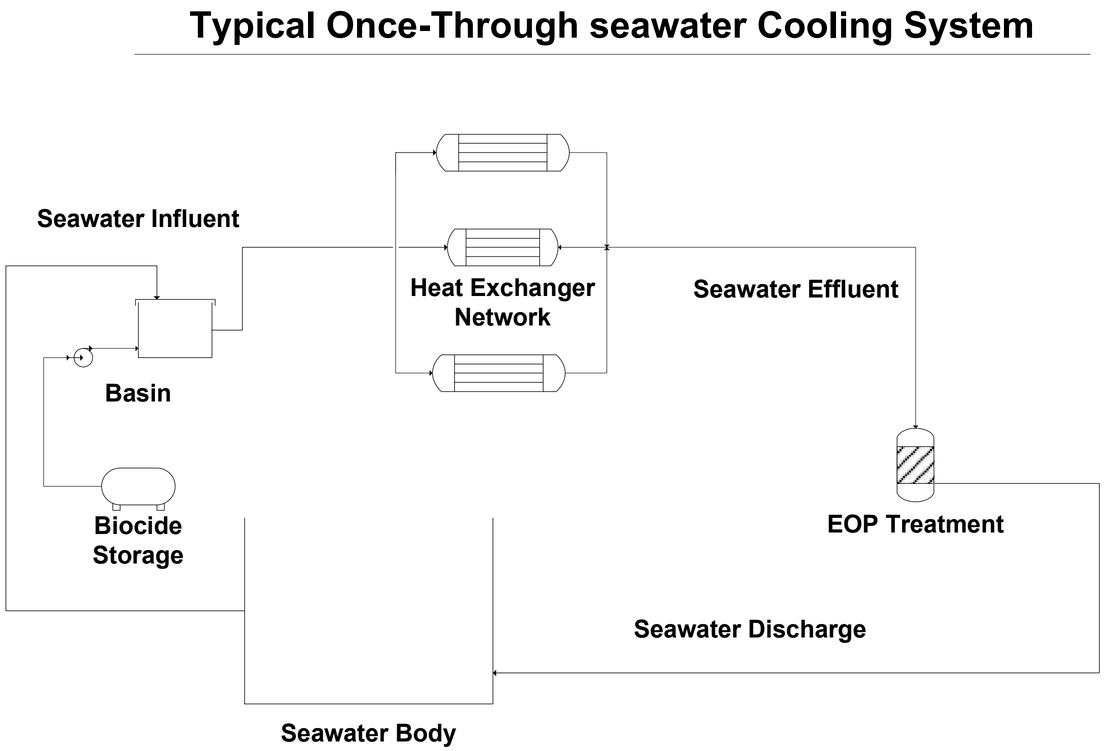

Figure 6.6. Segment Representation of the Process.

The segmented diagram starts by adding the biocide solution to seawater in a basin before entering the cooling system. Seawater is pumped from the body of the sea and screened from large objects to be ready for cooling use. At the basin seawater is well mixed with the biocide. The assumption is that the reaction of biocide and seawater is immediate and complete instantaneously. The flow of seawater is much larger the flow rate of biocide. The flow rate of seawater is constant and therefore the volume of seawater inside the basin is constant. The products of the reaction of biocide with seawater are some byproducts (Seawater demand) and biocide residuals. Since, biocide is added to natural water like this case seawater, biocide will be reacting with organic materials and metals that are naturally exist before treatment. The assumption of biocide residuals is that has the capability of controlling the biofouling development. Therefore, the concern of the concentration of biocide residuals is taking under consi deration to determine its influence on biofouling control. The biocide residuals are going to decay depending on many factors including residence time, temperature, initial concentration of biocide, and characterization of seawater including pH, salinity, nutrients, etc.

The annual operating time is discretized into N_t time intervals. Within each interval (period), t, the operation is assumed to be steady state. The number of intervals is selected in a way that balances accuracy (e.g., the intervals must capture seasonal variations, action points such as changes in biocide dosage, operational variations such as increases in flow rate of product and/or seawater) versus computational effort (size of the optimization problem and computing time).

Let us use the index j to denote the key components to be tracked in the system. These include the biocide (given an index j = 1) as well as the biocide residuals (which impact biofouling development) and other byproducts (which are also contribute to the consumption of biocide but do not affect the biofilm. These residuals and byproducts are described by the index j (where j = 2, 3, …, Nc).

Time Intervals:

N_t: Number of time periods to which the annual operation is discretized

t: is the time interval

Key Components:

j : is an index denoted to a key component, j=1 for the biocide.

N_C : is the number of key components tracked in the cooling system.

Process Segments:

i: is an index denoted to a process segment, i=1 for the basin.

N_S : is the number of the process segments (a portion of pipeline or a heat exchanger) in the cooling system.

The following terms are used for each time interval t:

Seawater Influent:

$C_{j,t}^{SW}$: Composition of the, j, key component of the biocide in fresh seawater as a function of, t, time interval.

F_t^{SW} : Flow rate of fresh seawater into the basin as a function of, t, time interval.

pH_t^{SW} : the pH of the seawater at the influent at time interval t.

T_t^{SW} : the temperature of the seawater at the influent at time interval t.

Biocide Storage:

$C_{j=1,t}^{B}$: Composition of biocide in the added biocide solution from the biocide storage into the basin as a function of, t, time interval.

F_t^{B} : Flow rate of the biocide solution into the basin as a function of, t, time interval.

Basin:

$C_{j,t}^{Ba\sin}$: Composition of the, j, key component of the biocide in the basin as a function of, t, time interval.

$pH_t^{Ba\sin}$: the pH of the treated seawater at the basin at time interval t.

$T_t^{Ba\sin}$: the temperature of the treated seawater at the basin at time interval t.

$\tau_t^{Ba\sin}$: is the residence time at the basin at time interval t.

$V_t^{Ba\sin}$: Volume of the water inside the basin as a function of, t, time interval.

Inlet of Cooling System:

i = 1.

Process Segment (i):

$C_{i,j,t}$: Composition of the, j, key component of biocide in the process segment, i, of the cooling system as a function of, t, time interval.

$F_{i,t}$: Flow rate of the treated seawater through the process segment, i, of the cooling system as a function of, t, time interval.

$pH_{i,t}$: the pH of the treated seawater inside the process segment, i, of the cooling system at time interval t.

$T_{i,t}$: the temperature of the treated seawater inside the process segment, i, of the cooling system at time interval t.

$\tau_{i,t}$: is the residence time inside the process segment, i, of the cooling system at time interval t.

$$\tau_{i,t} = \frac{V_{i,t}}{F_{i,t}}$$

$V_{i,t}$: Volume of the seawater inside the process segment, i, of the cooling system as a function of, t, time interval.

Outlet of Cooling System:

$i = N_s - 2$

End Of Pipe Treatment (EOP):

$C_{N_s-1,t}^{Chem}$: Composition of the key component of chemicals at the end of pipe treatment unit as a function of, t, time interval.

$i = N_s - 1$

Chemical Storage:

C_t^{Chem} : Composition of the chemicals out of the storage and going to the end of pipe treatment unit as a function of, t, time interval.

