Reuse of Treated Internal or External Wastewaters in the Cooling Systems of Coal-Based Thermoelectric Power Plants

September 2009

Final Technical Report

July 1, 2006 – June 30, 2009

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Cooperative Agreement Number: DE-FC26-06NT42722

Pilot-scale cooling towers installed at FTMSA, PA

Submitted to:

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ABSTRACT

This study evaluated the feasibility of using three impaired waters – secondary treated municipal wastewater, passively treated abandoned mine drainage (AMD), and effluent from ash sedimentation ponds at power plants – for use as makeup water in recirculating cooling water systems at thermoelectric power plants. The evaluation included assessment of water availability based on proximity and relevant regulations as well as feasibility of managing cooling water quality with traditional chemical management schemes. Options for chemical treatment to prevent corrosion, scaling, and biofouling were identified through review of current practices, and were tested at bench and pilot-scale.

Secondary treated wastewater is the most widely available impaired water that can serve as a reliable source of cooling water makeup. There are no federal regulations specifically related to impaired water reuse but a number of states have introduced regulations with primary focus on water aerosol "drift" emitted from cooling towers, which has the potential to contain elevated concentrations of chemicals and microorganisms and may pose health risk to the public.

It was determined that corrosion, scaling, and biofouling can be controlled adequately in cooling systems using secondary treated municipal wastewater at 4-6 cycles of concentration. The high concentration of dissolved solids in treated AMD rendered difficulties in scaling inhibition and requires more comprehensive pretreatment and scaling controls. Addition of appropriate chemicals can adequately control corrosion, scaling and biological growth in ash transport water, which typically has the best water quality among the three waters evaluated in this study. The high TDS in the blowdown from pilot-scale testing units with both passively treated mine drainage and secondary treated municipal wastewater and the high sulfate concentration in the mine drainage blowdown water were identified as the main challenges for blowdown disposal. Membrane treatment (nanofiltration or reverse osmosis) can be employed to reduce TDS and sulfate concentrations to acceptable levels for reuse of the blowdown in the cooling systems as makeup water.

ACKNOWLEDGEMENTS

This report is based upon work supported by the U.S. Department of Energy, National Energy Technology Laboratory under Award Number DE-FC26-06NT42722. Additionally, we thank the following individuals for serving on our project advisory board: Richard Aull (Brentwood Industries), John Holsapple (Energy and Environment Alliance of New York), Kareen Milcic (PA DEP), Richard Miller (Baltimore Air Coil), William Skalitzky (Alliant Energy), Alan Tennant (Allegheny Energy), David Velegol (Chester Engineers), Stephanie Yauger (Reliant Energy). We are also grateful to our industrial partners: Richard Aull of Brentwood Industries (Reading, PA), Louisa Scandolari of Kroff Chemical Company (Pittsburgh, PA), David Christophersen of Crown Solutions (Vandalia, OH) for their assistance with various aspects of this project. We thank Franklin Township Municipal Sanitary Authority (Murrysville, PA), and especially James Brucker and Gene Greco, for providing access to the FTMSA wastewater treatment facility for sampling and for pilot-scale field testing (the photograph of the FTMSA test site on the report cover is used with permission); St. Vincent College (Norman Hipps and Angela Belli) for access to their AMD passive treatment system for sampling; Reliant Energy (Thomas Teitt and Stephanie Yauger) for access to the Cheswick Power Station ash sedimentation ponds for sampling; and Robert Hedin of Hedin Environmental for helpful discussions related to AMD and site selection.

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EXECUTIVE SUMMARY

As the availability of freshwater for use in cooling in thermoelectric power production becomes increasingly limited, alternative sources of water for power plant cooling are of interest for both existing and future power plants. This study evaluated the feasibility of using three impaired waters – secondary treated municipal wastewater, passively treated abandoned mine drainage (AMD), and effluent from ash sedimentation ponds at power plants – for use as makeup water in recirculating cooling water systems at thermoelectric power plants. The evaluation included assessment of water availability based on proximity and relevant regulations as well as feasibility of managing cooling water quality with traditional chemical management schemes. Options for chemical treatment to prevent corrosion, scaling, and biofouling were identified through review of current practices, and were tested at bench and pilot-scale.

Secondary treated municipal wastewater is the most widely available impaired water while passively treated mine drainage is only available in the coal and metal mining regions of the U.S. Ash transport water is available at many thermoelectric power plants and could be internally reused for cooling without much additional treatment. Secondary treated wastewater from 1-2 large publicly owned treatment works (POTWs) located within a 25 mile radius could meet 75% of the existing cooling water demand and 97% of the demand by the proposed power plants. There are no federal regulations specifically related to this type of water reuse but a number of states have introduced regulations with primary focus on water aerosol “drift” emitted from cooling towers, which has the potential to contain elevated concentrations of chemicals and microorganisms and may pose health risk to the public.

Use of Secondary Treated Municipal Wastewater as Cooling System Makeup Water

It was determined that corrosion, scaling, and biofouling can be controlled adequately in cooling systems using secondary treated municipal wastewater at 4-6 cycles of concentration. While aluminum exhibited pitting corrosion, corrosion of mild steel, copper and cupronickel was not a concern even without addition of any corrosion inhibitors. The low corrosivity of this water was due to the high scaling potential that resulted in a protective layer of scales on metal surfaces. Phosphorous-based corrosion inhibitors are not appropriate due to their reversion to orthophosphate and subsequent precipitation. Scaling control can be achieved by adding commonly used polymer-based scaling inhibitors. Polymaleic acid (PMA) was very effective at scaling inhibition at 10-20 ppm level but its effectiveness can be compromised by free chlorine, often used as a biocide in cooling systems, as PMA was destroyed by this oxidizing agent. Monochloramine was found to be less aggressive with respect to PMA than free chlorine, while still being an effective biocide. It was determined that maintaining a monochloramine residual above 1 ppm as Cl_2 in the cooling system could effectively limit the growth of planktonic heterotrophic bacteria in the recirculating water. A residual concentration between 1-3 ppm as Cl_2 was required to control the growth of biofilm-forming attached bacteria under 10^4 CFU/cm^2. Pre-formed monochloramine yielded better biocidal control than that formed in situ due to unstable ammonia concentrations in the cooling system.

Use of Passively Treated Mine Drainage as Cooling System Makeup Water

The unique challenges of using treated AMD relate to the high concentration of dissolved solids and appreciable amount of particulate matter. When reusing passively treated mine drainage in cooling towers operated at CoC 4 and 40°C with the addition of monochloramine to control biomass growth, cupronickel exhibited acceptable corrosion rate without corrosion inhibitor. Addition of an inhibitor mixture consisting of 5 ppm as PO_4 of orthophosphate, 2 ppm of tolyltriazole (TTA) and 15-25 ppm of PMA reduced the corrosion rates of mild steel and copper to acceptable levels. Aluminum exhibited pitting corrosion and is not suitable for use. The high concentration of dissolved solids rendered difficulties in scaling inhibition and requires more comprehensive pretreatment and scaling controls. PMA at concentrations of 15-25 ppm lent some stability to suspended mineral solids and there was less deposition in the pipe flow sections of the cooling towers tested. Deposits from the AMD exhibited varied affinities to different surfaces. Significant deposits were observed at the bottom of the tower sump, especially in the tower receiving no PMA treatment. Microbial activity in the raw AMD selected for this study was rather limited in both bench- and pilot-scale tests and chlorination could control biofouling with a minimal dosage of 0.5 ppm as Cl_2. Chloramination exhibited higher disinfection efficiency and lower decay rate than chlorination. Monochloramine residual concentration of 1-2 ppm was sufficient to suppress biomass growth in the pilot-scale cooling tower tests.

Use of Ash Transport Water as Cooling System Makeup Water

When using ash transport water as cooling water at CoC 4 and 40°C with the addition of monochloramine to control biomass growth, cupronickel was found to be the most corrosion resistant material, even in the absence of corrosion inhibitor. Protection of copper required the addition of TTA at 2 ppm. Aluminum exhibited pitting corrosion even in the presence of corrosion inhibitors. Protection of mild steel required phosphorous-based corrosion inhibitor, such as tetra-potassium pyrophosphate (TKPP) at 20 ppm as PO_4. Scaling was less of a problem and addition of 10 ppm of PMA or 10 ppm of PBTC was very effective in suppressing scaling to minimal levels. Both of these scale inhibitors prevented calcium from forming deposits and their effectiveness lasted longer than that of polyacrylic acid (PAA). Bench-scale batch and recirculating system results revealed that chlorination can be an effective biocidal control option even at a low free chlorine residual close to 0.5 ppm as Cl_2 since this water has a low organic load. Addition of scaling and corrosion inhibitors with free chlorine residual does not affect biofouling control.

Blowdown Management

The primary objective of blowdown management is to treat blowdown to attain quality that is equal to or better than the makeup water so that it can be reused as makeup water. The high TDS in the blowdown waters from pilot-scale testing units with both passively treated mine drainage and secondary treated municipal wastewater and the high sulfate concentration in the mine drainage blowdown water were identified as the main challenges for treatment. Equilibrium calculations predicted that lime-soda ash softening treatment could effectively remove Ca and Mg but neither TDS nor sulfate could be substantially affected. Nanofiltration with a BW30 membrane was effective for treatment of blowdown from the pilot-scale testing with secondary treated municipal wastewater. The blowdown from the pilot-scale testing with passively treated AMD needed sequential treatment with two nanofiltration membranes (NF90 followed by BW30). In both cases, a trans-membrane pressure of 135 psi provided acceptable water flux. Overall, the testing with the blowdown waters demonstrated that membrane treatment can be employed to reduce TDS and sulfate concentrations to acceptable levels for reuse of the blowdown in the cooling systems as makeup water.

1.0 Introduction

The issue of water shortage is becoming more prominent in the U.S. as population increases and global warming affects water supplies (Hinrichsen et al., 1997). The freshwater usage in the U.S. has increased from 341 to 378 billion per day between 1995 and 2000 (USGS, 2000). The major freshwater users are irrigation (39%) and thermoelectric power generation (38%-39%). Water needs in a thermoelectric power plant include water for cooling, water for operation of pollution control devices, such as flue gas desulfurization (FGD), as well as for ash handling, wastewater treatment, and wash water.

Cooling tower operation is based on evaporative condensation and exchange of sensible heat. Depending on the technology used for cooling, the amount of water usage can be quite different. For a once-through cooling tower, 20–50 gallons of water are required to generate each kW-hour of electricity. On the other hand, modern recirculating cooling towers need 0.2 to 0.6 gallons of water to generate each kW-hour electricity (Veil, 2007).

It is estimated that water demand for energy generation will increase by 50% by 2030 (USDOE, 2008). Fierce competition for this valuable resource will force difficult decisions about allocation priorities and water availability for electric power production. Therefore, alternative sources of water for cooling tower operation are likely to be in even greater demand in the future.

Potential alternative sources of cooling water include treated municipal wastewater, treated mine drainage, and ash transport water from coal-fired power plants. It has been shown that impaired waters can be used as cooling water in electric power plants (Richard, 1964; Paul and Ken, 2003; and Veil, 2003). However, most of these reuse applications employ fairly limited addition of wastewater to cooling tower as make up water. In addition, these applications represent special circumstances (e.g., both POTW and power plant owned by the same company, close proximately of the two, demonstration project, etc.) and there is no reliable information about the true potential of these alternative water sources to meet cooling water demand of power industry.

This study was designed to evaluate key regulation incentives and obstacles for water reuse in cooling applications and to provide comprehensive assessment of the availability of secondary effluent from POTWs to meet the cooling water needs of existing and proposed thermoelectric power plants. In addition, technical issues associated with the use of selected impaired waters were evaluated in both lab- and pilot-scale studies together with potential operating strategies that would ensure proper performance of these critical systems in thermoelectric power plants.

1.1 Water Availability in the United States

Although 70% of the earth's surface is covered with water, most of that is saltwater. By volume, only 3% of all water on earth is fresh-water, and most of it is largely unavailable (Duddin and Hendrie, 1998) since it exists in the form of ice located in remote areas far away from most human habitation; only about 1% of all available water is easily accessible, surface freshwater. This is mainly the water found in lakes and rivers. In sum, only 0.007% of the world's total supply of water is considered easily accessible for human use (Lefort, 1996).

The U.S. population has been steadily increasing from 1990s to 2000s. Figure 1.1 shows the resident population change between 1990 and 2000 in the 50 states. Among the 50 states, Nevada and Arizona experienced the highest population increase rates, which are 66 % and 40 %, respectively. The intermountain states have an average increase of 30%. Apparently, the southern states have faster population increase because of the available undeveloped territory and immigration. The future population in the U.S. is also estimated to increase by as much as 82% (from 296 to 438 million) in the U.S (Passel and Cohn, 2008).

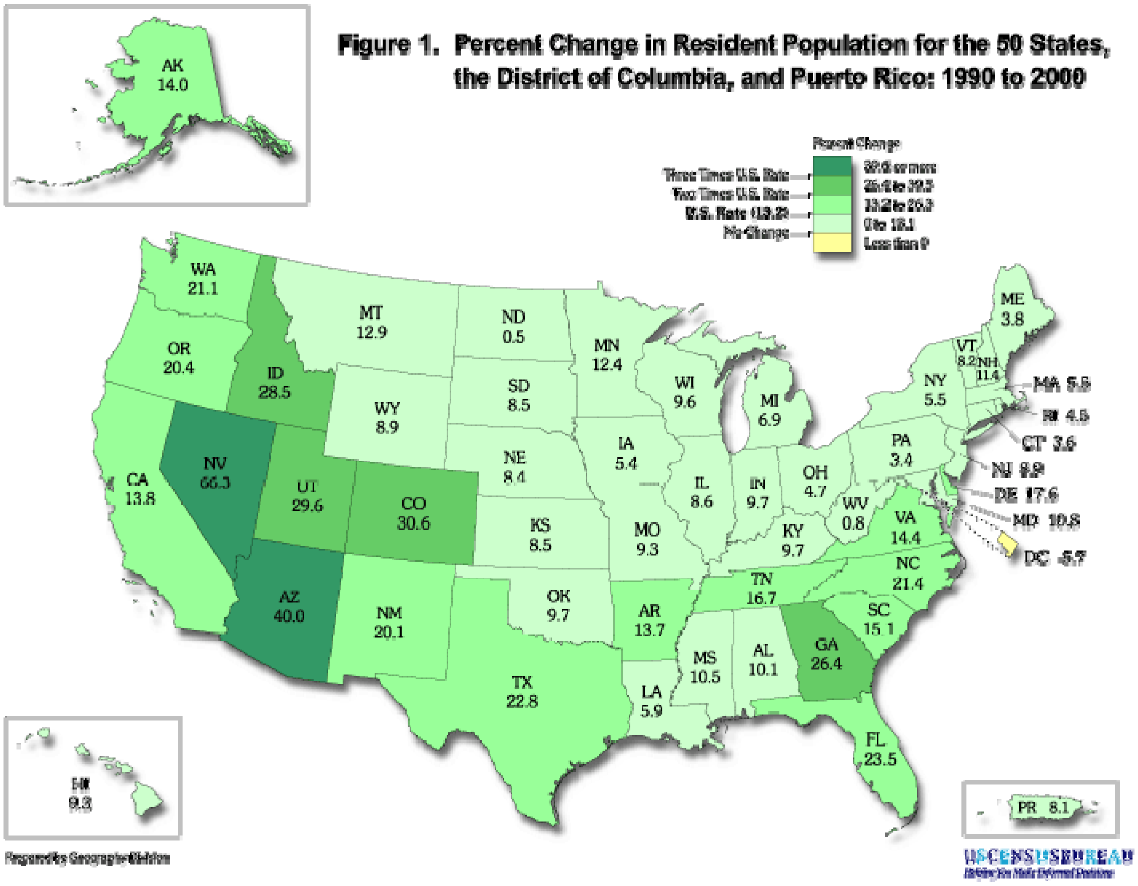

Figure 1.1. Population change in the U.S. from 1990 to 2000. Darker color indicates the higher increase rate (Adapted from US Census, 2000).

Figure 1.2 shows the drought monitor in the U.S. in October, 2007. A comparison of Figures 1.1 and 1.2 shows that the areas where the population is high also have intensive drought, especially in southwestern and southeastern U.S. It is clear that these conditions represent significant challenges for industrial water uses and that the industry will most likely have to find alternative solutions to their current water needs.

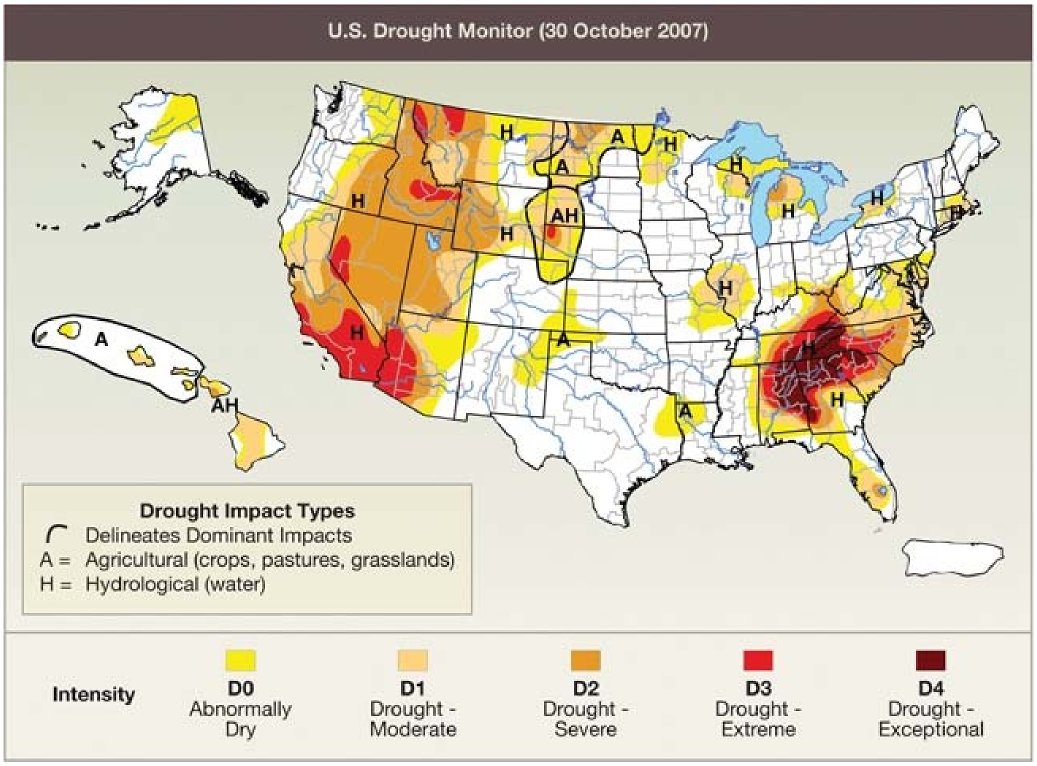

Figure 1.2. U.S. Drought monitor. Drought Monitor integrates information from a range of data on rainfall, snowpack, streamflow, and other water supply indicators into a comprehensible picture. (Adapted from USGCRP group, 2007).

1.2 Water and Energy Issues

Following the rapid population growth is the increase in energy demand. In order to satisfy the developing communities and businesses, more energy will be produced; in other words, more water will be needed. Thermoelectric power generation, which represents about 91% of electrical power produced in the U.S. (Figure 1.3), (USEIA, 2007), requires an abundance of water for its operation. In addition, the total thermoelectric generating capacity is expected to increase by nearly 18 % between 2005 and 2030. The increasing energy demand in next decades would certainly aggravate the water shortage problem, especially the availability of water used for electricity generation (USDOE, 2008).

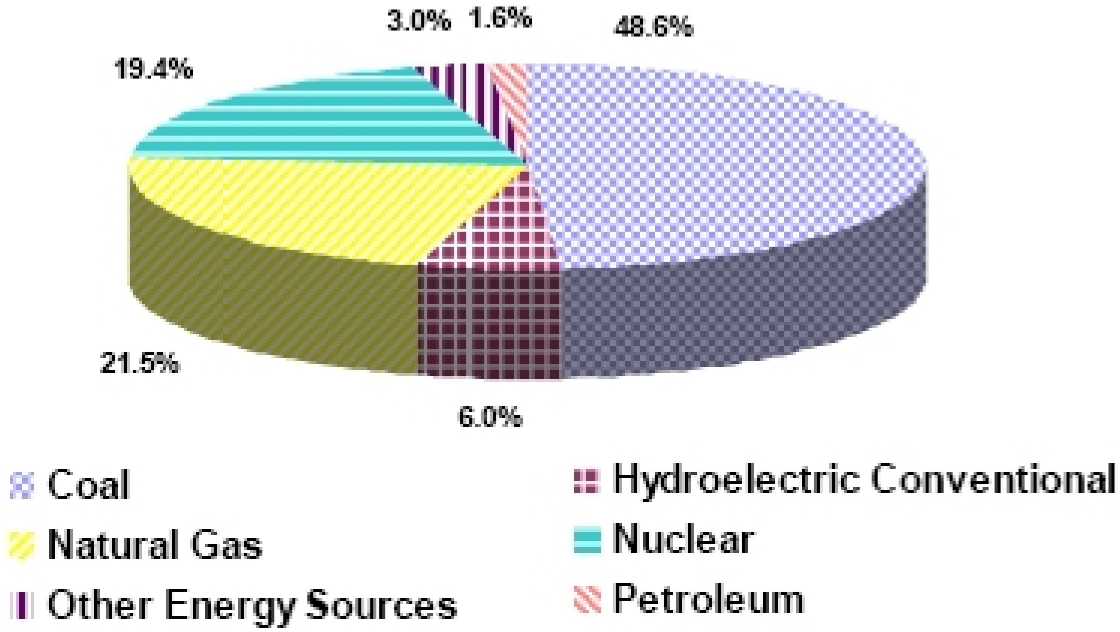

Figure 1.3. Net Generation Shares by Energy Source: Total (All Sectors), Year-to-Date through December (EIA 2007).

During the electricity generation process, process water is converted to steam to drive the turbine and generate electricity. Steam is then exhausted from the turbine and condensed for reuse. Coolant, such as water, is introduced to absorb heat from the exhaust steam so that the process water can be recycled. Therefore, the design and operating parameters of the cooling system are critically important for the overall power generation efficiency. At higher condenser cooling water inlet temperatures, the steam condensate temperature is higher and subsequently turbine backpressure is higher. The turbine backpressure is inversely related to power generation efficiency (i.e., the higher the turbine backpressure, the lower the power generation efficiency).

There are three major types of wet cooling procedures currently used by thermoelectric power generation, including once-through cooling system, wet recirculating system, and a cooling pond. Once-through cooling system draws surface water from lake, river, or the ocean for one time cooling and then discharges the heated water back to the water body. For once-through cooling system, the water withdrawal is high, but the water consumption is low. However, the higher temperature effluent usually causes the changes in aquatic ecology and damages the local natural habitats. The construction of once-through cooling systems is highly restricted in many states because of 316(b) Federal regulation (FWPCA, 2002). Clean Water Act section 316(b) introduced technology-based standards to reduce the harmful effects associated with cooling water intake structures on marine and estuarine life, such as trapping fish and small mammals against the intake screen, sucking in immature larvae and eggs, etc. In addition, the National Pollutant Discharge Elimination System (NDPES) program is involved in any point discharge source, thus making the construction of once-through cooling tower quite challenging.