F_t^{Chem} : Flow rate of the chemicals to the end of pipe treatment unit as a function of, t, time interval.

Seawater Effluent:

$C_{N_s,t}^{Chem}$: Composition of the key component of chemicals out to the environment as a function of, t, time interval.

$i = N_s$

Typically, the flow rate of the treated seawater is significantly larger than the flow rate of the biocide solution, i.e.,

$$F_t^{SW} >> F_t^B \quad \forall t \qquad \text{Equation 6.23}$$

The flow rates of the incoming seawater and of the treated seawater leaving the basin are taken to be equal to avoid any accumulation of water at the basin. Therefore, biocide flow rate can be neglected in the calculations of the residence time and of the treated seawater flow rate leaving the basin. The component material balances for any key component tracked species, j, at any process segment, i, of the cooling system at any, t, time interval are given by:

$$C_{j,t}^{Basin} = B_{j,t}\begin{pmatrix} F_t^{B}, C_{j=1,t}^{B}, F_t^{SW}, C_{j=1,t}^{SW}, T_t^{SW}, pH_t^{SW}, \\ V_t^{Basin}, \tau_t^{Basin}, \ldots, C_{j=1,t}^{Basin}, \ldots, C_{j,t}^{Basin}, T_t^{Basin}, pH_t^{Basin}, F_{i=1,t} \end{pmatrix} \quad \forall t \qquad \text{Equation 6.24}$$

where $B_{j,t}$ is the function characterizing the reactive model of key component species, j, within the basin at, t, time interval. For instance, if the basin is modeled as a completely mixed system, the component material balance for the biocide is given by:

$$F_t^{B} C_{j=1,t}^{B} + F_t^{SW} C_{j=1.t}^{SW} - F_{i=1,t} C_{1,1,t} = r_{1,t}^{Basin} V_t^{Basin} \quad \forall t \qquad \text{Equation 6.25}$$

where $r_{j=1,t}^{Basin}$ is the rate of depletion of the biocide in the basin per unit volume.

Within the process, given the specific path of seawater inside the process, a "path" model is developed to account for the biocide reaction kinetics throughout the process. The seawater goes through a number of pipes and units. The process is discretized into a number of segments. Each segment, i, represents a portion of the seawater pipeline or a heat exchanger (e.g., cooler, coil in a hot unit, cooling jacket of a unit, etc.). Consider the N_c key species and refer to the concentration of key component j in segment i during period t as $C_{j,i,t}$ .. For the j^th species, in the i^th segment, and at t^th period, the following kinetic expression may be written as:

$$C_{i,j,t} = \Psi_{i,j,t}\left(F_{i,t}, C_{i-p,1,t}, \ldots, C_{i-p,j,t}, \ldots, C_{i-p,N_C,t}, V_{i,t}, \tau_{i,t}, T_{i,t}, pH_{i,t}\right) \quad \forall i, \forall t \qquad \text{Equation 6.26}$$

where the subscript, i-p, is referring to the previous process segment of the cooling system before process segment i. The thickness of the biofilm in the i^th segment at the end of the t^th period is given by the following equation:

$$d_{i,t} = d_{i,t-1} * \left(1 - I_{i,t-1}\right) + \Delta d_{i,t}(C_{i,1,t}, \ldots, C_{i,j,t}, \ldots, C_{i,N_C,t}, T_{i,t}, pH_{i,t}, , \tau_{i,t})$$

Equation 6.27

where $I_{i,t-1}$ is a binary integer variable defined as:

$I_{i,t-1} = 1$ if maintenance/cleaning is carried out at the end of period t-1

$I_{i,t-1} = 0$ if no maintenance/cleaning is carried out at the end of period t-1

The effect of the binary in the previous equation is to set the thickness of the biofilm to zero (i.e., a clean surface) after the cleaning is carried out. The biofilm growth function $\Lambda d_{i,t}$ is described in terms of the compositions of the biocide and residual byproducts, as well as the average temperature and pH of the seawater in segment i.

In addition to the economic aspects of determining when cleaning is scheduled, there is also mandatory cleaning if the biofilm thickness reaches a maximum allowable level:

$$d_{i,t} < d_{i,t}^{\max} \quad \forall i, \forall t$$ Equation 6.28

$d_{i,t}$: the biofilm thickness at process segment i and at time interval t.

$d_{i,t}^{\max}$: the maximum allowable biofilm thickness at process segment i and time interval t.

$d_{i,t}^{\infty}$: the highest level of biofilm thickness at process segment i at time interval t.

The biofilm thickness grows seasonally up to a certain level defined as d_i^{∞}, This thickness depends on the biological and process conditions. The loss in performance of the ith heat exchanger resulting from the cumulative formation of the biofilm at the end of period t is given by:

$$\Delta Q_{i,t} = \Phi_{i,t}(d_{i,t}, d_{i,t-1}, d_i^{\infty}) \quad \forall i, \forall t$$ Equation 6.29

where $\Phi_{i,t}$ is the function characterizing the heat transfer reduction model in the process segment i at, t, time interval.

6.7. BIOCIDE KINETICS

6.7.1. REACTION KINETICS

Biocide + Seawater → Biocide Residuals + Byproducts (Seawater demand)

Equation 6.30

$$B + SW \rightarrow BR + BP \qquad \text{Equation 6.31}$$

r_{BR} : Rate of appearance (reaction) of biocide residuals (mass/ [time. Volume]^n)

$(r_{BR} = k_I [C_B]^n)$

r_{BP} : Rate of appearance (reaction) of biocide byproducts (mass/ [time. volume]^n)

$(r_{BP} = k_{II} [C_B]^n)$

where n is the order of the reaction.

6.7.2. DECAY KINETICS

Biocide residuals + Seawater → Byproducts Equation 6.32

$$BR + SW \rightarrow BP \qquad \text{Equation 6.33}$$

r_{BR} : Rate of disappearance/ decay of biocide residuals (mass/ [time. Volume]^{m}) ($r_{BR} = k_D \left[C_{BR}\right]^m$)

k_D: Reaction rate constant (time^{-1} [mass/ Volume]$^{-m}$)

n & m : Reaction orders

There are some assumptions considered:

1) $F^{SW} >> F^{B} \Rightarrow V_B$ therefore, the volume of the basin can be considered as a constant
2) Therefore, the reaction inside the basin considered to be as a plug flow reactor
3) The reaction of seawater with biocide in the basin is a single irreversible complete and instantaneous reaction:

Biocide + Seawater → Biocide Residuals + Byproducts Equation 6.34

B + SW → BR + BP Equation 6.35

4) There is no change in the number of moles
5) There is no change in temperature inside the basin
6) The products of the reaction are biocide residuals (BR), which have major effects on biofouling development

7) Other products are called byproducts (BP) which are considered as consumption of biocide or seawater demand

8) $C_j^{Ba\sin}$ is biocide residuals and byproducts' concentrations are uniform inside the basin

9) Water is well-mixed with biocide inside the basin, so there is no accumulation

10) $F^{SW} \& F_i$ the volumetric flow rate of seawater and treated seawater in and out of the basin are constants, therefore the volume of the water inside the basin is constant

The mass balance on biocide residuals around the basin is represented by:

[Flow into the basin] + [Rate of generation] = [Rate of consumption/ decay] + [Rate of accumulation] + [Flow out of the basin] Equation 6.36

After considering the assumptions:

[Rate of generation] = [Rate of consumption/ decay] + [Flow out of the basin]

Equation 6.37

$$F_t^{SW} * \left(r_{BP} = k_{II}\left[C_B\right]^n\right) = V_B * \left(r_{BR} = k_D\left[C_{BR}\right]^m\right) + F_{i=1,t} \quad \text{Equation 6.38}$$

$$F_t^{SW} * k_{II} \left[C_B \right]^n = V_B * k_D \left[C_{BR} \right]^m + F_{i=1,t} \qquad \text{Equation 6.39}$$

Mass balance on biocide residuals around Heat exchangers network (HEN):

[Flow in to HEN] + [Rate of generation] = [Rate of consumption/ decay] + [Rate of accumulation] + [Flow out of HEN] Equation 6.40

After considering the assumptions:

- There will be a slight change in temperature of seawater trough HEN
- The residence time τ of seawater inside HEN
- VHEN is the volume of seawater inside the HEN
- $F_{i=1,t} \& F_{i=N_S-2,t}$ are volumetric flow rate of treated water out of the basin and out of HEN respectively.

[Flow in to HEN] = [Rate of consumption/ decay] + [Flow out of HEN]

Equation 6.41

$$F_{i=1,t} * \left[C_{i=1,j,t} \right] = F_{i=1,t} * \left(r_{BR} = k_D \left[C_{i=1,t} \right]^m \right) + F_{i=1,t} * \left[C_{i=1,j,t} \right] \qquad \text{Equation 6.42}$$

$$F_{i=1,t} * \left[C_{i=1,j,t} \right] = F_{i=1,t} * k_D \left[C_{i=1,t} \right]^m + F_{i=1,t} * \left[C_{i=1,j,t} \right] \qquad \text{Equation 6.43}$$

After considering the assumptions:

1) There will be no change in temperature of seawater through EOP
2) The residence time τ of seawater inside EOP equals flow rate/EOP volume
3) $F_{i=N_S-1,j,t}$ is the volume of seawater inside the EOP
4) $F_{i=N_S-2,j,t}$ & $F_{i=N_S,j,t}$ are volumetric flow rates of effluent water out of HEN and out of EOP respectively.
5) Decay kinetics:

$$\text{Biocide residuals + EOP Agent} \rightarrow \text{Byproducts} \qquad \text{Equation 6.44}$$

$$BR + RA \rightarrow BP \qquad \text{Equation 6.45}$$

r_{BR} : Rate of removing of biocide residuals (mass/ [time. volume]^{o})

$(r_{BR} = k_R\left[C_{i=N_S-2,j,t}\right]^{o})$

k_R : Removing rate constant (time^{-1} [mass/ Volume]$^{-o}$)

o : Reaction orders

6) [Flow in to EOP] = [Rate of consumption/ decay] + [Flow out of EOP]

Equation 6.46

$$F_{i=N_S-2,j,t} * \left[C_{i=N_S-1,j,t}\right] = F_{i=N_S-1,j,t} * \left(r_{BR} = k_R \left[C_{i=N_S-2,j,t}\right]^{o}\right) + F_{i=N_S,j,t} * \left[C_{i=N_S,j,t}\right]$$

Equation 6.47

$$F_{i=N_S-2,j,t} * \left[C_{i=N_S-1,j,t}\right] = F_{i=N_S-1,j,t} * k_R \left[C_{i=N_S-2,j,t}\right]^{o} + F_{i=N_S,j,t} * \left[C_{i=N_S,j,t}\right]$$

Equation 6.48

The relation between the chemical added to seawater at the basin and its influence on how it controls the fouling can be shown in the following model. The thickness of biofilm inside the heat exchangers tubes is a function of chemical concentration and scheduled dosage:

$$X_{t_{\Pr d}} = X_0 \left[e^{\beta * t_{\Pr d}} - e^{\gamma * t_{Dsg}}\right]$$

Equation 6.49

where $X_{t_{\Pr d}}$: is the biofilm thickness at the end of the period

X_0 : is the initial biofilm thickness

β : is the biofilm growth rate constant

γ : is the biofilm destruction rate constant from the influence of biocide

t_{Dsg} : is chemical dosage schedule in hours per day

The biofilm growth rate constant, β, can be calculated by letting the biofilm grow for some time with no chemical added to control it. Then, a graph is generated for the biofilm thickness versus time in days. By using regression analysis, the growth rate β can be calculated from the exponential kinetic growth. This kind of experiment can be repeated at different months/ seasons to generate β at each month/season.

The biofilm destruction rate constant, γ, is based on the relationship between the kinetic of biofilm destruction by chemicals and disinfection kinetics of suspended bacterial systems. Then, a graph is constructed to show different disinfection rate constants, K , for bacteria that dies off versus different biocide concentration $[C_B]$ dosages. The mathematical relation, which can be linear, that represents the relationship between the rate constants with chemical concentration is:

$$\kappa = a * [C_B] + b$$ Equation 6.50

The disinfection rate constant, K, has to be calibrated by ϕ, which can be determined by dosing the plant that is going to use this model with a certain chemical concentration for one hour per day and developing a graph from the data collected to represent the biofilm thickness versus time in days. By using a regression analysis for the curve, the destruction rate constant can be determined. From the disinfection rate constant K and destruction rate constant at the same dosage, ϕ can be calculated as follows:

$$\gamma = \phi * \kappa$$ Equation 6.51

The biocide residual concentration, $\lfloor C_{i=N_S-2,j,t} \rfloor$, at the effluent before discharge or biocide removal treatment can be determined by developing a kinetic model of the process. The consumption of chemicals is due to the reaction with organic and nonorganic compounds, biofilm, and corrosion. The chemical decay in kinetics in a batch cooling system (Xin et al. 2003) may be described as follows:

$$\frac{dC}{dt} = \frac{K_W * C_W}{r_h} - \frac{W}{r_h} - K_b C$$

Equation 6.52

Based on examining numerous experimental results for the kinetics of seawater treated with a chemical (e.g., chlorine), decay kinetics have been correlated to several factors, including temperature, pH, and contact time, but mainly on the ratio of chlorine dosage to ammonia (e.g., Haag 1981). The reduction or decay of chlorine in seawater is due to reactions with organic and nonorganic compounds in seawater. The chlorine decay occurs in three stages, starting with a very fast rate during the first the two minutes, due to a reaction with inorganic reducing agents. The second phase is slower and usually does not last more than two hours. It mainly involves reactions with the organic compounds that started in the first phase. Then, chlorine decays continuously via a very slow rate.

Of particular importance is the dependence on residence time and temperature. Given the specific path of seawater inside the process, the following model is developed to account for chlorine decay throughout the process. The seawater goes through a number of pipes and units. The process is discretized into a number of segments. Each segment, i, represents a portion of the seawater pipeline or a heat exchanger (e.g., cooler, coil in a hot unit, cooling jacket of a unit, etc.). Consider the N_S key species and refer to their concentrations in segment i as: $C_{i,1}, C_{i,2}, \ldots, C_{i,j}, \ldots, C_{i,N_S}$ ..