In a wet re-circulating cooling system, warm water is transferred to a cooling tower and exposed to ambient air for cooling through evaporation. Contact between water and air is enhanced by the use of packing material in the cooling tower and the natural draft is used to pull air through the tower. Since the water keeps recycling in the system, the total water withdrawal decreases, but the total water consumption increases because of significant evaporative loses.

Cooling pond uses the same mechanism as the re-circulating system but it relies on the natural heat transfer from the water to the atmosphere.

Dry cooling systems are also used in either direct cooling or indirect cooling arrangement. High flowrate of air is blown to the surface of an air-cooled condenser to absorb the heat via convective heat transfer, which is called direct dry cooling. Indirect dry cooling uses the same water-cooled condenser but uses air instead of water as a coolant. Therefore, both processes have no loss of cooling water and the freshwater withdrawal and consumption are minimized. However, due to significantly lower heat capacity of air as compared to water, dry cooling systems are usual larger and require significantly larger capital costs.

For wet recirculating systems, each kW-hour of electricity generation requires 20-50 gallons of water in once through cooling systems, while only 0.3-0.6 gallons of water is required to generate each kW-hour of electricity in modern re-circulating systems (Veil, 2007). About 136 billion gallons of freshwater was withdrawn per day in 2000 for thermoelectric power generation, which is 39% of the overall freshwater withdrawal in the U.S. (Figure 1.4, USGS, 2004).

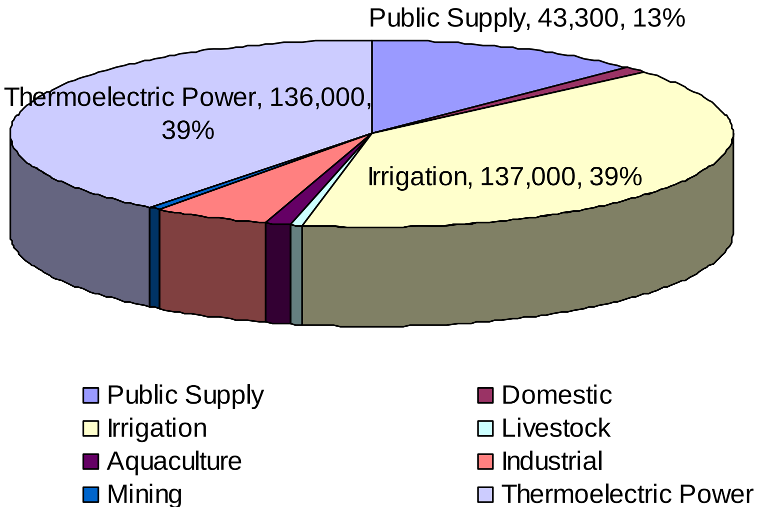

Figure 1.4. Daily freshwater withdrawn in the United States in billion gallons per day (USGS, 2004).

In addition to water withdrawal, USGS also has evaluated the overall freshwater consumption in the U.S. (Figure 1.5, USGS, 2000). The thermoelectric power generation represents 3%, (3 billion gallons per day) of the overall freshwater consumption in the U.S., while the irrigation represents the largest portion of freshwater consumption at 81%. As opposed to the huge amount of freshwater withdrawn for thermoelectric power generation, only 0.47 gallons of freshwater is evaporated per kWh of electricity at the point of end use (Trocellini et al., 2003).

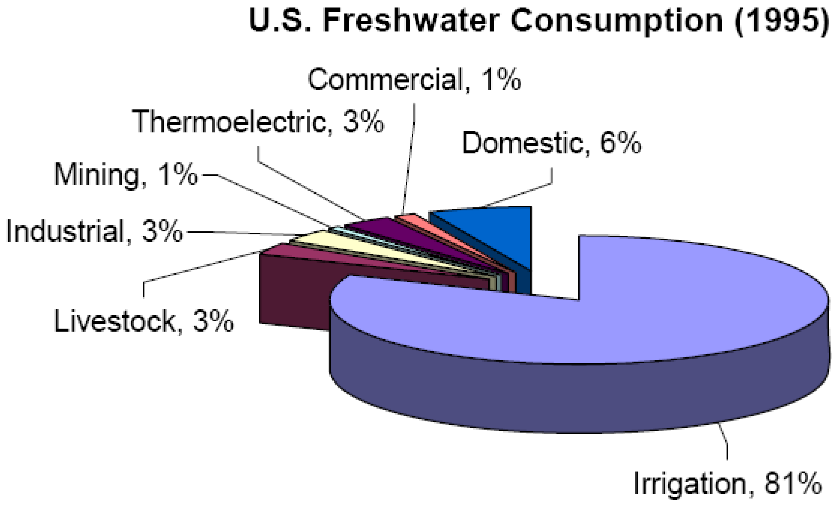

Figure 1.5. Freshwater consumption percentage divides into different categories in the United States (USGS, 2000).

A forecast of freshwater usage in 2030 was done by National Energy Technology Laboratory using different assumptions about cooling system deployment in the U.S. (USDOE, 2008). The results indicate that freshwater withdrawal will remain the same or even decrease when most aged power plants are replaced with modern generation units and recirculating cooling systems. However, the freshwater consumption in 2030 will increase by 27~49% when compared to freshwater consumption in 2005.

Existing and new power plants, including coal-based thermoelectric plants, will be faced with increasingly stringent restrictions on water use in some regions of the U.S. Figure 1.6 shows the Cooling Constraint Index for thermoelectric power plants (Roy et al., 2003). Indeed, the lack of available freshwater has already prevented the siting and permitting of new power plants in some regions (Feeley and Ramezan, 2003; Dishneau, 2007). Furthermore, Section 316(b) of the Clean Water Act limits the amount of freshwater that can be withdrawn by power plants, thereby requiring the installation of wet or dry closed-loop cooling systems.

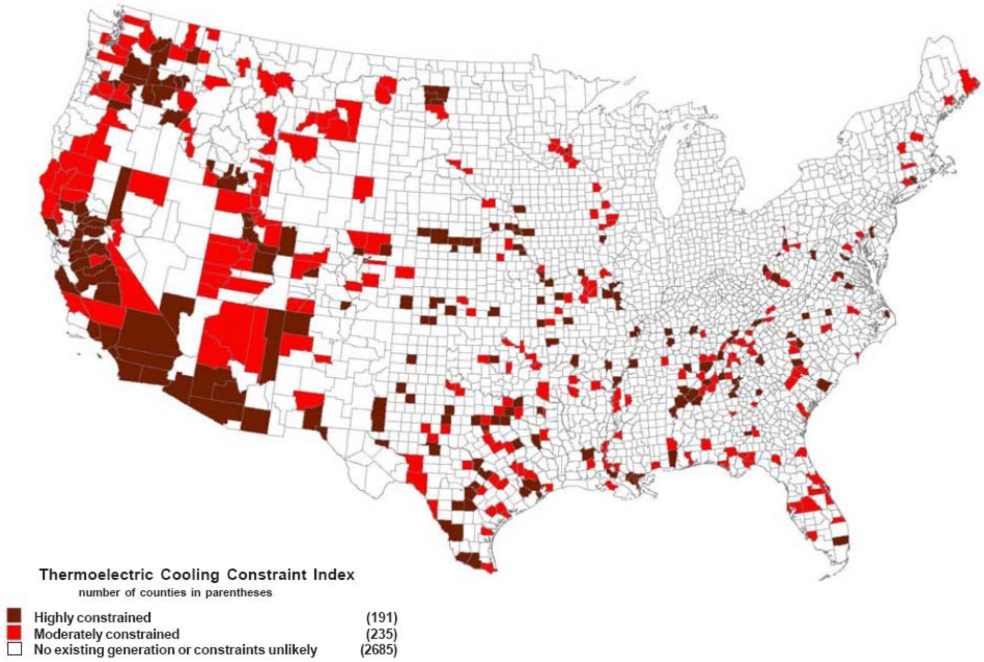

Figure 1.6. Thermoelectric Cooling Constraint Index. The colored areas indicate the cooling water supply is limited (Roy et al., 2003).

In conclusion, water and energy issues are intricately related and cannot be addressed in isolation. With the increasing population and energy demand, the scarcity of freshwater will become a nationwide phenomenon. Impaired waters could serve as potential alternative water sources and help meet power plant cooling needs. There is already some experience with the use of impaired waters, especially treated municipal wastewater as cooling water sources. Therefore, finding alternative water resources to replace freshwater demand for cooling purposes is inevitable and urgent.

1.3 Study Objectives

This study is designed to assess geographic proximity, available quantities and regulatory and permitting issues that are relevant for application of these impaired waters in cooling systems, as well as key design and operating parameter that would ensure successful use of these impaired waters without detrimental impact on the performance of the cooling system (e.g., heat rejection capacity, corrosion, biofouling and scaling issues). Another important objective of the proposed work is to develop and demonstrate the efficacy of small pilot-scale cooling towers for side-by-side evaluation of the use of impaired waters under different operating conditions. As consideration of alternative sources of water for cooling purposes increases in the years ahead, it will be important to have methods in place for rapid and accurate evaluation of performance of these waters in cooling systems.

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2.0 Availability of Impaired Waters for Cooling in Power Plants

Potential alternative sources of cooling water addressed in this study include treated municipal wastewater, treated mine drainage, and ash transport water from coal-fired power plants. It has been shown that impaired waters can be used for cooling needs in electric power plants (Richard, 1964; Paul and Ken, 2003; and Veil 2003). However, most of these reuse applications employed fairly limited addition of wastewater to cooling tower as make up water. In addition, these applications represent special circumstances (e.g., both POTW and power plant owned by the same company, close proximately of the two, demonstration project, etc.) and there is no reliable information about the true potential of these alternative water sources to meet cooling water demand of power industry.

When assessing the feasibility of using impaired waters for cooling in power plants, it is important to asses both water quality parameters and the availability of different impaired waters to meet power plant needs. Among all possible sources of impaired water that could potentially be used in power production, secondary treated municipal wastewater is the most common and widespread source in the U.S. Therefore, particular attention is given to comprehensive analysis of the quantities, availability and proximity of this impaired water for use in existing and future power plants.

2.1 General Water Quality and Availability of Secondary Treated Municipal Wastewater

Municipal wastewater is a complex mixture of organic waste, suspended solids, debris and a variety of chemicals that come from residential, commercial and industrial activities. Secondary treatment of municipal wastewater, the minimum standard for municipal wastewater treatment under the Clean Water Act, usually involves debris and grit removal, primary settling of particles, aerobic biological treatment for the removal of readily biodegradable organic matter, secondary sedimentation, and disinfection.

The characteristics of typical secondary effluent reported in literature were compiled in this study and the results are shown in Tables 2.1 and 2.2. Data for secondary effluent that is currently used as makeup for cooling water systems were also included. The secondary effluent quality in Table 2.1 can be used as an indication of the concentration range for the constituents that are of importance if the effluent is used as cooling tower makeup water. The range of concentrations for general constituents of treated wastewater used for cooling needs is shown in Table 2.2.

After treatment, BOD and ammonia concentration are reduced to low levels, thus causing less adverse impact when using this impaired water in cooling systems. However, total dissolved solid and several neutral salts, such as sodium and potassium are comparatively higher than other chemicals because of less strict limitations. Organic nutrients, calcium and magnesium, which may cause biofouling, corrosion, and scaling problems, show a wide range in the treated wastewater.

Table 2.1. Water quality of secondary treated municipal wastewater effluent from different U.S. locations

Parameters	General Treated Wastewater Quality	
	After Williams, 1982 (1)	After Weinberger et al., 1966 (2)
BOD (mg/L)	11	25
COD (mg/L)	71	
TSS (mg/L)	17	
TDS (mg/L)		730
Alkalinity (mg/L as $CaCO_3$)	131	250
Hardness (as $CaCO_3$)		270
Turbidity (TU)	11	
Color (P-C unit)	29	
Forming Agent (mg/L)	0.45	
Oil and Grease (mg/L)	3.7	
TOC (mg/L)	11	
Organics (mg/L)		55
Na (mg/L)		135
K (mg/L)		15
Ca (mg/L)		60
Mg (mg/L)		25
Cl (mg/L)		130
NH_3-N (mg/L)		16
NO_3-N (mg/L)		3
NO_2-N (mg/L)		0.3
HCO_3 (mg/L)		300
SO_4 (mg/L)		100
PO_4 (mg/L)		8
SiO_2 (mg/L)		50

(1) Williams, R.B., (1982), "Wastewater Reuse -- An Assessment of The Potential and Technology," Water Reuse, Chapter 5,, Ann Arbor, Michigan.

(2) Weinberger, L.W., Stephan, D.G., Middleton, F.M. (1966), "Solving Our Water Problems -- Water Renovation and Reuse" Ann. N. Y. Acad. Sci. 136, pp. 131-154.

Table 2.2 Range of chemical constituent concentrations in secondary treated municipal wastewater effluent

Parameter	Range*
pH	7 -8
BOD (mg/L)	3 – 30
TDS (mg/L)	130 – 1600
Alkalinity (mg/L as $CaCO_3$)	100 – 250
Ca (mg/L)	28 – 185
Mg (mg/L)	23 – 150
NH_3-N (mg/L)	3 – 73
HCO_3 (mg/L)	137 - 396
SO_4	60 – 293
PO_4	0.6 – 51
SiO_2	8.3 – 50

*The range of concentration is determined from:
(1) General water quality gathered from (Williams, R.B., 1982) and (Weinberger et al., 1966).
(2) Sewage effluent quality used for power plant cooling water makeup from Goldstein (1982), Breitstein et al., (1986).
(3) Specific sites from American Water Works Association Research foundation (1978), Goldstein et al., (1982), Tsai (2006), and Masri et al., (2003).

2.2 Feasibility Analysis of Using Secondary Treated Wastewater for Cooling Purposes

Regional and local wastewater availability for selected power plants was evaluated using standard geoprocessing tools. The analysis was performed using ArcGIS (Version 9.2, ESRI). Database of publicly owned treatment works with NPDES permits was extracted from EnviroMapper of Water, USEPA. Database of power plants included proposed power plants listed by Energy Information Administration, Form EIA-860, "Annual Electric Generator Report" and the existing coal-fired power plants from DOE database (USDOE, 2007)

For each of the power plants in the database, the sources of treated municipal wastewater within a 10 and 25-mile radius from the plant was catalogued together with the distance and average flow characteristics. The number of POTWs required to satisfy the cooling water demand of each power plants is determined to provide an initial assessment of water distribution network needed to meet cooling water needs.

2.2.1 Feasibility Analysis Methodology

2.2.1.1 Analysis Steps

Figure 2.1 provides a flowchart depiction of the methodology used to conduct the analysis. Each step in the process is briefly described in the following sections while the additional details are given in Appendix A.

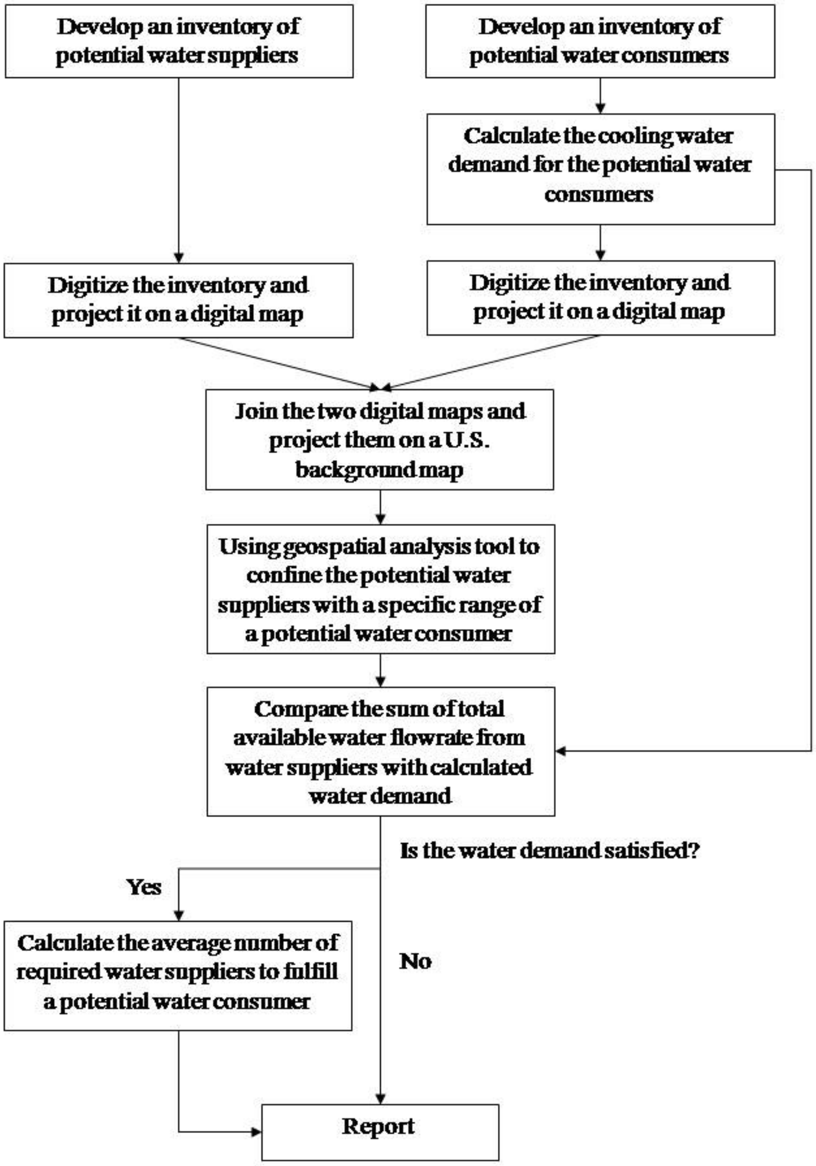


Figure 2.1. Methodology for the Feasibility Analysis of using secondary effluent as cooling water.

2.2.1.2 Develop an inventory of Potential Water Suppliers and Consumers

Water Suppliers – Publicly Owned Treatment Works (POTWs)

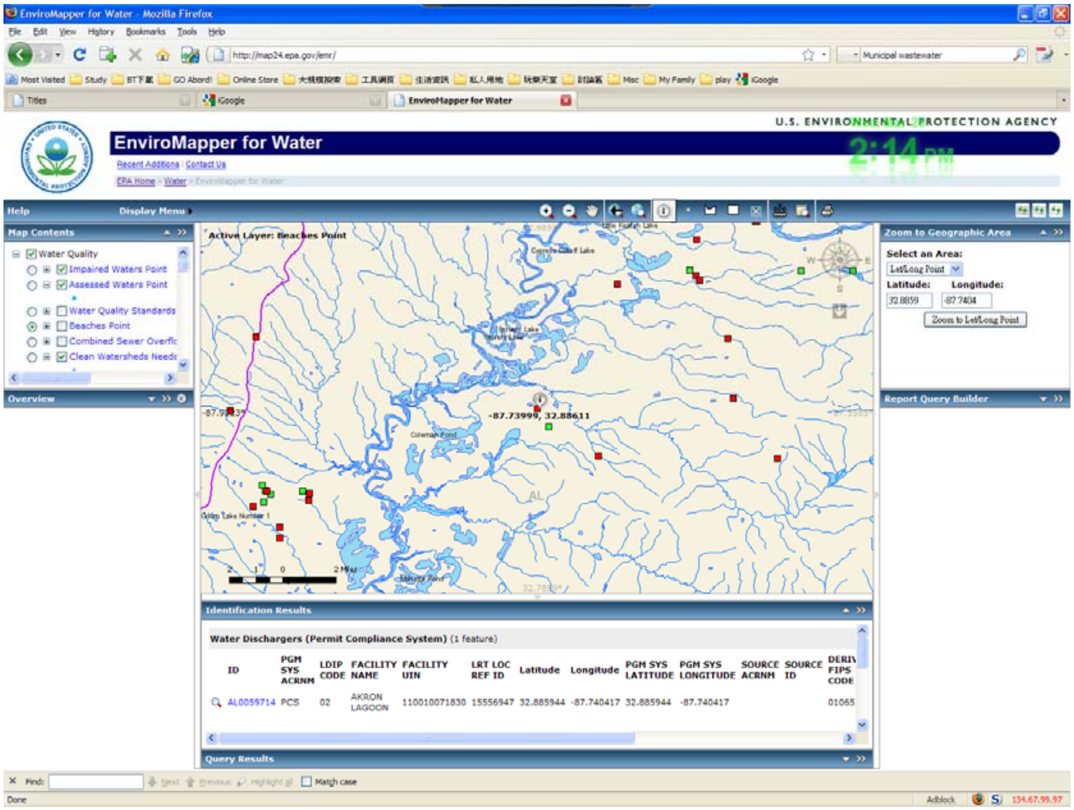
The first step was to acquire a database containing information about wastewater treatment facilities. Database created for the Clean Watersheds Needs Survey (CWNS), which was used in CWNS 2000 data report to congress (USEPA, 2003), was chosen and the information about POTWs was extracted from the original database.

The database has a list of 33,852 wastewater discharge records and includes wastewater flow discharged from household, city sewer, treatment plant, industry, etc. However, it includes both abandoned facilities and proposed facilities to be built in the future. Therefore, the database was screened based on the following requirements:

- Reflects publicly owned treatment works,
- Minimum level of treatment is secondary treatment
- Includes latitude and longitude information
- Plant currently in operation instead of abandoned or proposed.

After the screening, the total number of POTWs that could be used for this survey was reduced to 17,864, including wastewater treatment plants, sewage treatment plants, water recycling plants, water pollution control plants, and lagoons. Data for each POTW included information about present and future discharge flowrates. Since this study was based on geospatial analysis, the geographic location and available wastewater flowrate of these POTWs would significantly affect the accuracy of the results and required data validation. First, authorized permit number by the National Pollutant Discharge Elimination System (NPDES) was related to facility name in the database. Furthermore, a number of random POTWs was verified on the GIS query tool, EnviroMapper, to ensure the reliability of the information (USEPA, 2008). EnviroMapper is an online based GIS developed by EPA and can provide information about any point discharge source in the U.S. Querying with NPDES permit number, geographic information and daily discharge flowrate can be compared with information in POTW database.

Figure 2.2 shows an example of verifying the water supplier, Akron Lagoon, Alabama, on EnviroMapper with latitude and longitude query.



Water Dischargers (Permit Compliance System) (1 feature)

ID	PGM SYS ACRNM	LDIP CODE	FACILITY NAME	FACILITY UIN	LRT LOC REF ID	Latitude	Longitude	PGM SYS LATITUDE	PGM SYS LONGITUDE	SOURCE ACRNM	SOURCE ID	DERIV FIPS CODE
AL0059714	PCS	02	AKRON LAGOON	110010071830	15556947	32.885944	-87.740417	32.885944	-87.740417			01065

Figure 2.2. EnviroMapper, the online GIS query tool (EPA, 2008).