6.8. OBJECTIVE FUNCTION FOR OPTIMUM DOSAGE

Based on the proposed holistic approach, all scenarios from the chemical dosing of treatment and post-treatment, and all of the costs incurred from heating loss due to fouling and heat exchanger cleaning, have to be incorporated in the decision for any design or operation changes. The objective function is built on the economic criterion. It will permit the most feasible solution that would also cost the least to operate the plant.

This approach might allow for biofilm growth and removal by periodic heat exchanger cleaning at the minimum overall operating cost. On top of that, there are a variety of options for chemical dosing. For each dosing course, the response of biofouling development will vary accordingly. Thus, there will be an impact on the other operating costs. Also, the nitration and the ambient temperature variations through different seasons of the year will govern the microorganisms' behavior inside the cooling system. All of the different aspects have to be integrated to make one plan that considers the impact on all of the related design and operation changes. The dynamics of the process itself will add difficulty to selecting the optimal scenario among the options.

The objective function is to minimize the annual total cost that is incurred directly and indirectly from fouling. It will include the annual operating cost of chemicals (chlorine) used to treat the cooling water against biofouling, the annual fixed and operating costs of removing chemical residuals from the effluent water, the cost of cleaning heat exchanger units, the cost of the loss incurred by biofouling, and the annual gross profit loss from shutting down the operation for cleaning the heat exchangers.

The annual operating time in discretized into N_t time intervals t = 1, 2,….., Nt under the assumption of steady state at each t (time interval). The key components are tracked in the cooling system as j = 1,2,…, N_c with j=1 for biocide added. The cooling system is discretized into number of segments i = 1, 2,…, Ns. Those segments are portions of pipeline or heat exchanger unit. The objective function is to minimize the total annualized cost which includes all direct and indirect costs. Hence:

Annual Total Cost = Annual Cost of Biocide to Treat the Seawater +

Annual Costs of Chemicals at EOP Treatment Unit for Removing the effect of Biocide Residuals +

Annual Costs of Heat Exchanger Cleaning, Heat Loss Due to Fouling, and Gross Profit Loss Due to Shutting Down the Process for Heat Exchanger Cleaning.

Mathematically, the objective function is described by:

$$Minimize\ Total\ Annualized\ Cost = \sum_{t=1}^{N_t} \left[Cost_t^B + Cost_t^{EOP} + \sum_{i=1}^{N_S} (Cost_t^{LP} + Cost_i^{Cleaning} * I_{i,t}) \right]$$

Equation 6.53

The cost of biocide during period t is expressed as:

$$Cost_t^B = Cost\_Biocide(F_t^B, C_t^B)$$ Equation 6.54

The cost of end-of-pipe treatment during period t is given by:

$$Cost_t^{EOP} = Cost\_EOP(F_t^{Chem}, C_t^{Chem}, F_{i=N_s-2,t}, C_{N_s-2,1,t}, \ldots, C_{N_s-2,j,t}, \ldots, C_{N_s-2,N_c,t})$$

Equation 6.55

Loss of production can be defined as loss due to reduction in heat transfer in the heat exchanger units, as well as the loss of production due to shutting down the process for maintenance. The cost of loss of production is given by:

$$Cost_t^{LP} = Cost\_LP(\Delta Q_{i,t}, I_{i,t})$$ Equation 6.56

6.9 ENVIRONMENTAL AND QUALITY CONSTRAINTS

In addition to the aforementioned technical constraints, the minimization of the cost objective function is also subject to environmental and quality constraints from the process and from the environment. There is a minimum requirement from the process technical specification of the plant on the concentration of biocide residual to insure minimum biofouling development. Also, another constraint on the thickness of biofilm is to not exceed a certain thickness, $d_{i,t}^{\max}$.

$$C_{N_s-2,j,t} > y_{j,t}^{Tech}$$

Equation 6.57

$$d_{i,t} \leq d_{i,t}^{\max}$$

Equation 6.58

The concentration of key component, j, of biocide residual must comply with the environmental regulations. Also, the concentration of chemicals added to reduce the effect of the biocide residuals is regulated by the environmental requirements. Hence,

$$C_{N_s,j,t} > y_{j,t}^{Env}$$

Equation 6.59

$$C_{N_s,j,t}^{Chem} > y_{Chem}^{Env}$$

Equation 6.60

Gross profit is the revenue or sales after deducting all directed costs like manufacturing expenses, feed, labor, and selling/marketing expenses. The gross profit loss is how much of the gross profit would have been generated if the production had not been stopped for heat changer cleaning. The daily gross profit (DGPft) can be calculated by taking the revenue of a company over a period of time, with no shutdown in production, and dividing it by the number of days of that period.

6.10.CASE STUDY

The case study is for a plant producing Acrylonitrile from propane with annual capacity of 200 million pounds. The discharged amount of biocide residuals is higher than newly enacted environmental regulations of 0.002 ppm of total residual chlorine. This problem is normally solved by a conventional end-of-pipe treatment approach. The purpose of the case study is to develop optimal design modifications and operating and scheduling strategies for biocide usage and cleaning maintenance. The current usage of seawater and the heating and cooling utilities of the process are given in Table 6.1. First, thermal pinch analysis is carried out to minimize the heating and cooling utilities. The results of heat integration lead to a targeted reduction of 92% and % 60% in heating and cooling utilities, respectively. The amount of seawater and utilities for the target reduction by heat integration tools is compared to the current usage and shown in Table 6.1. A simplified diagram depicting the cooling system is shown by Figure 6.7.

Table 6.1. Heating and Cooling Utilities Required for the Acrylonitrile Plant.

Heating & Cooling Utilities						
Utility		**Current**		**Heat Integration Target**		**% of Red.**
		Seawater	**Heat Load**	**Seawater**	**Heat Load**	
		m3/hr	**MM Btu/hr**	**m3/hr**	**MM Btu/hr**	
Cooling	**Seawater**	**9328**	**228**	**4337**	**91**	**60**
	Refrigeration	**---**	**39**	**---**	**39**	**0**
Heating		**---**	**173**	**---**	**36**	**79**

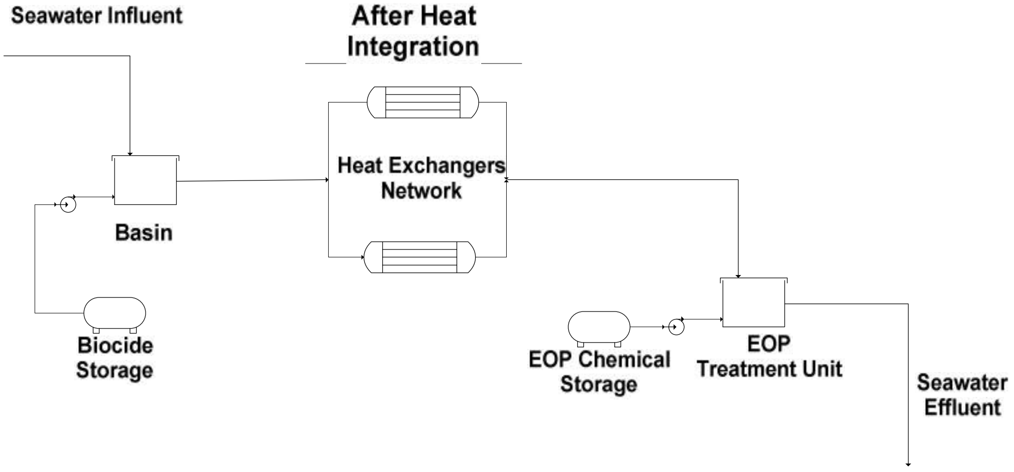

Figure 6.7. Seawater Cooling System for the Acrylonitrile Plant.

The next step is to develop the biocide kinetic model and the biofilm growth model for the heat exchangers in the plant. The objective is to develop chlorine residual model to predict the chlorine concentration over a period of time throughout the process. Chlorine is used as the biocide and the original plan is to introduce chlorine dosing at 5 mg/L three times for about 30 minutes and to switch to continuous chlorination to prevent mussels during 2-4 week of breeding season at residual chlorine not less than 0.5 mg/L. Decay of chlorine is due to volatilization to the atmosphere and reaction with ammonia-nitrogen in natural water. This reaction takes place when the ratio of the concentration of free available chlorine to chloramines ([HOCl]/[NH2Cl + NHCl2]) is 8 to 10. This reaction is known as a breakpoint reaction as shown in the following reaction.

$$NH_2Cl + NHCl_2 + HOCl \rightarrow N_2O + 4H^+ + 4Cl^- \qquad \text{Equation 6.61}$$

Other factors participating in reducing chlorine residual to chloride is reacting chlorine with in-organic species like S--, Fe++, and NO2-. Also, chlorine can be reduced to chloride by reaction with organic species to produce higher level compounds or decomposed to CO2 and H2O. Moreover, hypochlorous acid is decomposed at very low rate to produce oxygen.

$$HOCl \leftrightarrow 1/2\ O2 + H+ + Cl- \qquad \text{Equation 6.62}$$

Chlorine residual is detected by diethyl-p-phenylenediamine DPD method at range of 0.05 to 5.00 mg/L chlorine. This method is the titration of Fe++ ions at the presence of iodide and diethyl-p-phenylenediamine. The samples from the seawater are examined at different points of time with known initial chlorine dosing. The results then plotted in graphs of residual chlorine concentrations versus time. These data are used in building a kinetic model of chlorine residual over time.

Due to the complexity of the reaction of chlorine with seawater, the consideration is just for one reactant which is chlorine residual. The kinetics of chlorine residual disappearance happens in two phases. It starts with a very fast decay rate, then it moves to a slow rate. The following reactions are considered: The first equation is dominant until organic species are consumed, then the second reaction becomes dominant.

$$Cl2 + Organics \rightarrow products \qquad \text{Equation 6.63}$$

$$r1 = - k1\ CCl2\ COrg \qquad \text{Equation 6.64}$$

$$Cl2 \rightarrow products \qquad \text{Equation 6.65}$$

$$r2 = k2\ CCl2 \qquad \text{Equation 6.66}$$

There is a limitation of this model. It cannot be used for long periods (over 18 hours) nor can it be used for very small periods of time and low initial chlorine concentrations. Alternatively, a second order kinetic model is used for the second reaction:

$$Cl2 \rightarrow products \qquad \text{Equation 6.67}$$

$$r = dCCl2 /dt = - k\ C2Cl2 \qquad \text{Equation 6.68}$$

$$1/[CCl2\ ] = k\ t + 1/[CCl2\ ]o \qquad \text{Equation 6.69}$$

The collected data were graphed as reciprocal residual chlorine 1/ C2Cl2 versus time. A linear relationship indicating that this reaction is indeed a second order reaction. The assumption is that the instantaneous disappeared amount of chlorine is [CCl2]d.

For low initial chlorine concentrations [CCl2]o, the disappearing concentration is equal to the remaining concentration [CCl2]o = [CCl2]r.

Amount of disappeared chlorine = Initial chlorine – remaining chlorine Equation 6.70

$$[CCl2\ ]d = [CCl2\ ]o - [CCl2\ ]r$$ Equation 6.71

Therefore, the concentration of remaining chlorine [CCl2]r after the initial instantaneous disappearance [CCl2]d will be considered as the initial chlorine concentration for the second order kinetic reaction:

$$1/[CCl2\ ] = k\ t + 1/[CCl2\ ]r$$ Equation 6.72

There is a linear relationship between disappeared chlorine with initial chlorine concentration. As the initial chlorine increases, the pH of seawater increases slightly. Thus, the value of k changes as appears from the obtained data from the experiment of Wang 2008. The data for [CCl2]r and k are obtained from the graph with the corresponding initial chlorine concentration [CCl2]o:

$$k = 0.6925\ e\text{-}0.8124[Ccl2]o$$ Equation 6.73

The temperature effect on the k value was accounted for using the work of Wang, 2008.

It is important to track the biocide residuals concentration inside the cooling system through each process segment. The biofilm growth is controlled by biocide residual concentration. Determining the amount of residual chlorine [CCl2] after time t in minutes requires the result of the kinetic study depending on water quality and the time of the year. Also, for different temperatures, the changes in decay rate constants are considered. The works of Wang et al. (2008) and Xin et al. (2003) were used in developing the kinetic model for chlorine. The general form of chlorine decay in seawater was taken as follows:

$$C = A\ e\text{-}kt \qquad \text{Equation 6.74}$$

It was considered that the first chlorine decay was very rapid in the first few minutes (Characklis et al., 1980). After the first five minutes, the data are fitted to the exponential form shown above (Xin et al., 2003).

The decay of biocide inside the cooling system for this case study follows this function:

$$C_{i,j,t} = C_{i-p,j,t} e^{-k_t * \tau_{i,t}} \qquad \text{Equation 6.75}$$

where:

$C_{j,i,t}$:is the concentration of biocide key component j at process segment, i, at time interval t in (mg/l).

$C_{j,i-p,t}$:is the concentration of biocide key component j at process segment, i-p, which precedes process segment i at time interval t.

The decay constant (1/min) has a proportional relationship with temperature (Nebot et al., 2007). As temperature increases, the decay of chlorine increases following this equation:

$$k_{i,t} = \eta * T_{i,t} \qquad \text{Equation 6.76}$$

where T is measured in Celsius.

$\kappa_{j,t}$: is the disinfection kinetics rate constant for key component j at time interval t.

η: is the coefficient of the decay constant of biocide by-products $\eta = 6.8 * 10^{-4}\ (1/\min.^{o}C)$.

$T_{i,t}$ the temperature in (oC) at process segment i and time interval t.

Data for the residual chlorine is in seawater at temperature range from 20 to 24C were extracted from Hostgaard-Jensen et al. (1977).