A number of POTWs were validated through this procedure and all information matched with the database used in this study. However, some limitations of the database are: (1) Both point or non-point source of discharge are included in the inventory; (2) POTWs matching the requirements listed above were included in the database regardless of discharge destination (e.g. surface discharge, groundwater recharge, ocean discharge, etc.); (3) POTWs matching the requirements listed above were included in the database regardless when the information was last updated.

Since 1996, the water discharge data were collected and updated every four years and the latest update was in 2004. However, the database still included dated information for some facilities. According to the USEPA website, the CWNS group plans to move the data entry to the Internet to enable direct entry into CWNS 2008 by the responsible parties.

The information about 17,864 POTWs extracted from CWNS 2000 was imported into a geographic information system (GIS). ArcGIS version 9.2 was used as the software package for this study. The U.S. background was acquired from ESRI – U.S. Street Map DVD. The geographic coordinate system for the map was World Geodetic Survey 1984 (WGS 84) and the datum for the map was also WGS 84. The distribution of POTWs is shown on Figure 2.3. Each node represents a POTW on the map and the scale/color of the point reflects the present flowrate discharged from the POTW.

Most POTWs are located in the Eastern and middle U.S. and most large treatment facilities are located in major cities, such as Chicago, New York, etc.

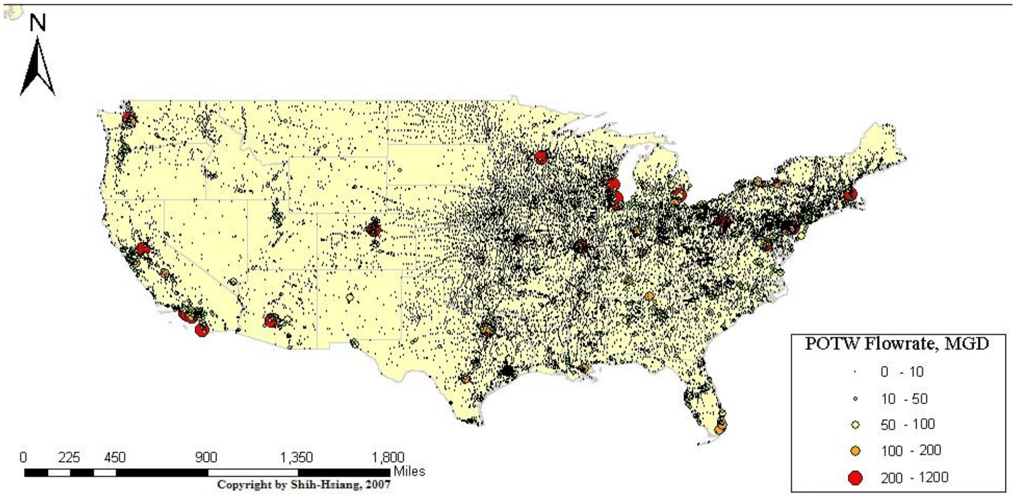


Figure 2.3. Publicly owned treatment works in continental U.S.

Water Consumers –Power Plants Proposed for Construction

Power plants which were proposed to start construction in 2007 were selected to represent potential water consumers in this study. The original database was compiled from the EIA-860, Annual Electric Generator Reports. The EIA-860 reports includes specific information about generators at electric power plants owned and operated by electric companies, including independent power producers, combined heat and power producers, and other industrial facilities. The file contains generator-specific information, such as initial date of commercial operation, generation capacity, energy sources, status of existing and proposed generators, proposed changes to existing generators, etc. A total number of 110 power plants proposed in 2007 were used to assess the feasibility of using secondary effluent to meet cooling water needs for new power plant.

Figure 2.4 depicts tentative locations of these new plants. The geographic coordinate system for the map was World Geodetic Survey 1984 (WGS 84) and the datum for the map was also WGS 84. The U.S is divided into 13 different North America Electric Reliability Council

(NERC) regions. The NREC regions were formed by the electric utility industry in 1968 to ensure that the main electric system in North America is reliable, adequate, and secure. The full name of each region is provided in Table 2.3.

The region boundaries used in this study were those originally established by the NERC Regional Council. Regional boundaries have been changed to include eight regions as shown in Figure 2.5. Due to the lack of information on new boundaries and reliable digitized maps, the analysis conducted in this study focused on the original NERC regions.

Only 11 NERC regions were included in this survey because no power plants were proposed to be built in Mid-Atlantic Area Council (MACC) and Western Electricity Coordinating Council/New England (NPCC/NE).

It is also important to note that the exact geographic locations of the proposed power plants have not yet been confirmed. As a result, the center of the city/county was designed as the location for the new plant and used in this study.

Table 2.3. Full names of NERC regions.

Abbreviation	Region
ECAR	East Central Area Reliability Coordination Agreement
ERCOT	Electric Reliability Council of Texas
MAAC	Mid-Atlantic Area Council
MAIN	Mid-America Interconnected Network
MAPP	Mid-Continent Area Power Pool
NPCC/NY	Northeast Power Coordinating Council/New York
NPCC/NE	Northeast Power Coordinating Council/New England
FRCC	Florida Reliability Coordinating Council
SERC	Southeastern Electric Reliability Council
SPP	Southwest Power Pool
WECC/NWCC	Western Electricity Coordinating Council/Northwest Power Pool
WECC/RM	Western Electricity Coordinating Council/Rocky Mountains AZ NM Southern NV
WECC/CA	Western Electricity Coordinating Council/California

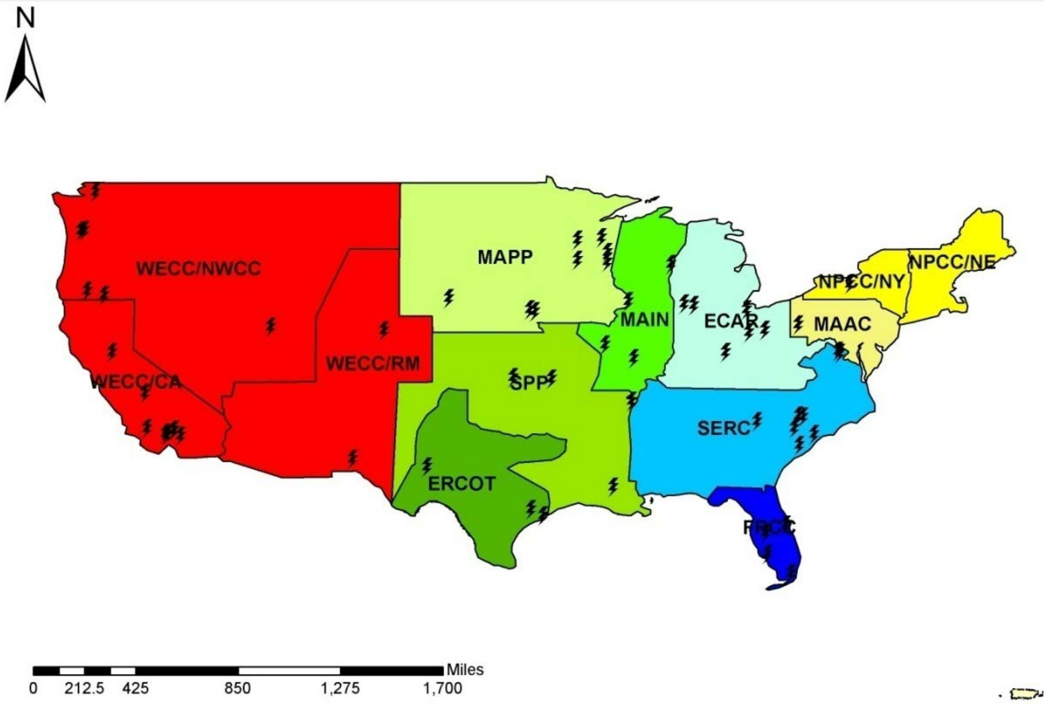


Figure 2.4 Power plants proposed in 2007 listed by EIA in continental U.S.

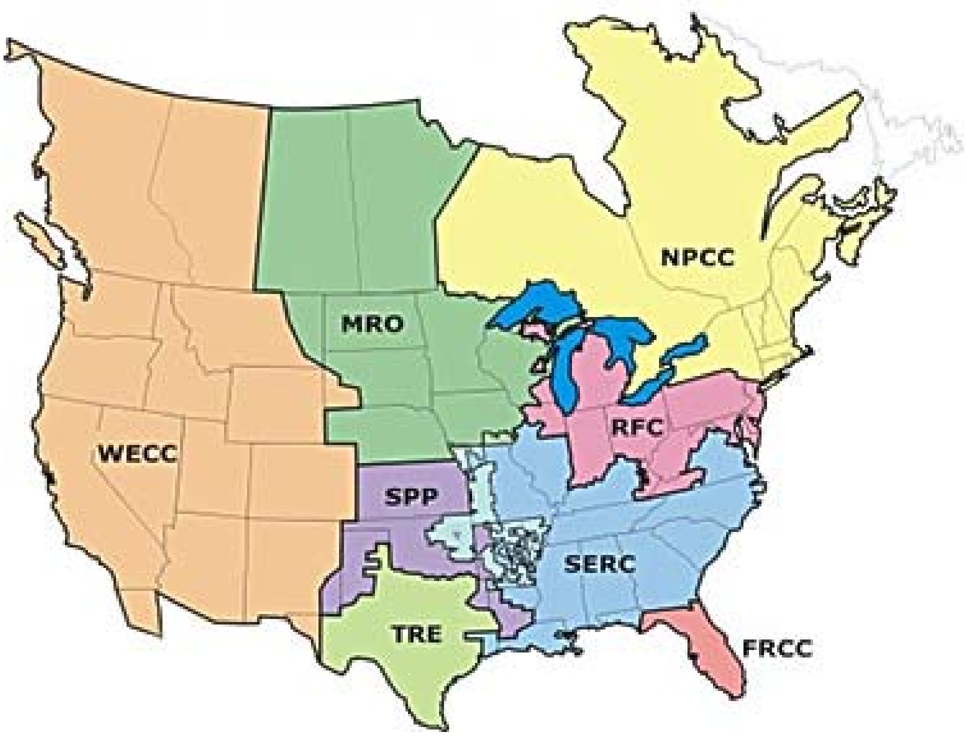


Figure 2.5 Current Map of the Eight NERC Regions (Starting from January 1, 2006).

Water Consumers –Existing Power Plant Units as of 2007

To better understand the potential connection between treated wastewater and power generation, database of existing coal-fired power plants compiled by NETL (USDOE, 2007) was evaluated in this study. A total of 1929 generating units were listed individually although a single power plant may have multiple generating units. The average generating capacity of existing power plants is 547 megawatts per hour. Total numbers of power plants used in the study is 407 in 43 states as shown in Figure 2.6. The geographic coordinate system for the map was World Geodetic Survey 1984 (WGS 84) and the datum for the map was also WGS 84.

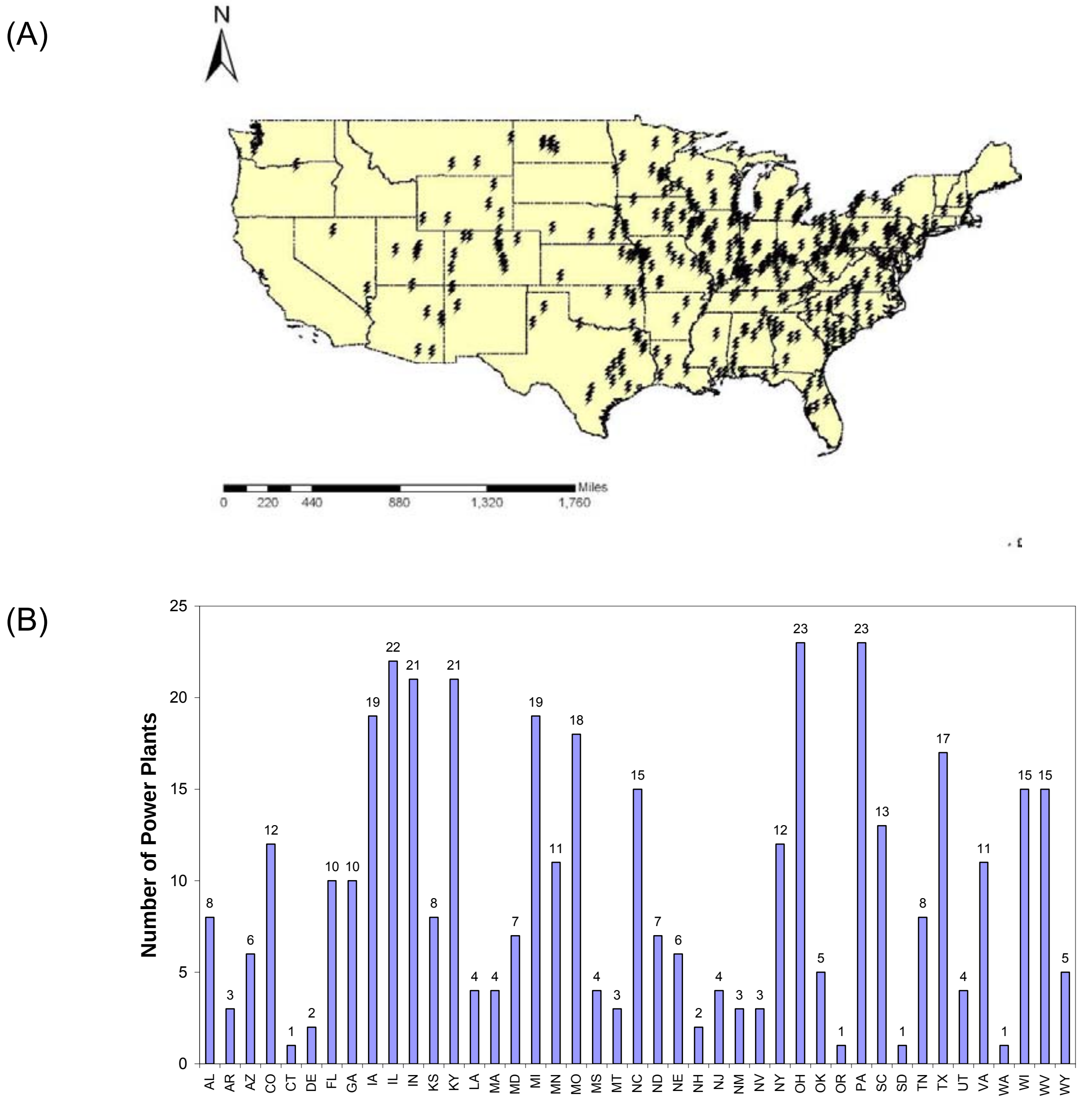


Figure 2.6. Existing Coal-fired power plants listed in NETL Thermoelectric Power Plant Database, 2007. A total of 407 plants are included in the database. (A) Geographical distribution of existing power plants; (B) Summation of the existing power plants in each state.

2.2.2 Estimation of the Cooling Water Demand

The next step was to estimate the cooling water needs for each proposed power plant so that a comparison with the total available wastewater that can be made. Two methods for estimating water needs of a specific power plant are described below.

The first method calculates water demand based on plant capacity, water to energy ratio, capacity factor and operating hours based on the following equation:

$$E = C \cdot R \cdot F \cdot T$$

Where,

E = Estimated water demand, gal/day
C = Maximum generating capacity (Summer capacity), MW
R = Water to energy ratio = 1200 gal/MW*h
F = Capacity factor = 0.75 (dimensionless)
T = Operating hours, hours/day

Water to energy ratio of 1200 gallons of water per MWh of energy was derived from the EIA's report (EIA, 2000) and it is an estimate of average water withdrawal for wet re-circulating cooling systems based on the data collected in 2000. The water to energy factor has since been updated to reflect specific generation type, the boiler type, and the design of the turbine and has been renamed to withdrawal factor (USDOE, 2008). Table 2.4 summarizes withdrawal factors adapted from NETL report, Estimating Freshwater Needs to Meet Future Thermoelectric Generation Requirements (USDOE, 2008). The withdrawal factor for coal-fired power plants includes: 1) boiler make-up water, 2) FGD make-up water, and 3) cooling water. Apparently, the water to energy factor of 1,200 gal/MWh used in this study is overestimating the cooling water demand by power plants, which provides a conservative assessment of water availability for cooling.

Table 2.4. Withdrawal factors for specific applications.

Applications	Withdrawal Factor (gal/MWh)
Freshwater, Re-circulating System, Coal-fired power plants	~600
Freshwater, Re-circulating System, Nuclear power plants	~1100
Freshwater, Re-circulating System, Non Coal-fired power plants	~250
Freshwater, Re-circulating System, NGCC power plants	~150
Freshwater, Re-circulating System, IGCC power plants	~226

Summer capacity is usually regarded as the design capacity of a power plant. The capacity factor is the average output of a power plant as a fraction of the full load of a power plant. A seventy five percent capacity factor was assumed for this analysis considering a steady, normal output condition and variations between seasons. The operating hours were set at 24 hours per day. Using this equation for the Freeport Energy Center owned by Dow Chemical Company in Texas, for example, a cooling water makeup flowrate is estimated at 3.34 MGD for this 154.80MW power plant.

The second method to estimate the water demand for cooling was to analyze the existing power plants that are using reclaimed water for cooling purposes. From the inventory of 48 plants provided in a technical report (Vidic and Dzombak, 2007), it is estimated that an average of 0.0095 MGD of cooling water is required per MW of power generated per day. Using this ratio for the Freeport Energy Center (the same 154.80MW power plant used in the previous example), a cooling water make up is estimated at 1.47 MGD.

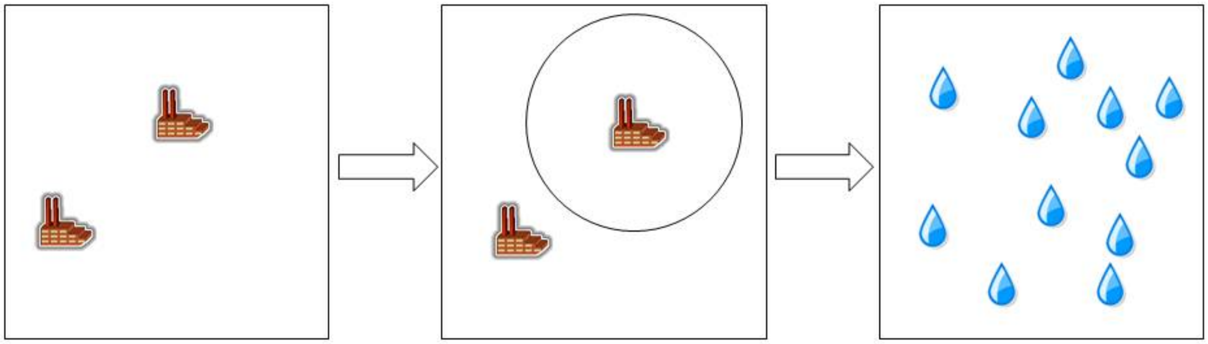
The water consumption estimated by the second method is much lower than the value derived using the first method. One possible explanation is that the second method only considers the amount of impaired water used for cooling as reported by these plants. However, not all of these 48 power plants use only reclaimed water for cooling and may add water from other sources. Therefore, the first method was selected for further analysis.

2.2.3 Geospatial Analysis

The goal of this study was to identify the total amount of secondary effluent discharged from POTWs that is available within a specific distance from each power plant. To accomplish this goal, several geoprocessing tools, such as buffer, overlay, select, and summary were used.

The geoprocessing steps are shown in Figure 2.7. Generating a buffer zone is the first operation to perform in order to create a correlation between two point attribute datasets. The buffer zone is then overlaid on the POTW layer to produce a list of POTWs contained within the buffer zone. In this way, a list of all POTWs available to meet the cooling water needs of a proposed power plant is extracted from the database.

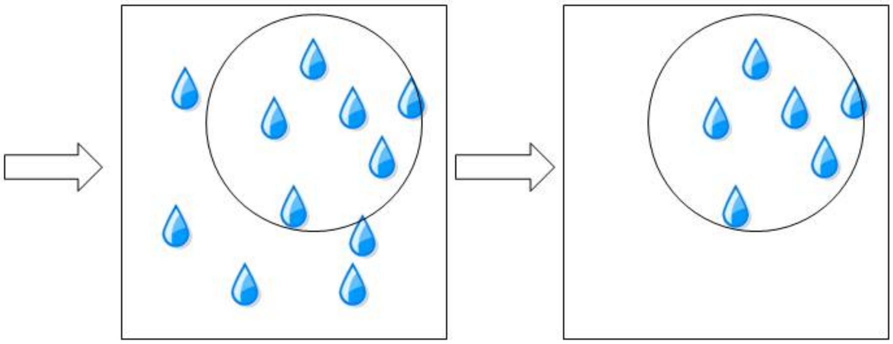
The buffer zones selected for this study had a radius of 10 and 25 miles. The reason to limit the distance from a given power plant to 10 and 25 miles is the cost of transporting the water from a POTW to a power plant. These numbers were selected arbitrarily based on the example of Redhawk Power Plant (RPP) in Arizona. The RPP is one of the power plants that uses 100% reclaimed water for cooling proposes with an average daily cooling water flowrate of 6.48 MGD. The wastewater is transported 40 miles from a wastewater treatment facility, which is located at a higher elevation than the power plant. Therefore, it is assumed that 10-25 miles would likely be a reasonable distance for transporting wastewater in the areas where other sources of the waters are not available.



1. Select a location

2. Generate a buffer zone around the selected power plant

3. Identify the POTW locations in a separate layer



4. Overlay the buffer zone from step 2 with the POTW layer in step 3

5. Select the POTWs included in the buffer zone and produce a report

Figure 2.7. Geoprocessing steps used for this study.

Selected POTWs were extracted from the POTW layer and related to the proposed power plants. The total wastewater discharged from POTWs within a specified distance from the selected power plant was calculated and compared to estimated cooling water demand of the power plant.

Power plants having sufficient wastewater to meet their cooling water demand were subjected to further analysis to determine the total number of POTWs needed to meet its cooling water needs. Publicly owned treatment works within a specified distance from the power plant were ranked in a descending manner based on their flowrate. The estimated cooling water demand was compared to the summation of wastewater flowrate from the POTW series until the estimated value was less than the summation of wastewater flowrate. The total number of POTWs required to satisfy the cooling water demand for each power plant was also reported.

2.2.4 Wastewater Availability for Future Power Plants

Table 2.5 shows the total cooling water needs for all proposed power plants in each NERC region in comparison to the total secondary wastewater available in that region. The amounts of cooling water needed for proposed power plants are highest in WECC/NWCC region, followed by FRCC and SERC regions. This trend matches the projection of energy demands for water resources by Department of Energy, which states that the main increase in energy demands will be in Southeast, Southwest, and Far West (USDOE, 2008). It is evident from the last column of Table 2.5 that the cooling water needs of the proposed power plants in most regions do not exceed 1% of the total available wastewater in that region, except for FRCC, MAPP and WECC/NWCC regions.

As mentioned earlier, there are 110 proposed power plants that were included in this survey and a large percentage of them are located in WECC, SERC, ECAR regions. The number of power plants in a given region does not accurately reflect the total cooling water needs. For example, there are only six proposed plants in the FRCC region. However, because of the 1053 MW Turkey Point Power Plant, the total daily cooling water needs in FRCC is much greater than that in ECAR, which includes 21 proposed power plants.

The average percentage of available wastewater needed for cooling is 1.10%. The real available wastewater flowrate can be higher because this survey does not include private or commercial wastewater plants. In addition, the guidelines for Water Reuse indicate that the total wastewater reuse in California and Florida only accounts for 358 MGD and 584 MGD, respectively (USEPA, 2000). This indicates that plenty of wastewater is still available for further reuse.

The key outcome of this part of the study is that the amount of wastewater available in each region can easily satisfy cooling water needs of the proposed power plants.

Table 2.5. Comparison of total cooling water required for the proposed power plants and total available wastewater from POTWs in NERC regions.

NERC Region	Total daily cooling water needs, MGD	Total daily wastewater flow rate, MGD	Percentage of available wastewater needed for cooling, %
ECAR	27.5	4873	0.56
ERCOT	15.0	1994	0.76
FRCC	42.9	1374	3.12
MAIN	1.6	3318	0.05
MAPP	25.8	1167	2.20
NPCC/NY	0.1	1112	0.01
SERC	28.2	3915	0.72
SPP	17.5	2077	0.84
WECC/CA	22.5	3636	0.62
WECC/NWCC	44.9	1910	2.35
WECC/RM	9.3	1061	0.88

Table 2.6 and Figures 2.8 and 2.9 provide the results of the analysis performed for individual power plants. GIS-based analysis provided information about the total wastewater flowrate available within a 10 and 25 mile radius around each proposed power plant.

The data in Table 2.6 show that about 81% of proposed power plants could completely meet their water needs by the POTWs within a 10 mile radius. On the same Table, it is shown that 97% of proposed power plants can satisfy their cooling water needs from POTWs within a 25 mile radius.

Figure 2.8 shows the percentage of power plants that can meet their cooling water needs from POTWs in each NERC region when considering wastewater available with a 10 mile radius. Only SPP and WECC/RM could not satisfy the needs of more than half of their proposed plants with the treated wastewater from POTWs within 10 mile radius, despite the fact that both SPP and WECC/RM have more than 1500 MGD wastewater available. Figure 2.9 shows the same analysis when considering wastewater available with a 25 mile radius. With the increase in coverage, SPP and WECC/RM could completely satisfy the water demand for their power plants with secondary effluent. This result is important because it indicates that treated municipal wastewater can be a major cooling water resource for the future power plants.

Table 2.6. Proposed power plants that have sufficient wastewater for cooling provided by POTWs within 10 and 25 mile radius

Region	Number of proposed power plants that have sufficient wastewater within 10 miles	Proposed power plants that have insufficient wastewater within 10 miles	Proposed power plants that have sufficient wastewater within 25 miles	Proposed power plants that have insufficient wastewater within 25 miles
ECAR	18	3	21	0
ERCOT	5	3	8	0
FRCC	5	1	6	0
MAIN	3	1	4	0
MAPP	10	1	10	1
NPCC/NY	4	0	4	0
SERC	18	1	19	0
SPP	1	5	6	0
WECC/CA	11	0	11	0
WECC/NWCC	13	4	15	2
WECC/RM	1	2	3	0
Average Percentage	**81%**	**19%**	**97%**	**3%**

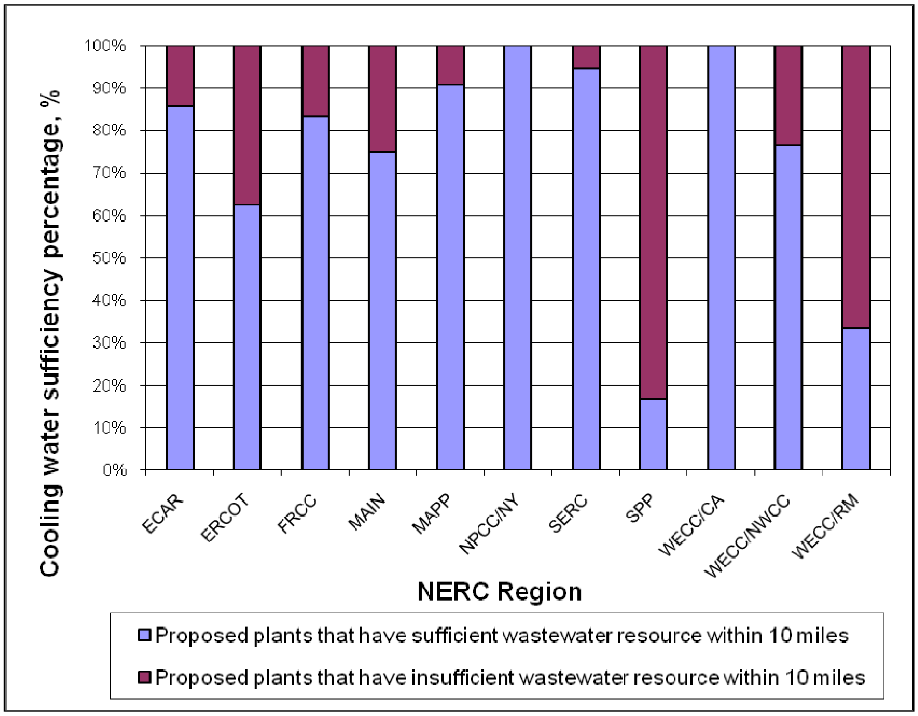


Figure 2.8. Percentage of proposed plants which have sufficient wastewater within 10 miles.

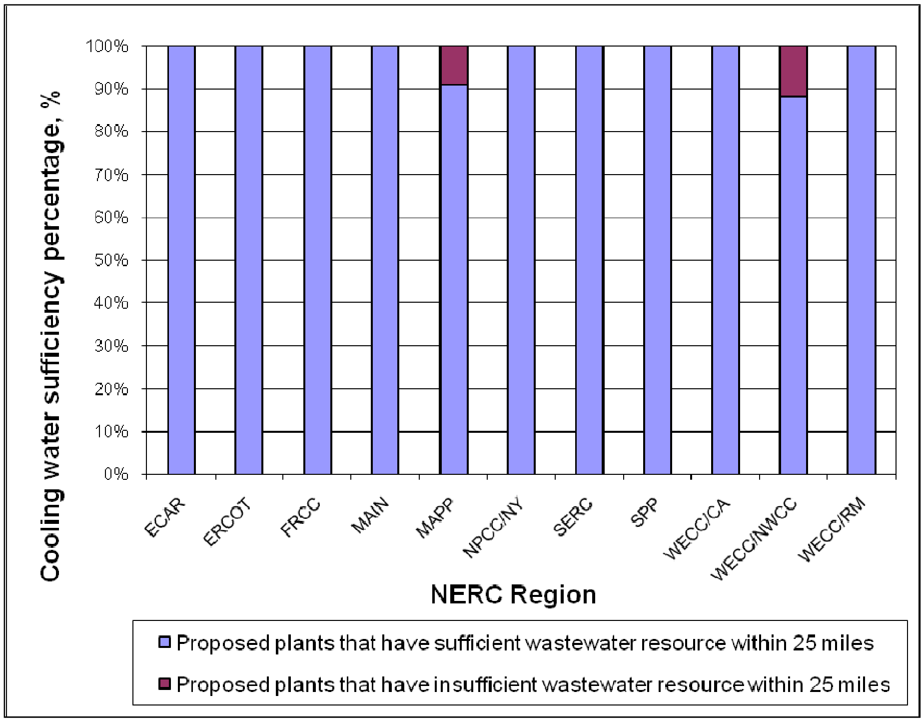


Figure 2.9. Percentage of proposed plants which have sufficient wastewater within 25 miles

Tables 2.7 and Table 2.8 provide information about the ability of proposed power plants to satisfy their cooling water needs considering POTWs in each region. For both tables, column 2 provides the total percentage of all proposed power plants in a given NERC Regions that can satisfy their cooling water needs from POTWs located within 10 and 25 mile radius, respectively. Column 3 lists the average number of POTWs located within 10 and 25 mile radius from each proposed power plant, respectively. Last column provides information about the average number of POTWs with a 10 and 25 mile radius that can satisfy cooling water needs for proposed power plants in each NERC region, respectively.

The data provided in Table 2.7 indicate that each power plant has an average of 3.48 POTWs within a 10 mile radius. However, only 1.15 POTWs are needed to satisfy cooling water needs of the proposed power plants. If the coverage is extended to 25 miles, it can be seen in Table 2.8 that the proposed power plants have an average of 18.4 POTWs within that radius. However, only 1.10 POTWs are needed to satisfy cooling water needs of the proposed power plants.

Figures 2.10 and 2.11 show that the MAIN region has the largest number of POTWs in either 10 or 25 mile radius around the power plants proposed for that region. On average, regions around the Great Lakes and the regions in the western part of the US have higher total wastewater flows available. In addition, in the western regions (e.g., WECC), only one POTW can satisfy water demand of the proposed power plants.

The fact that a fairly low number of POTWs (i.e., close to one) can meet the cooling water needs of the proposed power plants suggests that the cost of transporting wastewater can be kept at a minimum (i.e., only one or two pipes may be needed to transport the cooling water to each power plant). Therefore, using reclaimed water for cooling purposes can be both economical and reliable and can facilitate the development of coal-fired power plants in the regions where other water sources may not be readily available.

Table 2.7. Number of POTWs within 10 mile radius that can satisfy the cooling water demand of the proposed power plants.

Region	Percentage of proposed power plants that have sufficient wastewater water within 10 miles to satisfy their cooling water needs, %	Average number of POTWs within a 10 mile radius of a proposed power plant	Number of POTWs within a 10 mile radius needed to satisfy cooling water needs
ECAR	86	2.89	1.06
ERCOT	63	3.00	1.20
FRCC	83	4.60	1.40
MAIN	75	7.00	1.00
MAPP	91	3.10	1.00
NPCC/NY	100	4.00	1.00
SERC	95	2.06	1.00
SPP	17	2.00	2.00
WECC/CA	100	4.91	1.00
WECC/NWCC	76	2.85	1.00
WECC/RM	33	2.00	1.00
Average	**81**	**3.48**	**1.15**

Table 2.8. Number of POTWs within 25 mile radius that can satisfy the cooling water demand of the proposed power plants.

Region	Percentage of proposed power plants that have sufficient wastewater water within 25 miles to satisfy their cooling water needs, %	Average number of POTWs within a 25 mile radius of a proposed power plant	Number of POTWs within a 25 mile radius needed to satisfy cooling water needs
ECAR	100	20.29	1.05
ERCOT	100	9.88	1.25
FRCC	100	14.50	1.17
MAIN	100	28.50	1.00
MAPP	91	14.30	1.00
NPCC/NY	100	26.00	1.00
SERC	100	12.68	1.00
SPP	100	23.67	1.67
WECC/CA	100	20.18	1.00
WECC/NWCC	88	8.47	1.00
WECC/RM	100	24.00	1.00
Average	**97**	**18.40**	**1.10**

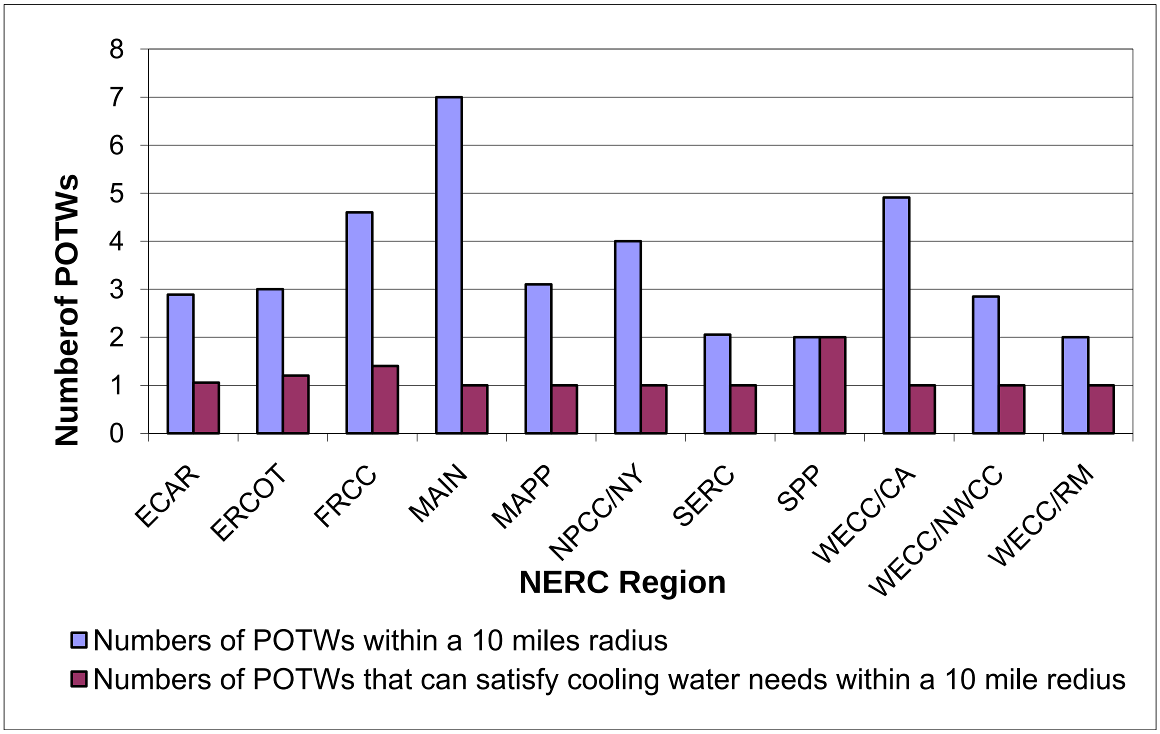


Figure 2.10. Total number of POTWs within a 10 mile radius and the number of POTWs that are needed to provide sufficient wastewater for cooling.

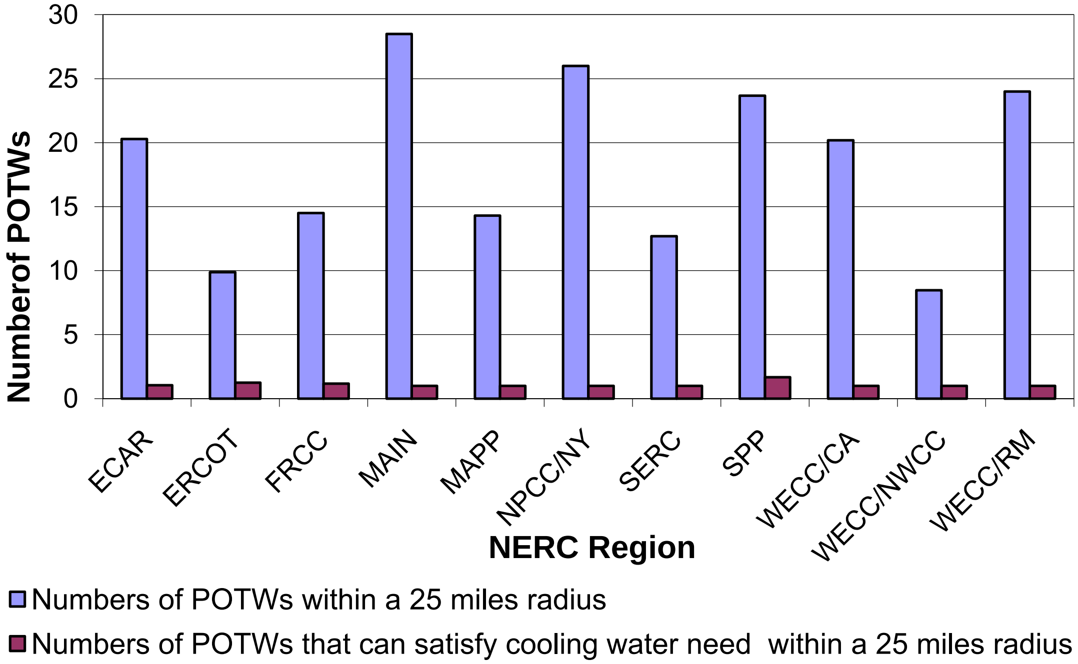


Figure 2.11. Total numbers of POTWs within a 25 mile radius and the number of POTWs that are needed to provide sufficient wastewater for cooling.

2.2.5 Wastewater Availability for Existing Power Plants

Figure 2.12 shows the availability of secondary effluent for power plants in each state. The cooling water demand to available wastewater ratio is the total estimated cooling water divided by the available wastewater flow in each state. On average, cooling water for existing power plants will require less than 50 % of available municipal wastewater from POTWs in most states. North Dakota, West Virginia, and Wyoming have the least available wastewater flow.

In Table 2.9, the average POTWs inside a 10/25 mile radius range of existing power plants is given for each state. Western states, like Arizona, New Mexico, Nevada, and Oregon, have lower number of available POTWs near the exiting power plants. On the other hand, Pennsylvania, Connecticut, Kansas, and West Virginia have the largest number of available POTWs. On average, each power plant has at least 4.9 POTWs within 10 miles and 25.3 POTWs within 25 miles.

Figure 2.13 shows the percentage of power plants that have sufficient wastewater to meet their cooling water demand. Results indicate that only 49.4% of existing power plants would have sufficient wastewater from POTWs within 10 miles. For these power plants having sufficient wastewater, only 1.14 POTWs are needed to meet their demand. If the range is extended to 25 miles, percentage of power plants having sufficient wastewater supply increases to 75.9% and an average of 1.46 POTWs are needed to meet their demand.

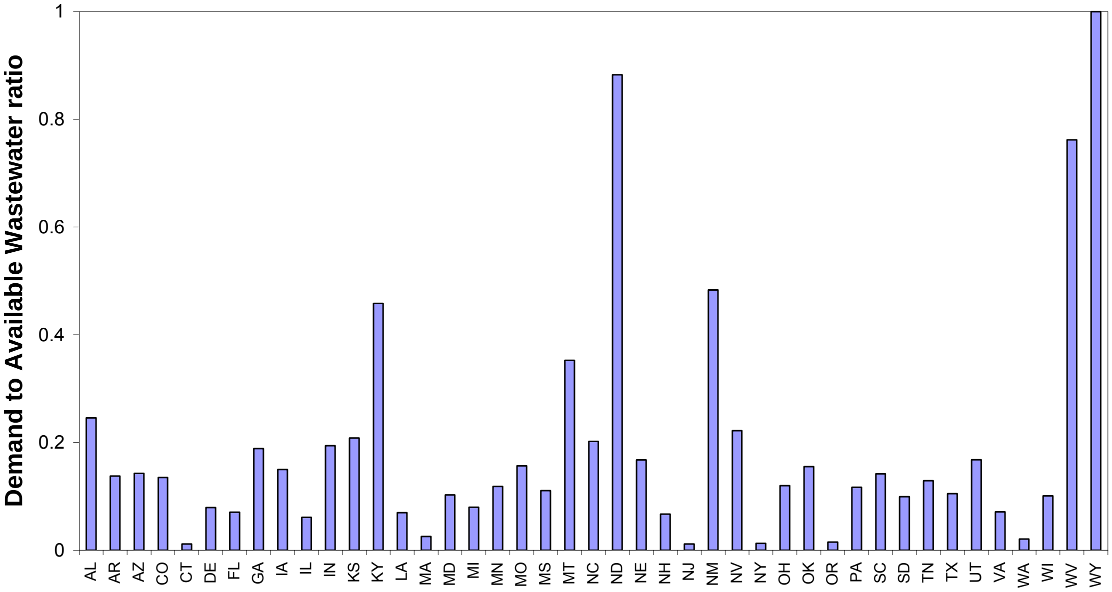


Figure 2.12. Total cooling water demand to total available secondary effluent in each state. Higher values indicate the scarcity of secondary effluent that can be used for cooling purposes.

Table 2.9 Average POTWs of existing power plants within 10 or 25 mile radius

State	Number of Power Plants	Average POTWs within 10 miles	Average POTWs within 25 miles
AL	8	2.4	12.3
AR	3	3.0	20.0
AZ	6	1.8	5.2
CO	12	4.4	16.5
CT	1	5.0	43.0
DE	2	5.5	34.5
FL	10	2.9	14.3
GA	10	2.8	14.9
IA	19	4.8	31.3
IL	22	6.3	33.1
IN	21	3.9	23.2
KS	8	9.8	43.8
KY	21	3.4	20.6
LA	4	3.8	18.3
MA	4	6.8	27.8
MD	7	4.9	27.0
MI	19	3.2	12.8
MN	11	2.4	16.1
MO	18	7.9	39.6
MS	4	3.3	13.5
MT	3	1.0	3.7
NC	15	4.4	21.9
ND	7	1.6	8.1
NE	6	4.7	25.2
NH	2	6.5	25.5
NJ	4	3.5	30.8
NM	3	0.0	1.3
NV	3	1.3	4.3
NY	12	6.4	30.0
OH	23	8.1	40.7
OK	5	2.8	18.2
OR	1	0.0	4.0
PA	23	11.7	62.5
SC	13	2.2	10.6
SD	1	2.0	11.0
TN	8	3.9	15.8
TX	17	3.0	17.0
UT	4	0.8	5.0
VA	11	3.0	14.0
WA	1	2.0	11.0
WI	15	3.9	25.4
WV	15	8.8	41.1
WY	5	1.8	4.4
Average	**-**	**4.9**	**25.3**

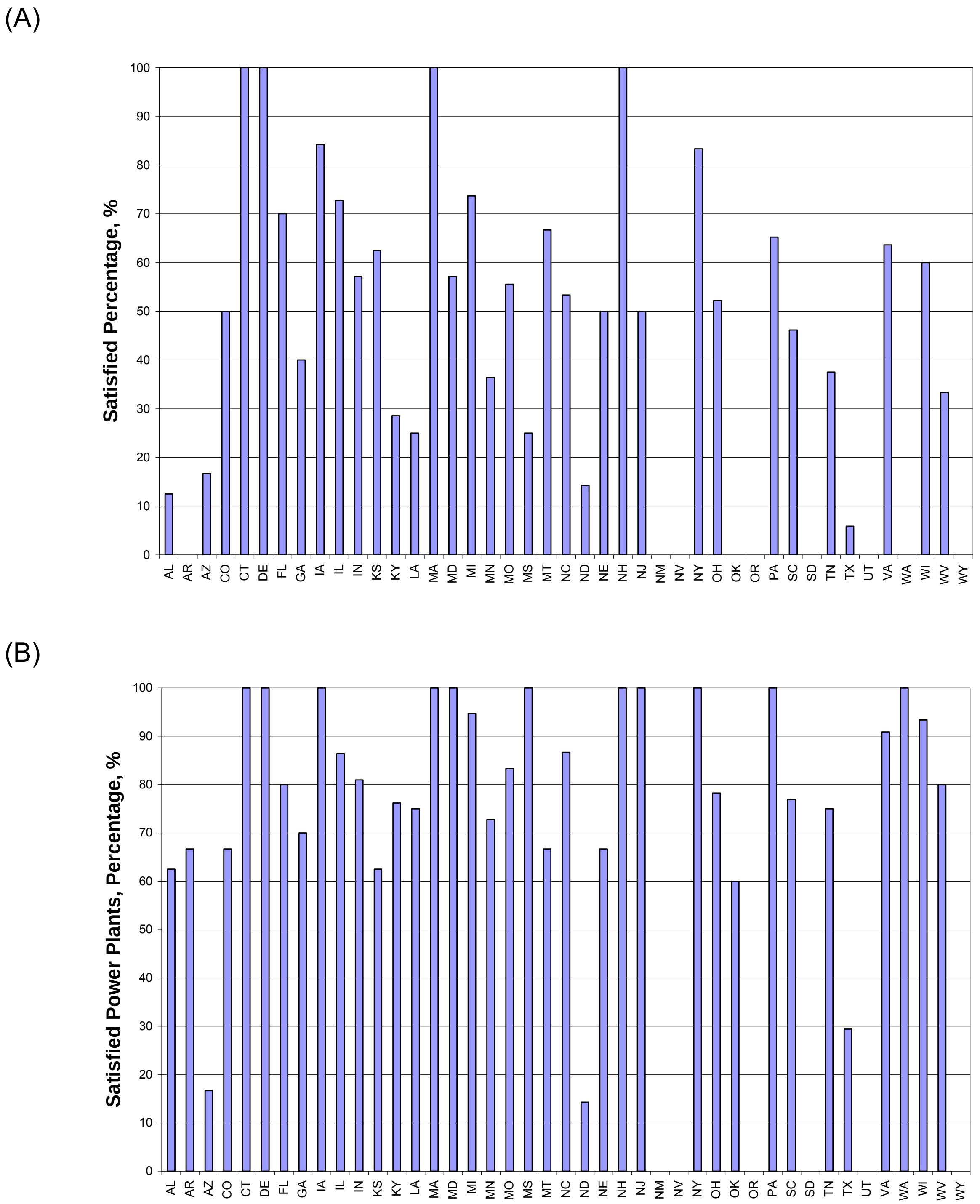


Figure 2.13 Percentage of existing power plants that have sufficient wastewater for cooling within (A) 10 mile radius and (B) 25 mile radius. Although extending the radius form 10 to 25 miles significantly improves availability of wastewater for cooling, the power plants in New Mexico, Nevada, Utah, and Wyoming still cannot meet their cooling needs.