The biofilm development model is integrated in the optimization model to track the thickness of biofilm on the inside surface of the tubes of the heat exchanger. The biofilm development is influenced by many factors including the variation in temperature through the cooling systems after passing through heat exchanger units. The other factor is the seasonal temperature variations of fresh seawater. This factor influences the biological activities of microorganisms that contribute to the development of the biofilms. Therefore, the optimization model includes constraints that track the biofilm thickness which reduces the heat transferred across the tube surface. The influent seawater temperature varies and after passing through heat exchanger units. It becomes:

$$T_{i,t} = \frac{Q_{i,t}}{F_{i,t}\rho^{SW} C_p^{SW}} + T_{i-p,t}$$ Equation 6.77

$T_{i-p,t}$: is the temperature of seawater at process segment i-p, preceding segment i at time interval t

$Q_{i,t}$: the heat transfer at process segment (in the heat exchanger) i and at time interval t.

$Q_{i,t}^{\mathrm{Re}q}$: is the heat transfer required for process segment i at time interval t (Btu/hr).

The heat transfer rate would decrease from $Q_{i,t}^{\mathrm{Re}q}$ *to* $Q_{i,t}$ as the biofilm accumulates.

The required output of the plant requires an operational schedule to maintain certain process conditions. Thus, the heat load required to be transferred at each process segment (in the heat exchanger) is assigned accordingly. This amount of heat load for each process segment i at time interval t is called $Q_{i,t}^{\mathrm{Re}q}$. The transferred heat load, $Q_{i,t}$, must be kept e within the designed margin after any reduction due to fouling according to the equation below (Nebot et al., 2007). From the percentage reduction in heat transfer in the heat exchanger, the heat transferred can be calculated from the designed value.

$$Q_{i,t} = Q_{i,t}^{\mathrm{Re}q} * \left(1 - \frac{\% H.T.R_{i,t}}{100}\right)$$ Equation 6.78

Therefore, $Q_{i,t}$ is the actual heat load transferred at unit i and time interval t, which has to be less than or equal to the unit i is designed for. $Q_{i,t} \leq Q_i^{Des}$ where %HTRi,t is the percentage of heat transfer reduced at heat exchanger i at time interval t. The reduction in the designed heat transfer of a heat exchanger can be related to the biofilm thickness. However, biofilm thickness is not directly related to the reduced heat transfer because biofilm density changes with time. But, for simplicity in this model, it is considered that heat transfer reduction is calculated from biofilm thickness.

$$\% HeatTransfer\,\mathrm{Re}duction = \% HTR_{i,t} = \varepsilon * d_{i,t}$$ Equation 6.79

$\% H.T.R_{i,t}$:is the percentage of heat transfer reduced for process segment i and at time interval t.

$$\varepsilon = 0.2156(1/\mu m)$$ Equation 6.80

ε : is the coefficient in the heat transfer percentage equation.

The biofilm thickness increases over time by accumulating on the tubular surface of the heat exchangers (Turakhia et al.1984). The biofilm thickness depends on the net between the rates of attachment, growth, and detachment, as well as the destruction rate of biofilm due to the biocide effect (Sriyutha Murthy et al., 2004; Morgan et al., 1969). This complex relation is expressed through a function that takes care of the biofilm growth over the variation of seawater condition with the destruction effect of biocide residuals. This can be described by the following equation (Bryers et al., 1982):

di,t= net development from growth and destruction

$$d_{\;i,t} = d_i^{\infty} * \left\lfloor 1 - e^{\left(-\beta_{i,t} * \sigma i_{i,t}\right)} \right\rfloor / \; e^{(\gamma_{i,t} * \varpi)}$$ Equation 6.81

$$\beta_{i,t} = \phi * T_{i,t}$$ Equation 6.82

$\beta_{i,t}$: is the biofilm growth rate constant for process segment i at time interval t (1/min);

(phi) $\phi = 2.909 * 10^{-7}\ (1/\min.^{o}C)$ Equation 6.83

ϕ : is the coefficient of biofilm growth rate constant [1/ (min.oC)].

ω : is the duration of a single time interval (day).

$$\sigma_{i,t} = \omega + \left[\left(\frac{-1}{\beta_{i,t-1}}\right) * \ln\left(1 - \frac{I_{i,t-1} * d_{i,t-1}}{d_i^{\infty}}\right)\right],$$ Equation 6.84

$\sigma_{i,t}$: is the biofilm growth rate constant considering the growth from the previous time interval for process segment i and at time interval t (min).

$$\alpha = 0.0225\left(\frac{\mu m}{\min}\right)$$

Equation 6.85

where α : is the coefficient of biofilm growth from the previous time segment.

When the biofilm thickness reaches the maximum allowable thickness, a decision for maintaining that unit has to be made. Here, this has been accounted for by multiplying the maximum allowable thickness by a 0/1 binary integer variable, Ii,t. When biofilm thickness di,t-1 of unit i at time interval t-1 exceeds the allowable level diMax , then Ii,t for unit i and time interval t-1 is equal to zero. Otherwise, Ii,t is always equal to one. The maximum allowable level of the biofilm thickness has to be less than d_i^{∞} .

$$I_{i.t-1} = \begin{bmatrix} 0 \ \ when \ \ d_{i,t-1} > d_i^{Max} \\ 1 \ \ when \ \ d_{i,t-1} \ \underline{< d_i^{Max}} \end{bmatrix}$$

Equation 6.86

$$0 - d_i^{Max} \ * I_{i,t} < d_{i,t} - d_i^{Max} \underset{-}{<} \left(10000 - d_i^{Max}\right) * \left(1 - I_{i,t}\right)$$

Equation 6.87

$$d_i^{Max} < d_i^{\infty}$$ Equation 6.88

$$d_i^{\infty} = 250\mu m$$ Equation 6.89

$I_{i,t}$: is a binary integer variable for making decisions in order to maintain process segment i at time interval t.

The destruction rate of the biofilm due to the biocide depends on the biofilm thickness of the same unit i at the pervious time interval t-1 and the concentration of biocide residual coming from the previous process segment pi at the pervious time interval t-1 (Platon et al., 1985):

$$\gamma_{i,t} = \lambda * C_{p_i,t-1}, \quad \gamma : (1/\min)$$ Equation 6.90

$$\lambda = 2.829*10^{-4}\left(\frac{1}{\min.(mg/l)}\right)$$ Equation 6.91

$\gamma_{i,t}$: is the biofilm destruction rate constant for process segment i and time interval t (1/min).

λ: is the coefficient of biofilm destruction rate constant (Gamma) of biocide residual

Additional constraints used in the case study:

- The maximum allowable biofilm thickness is 70um.