2.2.6 Synopsis of Feasibility Analysis

Water to energy factor is introduced to estimate the cooling water demand of proposed thermoelectric power plants. This factor varies depending on the type and configuration of the power plant but the analysis performed in this study used high water to energy factors to be able to account for the worst case of cooling water demand. The total wastewater flowrate available from POTWs within a 10 or 25 mile radius from each proposed power plant was calculated and compared to the estimated cooling water demand.

Limited freshwater sources have becoming more of a public concern and the shortage of freshwater supply will inevitably impact the power industry. Wastewater availability analysis with proposed power plants demonstrated the real possibility of employing impaired water for cooling systems both in terms of quantity and proximity. Considering POTWs within 25 miles, 97 percent of the proposed power plants can meet their cooling needs by utilizing secondary treated wastewater from POTWs. Results of geospatial analysis suggest that one fairly large POTW can fulfill most of the cooling water needs for majority of the 110 proposed power plants. This implies that the cost of transporting wastewater can be kept reasonably low (i.e., only one or two pipes may be needed to transport the cooling water to the power plant).

Thermoelectric power plants are categorized as major freshwater withdrawal and consumption sources. Analysis of existing coal fired power plants revealed that the secondary treated wastewater from POTWs within 25 miles can satisfy more than 75% of their cooling water demand.

This analysis showed that using reclaimed water for cooling purposes can be both economical and reliable and can facilitate the development of coal-fired power plants in the regions where other sources are not readily available.

2.3 General Water Quality and Availability of Abandoned Mine Drainage

Acid mine drainage refers to the discharge of acidic water from an abandoned coal mine. Because of the oxidized iron precipitation, streams receiving AMD will have different color sediments at the bottom or on the riverside. The acidic discharge may also contain heavy metals, such as copper, lead, mercury, which will endanger the aquatic and botanic life.

The formation of AMD is the result of reactions involving pyrite, FeS_2. Once FeS_2 is exposed and reacts with air and water, sulfuric acid and dissolved iron are formed according to the following equations (Stumm and Morgan, 1996):

$$FeS_2 + \frac{7}{2}O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4{}^{2-} + 2H^+ \qquad (1)$$

$$Fe^{2+} + \frac{1}{4}O_2 + H^+ \rightarrow Fe^{3+} + \frac{1}{2}H_2O \qquad (2)$$

$$FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4{}^{2-} + 16H^+ \qquad (3)$$

$$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3 + 3H^+ \qquad (4)$$

Pyrite can be oxidized by oxygen and ferric iron, Fe^{2+}, as shown by Equation (1) and (3). The produced ferrous iron from Eq. (1) can then be oxidized by oxygen to form ferric iron, as seen in Eq. (2), which produces more ferrous iron (Eq. (3)) to keep reactions (2) and (3) active. Ferric iron can also form amorphous precipitate, hydrous ferric oxide (Eq. (4)). Those equations indicate that oxidation of pyrite contributes to the increase of acidity and that the oxygen level plays a key role in the production of AMD. Studies have shown that the production of AMD can be limited by controlling the oxygen level in water or coal system (Watzlaf, 1992). Recent studies have shown that the better quality of water was observed from flooded mines than that from partially flooded or unflooded mines (Lambert et al., 2004).

AMD has a wide range of chemical characteristics in North America and might even have different water characteristics among mines located at identical geographic locations. Typically, AMD contains elevated concentrations of sulfate, iron, manganese, aluminum, and several common elements, such as calcium, sodium, potassium, and magnesium (PADEP, 1998). Different composition of these elements leads to different pH values, ranging from acidic to alkaline. The range of pH is commonly within either 3 to 4.5 or 6 to 7; however, intermediate values or extreme values might occur as well. Abandoned coal mines could reach steady-state conditions approximately 25-30 years after the mine pool flooded (Lambert et al., 2004).

The most serious problems with acid mine drainage are confined to Western Maryland, Northern West Virginia, Pennsylvania, Western Kentucky, and along the Illinois-Indiana border (USEPA, 1995). Table 2.10 shows the concentrations of constituents in the coal mine drainage for the U.S., Illinois, Kentucky, Maryland, and West Virginia. The concentrations of the major contaminants in the U.S. were compiled by Wildeman et al. (1993). The values given in Table 2.10 are 10 and 90 percentage concentration of AMD from 23 coal mines in the U.S. The data shown for Illinois were the median of 110 coal disposal sites in Southern Illinois, collected by Proudan et al. (1982). The regional concentration range in Kentucky was estimated by Caruccio et al. (1977). The example in Maryland was from Frazee Mine (Leonardo, 1999), which is the underground coal mine that was abandoned since the 1960's. The example in West Virginia was a bond-forfeited coal mine site (Upper Freeport seam) located in north central West Virginia and was collected in an underground pool and pumped to a treatment channel on the surface (Xinchao et al., 2005).

Table 2.10 also shows that the AMDs are quite similar among these states. The pH values are about 3 and the concentration of sulfate reaches 1000 mg/L in all states. The iron concentration among all regions compares well with the values for the entire U.S. Most metals are within the values for the entire U.S. except for the concentrations of Zn and Mn in West Virginia. Factors that may influence the concentration of specific constituents include temperature, precipitation, hydraulic head, conductivity, fractures, floor leakages, etc. (Stumm and Morgan, 1996).

Pennsylvania has abundant coal resources that have been mined for a very long time. Hence, there are plenty of AMD sources in PA. Studies of 136 mine discharges in the syncline were done in 1974-1975. A reevaluation of discharges in 21 out of the 136 mines was done in 1998-2000 (Lambert et al., 2004). The results show that the AMD characteristics changed with time as the hydraulic condition changed (McDonough et al., 2005).

Table 2.11 shows the concentrations of constitutes from two regularly sampled mines located in Clarion County, Pennsylvania (PADEP, 1998).

Table 2.10. Water Quality of mine drainage in North America

Substance	U.S. (1)	Illinois (2)	Kentucky (3)	Maryland (4)	West Virginia (5)
pH	3.2-7.9	3	1.8-3.5	3.6–6.0	2.6±0.1
Acidity $CaCO_3$ (mg/L)	-	-	-	90-438	-
SO4- (mg/L)	-	1300	500-12000	620-1600	1527±12
Ca (mg/L)	-	-	-	183-489	191±10
Mg (mg/L)	-	-	-	17-48	50.5±3.9
Fe (mg/L)	0.6-220	57	57-500	28-92	162±23
Mn (mg/L)	0.3-12	6.4	-	2-5.5	203±0.21
Al (mg/L)	-	37	-	4.0-28	80.8±7.4
Cu (mg/L)	0.01-0.17	-	-	ND-0.08	0.08±0.02
Ni(mg/L)	-	-	-	0.57-1	1.01±0.15
Zn (mg/L)	0.03-2.2	-	-	0.5-3	2.72±0.34
Cd (mg/L)	0.01-0.10	-	-	-	-
Pb (mg/L)	0.01-0.40	-	-	-	-
As (mg/L)	0.002-0.20	-	-	-	-

Note: ND = non-detectable,

Reference: (1) Wildeman et al, 1993 (2)Prodan et al., 1982 (3) Caruccio et al., 1977 (4) Leonardo, 1999 (5) Xinchao et al., 2005.

The number of unreclaimed, abandoned, hardrock mines in the US is estimated at 550,000 to 560,000 (Aston, 2001). West Virginia, Pennsylvania, and Kentucky have long history of mining and a large number of abandoned mine sites. With more than 250,000 acres of abandoned mine lands, Pennsylvania has the highest number of abandoned mines (PADEP, 1997). Studies have also revealed that Pennsylvania and West Virginia have potentially 250 billion gallons of water stored in these abandoned mine sites (Veil, 2003).

Table 2.11. Water quality of mine drainage in Pennsylvania

Mine 1. Clarion County, C & K Mines 18, 19, and 20 (lat 41°04'15" N, long 79°26'45" W)										
Site name	**Depth, meters**	**Conductance, μS/cm**	**pH**	**Acidity, $CaCO_3$**	**Alkalin-ity, $CaCO_3$**	**SO_4**	**Ca**	**Mg**	**Fe**	**Mn**
LMS S2-5	1.5	4,370	7.0	0	750	2,300	560	210	0.04	6.60
LMS S1-15	4.6	3,550	6.9	0	600	1,600	610	220	1.80	19.00
LMS S2-15	4.6	3,890	6.9	0	730	1,900	650	230	5.70	7.50
WMS N2-1	17.4	2,900	6.1	64	120	2,200	320	240	30.00	59.00
WMS S4-1	20.1	2,310	6.3	30	360	1,400	410	180	0.70	16.00
WMS S1-1	28.9	2,330	6.7	0	500	1,300	380	130	0.76	5.10
Mine 2. Clarion County, C & K Mine #69 (lat 41°09'15" N, long 79°29'30" W))										
DMS 16	0	3,280	5.2	22	56	2,352	311	288	18.8	22.80
WMS 15B	16.3	5,030	2.6	1,660	0	3,457	331	287	375.0	36.10
WMB 15A	24.8	6,040	2.5	2,680	0	4,404	279	234	683.0	41.10
WUB 14A	33.2	2,960	5.4	122	54	2,251	325	229	62.8	24.10
WUB 14	33.3	3,030	5.2	136	33	2,049	308	215	63.4	26.60
WMB 15	36.4	4,840	3.4	1,604	0	3,675	353	270	477.0	48.30

The three-letter prefix of sample site name indicates sample type: W=well, L=lysimeter, M=mined, U=unmined, S=spoil, B= bedrock.

Feasibility analysis of using acid mine drainage for cooling needs at a specific site in Pennsylvania has been conducted by Donovan et al. (2004). However, detail analysis of acid mine drainage availability on a larger scale cannot be conducted due to the lack of precise geographic locations. In addition, unlike municipal wastewater that is available throughout the country, acid mine drainage is available in just a few states and at specific location so that its impact in meeting the cooling water needs of thermoelectric power plants is limited.

2.4 General Water Quality and Availability of Ash Pond Water

As coal is combusted, ash is generated and it either falls to the bottom of the boiler (bottom ash) or it travels together with a flue gas (fly ash). Bottom ash consists primarily of oxides of silica, aluminum, iron, magnesium, and calcium that represent over 95% of its weight. Bottom ash contains lower concentrations of trace elements, such as arsenic, beryllium, copper and vanadium, than fly ash (MDEQ, 2004). Exact chemical properties of fly ash are influenced, to a great extent, by those of the coal burned and the techniques used for handling and storage.

Recent study by Nevada Division of Environmental protection showed that the total flow of ash to the ponds from Reid Gardner Station power plant (650MW), including fly ash, bottom ash, and other coal combustion by products, was 286,000 gpd (NVDEP, 2005). It is very common that the cooling tower blowdown is used as a water supply for the scrubbers and bottom ash transport system (EPRI, 1980). When an ash settling pond is full, it is temporarily removed from service and allowed to dry so that the retained materials can be removed to the disposal site.

Fly ash transport waters are generated when the ash collected from the stack gases is mixed with water to form slurry, which is then pumped to ash settling ponds. Liquid used to transport fly ash may be either fresh water, diverted waste streams from other processes, or re-circulated slurry water from fly ash settling ponds. Table 2.12 summarizes the result of several studies investigating the characteristics of water in fly ash and bottom ash settling ponds.

TVA power plant uses a once-through ash pond where the fly ash is pumped to settling ponds to be removed by gravity settling so that the ash pond effluent can be treated and released to the environment. Colstrip power plant in Montana burns sub-bituminous coal and uses several ponds for disposal of fly ash and bottom ash. Water in these units comes from the ash transport water and from the wet venturi scrubbers that are used for particulate and sulfur dioxide control. The last column in Table 2.12 provides the average water quality from several bottom ash ponds compiled by Lagnese (1991).

Table 2.13 compares the characteristics of the fly ash and bottom ash pond waters to the quality of river water (Bohac, 1990). The bottom ash water quality is poorer than the fly ash pond water but these results indicate that the quality of the ash pond waters may not be that different from the quality of the river water, which is commonly used for cooling in coal-fired power plants. Such finding suggests that the ash pond water may serve the same purpose without much difficulty.

Table 2.12. Chemical characteristics of fly ash pond and bottom ash pond at different plants.

Parameter	TVA Fly Ash Pond (1)	TVA Bottom Ash Pond (1)	Colstrip Bottom Ash Pond 1&2 (2)	Colstrip Bottom Ash Pond 3&4 (2)	Bottom Ash Ponds (3)
Flow (GPM)	6212.5	16000	0	0	-
Total alkalinity ($CaCO_3$)	-	85	125	268	-
Conductivity (μmhos/cm)	810	322	5166	4119	-
Total Hardness ($CaCO_3$)	261	140	3768	985	-
pH	4.4	7.2	9.5	10	6.71
Dissolved Solid	508	170	5924	3089	209
Suspended solid	62.5	60	-	-	2.4
Al	7.19	3.49	0.27	0.42	<0.15
Ammonia as N	0.43	0.12	7.2	0.34	0.06
Ar	0.01	0.006	-	-	0.006
B	-	0	21.7	2.5	<0.05
Ba	0.25	0.12	-	-	0.063
Be	0.011	<0.01	-	-	-
Cd	0.037	0.0011	<0.002	<0.001	<0.0005
Ca	136	40	550	354	46
Cl	7.12	8.38	1.13	0.51	20
Cr	0.037	0.009	-	-	0.04
Cu	0.31	0.065	0.05	0.01	0.008
Cyanide	<0.01	<0.01	-	-	-
Fe	1.44	5.29	0.03	0.03	2.38
Pb	0.058	0.016	0.03	<0.01	<0.002
Mg	13.99	5.85	518	41	9.8
Mn	0.48	0.16	1.64	0.02	0.37
Hg	<0.0003	<0.0007	<0.001	<0.001	0.002
Ni	1.1	<0.059	0.08	0.01	<0.011
Total phosphate as P	0.021	0.081	0.04	0.04	-
Se	0.0019	0.002	0.014	0.01	<0.003
Silica	12.57	7.4	-	-	3.6
Ag	<0.01	<0.01	-	-	<0.0005
Sulfate	357.6	48.75	3790	1893	103
Zn	1.51	0.09	0.05	0.01	<0.001

Unit for all concentrations are in mg/L unless otherwise indicated.
TVA: Tennessee Valley Authority
Reference (1) EPRI, (1980), (2) MDEQ, 2004, (3) Lagnese, 1991.

Table 2.13. Comparison of fly and bottom ash pond water in TVA plant to river water.

	River water	Fly ash supernatant	Bottom ash supernatant*
TDS mg/L			72
SS mg/L			160
Al µg/L	110	<50	2200/<50
As µg/L		130	28/22
Ba µg/L		410	160/100
Cd µg/L		1.1	0.3/<0.1
Ca mg/L	25	38	15/14
Cl mg/L	4	4.5	3.5
Cr µg/L		10	3/<1
Cu µg/L	<10	<10	<10
B µg/L		170	<50
Fe µg/L	340	2	2500/60
Pb µg/L		<1	5/1
Mg mg/L	7.9	7.8	3.1/2.9
Mn µg/L	84	32	61/22
Na mg/L	5	5.6	3.2/3.1
Li µg/L		<10	<10
Se µg/L		14	<1
Silica µg/L			2200/1700
Sulfate mg/L	26	62	22/20
Zn µg/L	<10	10	30/30

* Total Concentration/Dissolved Concentration

Ash pond water is generally stored near the coal-fired power plants, which means that it is readily available for reuse in cooling systems. Newerow and Agardy showed the average volume of bottom ash pond overflow is 3,881 GPD/MW, while the average makeup water need in a recirculating cooling system is about 14,400 GPD/MW. (Newerow and Agardy, 1998; NETL, 2005). These results indicate that a small portion (25%) of freshwater demand for cooling can be easily replaced by ash pond water.

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3.0 Review of Regulations Governing the Use of Reclaimed Water for Cooling Purposes

Review of regulations will focus on four topics: (1) the basis of using reclaimed water in a re-circulating cooling system, (2) the discharge of utilized impaired water, (3) the air emission from cooling tower using reclaimed waters, and (4) transport of reclaimed water across regional boundaries.

All four topics will be evaluated on both federal and state level and, in addition to official regulatory requirements, and this chapter also offers guidelines suggested by federal and state environmental control agencies.

3.1 Federal Regulations

The operation of a water reuse program must be within the framework of federal and state regulations and these must be addressed in the earliest planning stages. Currently, there are no federal regulations directly related to the practices of water reuse in the U.S., including no specific federal regulations governing the reuse of reclaimed water as power plant cooling water. Many states, however, do have regulations pertaining to water reuse. At the federal level, the U.S. Environmental Protection Agency published “Guidelines for Water Reuse” for the benefit of utilities and regulatory agencies (USEPA, 2004). “Guidelines for Water Reuse” provides an overview of (1) types of reuse applications, (2) related technical issues, (3) water-reuse regulations/guidelines established by each state, (4) legal and institutional issues, (5) funding water reuse systems, (6) public involvement programs, and (7) water reuse in other countries. For those states having no water reuse regulations/guidelines, the USEPA guideline document provides suggestions about treatment, reclaimed water quality, reclaimed water monitoring, and minimal distance between wastewater source and public area.

3.1.1 Water Reuse Regulations

Currently, there are no federal regulations governing water reuse in cooling systems. “Guidelines for Water Reuse” suggests treatment and desired reclaimed water quality for water reuse in industrial cooling systems, including once-through cooling and re-circulating cooling towers. The reclaimed water quality for industrial reuse suggested by the USEPA is summarized in Table 3.1. Since the general focus of reclaimed water use is on municipal wastewater, suggested standards for cooling towers are correlated to the municipal wastewater discharge standards. Any effluent leaving the wastewater treatment plant is regulated by technology-based limits on BOD_5, TSS, and pH.

Federal regulations do not govern how the power plant uses reclaimed water inside their facility. Therefore, the water quality requirements are established by the local government based on the operational requirements. For example, the suggested guidelines for fecal coliform and chlorine residual are focused on bacteria levels in the drift, which may travel through the air and cause increased health risk.

Table 3.1. Summary of reclaimed water quality when used in cooling water system (USEPA, 2004)

System	Treatment	pH	BOD_5	TSS	Fecal Coliform	Cl_2 Residue
Once-through cooling	Secondary, disinfection	6-9 (monitored weekly)	30 mg/l (monitored weekly)	30 mg/l (monitored daily)	•200/100 mL (weekly median, monitored daily) •800/100 mL (max)	1 mg/l (minimum, monitored continuous)
Re-circulating cooling towers	Secondary, disinfection (chemical coagulation and filtration may be needed)	6-9 (variable depends on recirculation ratio)				

3.1.2 Water Discharge Regulations

Clean Water Act governs all discharges of pollutants into the surface water. Cooling tower is regulated and referred to as a point source. While there are no federal regulations focused specifically on the effluent discharge of reclaimed water from industrial cooling systems, Section 402 of the Clean Water Act requires that all point source discharges of pollutants to surface waters must be authorized by National Pollutant Discharge Elimination System (NPDES) discharge permits. Limits in NPDES permits can be technology-based or water-quality-related. Specific Clean Water Act regulations in the Code of Federal Regulations (40CFR423) provide effluent standards for steam electric power generating plant discharges, categorized as:

1. The best practicable control technology currently available (BPT);
2. The best available technology economically achievable (BAT);
3. New source performance standards (NSPS);
4. Pretreatment standards for existing sources (PSES); and
5. Pretreatment standards for new sources (PSNS).

As noted by the California Energy Commission (2003), the only aspect of BPT that applies to any current or future power plant discharges is pH limits of 6.0~9.0. Other BPT controls are superseded by BAT. A summary of effluent standards from 40CFR423 is shown in Table 3.2.

Table 3.2. Summary of 40CFR423 related to BPT, BAT, NSPS, PSNS, and PSES in once through cooling water and cooling tower blowdown.

			pH	**Free available Chlorine**		**Total Chromium**		**Total Zinc**	
				One day maximum (mg/l)	Average (30 consecutive days) (mg/l)	One day maximum (mg/l)	Average (30 consecutive days) (mg/l)	One day maximum (mg/l)	Average (30 consecutive days) (mg/l)
Once through cooling water	BPT			0.5	0.2				
	BAT/NSPS	≥25MW		0.2					
		<25MW		0.5	0.2				
Cooling tower blowdown	BPT		6~9	0.5	0.2				
	BAT, NSPS		6~9	0.5	0.2	0.2	0.2	1.0	1.0
	PSNS					0.2		1.0	
	PSES					0.2		1.0	

Notes: 1) For BAT, NSPS, PSNS, and PSES, the 126 priority pollutants (except chromium and zinc) contained in chemicals added for cooling tower maintenance should be in non-detectable amounts.
2) The 126 priority pollutants are listed in Appendix A to 40CFR423

Free chlorine is a general biocide for controlling the bacteria population in the cooling tower system. Inactivation and suppression of pathogenic microorganisms, e.g., Legionella, requires a chlorine level above 3 mg/L (Skaliy et al., 1980). Therefore, the suggested chlorine residual in cooling tower system has a minimum at 1 mg/L. However, elevated free chlorine concentrations contributes to the production of trihalomethanes and other byproducts that are carcinogenic or mutagenic (Morris et al., 1993).

Other commonly regulated additives are Chromium and Zinc, which are usually used as corrosion inhibitors. Hexavalent chromium-based compounds are among the most available and efficient corrosion inhibitors for cooling towers, but have been categorized as suspected carcinogens with high toxicity (IARC, 1997). Traces of zinc are not directly hazardous to human body. However, elevated concentration of Zinc will cause adverse impact on the aquatic life and cause a wide range of problems in mammals, including cardiovascular, developmental, immunological, liver and kidney problems, neurological, hematological, pancreatic, and reproductive issues (Eisler, 1993; Domingo, 1994).

NSPS are federal emission standards for point sources which cause or contribute significantly to air pollution, such as cooling towers. Any sources which have been constructed or modified since the proposal of the standards are regulated under this section. This act ensures the use of best air pollution control technologies in the future.

In 40 CFR 403, government proposed PSES and PSNS in order to establish responsibilities of federal, state, local government, industry, and public for the pollutant discharge. These standards regulate all non-domestic sources which introduce pollutants into POTWs and are enforced through a pretreatment program established by individual plants.

Another type of NPDES permit is water quality-based limits that consider the water quality of receiving water body and possible dilution factor of the water body. Limits may be set on trace metals, nutrients, organic compounds, BOD_5, etc. based on state or local regulations.

3.1.3 Air Emission Regulations

Evaporative condensation of water occurs when the warm water gets in contact with air in wet re-circulating cooling towers. Millions of small droplets, also called "drift", are exhausted with air into the atmosphere from these towers. The "Guidelines for Water Reuse" recommended that when reclaimed water is used in industrial cooling, windblown spray should not reach areas accessible to workers or the public. The drift usually contains highly concentrated elements, including metals, nutrients, and microorganisms, which may increase the health risk for residents in the vicinity of the power plant. Cooling tower drift can contain all the chemicals present in the recirculating cooling water (USEPA, 2004).

The federal government does not offer specific limitations on air emission from industrial cooling systems using reclaimed water for cooling purposes. Nonetheless, there are regulations related to air emissions from cooling towers. According to USEPA (2005), cooling towers are categorized as potential point emission sources of volatile organic compounds (VOC), PM_{10}, $PM_{2.5}$, and NH_3. USEPA (1995) provides a compilation of emission factors for these air pollutants for estimation purposes, but the values listed are neither EPA-recommended emission limits (e.g., best available control technology or BACT, or lowest achievable emission rate or LAER) nor standards (e.g., National Emission Standard for Hazardous Air Pollutants or NESHAP, or New Source Performance Standards or NSPS). Detailed discussion of particulate emission calculations pertinent to cooling towers in the United States is given in Appendix B.

As mentioned before, chromium was commonly used as corrosion inhibitor in re-circulating cooling systems but has been banned for its toxicity to humans. The use of chromium in cooling water is regulated in 40CFR63.402 (National Emission Standards for Hazardous Air Pollutants for Industrial Process Towers): "No owner or operator of an IPCT (industrial process cooling tower) shall use chromium-based water treatment chemicals in any affected IPCT."

3.1.3.1 Particulate Emission Regulations Pertinent to Cooling Towers in the United States

Particulate matter emissions from cooling towers are a concern primarily because they are aerosols that may be easily inhaled and deposited into the respiratory system. Drift eliminators are able to reduce the amount of cooling water lost as a drift to a range between 0.0005-0.002% of the total recirculation flow rate. However, most of the loss is as PM_{10} which is the particle size of highest concern. Regulations pertaining to cooling towers are similar to those in place for vehicles and power plants and therefore are set in terms of particle mass per airflow volume ($\mu g/m^3$). National ambient air quality standards (NAAQS) set particulate matter criterion, whereas each state regulates the amount of water used for cooling purposes. If the total dissolved solids in the cooling water are established, total particulate emissions can be estimated using the drift loss. If there are no data for total dissolved solids in the cooling water, particulate emissions can be estimated using PM_{10} emission factor (EPA,1995) resulting in total drift to PM_{10} ration of 89.5:1.

3.1.3.2 National Ambient Air Quality Standards (NAAQS)

Particulate matter regulations were issued together with six criteria pollutants in 1971 and then revised in 1997 (USEPA, 2009). In 1990, the Clean Air Act required EPA to set up standards for all pollutants that are considered harmful to public health and the environment, which are known as National Ambient Air Quality Standards (40 CFR part 50). Both primary and secondary standards are introduced to limit the potential adverse impacts. Primary standards are mainly concerned with protecting public health and secondary standards are about protecting public welfare, including protection against decreased visibility, damage to animals, crops, vegetation, and buildings. The specific standard for total particulate matter was introduced in 1987 by NAAQS, with maximum concentration in a 24-hour period of 150 $\mu g/m^3$ and annual average of 50 $\mu g/m^3$. This standard was later referred as PM_{10}. In 1997, EPA established new NAAQS for PM, which included standards for particles smaller than 2.5 μm ($PM_{2.5}$) and smaller than 10 μm (PM_{10}) (EPA, 1997). The PM criteria are listed in Table 3.3.

Table 3.3. Particulate Matter Criteria issued in NAAQS

Pollutant	Primary Standards.	Averaging Times	Secondary Standards.
Particulate Matter (PM_{10})	Revoked*	Annual (Arith. Mean)	
	150 µg/m^3	24-hour	
Particulate Matter ($PM_{2.5}$)	15.0 µg/m^3	Annual (Arith. Mean)	Same as Primary
	35 µg/m^3	24-hour	

Note: *Due to a lack of evidence linking health problems to long-term exposure to coarse particle pollution, the agency revoked the annual PM_{10} standard in 2006 (effective December 17, 2006)
Source: National Ambient Air Quality Standards, USEPA, 2006

3.1.4 Interbasin Water Transfer Regulations

The use of treated wastewater or other impaired waters in power plants may involve the transfer of water/wastewater from one water drainage basin to another, and perhaps even across state boundaries. Such water/wastewater transfer could raise public concern, especially in regions with limited water resources where the competition for those resources is fierce. Both federal and state laws and regulations pertaining to interbasin water transfer were evaluated in this study. Regulations that govern interbasin water transfers vary from region to region, and interstate or intrastate water transfer is mainly governed by individual states. This stems from having no federal interbasin transfer regulations and the fact that many large watersheds have their own regulatory commissions. These commissions often govern water rights and have very prohibitive transfer policies between basins, such as in the Great Lakes and Colorado River regions. Previous cases show that most transfer events were evaluated on a case-by-case basis and indicate few prohibitions against water transfer.

Water rights are legal rights to possess water, use it, dispose of it and prohibit anyone else from interfering with its use for an indefinite period of time (Goldfarb, 1988). In the US, the concept of water rights is divided into two different systems. States east of the Mississippi River, except Mississippi, Arkansas, Iowa, and Missouri, mostly define water rights as “riparian rights” (Getches, 1997). Riparian rights are the rights held by the owners of the land along the banks of bodies of water. The western US states rely on the appropriation rules, which can be described as “the first in time, the first in right” (Getches, 1997). Under this approach, a person who uses water in a beneficial and legal way can continue to do so as long as water is available. The appropriation system under the law that governs interbasin water transfer in the western US creates no fundamental barrier to taking water from one watershed to another and that water is not legally tied to the land or to the watershed. In contrast, the riparian system that prevails in the eastern US discourages interbasin transfers of water by arbitrary limitation on water users (Goldfarb, 1988).

Existing federal laws are not directly governing interbasin water transfer, but some environmental laws can influence interbasin water transfer. Table 3.4 shows that several laws, including the National Environmental Policy Act (NEPA), the Clean Water Act (CWA), and the Endangered Species Act (ESA), indirectly relate to interbasin water transfer. The major concern is mainly about the potential impacts on environment caused by transporting water from one basin to another. As stated in the CWA, interbasin transfers are usually governed by states except in special cases such as Great Lakes and federally authorized reclamation projects which involve interstate impacts (Craig, 2007).

Table 3.4. Federal environmental laws that indirectly affect interbasin water transfer.

Law	Description
The National Environmental Policy Act (NEPA)	Federal agencies are required to assess potential environmental impacts of proposed “major federal actions”. The agencies must hold hearings that allow public participation and then prepare an “environmental impact statement” document.
The Clean Water Act (CWA)	Although the Clean Water Act does not regulate interbasin water transfer, the depletion of a stream used by the transfer of water to other basin can adversely impact water quality. Section 404 of the CWA requires the U.S. Army Corps of Engineers to review the impacts and require mitigation for the impacts of a water development on the basin of origin.
The Endangered Species Act (ESA)	The ESA prohibits any action that would jeopardize the existence of an endangered species.

3.2 State Regulations

As summarized in "Guidelines of Water Reuse" (USEPA, 2004), most states have established regulations and/or guidelines on water reuse for different purposes. Among those states, California, Florida, Hawaii, New Jersey, North Carolina, Oregon, Texas, Utah, and Washington have regulations and guidelines for industrial reuse of reclaimed water. The regulations/guidelines for reclaimed water use in industrial cooling water systems in these ten states are reviewed.

Although Arizona, Maryland, and Wyoming do not have regulations or guidelines related to reclaimed water reuse as industrial cooling water, they were chosen to illustrate the applicability of their general regulations/guidelines pertaining to reclaimed water reuse. In addition, all these states are selected for further analysis because they either have potential for severe water shortage or have documented experience with water reuse for cooling in thermoelectric power plants.

Table 3.5 summarizes the states having regulations and guidelines for different water reuse applications. In section 3.2.1, pertinent regulations developed by each state to govern water reuse and water discharge are outlined in more details.

Another critical concern with water reuse is the exposure of public or workers to reclaimed waters. When public or workers have the chance to contact the reclaimed water, higher reclaimed water quality may be required. Drift/mist/aerosol created from cooling towers is the key concern in air emission regulations because of the potential for human exposure. Pertinent regulations are also reviewed in Section 3.2.1.

Interbasin water transfer regulations developed by the states are also relevant to the use of impaired waters in cooling water systems of power plants. State interbasin water transfer regulations are described in Section 3.2.2.

3.2.1 State Regulations on Water Reuse

Table 3.6 summarizes specific state rules and regulations governing water reuse, water discharge and air emissions in 12 states selected for further evaluations. Specific guidelines and regulations developed by these states are reviewed in the rest of the Section 3.2.1.

Table 3.5. Summary of water reuse regulations and guidelines by states*

State	Regulations	Guidelines	No regulation/Guideline	Unrestricted Urban Reuse	Restricted Urban Reuse	Agricultural Reuse Food Crops	Agricultural Reuse Non-Food Crops	Unrestricted Recreational Reuse	Restricted Recreational Reuse	Environmental Reuse	Industrial Reuse	Groundwater Recharge	Indirect Potable Reuse
Alabama		●			●		●						
Alaska	●						●						
Arizona	●			●	●	●	●		●				
Arkansas		●		●	●	●	●						
California (3)	●			●	●	●	●	●	●		●	●	●
Colorado	●			●	●	●	●	●	●				
Connecticut			●										
Delaware	●			●	●		●						
Florida	●			●	●	●	●			●	●	●	●
Georgia		●		●	●		●						
Hawaii		●		●	●	●	●		●		●	●	●
Idaho	●			●	●	●	●						
Illinois	●			●	●		●						
Indiana	●			●	●	●	●						
Iowa	●				●		●						
Kansas		●		●	●	●	●						
Kentucky			●										
Louisiana			●										
Maine			●										
Maryland		●			●		●						
Massachusetts		●		●	●		●					●	●
Michigan	●					●	●						
Minnesota			●										
Mississippi			●										
Missouri	●				●		●						
Montana	●			●	●	●	●						
Nebraska	●				●		●						
Nevada	●			●	●	●	●	●	●				
New Hampshire			●										
New Jersey		●		●	●	●	●				●		
New Mexico		●		●	●	●	●						
New York		●			●		●						
North Carolina	●			●							●		
North Dakota		●		●	●		●						
Ohio		●		●	●		●						
Oklahoma	●				●	●	●						
Oregon	●			●	●	●	●	●	●		●		
Pennsylvania		●			●		●						
Rhode Island			●										
South Carolina	●			●	●		●						
South Dakota		●		●	●		●						
Tennessee	●			●	●		●						
Texas	●			●	●	●	●	●	●		●		
Utah	●			●	●	●	●	●	●		●		
Vermont	●						●						
Virginia			●										
Washington		●		●	●	●	●	●	●	●	●	●	●
West Virginia	●				●	●	●						
Wisconsin	●				●		●						
Wyoming	●			●	●	●	●						

*Adapted from "Guidelines of Water Reuse", USEPA, 2004.

**States reviewed in this study are those that are shaded in this table.

Table 3.6. Summary of regulations and guidelines reviewed in the twelve selected states.

	Water Reuse Regulations	Water Discharge Regulations	Air Emission
Arizona	*AAC, R18-9, Article 7	• AAC, R18-9 Article 9	
California	* State Water Resources Control Board, Resolution No.75-58 * Warren-Alquist Act, Section 25602 * Water Code, Section 462 * 22CCR60306	* State Water Resources Control Board, Resolution No. 75-58	* 22CCR60306 • 17CCR93103
Florida	* FAC 62-610-668	• FAC 62-302-520 • FAC 62-660.400	* FAC 62-610-668
Hawaii	* Guidelines for the Treatment and Use of Recycled Water, III, C (Dep. of Health, 2002)		* Guidelines for the Treatment and Use of Recycled Water, III, C (Dep. of Health, 2002)
Maryland		• COMAR26.08.03.06	
New Jersey	* Reclaimed Water for Beneficial Reuse (Dep. of Env. Pro., 2005)		
North Carolina	* 15A NCAC 02T.0906 * 15A NCAC 02T.0910	• 15A NCAC 02B.0208 • 15A NCAC 02B.0211 • Thermal (Temperature) Variances to North Carolina Water Quality Standards (USEPA, 2006)	
Oregon	* OAR 340-550-0012		* OAR 340-550-0012
Texas	* TAC 30-210.32 * TAC 30-210.33	• TAC 30-307.8	* TAC 30-210.32 * TAC 30-210.33 • TAC 30-113.220
Utah	* Water Reuse in Utah (Division of Water Resource, 2005) * UAC R317-3-11		* UAC R317-3-11
Washington	* RCW 90.46 * Water Reclamation of Reuse Standards (Dep. of Health & Dep. of Ecology, 1997)		* Water Reclamation of Reuse Standards (Dep. of Health & Dep. of Ecology, 1997)
Wyoming	• WQRS Chapter 21	• WQRS Chapter 2	

Notation: * Related to reuse of reclaimed water in power plant cooling water system.
• Related to power plant cooling water system.

3.2.1.1 Arizona

In the state of Arizona, the Arizona Revised Statutes (A.R.S.) authorizes the Arizona Department of Environmental Quality (ADEQ) to adopt water quality standards for the direct reuse of reclaimed water. Any reclaimed water use is regulated by Arizona Administrative Code (AAC), R18-9 and the requirement for direct use of reclaimed water is regulated in AAC R18-9, Article 7. The reclaimed water classification and relevant water quality is stated in AAC, R18-11 and the transportation of reclaimed water is regulated in AAC, R18-9, Article 6.

In the Regulation R18-9-704 G Prohibited Activities, Item 2-C, direct reclaimed water use is prohibited for evaporative cooling towers or misting. Using reclaimed water for cooling seems to be illegal in Arizona but there have been power plants using 100% reclaimed water for years. The answer was provided by the Reclaimed Water Office, ADEQ (Veil, 2007). The definition of “direct use” opens the opportunity for the power plants to utilize reclaimed water in cooling tower systems. The Regulation R18-9-701 states that “The use of industrial wastewater or reclaimed water, or both, in a workspace subject to a federal program that protects workers from workplace exposures” is not regarded as “direct use” of reclaimed water. In other words, as long as the power plant could provide safety programs for the workers, the use of reclaimed water will not be categorized as direct use and does not require a permit for its use. Another case is to acquire the reclaimed water from a treatment facility and discharge the blowdown back to the treatment facility. Under this circumstance, R18-9-701-a will activate and no permit is required.

Although any discharge of pollutant is regulated by Arizona Pollutant Discharge Elimination System (AZPDES), the power plants could avoid these regulations by sending cooling tower blowdown back to: 1) POTWs by indirect discharge, and 2) Discharge into a privately owned treatment works. Otherwise, the discharge of blowdown back to the surface water or other water body is regulated in R18-9 Article 9.

Regulation R18-9 Article 6 regulates two types of transportation of reclaimed water, “Open Water conveyance” and “Pipeline conveyance”. An open water conveyance does not include waters inside the United States and is not applied. “Pipeline conveyance” means any system of pipelines that transports reclaimed water from a sewage treatment facility to a reclaimed water blending facility or from a sewage treatment facility or reclaimed water blending facility to the point of land application or end use. In R18-9-602, F and G, the transportation of reclaimed water through pipelines should meet the minimum separation distance or have better material/joint design to ensure no contamination to drinking water. In addition, a notable sign with caution words is required; otherwise, the pipe must have light purple color.

3.2.1.2 California

California is one of two states (the other is Florida) having comprehensive regulations about water reuse. State Water Resources Control Board and the California Regional Water Quality Control Board are the two divisions of California Environmental Protection Agency (CEPA), which administer the state water quality control. Regional boards include (1) North Coast (2) San Francisco Bay (3) Central Coast (4) Los Angeles (5) Central Valley (6) Lahontan (7) Colorado River Basin (8) Santa Ana and (9) San Diego.

Two major regulations related to the reuse of reclaimed water in industrial cooling tower are 1) California State Water Resources Board, resolution No. 75-58: Water quality control policy on the use and disposal of inland waters used for power plant cooling; 2) California Health Laws Related to Recycled Water "The Purple Book" (CADOH, 2001) Excerpts from the Health and Safety Code, Water Code, and Titles 22 of the California Code of Regulations.

In addition to State Board Resolution No. 75-58, Warren-Alquist Act (Section 25602), and Water Code (462) also direct the administrator to evaluate water reuse in power plant cooling tower. In other words, the California government supports the use of recycled water for cooling purposes

Treated wastewater is defined as recycled water. The use of recycled water for cooling purposes is regulated by 22 CCR § 60306 (C) and recycled water used for industrial cooling that creates a mist shall be a disinfected tertiary recycled water. The recycled water quality required for cooling purposes is summarized in Table 3.7.

Table 3.7. The recycled water quality requirement for cooling water in CA

System	Treatment level	Treatment Requirement	Total Coliform	Turbidity
Industrial cooling involving cooling tower, evaporative condenser, or spraying that creates a mist	Disinfected Tertiary Recycled Water	oxidation, coagulation, filtration, and disinfection	23/100 mL (Av g) 240/100 mL (Max in 30 days) 2.2/100 mL as a weekly median	• coagulated and passed through natural undisturbed soil or a bed of filter media - 2 NTU (1-day average) - 5 NTU (not to exceed for more than 5% of 24 hr period) - 10 NTU (max) • passed through membrane - 0.2 NTU (not to exceed for more than 5% of 24 hr period) - 0.5 NTU (max)

*Adapted from “Guidelines of Water Reuse”, USEPA. 2004.

In addition, the California government also suggests sampling for total coliform at least once a week and continuous monitoring of turbidity following filtration.

In California State Water Resources Board, resolution No.75-58, Page 5, two kinds of discharges are prohibited:

1) The discharge to land disposal sites of blowdown waters from inland power plant cooling facilities shall be prohibited except to salt sinks or to lined facilities approved by the Regional and State Boards for the reception of such wastes.
2) The discharge of wastewaters from once-through inland power plant cooling facilities shall be prohibited unless the discharger can show that such a practice will maintain the existing water quality and aquatic environment of the State’s water resources.

In addition, the Regional Boards may grant exemption to these discharge prohibitions on a case-by-case basis in accordance with exception procedures included in the “Water Quality Control Plan for Control of Temperature in the Coastal and Interstate Waters and Enclosed Bays and Estuaries of California”.

Concerning the air emission, District Rule 4201, Section 3.1 limits the emission of total suspended particulate matters (PM) to 0.1 grain/dry standard cubic foot of gas. Another concern is the hexavalent chromium compounds in the cooling tower. In 17 CCR s 93103, restrictions of chromate use in cooling towers includes: (1) Not adding any hexavalent chromium-containing compounds to the cooling tower circulating water; (2) The hexavalent chromium concentration should be less than 0.15 milligrams hexavalent chromium per liter of circulating water; (3) The concentration of hexavalent chromium should be tested every six months.

The air emission from cooling tower using recycled water is also regulated by 22 CCR § 60306 (C). Whenever a cooling system using recycled water in conjunction with an air conditioning facility utilizes a cooling tower which creates a mist that could come into contact with employees or members of the public, the cooling system shall comply with the following:

(1) A drift eliminator shall be used whenever the cooling system is in operation.

(2) A chlorine, or other, biocide shall be used to treat the cooling system re-circulating water to minimize the growth of Legionella and other micro-organisms. Moreover, the volatile organic compound emission is not expected from cooling towers in power plant facilities.

3.2.1.3 Florida

In the state of Florida, the water quality specific to cooling tower is regulated in FAC 62-610.668. Reclaimed water may be used in once-through cooling towers and open cooling towers with at least secondary treatment. Once-through cooling towers may use non-disinfected secondary effluent in a closed system and return the used water back to the domestic wastewater treatment facilities. For open cooling systems (wet re-circulating systems), reclaimed water must be at least secondary treated with basic disinfection before use. A 300-foot setback distance shall be also provided to inform the workers and the cooling tower shall be designed and operated to minimize aerosol drift to areas beyond the site property line that are accessible to the public.

If the system design does not meet the requirements in Part III of Chapter 62-610, F.A.C., alternative requirements shall be addressed in the industrial wastewater permit, including high level of disinfection, filtration, and continuous monitoring of total suspended solids, chlorine residual, Giardia and Cryptosporidium. Moreover, total chlorine residual of at least 1 mg/l after a minimum acceptable contact time of 15 minutes is required at peak hourly flow. The water quality required for cooling systems is summarized in Table 3.8.

Table 3.8. The minimum reclaimed water quality requirement for cooling water in Florida

System	Treatment level	$CBOD_5$	TSS	Fecal Coliform	pH
Once-through cooling tower	secondary treatment (used in closed systems)	60 mg/L*	60 mg/L*	NS	6-8.5
Open Cooling tower	Secondary treatment and basic disinfection	20 mg/L	5 mg/L**	25/100 mL***	

Notes: For once-through cooling tower: 1) the reclaimed water must be conveyed and used in closed systems which are not open to the atmosphere and 2) The reclaimed water must return to the domestic wastewater treatment facility.
*20 mg/l for annual average, 30 mg/L for monthly average, 45 mg/L for weekly average, and 60 mg/L for single sample.
**Single sample to be met after filtration and prior to disinfection.
***Over 30-day period, 75 percent of samples below detection limits.

Discharges from once-through cooling towers using reclaimed water must return the effluent back to the domestic wastewater treatment facility. Although no regulation is related to the effluent discharge of used reclaimed water from open cooling system, the discharges into waters of the state is still regulated by FAC, 62-302.520, which regulates the thermal water discharge and FAC, 62-660.400 which addresses effluent limitations.