- Cleaning (maintenance) of heat exchangers is only considered at the end of each month and no more than three maintenances are allowed per year.
- The objective function is considering all costs directly or indirectly incurred by biofilm developments. Those costs include biocide and EOP chemical dosing. The optimal solution would include also the heat exchanger maintenance schedules. The maximum allowable biofilm thickness is 70 micrometer.
- The annual operating time is discretized into Nt = 365 time intervals (i.e., the optimization formulation is developed on a daily basis). The key components are tracked in the cooling system for an accumulation of biocide residuals. The cooling system is discretized into numbers of segments i = 1, 2,…, Ns. Those segments are portions of the pipelines or heat exchanger units.

$$Minimize\ Total\ Annualized\ Cost = \sum_{t=1}^{N_t}\left[Cost_t^B + Cost_t^{EOP} + \sum_{i=1}^{N_S}(Cost_t^L * I_{i,t})\right] \qquad \text{Equation 6.92}$$

Total Annual Cost of Biocide:

$$Cost_t^B = \left[\sum_t^{N_t} F_t^B * \omega\right] * Biocide \qquad \text{Equation 6.93}$$

The total annual cost of biocide is the summation of the volumetric flow rate of biocide F_t^B over all time intervals Nt, multiplied by the duration of each time interval ω. This total is multiplied by the cost of biocide ($/m3). Total annual cost of end-of-pipe treatment is calculated as follows:

$$Cost_t^{EOP} = \left[\sum_t^{N_t} F_t^{Chem} * \omega \right] * Chemicals$$

Equation 6.94

Total annual cost of end of pipe treatment is equal to the summation of the volumetric flow rate of chemicals (m3/hr) multiplied by the duration of each time interval over all time intervals, Nt. The total summation is multiplied by the cost of chemicals ($/m3).

Total annual cost for production loss due to heat reduction in heat exchangers caused by fouling and shutting down the process for heat exchangers cleaning is given by:

$$Cost_t^L = \left[\sum_{i=1}^{N_S} Maintenance_i \right] \quad \forall t$$

Equation 6.95

where maintenance is the cost for maintaining process segment I with a loss of production due to the reduction in heat transfer and being out of the process for cleaning.

The total annual cost for heat exchangers' maintenance is the summation of the multiplication of binary number Ii,t by the cost of the maintenance of a single process segment over all process segments Ni and over all time intervals Nt.

6.11. RESULTS

The optimal schedule is for continuous monthly chlorine dosing that depends on seasonal variations. In response, the chemical dosing at the EOP treatment unit is eliminating or reducing the effect of biocide on aquatic life in the seawater. The achieved reduction in heating and cooling utilities was 79 % and 51 %, respectively, which is shown in Table 6.2. This is the most economically feasible reduction of the utilities.

Table 6.2. Comparison of Current and Achieved Heating and Cooling Utilities Required for the Acrylonitrile Plant.

Heating & Cooling Utilities		
Utilities	Heating	Cooling
	MM Btu/hr	MM Btu/hr
Current	173.4	266.90
H.I. Target	14.05	107.55
% of Current	91.8973	59.70
Achieved	36.4	129.90
% of Current	79.0	51.3

The comparison between the current and the proposed reduction in the usages of heating and seawater cooling utilities as well as the amount of seawater is shown in Figure 6.8. A significant reduction (percentagewise) was made for the heating utilities.

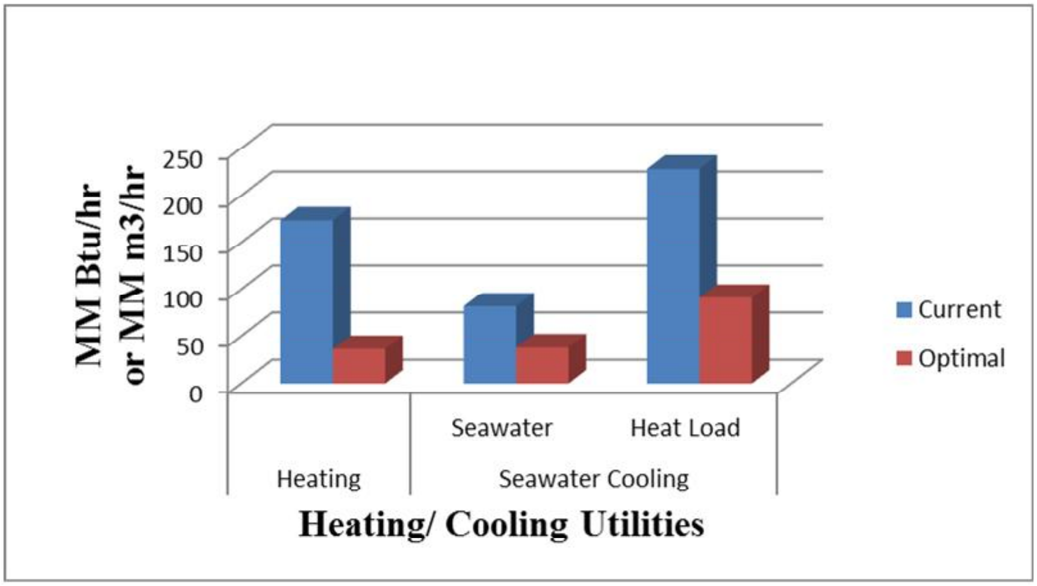

Figure 6.8. Comparison Between Current and Achieved Heating and Cooling Utilities Including Seawater Usage.

The majority of annual savings is attained through the reduction of heating utilities of $3.5 MM. Then, the next annual savings is achieved from the reduction in biocide dosing of $ 2.7 MM. Furthermore, savings is about $ 1 MM in usage of seawater. There is a small annual savings in EOP chemical dosing because the aim was to lower the biocide residual concentration beyond well below the current discharge to reach 0.002 ppm. There is no saving in the maintenance of heat exchangers because the current maintenance although the timing has changed. A summary of these savings is shown in Figure 6.9.

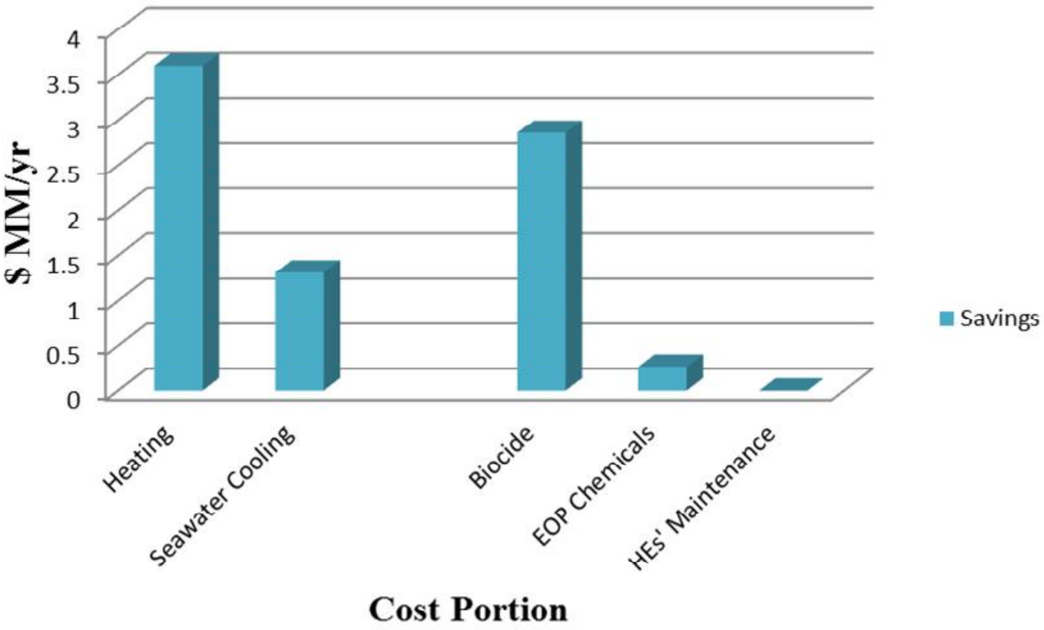

Figure 6.9. Annual Savings from Current to Proposed Schedule in Millions of Dollars.