Discharges from steam electric generating plants existing or licensed by July 1st, 1984 shall not be required to be treated to a greater extent than may be necessary to assure:

- That the quality of non-thermal components of discharges from non-recirculated cooling water systems is as high as the quality of the make-up waters; or
- That the quality of non-thermal components of discharges from re-circulated cooling water systems is not lower than is allowed for blowdown from such systems; or
- That the quality of non-cooling system discharges, which receive make-up water from a receiving body of water that does not meet applicable Department water quality standards, is as high as the quality of the receiving body of water.

3.2.1.4 Hawaii

Currently, Hawaii has no regulation related to water reuse. However, the Department of Health published “Guidelines for the Treatment and Use of Recycled Water” in 2002. The reuse of recycled water in evaporative cooling towers is referred to the uses of R-1 type water and it stipulates that the following requirements shall be met:

1. A high efficiency drift reducer is used and the system is maintained to avoid greater rate of generation of drift than that with which a high efficiency drift reducer is

associated;

2. A continuous biocide residual, sufficient to prevent bacterial population from exceeding 10,000 per milliliter, is maintained in circulating water; and
3. The system is inspected by an operator, capable of determining compliance with this subdivision, at least daily.

For R-1 type recycled water, a continuous recording of turbidity shall be installed after a filtration process as a measure of the coagulation-flocculation-sedimentation-filtration process effectiveness and as means of assuring a quality effluent upon disinfection. The turbidity of filtered effluent shall not exceed 2 NTU at any time.

No evaporative cooling towers can use lower quality recycled water, R-2 type water, for cooling purposes. R-2 type recycled water does not require a filtration process; however, new R-2 facilities constructed after May 30, 2002, will be required to install a continuous recording turbidimeter at a point after the secondary treatment. A continuous monitoring is required at this stage.

The water quality of two types of cooling systems is summarized in Table 3.9. Disinfected secondary-23 recycled water, means secondary treatment with disinfection to achieve a median fecal coliform limit of 23 per 100 mL based on the last seven days for which analyses have been completed.

Table 3.9. The least reclaimed water quality requirements for cooling water in Hawaii

System	Treatment level	Fecal coliform	Cl_2 Residue	Turbidity
Cooling water that doesn't emit drift	R-2 water: oxidized and disinfected	• 23/100 mL (7-day median) • 200/100 mL (not to exceed in more than one sample in 30-day)	0.5 mg/L (minimum; theoretical contact time 15min, actually contact time 10min)	NS
Cooling water that emits drift	R-1 water: oxidized, filtered, disinfected	• 2.2/100 mL (7-day median) • 23/100 mL (not to exceed in more than one sample in 30-day) • 200/100 mL (max)	5 mg/L (minimum; theoretical contact time 15min, actually contact time 10min)	2 NTU

In addition to the minimum reclaimed water quality requirements, continuous monitoring of daily flow, turbidity prior and after filtration procedure, fecal coliform, and chlorine residual are mandatory. Besides these, BOD_5 and suspended solids shall also be measured weekly.

3.2.1.5 Maryland

The "Guidelines for Land Treatment of Municipal Wastewaters" (MDOE, 2003) reveals that the majority of wastewater reuse in Maryland is spray irrigation systems installed for agricultural crops.

Maryland's regulations applicable to thermal discharges and cooling water intake structures were based on the State's then-current scientific and technical knowledge of the factors influencing the type and magnitude of impacts expected to occur, and following a logical conceptual framework. Code of Maryland, 26.08.03.06 indicates the standards for the effluent discharged from steam electric power stations using the cooling system. The biocide concentration in the cooling water is regulated to prevent adverse impact on aquatic life in the receiving water bodies. The information is summarized in Table 3.10.

Table 3.10 Standard of effluents discharge contained chlorine

System	Type (capacity)	Total residual chlorine (daily max)	Free available chlorine (daily max)
Once-through cooling tower	> 25MW	0.2 mg/L	
	<25MW	0.2 mg/L	0.5mg/l
Cooling tower blowdown		0.2 mg/L	0.5mg/l

3.2.1.6 New Jersey

The state of New Jersey does not have specific regulations regarding the use of reclaimed water as industrial cooling water. However, "Reclaimed Water for Beneficial Reuse" provides the guidelines on using reclaimed water for different purposes (NJDEP, 2005). Industrial reuse for cooling equipment is listed as Type IV Reclaimed Water for Beneficial Reuse (RWBR). It is mentioned that type IV RWBR can be used as industrial cooling water but there are no established standards. Otherwise, all industrial reuse systems require a case-by-case review by NJDEP.

Non-contact cooling water, as mentioned in the document, is an example of little or no level change of treatment before use because the water has already been treated by the wastewater treatment plant. Furthermore, only workers who receive specialized training on dealing with the RWBR systems would be in contact with the reclaimed water. In addition to criteria listed in Table 3.11, other requirements include following the Submission of Standard Operations Procedure that ensure proper material handling and submitting a User/Supplier Agreement Annual usage report.

Table 3.11. The minimum reclaimed water quality requirements for cooling water in New Jersey

System	Type of Water	TSS	Cl_2 Residue	Fecal Coliform
Cooling water	Type IV RWBR, secondary treatment	Specified in the NJDEP permit for the existing treatment requirements	1 mg/L (minimum; after a minimum acceptable contact time of 15 min at peak hourly flow)	• 200/100 mL (30-day average) • 400/100 mL (max, single sample)

3.2.1.7 North Carolina

In North Carolina Administrative Code, Subchapter 02T, Chapter 15A, Section 0910 Reclaimed Water Utilization, the use of reclaimed water for cooling tower is approved once the following requirements are met:

1. Notification is provided to inform the public or employees of the use of reclaimed water (Non-Potable Water) and that the reclaimed water is not intended for drinking,
2. The reclaimed water users received appropriate education and approval from the reclaimed water generator,
3. The distribution of reclaimed water is recorded by the reclaimed water generator, and
4. The pathway used to transport reclaimed water from the generator to end user is reviewed and inspected.

In Section 0906, the North Carolina Government mentions the reclaimed water effluent standards that could be used but they are not specific to cooling purposes. The reclaimed water should be treated (filtration or its equivalent) to achieve the tertiary quality before using for storage, distribution, or irrigation. The reclaimed water criteria are summarized in Table 3.12. However, if the power plant has its own treatment facility, the water quality of produced reclaimed water is not required to meet the same criteria if the water is used in the industrial process and the area of use has no public access.

Thermal discharge requirements are regulated in 15A NCAC 02B.0208, 0211, and

"Thermal (Temperature) Variances to North Carolina Water Quality Standards" (USEPA, 2006). The Commission may establish a water quality standard for temperature for specific water bodies other than the standards specified in Rules 0211 and 0220 of this Section, upon a case by case determination that thermal discharges to these waters, such as industrial cooling water, provide for the maintenance of the designated best use throughout a reasonable portion of the water body.

Table 3.12. The minimum reclaimed water quality requirement for cooling water in North Carolina

System	Treatment Level	BOD_5	TSS	NH_3	Total Fecal Coliform	Turbidity
Reclaimed water prior to storage, distribution, or irrigation	Tertiary treatment	10 mg/Ll (monthly) 15 mg/L (daily max)	5 mg/L (monthly) 10 mg/L (daily max)	4 mg/L (monthly) 6 mg/L (daily max)	14/100 mL (monthly) 25/100 mL (daily max)	10 NTU (max)

3.2.1.8 Oregon

Generally, different classes of water quality are required in accordance to different reuse purposes (there are four reuse levels). Public access to Class A, Class B, and Class C water should be prevented and controlled, respectively, while there should be no direct public contact when using Class D water.

Oregon Administrative Rules (OAR), Title 340, Division 55 Section 0012 declares that Class C recycled water can be used for industrial cooling if the specified requirements are met. Typical Class C recycled water must be an oxidized and disinfected wastewater. The total coliform must be monitored once per week at a minimum and meet target level in Table 3.13. If aerosols are generated when using recycled water for an industrial, commercial, or construction purpose, the aerosols must not create a public health hazard.

Table 3.13. The minimum reclaimed water quality requirements for cooling water in Oregon

System	Type of Water	Treatment	Total coliform
Industrial Cooling	Class C	Oxidized and Disinfected	• 240/100 mL (2 consecutive samples) • 23/100 mL (7-day median)

3.2.1.9 Texas

Texas Administrative Code, Title 30, Environmental Quality, Part 1, Chapter 210 regulates the use of reclaimed water for different purposes. For instance, two kinds of reclaimed water are:

1) Type I - reclaimed water that is used when the public may be present or the public may come in contact with the reclaimed water.
2) Type II - reclaimed water that is used when the public may not be present or the public may not come in contact with the reclaimed water.

Since Type I reclaimed water has better water quality than Type II, any Type I Reclaimed water can also be used for any of the Type II uses identified in TAC 30-210.32. Water quality requirements (TAC 30-210.33) for Type I and Type II Reclaimed Waters used in cooling systems are summarized in Table 3.14. The reclaimed water must meet standards for BOD_5 and fecal coliform and samplings must be conducted once per week.

The used reclaimed water discharged from cooling towers is also regulated by Texas Administrative Code, TAC, title 30, 113, 113.220 with regards to the Industrial Process Cooling Towers Maximum Achievable Control Technology standard as specified in 40 Code of Federal Regulations Part 63, Subpart Q. In addition, for once-through cooling systems, if the discharges do not measurably alter intake concentrations of a pollutant, the water-quality based effluent limits for that pollutant are not required (TAC, Title 30 Environmental Quality, Part 1, Chapter 307, Rule 307.8).

Although Type II Reclaimed Water can be used in cooling tower makeup water according to TAC 30-210.32, special requirements might be needed to control the air emission.

Table 3.14. The minimum reclaimed water on a 30-day average quality requirement in Texas

Type of reclaimed water		BOD_5	$CBOD_5$	Turbidity	Fecal Coliform	Fecal Coliform (Maximum)
Type I		5 mg/L		3 NTU	20 CFU/100 mL	75 CFU/100 mL
Type II	Others	20 mg/L	15 mg/L		200 CFU/100 mL	800 CFU/100 mL
	Pond system	30 mg/L			200 CFU/100 mL	800 CFU/100 mL

3.2.1.10 Utah

The use of reclaimed water as cooling water is regulated by Utah Administrative Code, R317-3-11 Use, Land Application and Alternate Methods for Disposal of Treated Wastewater Effluents. There are two types of reclaimed water identified in this session, 1) Type I, use of treated domestic wastewater effluent where human exposure is likely; 2) Type II, use of treated domestic wastewater effluent where human exposure is unlikely. Apparently, reclaimed water used for cooling water makeup is classified into Type II uses. The same session and “Water Reuse in Utah” NRDWR, 2005 also state that Type I effluent can also be utilized for any of the Type II uses based on its higher quality. Utah State Department of Natural Resources also published “Water Reuse in Utah” (2005), and “Utah’s Water Resources Planning for the Future” (2001) to help satisfy the need for more detailed information about water reuse and its potential in Utah.

Type II reclaimed water can be used as cooling water but use for cooling towers which produce aerosols in populated areas may have special restriction. The lowest requirements of water quality for cooling water are summarized in Table 3.15.

Table 3.15. The minimum reclaimed water quality requirement for cooling water in Utah

Type of reclaimed water	BOD_5	TSS	Turbidity	Daily Fecal Coliform	Total residual chlorine	pH
Type I	10 mg/L (monthly)		2 NTU (daily) 5 NTU (max)	none detected (weekly) 9 /100 mL (max)	1.0 mg/L	6-9
Type II	25 mg/L (monthly)	25 mg/L (monthly avg.) 35 mg/L (weekly avg.)		126/100 mL (weekly) 500 /100 mL (max)		

3.2.1.11 Washington

Four types of reclaimed water are classified in Revised Code of Washington (RCW) 90.46 Reclaimed Water Use:

1) Class A reclaimed water is at a minimum, at all times an oxidized, coagulated, filtered, disinfected wastewater.
2) Class B, C, and D reclaimed waters are at a minimum, at all times oxidized, disinfected wastewaters.

According to "Water Reclamation and Reuse Standards", article 4, section 15, reclaimed water used for industrial cooling purposes without creating aerosols or mist shall be class C reclaimed water or better. Reclaimed water used for industrial cooling purposes with creating aerosols or mist shall be Class A reclaimed water or better. "Water Reclamation and Reuse Standards" indicates the potential usage and the required reclaimed water quality (WADOH and WADOE, 1997) as summarized in Table 3.16.

Table 3.16. The minimum reclaimed water quality requirement for cooling water in Washington

System	Type of reclaimed water	Total Fecal Coliform	BOD_5	TSS	Turbidity	Cl_2 Residue
Cooling tower with creating mist	Class A (oxidized, coagulated, filtered, and disinfected)	2.2 /100 mL (weekly) 23/100 mL (max)	30 mg/L (monthly)	30 mg/L (monthly)	2 NTU (daily) 5 NTU (max)	Minimum Cl residue of 1 mg/L after a contact time of 30-min
Cooling tower without creating mist	Class C (oxidized, disinfected)	23/100 mL (weekly) 240 /100 mL (max)				

3.2.1.12 Wyoming

The state of Wyoming has not yet developed regulations for the use of reclaimed water as industrial cooling water. However, Water Quality Division (WQD), Department of Environmental Quality, provides regulations when using reclaimed water for irrigation. “Standards for The Reuse of Treated Wastewaters,” Chapter 21, regulates the use of reclaimed water in Wyoming. Three different types of reclaimed water, Class A, B, and C are classified by relative treatment and the maximum number of fecal coliform organisms (CFU/mL).

Although there is no regulation directly related to the effluent discharge of used reclaimed water from industrial cooling systems, standards have been established to address the primary health concerns associated with the reuse of treated wastewater. According to “Water Quality Rules and Regulations, Chapter 2, Permit, Regulations for Discharges to Wyoming Surface Waters”, the potential quantitative data for the pollutants or parameters needed for cooling water discharge include major parameters, such as pH, Total Suspended Solids (TSS), Total Organic Carbon (TOC), and Fecal Coliform (if believed present or if sanitary waste is or will be discharged), etc. Chemical parameters are Total Residual Chlorine (if chlorine is used), Chemical Oxygen Demand (COD), (if non-contact cooling water is or will be discharged), and Ammonia (as N). Moreover, temperature should be monitored during both summer and winter.

3.2.2 State Interbasin Water Transfer Regulations

Among the twelve states that have been reviewed in this study, seven states were found to have regulations that directly or indirectly relate to interbasin water transfer (Table 3.17). These states are Arizona, California, Florida, New Jersey, North Carolina, Texas, and Wyoming. Pennsylvania is also included in this study although there are no proposed regulations or guidelines by the state government. In general, no prohibition against interbasin water transfer was found in these states.

The beneficial use of water is the main concern at the state level. California Water Code Section 109, California Water Code Sections 480-484, Pennsylvania House Bill 2005 P.N. 2707, and Wyoming Statutes Annotated Section 41-4-503 all declare the transfer will be permitted if the transfer is beneficial to the state.

Most states declare that applying for interbasin water transfer is necessary to obtain the permission, while commissions should consider the welfare of the public in the origin basin and might need to hold hearings. Most states do not have limitations on transfer certifications. The only numeric limitation is the case of North Carolina where a transfer certificate is required for a new transfer of 2 million gallons per day (mgd) or more and for an increase in the existing transfer by 25 percent or more, if the total including the increase is 2 mgd or more.

Additional issues exist about the quality of transported water and the protection of conservation districts. For example, New Jersey Statutes clearly state that no individual shall transport ground or surface water in the Pinelands National reserve, or cause it to be transported more than 10 miles from the reserve. Water quality rules in Wyoming introduce restrictions on water transport to avoid contact between transported water and contaminants.

In Pennsylvania, there are instances of both drinking water and wastewater being transported across state lines into neighboring states. There are no regulations that apply specifically to interstate transport of impaired water above those that apply to intrastate transport of water in general. However, there may be interstate commissions that may regulate the transport of water. These include the Delaware River Basin Commission, the Susquehanna River Basin Commission, and the Great Lakes Commission. These commissions have the responsibility and authority to regulate the quantity and quality of water in their respective basins, whether it is interstate or intrastate (McLeary, 2007).

The transfer of water between different water regions sometimes requires certification for the right to carry out the process. An example of such a process is that implemented in North Carolina. In 1993, the Legislature adopted the Regulation of Surface Water Transfers Act (N.C.G.S. Section 143-215.22I) to regulate large surface water interbasin transfers by requiring a certificate from the Environmental Management Commission (EMC). In North Carolina, the certification process usually contains several stages. The first step is to send notification and hold a consultation to determine the original basin capacity. After a detailed evaluation, the state requests the applicant to make either an Environmental Assessment (EA) or an Environmental Impact Statement (EIS) for this event and submit a petition to Environmental Management Commission (EMC), which will evaluate the document and hold a public hearing (N.C.G.S. Section 143-215.22I). Integrating the public comments from the hearing, the applicant then completes a final EA/EIS and submits it to the EMC for final decision.

Table 3.17. Limitations on interbasin water transfers in eight selected states

State	Regulation	Description
Arizona	A.R.S. § 45-107	Water transfer beyond the boundary of irrigation districts subject to the approval of the district. *
	A.R.S. § 45-165	About the application for interstate operations, except as regulated by A.R.S. § 45-291 to 294, every application should not be denied.
	A.R.S. § 45-291-294	Approval is required to transport water out of state; application, criteria, hearing, and written periodic reports as required by the director.
	A.R.S. § 45-292	A person may withdraw, divert or transport water from the state for a beneficial use in other states as long as the application is approved. The annual amount of water in acre-feet for the application and studies of the probable hydrologic impact on the area from which the water is proposed to be transported are required.
	A.R.S. § 45-541 to 547	Regulate the transportation of groundwater instate.
California	C.W.C § 109	The State Water Resources Control Board should review proposed transfers to determine if they would cause an unreasonable effect on the economy in the area of origin or on fish, wildlife, or other water uses.*
	C.W.C § 480-484	The department shall seek to facilitate transaction only if the water to be transferred is already developed and being diverted from a stream for beneficial use or has been conserved.*
	C.W.C § 10501-10505.5	This code reserves for the county of origin all the water it may need for future development; this code also provides that the State Water Resources Control Board makes the determination of when, and to what extent, water is "necessary for the development of the country".*
	C.W.C § 11460-11463 (Watershed Protection Act)	The main idea of the act was to extend area of origin priorities to the entire watershed area and not limit them to the areas of precipitation.*
Florida	Florida Statutes §373.2295	This statute grants authority only to groundwater but not surface water. (Surface water inter-district transfer is not permitted under chapter 373**)
New Jersey	N.J.S. §58:1A-7.1	No individual shall transport, or cause to be transported, more than 10 miles outside the boundary of the Pinelands National Reserve, and ground or surface water there from. However, nothing in this section shall prohibit the continued transportation of any such water utilized for public water supply purposes prior to the effective date of this act.*
North Carolina	N.C.G.S. §143-215/22I	Without a certificate from the commission, no person may initiate an interbasin transfer of over than 2 MGD.*
Pennsylvania	House Bill 2005 P.N. 2707	This interbasin transfer of waters of the commonwealth shall be permitted only if it agrees with long-range water resource planning and proper management and use of the water resources of the commonwealth.*
Texas	T.W.C §11.085	No person may take or divert any state water from a river basin in this state and transfer such water to any other river basin without first applying for and receiving a water right or an amendment to a permit, certified filing, or certificate of adjudication from the commission authorizing the transfer.*
	T.W.C. §36.122	If an application for a permit or an amendment to a permit under section 36.113 proposes the transfer of groundwater outside of a district's boundaries, the district may also consider the provisions of this section in determining whether to grant or deny the permit or permit amendment.*
Wyoming	Wyoming Statutes Annotated §41-4-503	A special process to evaluate transfers considers potential economics losses to the community relative to the benefits of the transfer and the availability of other sources of water *
	Water quality rules and regulations, Chapter 2	The restriction of transport water is to avoid contact between transported water and contaminants

P.S. A.R.S. = Arizona Revised Statutes; C.W.C.= California Water Code; N.J.S.= New jersey Statutes; N.C.G.C = North Carolina General Statues; T.W.C.= Texas Water Code

*Integrated information from "Survey of Eastern Water Law", Janice A. Beecher, Ph.D et al., Center for Urban Policy and the Environment School of Public and Environmental Affairs Indiana University, Indianapolis, IN, September, 1995.

**R.A. Christland. "Sharing the cup: a proposal for the allocation of Florida's Water resources, "Florida State University Law Review. 1996.

3.3 Summary of Regulations

Review of state and federal regulations relevant to water reuse in power plant cooling systems shows that the federal government has not established regulations specifically related to this type of water reuse, but a number of states have done so. Among those states, California, Florida, Hawaii, New Jersey, North Carolina, Oregon, Texas, Utah, and Washington were investigated for specific regulations and/or guidelines related to water reuse in re-circulating, evaporative cooling water systems in power plants. Regulations pertaining to interbasin transfer of water were also examined, as some potential sources of impaired water for power plants will be in different drainage basins, and perhaps different states, than the power plant.

The state regulations focus commonly on water aerosol “drift” emitted from cooling towers, which has the potential to contain elevated concentrations of chemicals and microorganisms and thus pose a health risk to the public. Other regulations related to the use of impaired waters in cooling towers, appear to be much less limiting. Drift has the same water quality as the re-circulating cooling water. The possible presence of microorganisms in drift is of primary concern. With regard to regulation of drift from cooling towers, the various state regulations and guidelines include the following provisions:

1) require the reclaimed water to be secondary treated and disinfected or tertiary treated (EPA, CA, FL, HI, NJ, NC, OR, TX, UT, WA),
2) and/or require the chlorine residual to be above a certain amount after a period of contact time (EPA, FL, HI, NJ, WA),
3) and/or require
   - the cooling tower to be equipped with drift eliminator (CA, FL, HI)
   - or a demonstration of public health assurance (OR),
   - or invoke special requirements (EPA, TX, UT, WA),
4) and/or require the fecal/total coliform to be under a certain concentration (EPA, CA, FL, HI, NJ, NC, OR, TX, UT, WA).

Thus, the focus of existing regulations pertaining to reuse of reclaimed water in evaporative cooling systems is the potential exposure of workers and public to drift in air emissions from the cooling tower, and especially to the potential for exposure to microorganisms in the drift.

Transferring impaired water within a state or between states is possible but also strictly regulated by local committees constituted by adjacent state governments, such as Great Lake Commission. Request of transferring wastewater must coincide with beneficial use for the state/states. An environmental impact statement and public hearing are required to acquire permission authorized by Environmental Management Commission.