The optimal schedule for continuous monthly biocide dosing is proposed with heat exchanger maintenance at the end of May, August, and November. Figure 6.10 shows the optimal usage of the biocide and the chemicals used in end-of-pipe treatment. The biofilm thickness was tracked by using the model that represents biofilm growth. As shown in Figure 6.11, the biofilm thickness goes to zero at the proposed timing for the cleaning maintenance of the heat exchangers at the end of months 5, 8 and 11.

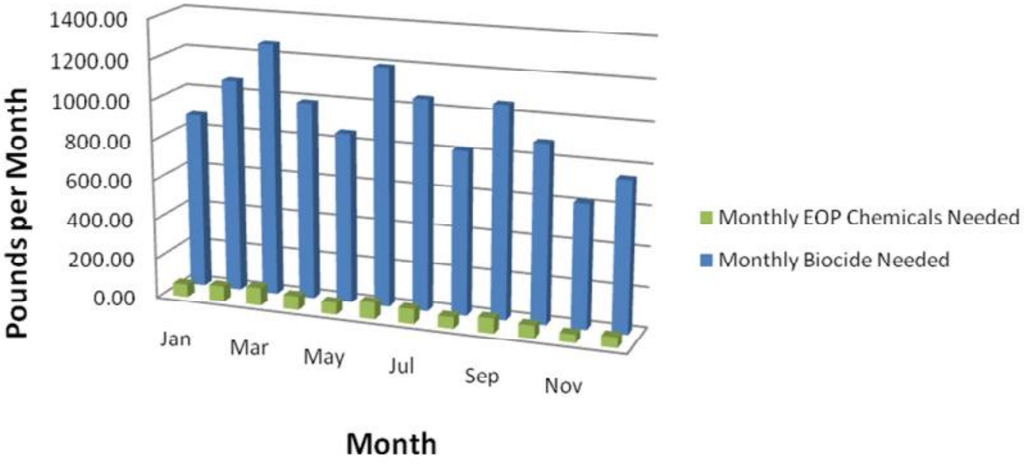

Figure 6.10 Proposed Monthly Biocide and EOP Chemicals Dosing for the Acrylonitrile.

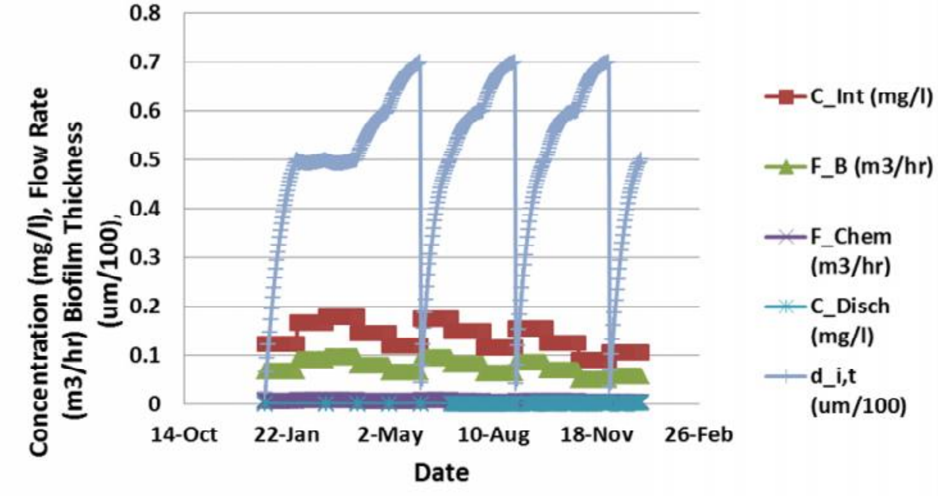

Figure 6.11. Biofilm Thickness with the Corresponding Biocide Dosing for the Proposed Schedule.

6.12. CONCLUSIONS

A systematic procedure has been developed for the optimization of biocide usage and discharge for seawater cooling systems. The devised procedure includes design modifications using heat integration and optimization of temperature profile. A kinetic model is developed for the reaction mechanism of biocide and its byproducts and is linked to the biofilm growth. A multi-period, multi-segment optimization model has also been developed to account for the various cost item, the technical performance, and the desired specifications and constraints. The case study of the plant for acrylonitrile from propane showed how the procedure can be effectively applied to determine optimal design changes and operating and scheduling strategies.

7. CONCLUSIONS AND RECOMMENDATIONS

This work has introduced systematic tools for the optimization of seawater cooling systems. Emphasis has been given to the use and discharge of biocide and the associated technical, economic, and environmental aspects. A comprehensive survey has been presented for the biocide-seawater chemistry to understand the key relations governing the effectiveness of the biocide dosing and the residual components exiting the plant.

There are many operating practices that impact the efficiency, performance, and cost of the plant. Adding more than the required amount of biocide would result in a higher performance of the heat exchanger units, but it would require additional treatment for seawater before it is discharged. Using less than the optimal doses of the biocide lead to reduction in heat transfer and process performance. Furthermore, there is a critical need to determine the timing of the cleaning maintenance of the heat exchangers.

Systematic procedures have been developed for the optimization of scheduling the dosing of biocide and dechlorination chemicals as well as cleaning maintenance for a power production/thermal desalination plant. A shortcut methods has been proposed to include simplified biocide kinetics in a process-integration scheme. Next, more detailed analysis of biocide chemistry and process characteristics were included. The annual operation has been discretized into operational periods and the process is discretized into two operating segments. A multi-period optimization formulation has been developed to determine the optimal levels of dosing, the relationship between the applied doses, the process conditions, and seawater characteristics for each time period. Applications were shown for general facilities and for combined power plants and thermal desalination systems. The technical and environmental considerations were also accounted for through case studies that have been solved to demonstrate the applicability of the devised procedures.

8. RECOMMENDATIONS FOR FUTURE WORK

The following topics are recommended for future work:

- Inclusion of process-modification changes: This work has focused on the seawater cooling system while accepting the process design and operation in their current form. It will be useful to allow changes in process design and operation to establish tradeoffs with the seawater cooling system.
- Molecular design of biocide: This work has assumed the selection of a specific biocide. Future research should include the problem of the molecular design and selection of biocides that provide the necessary controlling effect to the biofilms while exhibiting desirable technical, economic, and environmental performance.
- Integration with seawater dispersion models: This work has accepted a certain set of environmental regulations for biocide discharge. Future work should include dispersion models for the discharged biocide and relate such dispersion to the impact on aquatic lives.
- Inclusion of safety metrics: This work has focused on techno-economic and environmental criteria. It is important to include safety metrics in the assessment and screening of the design and operational strategies.

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