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Related Websites for Regulations

Code of Federal Regulations (CFR)	http://www.access.gpo.gov/
Arizona State Legislature (ASL)	http://www.azleg.state.az.us/
The Arizona Administrative Code (AAC)	http://www.azsos.gov/public_services/Table_of_Contents.htm
California Code of Regulations (CCR)	http://ccr.oal.ca.gov/linkedslice/default.asp?SP=CCR-1000&Action=Welcome
The Florida Administrative Code(FAC)	http://fac.dos.state.fl.us/
Code of Maryland (COMAR)	http://www.dsd.state.md.us/comar/search_all.htm
New Jersey department of environmental protection (NJDEP)	http://www.state.nj.us/dep/dwq/techman.htm
North Carolina Administrative Code(NCAC)	http://reports.oah.state.nc.us/ncac.asp
Texas Administrative Code (TAC)	http://info.sos.state.tx.us/pls/pub/readtac$ext.viewtac
Utah Administrative Code(UAC)	http://www.rules.utah.gov/main/index.php?module=Pagesetter&func=viewpub&tid=1&pid=9
Washington State Legislature (WSL)	http://apps.leg.wa.gov/RCW/default.aspx?cite=90.46
Warren-Alquist Energy Resources Conservation and Development Act	http://www.energy.ca.gov/2005publications/CEC-140-2005-001/CEC-140-2005-001-ED2.PDF
Clean Water Act (CWA)	http://www.epa.gov/region5/water/cwa.htm
New Jersey Administrative Code (NJAC)	http://michie.lexisnexis.com/newjersey/lpext.dll?f=templates&fn=main-h.htm&cp=uanjadmin
California Water Code	http://www.leginfo.ca.gov/calaw.html

4.0 Cooling Water Chemical Mass Balance and Chemical Equilibrium Modeling

Water chemistry modeling is essential to understanding and predicting the behavior of chemical constituents in a recirculating cooling tower system, especially when an impaired water is used as cooling system makeup water. This increases the challenge of managing cooling water chemistry to prevent scaling, corrosion, and biofouling due to higher concentrations of dissolved substances and suspended solids. To gain insight into the chemical and biochemical reactions in a recirculating cooling system, understanding the chemistry of the cooling water at different cycles of concentration is essential. In this study, water chemistry modeling was performed by chemical mass balance modeling and chemical equilibrium modeling.

Chemical mass balance modeling was developed by considering cooling system to behave as a completely mixed tank reactor with and without considering constituent generation by corrosion and loss by scaling. The mass balance modeling was performed to evaluate the rate and extent of build up of dissolved constituent concentrations in recirculating cooling water. Potential effects of corrosion and scaling were investigated. Simulations of the performance of the pilot-scale cooling towers were conducted.

The chemistry of the cooling water at different cycles of concentration was simulated using chemical equilibrium modeling to gain insight into the reactions controlling the chemical behavior of the system. Modeling was performed using the chemical equilibrium program MINEQL+ (Schecher and McAvoy, 1999). The modeling that was performed in this study was used to estimate the chemical composition and reactions that might occur in the pilot-scale cooling units operated at different cycles of concentration, and to interpret and understand the chemistries observed in the pilot-scale units during their operation.

4.1 Cooling Water Chemical Mass Balance Modeling

Abstract

A chemical mass balance model was formulated for the concentration of total dissolved solids in a circulating cooling system. The chemical mass balance modeling provided a number of useful insights into chemical behavior in recirculating cooling water systems, and also enabled predictions of cooling water chemistry evolution. A key finding was that it usually will not be beneficial to operate cooling systems above 10 cycles of concentration as additional reductions in blowdown volume are small at high cycles of concentration. The modeling also demonstrated that constituent generation by corrosion and loss by scaling can significantly affect the required blowdown when the generation rate by corrosion or loss rate by scaling follow first order or zero order rate laws. The chemical mass balance model simulation results for non-reactive constituents such as Mg^{2+} were in good agreement with the data from the field testing. The ability of the chemical mass balance model to describe accurately the performance of recirculating pilot-scale cooling systems and to predict the blowdown operation when starting up the cooling system demonstrated that chemical mass balance modeling can be a useful tool to predict water chemistry of non-reactive, conservative constituents in a cooling system.

4.1.1 Introduction

The main problem associated with impaired water for use in cooling systems is the high concentration of dissolved substances and suspended solids, which increases the challenge of managing cooling water chemistry to prevent scaling, corrosion, and biofouling. In recirculating cooling systems, the cooling water is concentrated through evaporation in the cooling tower, exacerbating the problem of cooling water management. Organic matter and nutrients in cooling water contribute to microbiological growth that contributes to the potential for deposits and microbiologically induced corrosion. Biofilm growth or chemical precipitation deposits can interfere with heat transfer and can cause corrosion directly through acid production (bacteria) or indirectly by shielding metal surfaces from water treatment corrosion inhibitors. Heat exchangers, cooling tower packing material, or cooling tower water distribution nozzles / sprays can be plugged by rapid growth of biofilm (Ludensky, 2005).

To gain insight into the chemical and biochemical reactions in a recirculating cooling system, understanding chemistry of the cooling water at different cycles of concentration is essential. Chemical mass balance modeling around the cooling tower can help to determine the operational parameters of the cooling system and identify the chemistries that should be exploited to control chemical and biochemical reactions of concern with respect to scaling, corrosion, and biofouling.

To simulate the chemistry of cooling water at different cycles of concentration and considering corrosion and scaling, a chemical mass balance for a power plant recirculating cooling system (including cooling tower and heat exchanger) was developed. One version of the mass balance model was developed without considering constituent mass gains from corrosion or mass losses from scaling. A second version of the model was developed with consideration of corrosion and scaling as source and sink terms. This model was employed to examine effects of corrosion and scaling on cycles of concentration. Simulations were also performed with both models to determine operational parameters for experiments with pilot-scale cooling towers.

4.1.2 Model Concept

In the model, the circulating cooling system loop including both the cooling tower and heat exchanger is chosen as the control volume. Figure 4.1.1 shows a schematic diagram of the cooling tower and the circulating water flow to and from the cooling tower. Figure 4.1.2 shows a diagram of the recirculating cooling water system control volume which includes the heat exchanger, cooling tower, and transfer piping.

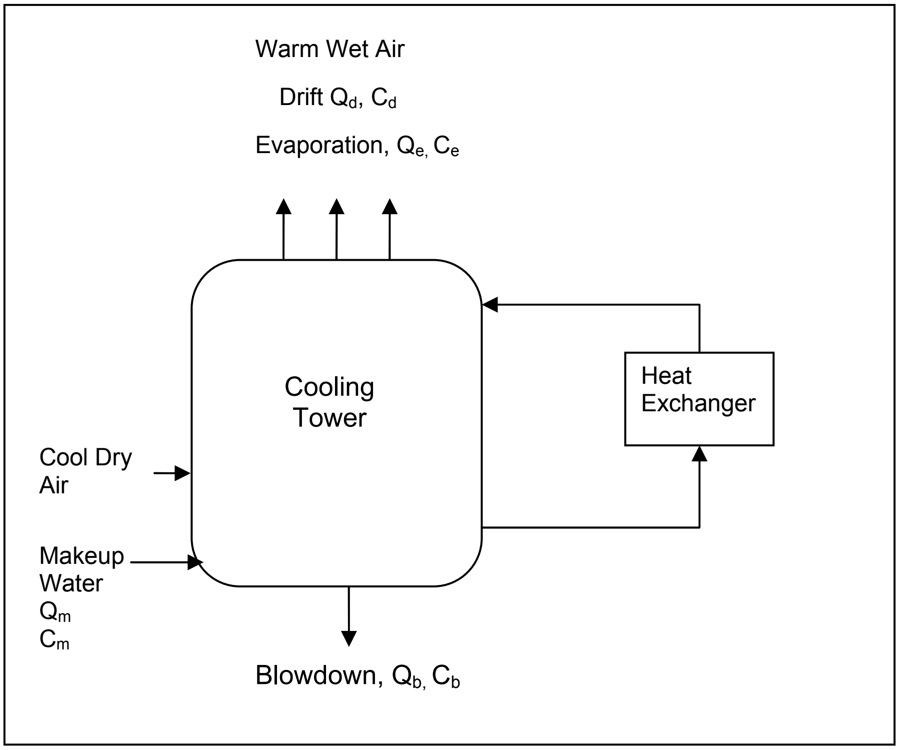

Figure 4.1.1 Schematic diagram of recirculating cooling tower operation

Two cases were considered in developing the chemical mass balance model:

- **Case 1:** no chemical loss/generation due to corrosion or scaling
- **Case 2:** chemical loss/generation due to corrosion or scaling

Case 1 applies to a conservative, non-reactive chemical constituent in the cooling water, e.g., total dissolved solids (TDS). Case 2 applies to specific constituents that may be lost from solution due to scaling, or that may build up in solution due to inputs from corrosion.

The chemical mass balance model was developed with the following simplifying assumptions:

- The cooling system was considered to behave as a completely mixed tank reactor (CSTR), i.e., the control volume was considered as total volume of water in the system.
- To consider the effects of corrosion and scaling, two empirical rate expressions were considered. Corrosion and scaling were modeled as zero order (constant rate) processes, and also as first order rate processes.

The general form of the chemical mass balance expression used to develop the mass balance model was as follows (Ramaswami et al., 2005):

$$\frac{dM}{dt} = \frac{dC}{dt}V = \dot{M}_{in}(C,t) - \dot{M}_{out}(C,t) + S(C,t) \pm Rxn(C,t) \tag{4.1.1}$$

where, M is the mass of chemical constituent in the system,

C is the constituent concentration in water, V is the system volume,

$\dot{M}_{in}(C,t)$ = mass in (MT^{-1})

$\dot{M}_{out}(C,t)=$ rate of mass outflow (MT^{-1})

$S(C,t)$ = rate of mass input from source (MT^{-1})

$Rxn(C,t)$ = rate of mass loss or gain from reaction (MT^{-1})

4.1.3 Development of Chemical Mass Balance Model

Two versions of the chemical mass balance model were developed reflecting the two different cases considered. In Case 1, scaling and corrosion contributions to chemical loss/generation were neglected. Scaling and corrosion contributions were considered in Case 2 assuming zero order and first order loss/generation models.

4.1.3.1 Case 1: No Chemical Loss/Generation Due to Scaling/Corrosion

In Case 1, a conservative, non-reactive chemical constituent was assumed, and no chemical loss/generation due to scaling or corrosion was considered. Water and chemical mass balances were developed for the system depicted in Figures 4.1.1 and 4.1.2. Chemical mass loss in aerosol drift shown in Figure 4.1.1 was included with the blowdown since the concentration of chemical constituent in drift is equal to that of blowdown.

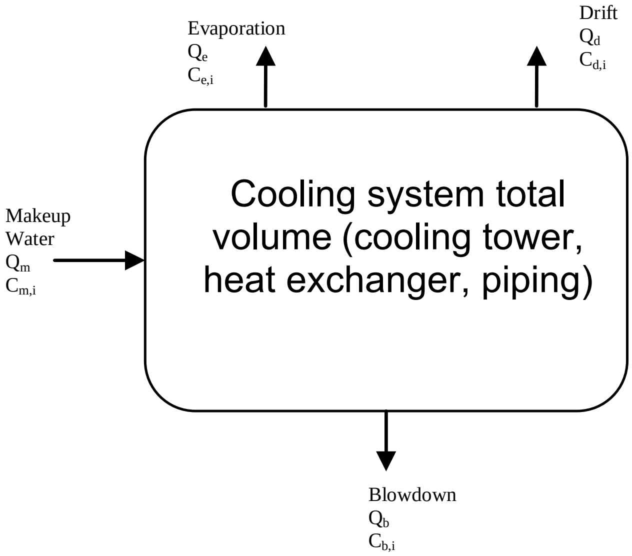

Figure 4.1.2 Diagram of cooling water system control volume including cooling tower, heat exchanger, and transfer piping.

The water flow balance around the cooling system control volume shown in Figure 4.1.2 is:

$$Q_m = Q_b + Q_e \tag{4.1.2}$$

where, Q_m is the makeup water flow rate, Q_b is the blowdown (plus drift) flow rate, and Q_e is the flow rate corresponding to evaporation.

Starting with the general mass balance expression in Equation 4.1.1, the chemical mass balance for a non-reactive constituent in the cooling system can be expressed by:

$$\frac{dC_i}{dt}V = Q_m C_{m,i} - Q_b C_i \tag{4.1.3}$$

where, C_i is the concentration of the chemical constituent in the circulating cooling system and $C_{m,i}$ is the concentration of the same constituent in the makeup water.

Integrating Equation (4.1.3) with respect to time yields:

$$C_{i,t} = \frac{Q_m C_{m,i}}{Q_b} + \left(C_{i,0} - \frac{Q_m C_{m,i}}{Q_b} \right) e^{-(t-t_0)\left(\frac{Q_b}{V}\right)} \tag{4.1.4}$$

$$N_{i,t} = \frac{Q_m}{Q_b} + \left(\frac{C_{i,0}}{C_{m,i}} - \frac{Q_m}{Q_b} \right) e^{-(t-t_0)\left(\frac{Q_b}{V}\right)} \tag{4.1.5}$$

where, $C_{i,0}$ is the initial concentration of chemical constituent *i* in the system, and $N_{i,t}$ is the number of cycles of concentration with respect to constituent *i*.

When time increases, the term $e^{-(t-t_0)\left(\frac{Q_b}{V}\right)}$ tends to zero and consequently

$$N_{i,t} = \frac{Q_m}{Q_b} \tag{4.1.6}$$

$$Q_b = \frac{Q_e}{N_{i,t} - 1} \tag{4.1.7}$$

$$Q_m = \frac{N_{i,t}}{N_{i,t} - 1} Q_e \tag{4.1.8}$$

Figure 4.1.3 shows the ratios Q_m/Q_e and Q_b/Q_e as a function of cycles of concentration, as calculated from Equations 4.1.7 and 4.1.8. Table 4.1.1 shows the decrease in blowdown flow rate with increasing cycles of concentration.

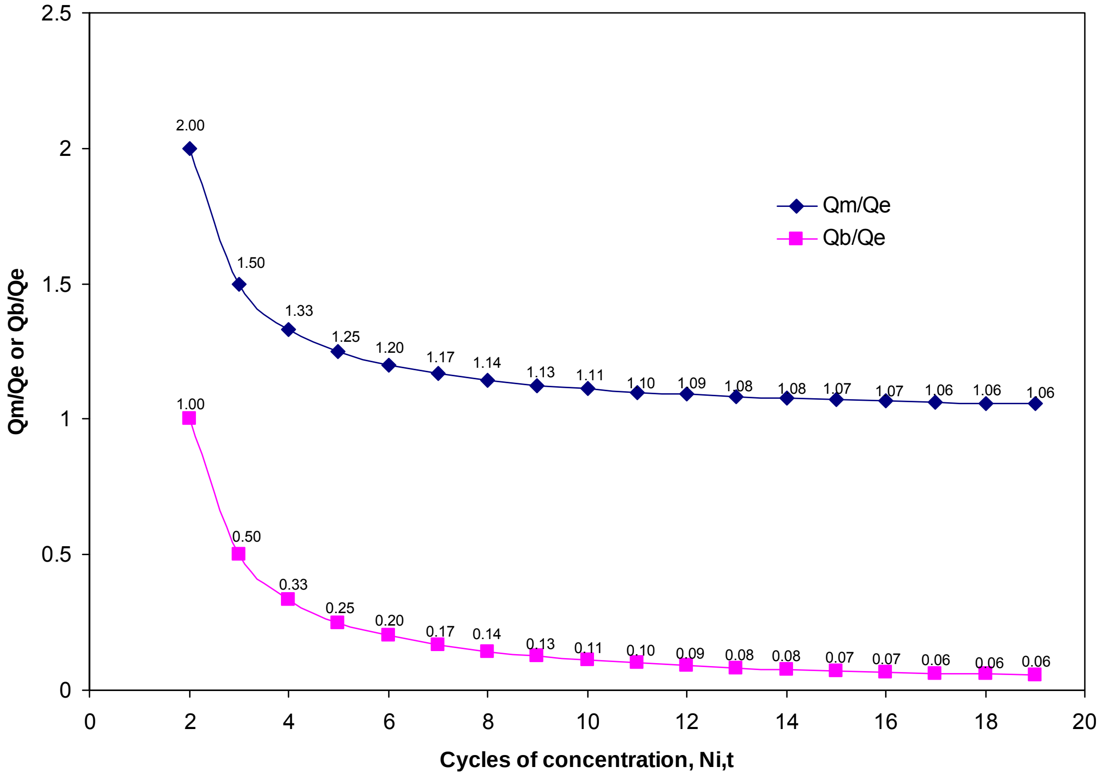

Figure 4.1.3 Flow rates ratios (Q_m/Q_e and Q_b/Q_e) versus cycles of concentration calculated with Equations 4.1.7 and 4.1.8

Table 4.1.1 Percent decrease of blowdown with cycles of concentration

Cycles of Concentration	**2**	**4**	**6**	**8**	**10**	**12**	**14**	**16**	**18**	**20**
Q_b/Q_e	0.996	0.329	0.196	0.139	0.107	0.087	0.073	0.062	0.055	0.048
Percent Decrease of Blowdown with respect to 2 cycles of concentration	-	67	80	86	89	91	93	94	95	95

From Figure 4.1.3, it may be seen that both blowdown and makeup flow rate decrease with increasing cycles of concentration. From Table 4.1.1, it is shown that at 10 cycles of concentration, blowdown rate is reduced by about 90% with respect to 2 cycles of concentration. Additional decrease of blowdown rate is small after 10 cycles of concentration. Thus, cooling tower operation beyond 10 cycles of concentration will have small benefit with respect to decreasing makeup water requirements and blowdown flow rate.

Figure 4.1.4 has been developed from Equation 4.1.4 for the six different operating conditions presented in Table 4.1.2. From Figure 4.1.4, it may be seen that at high blowdown rate (Condition 1), the concentration of chemical constituent does not significantly increase with time. At low blowdown rate, however, the concentration of chemical constituent increases significantly with time. After a long period, the constituent concentration becomes nearly constant. As time increases, the term $e^{-(t-t_0)\left(\frac{Q_b}{V}\right)}$ tends to 0 and concentration tends to $\frac{Q_m C_{m,i}}{Q_b}$. From Equation 4.1.5, it may be seen that blowdown has to be changed to maintain a particular cycle of concentration.

4.1.3.2 Case 2: Chemical Loss/Generation due to Scaling/Corrosion

In Case 2, constituent mass inputs from corrosion and mass outputs from scaling were considered in the model. For simplification, zero order and first order generation/loss models were considered for corrosion and scaling. For both rate models, different rate constant values were assumed and sensitivity analyses were performed. For the zero order model, the rate constant was designated as "k_0", and for the first order model, it was designated as "k_1". The value of this constant can be positive or negative, reflecting generation (input) or loss. A positive value means accumulation of chemical constituent in the circulating water due to corrosion and a negative value means loss of chemical constituent from the cooling water due to precipitation. The rate constants k_0 and k_1 have different units. The units of k_0 and k_1 are $ML^{-3}T^{-1}$ and T^{-1} respectively.

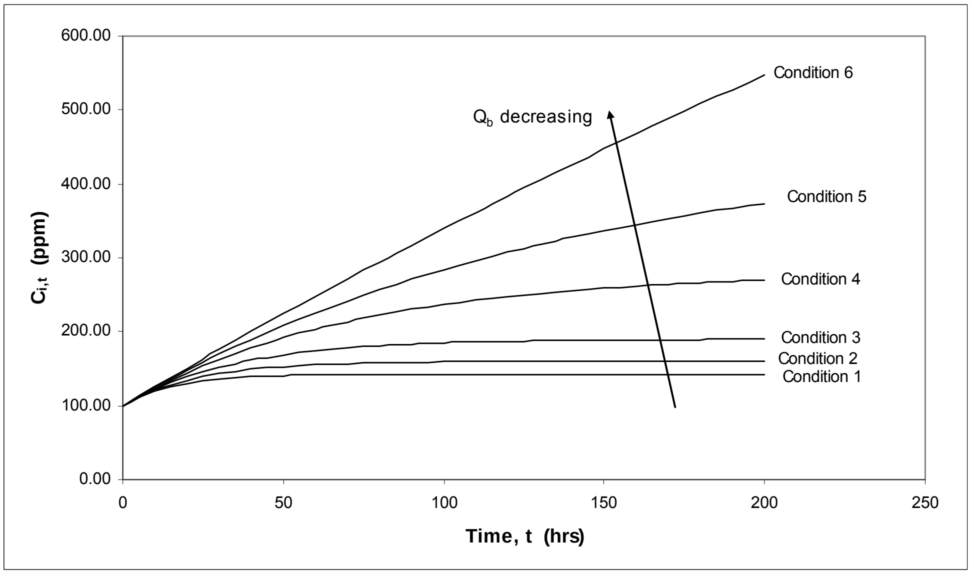

Figure 4.1.4 Concentration versus time without chemical mass generation calculated with Equation 4.1.4 for six operational conditions shown in Table 4.1.2

Table 4.1.2 Makeup water rate and blowdown rate values for different conditions

Condition	$C_{i,0}$ ppm	$C_{m,i}$ ppm	Initial CoC ($N_{i,0}$)	V Gallons	Q_e gph	Q_b gph	$Q_{m,}$ gph	Final CoC (Q_m/Q_b)
1	100	100	1	700000	18000	42000	60000	1.43
2	100	100	1	700000	18000	30000	48000	1.6
3	100	100	1	700000	18000	20000	38000	1.9
4	100	100	1	700000	18000	10000	28000	2.8
5	100	100	1	700000	18000	5000	23000	4.6
6	100	100	1	700000	18000	1000	19000	19

(Source: McCoy, 1974)

Zero Order Generation/Loss Model

In the zero order generation/loss model, the rate of generation or loss due to corrosion or scaling was considered to be constant. Thus,

$$r_{c,i} = k_0 \qquad (4.1.9)$$

where: k_0 = rate constant, $ML^{-3}T^{-1}$

$r_{c,i}$ = mass rate of loss/generation of chemical constituent “i” due to scaling or corrosion, $ML^{-3}T^{-1}$

Now, the mass balance of chemical constituent of “i” via Equation 4.1.1 yields

$$C_{i,t} = \frac{kV}{Q_b} + \frac{Q_m C_{m,i}}{Q_b} + \left(C_{i,0} - \frac{kV}{Q_b} - \frac{Q_m C_{m,i}}{Q_b} \right) e^{-(t-t_0)\left(\frac{Q_b}{V}\right)} \qquad (4.1.10)$$

$$N_{i,t} = \frac{k_0 V}{Q_b C_{m,i}} + \frac{Q_m}{Q_b} + \left(\frac{C_{i,0}}{C_{m,i}} - \frac{k_0 V}{Q_b C_{m,i}} - \frac{Q_m}{Q_b} \right) e^{-(t-t_0)\left(\frac{Q_b}{V}\right)} \qquad (4.1.11)$$

When time increases, $e^{-(t-t_0)\left(\frac{Q_b}{V}\right)}$ tends to zero and consequently

$$N_{i,t} = \frac{k_0 V}{Q_b C_{m,i}} + \frac{Q_m}{Q_b} \qquad (4.1.12)$$

$$Q_b = \frac{Q_e}{N_{i,t} - 1} + \frac{k_0 V}{(N_{i,t} - 1) C_{m,i}} \qquad (4.1.13)$$

Simulations performed with Equation 4.1.10 are plotted in Figures 4.1.5 and 4.1.6 for positive and negative values of rate constants for the zero order rate model. There it may be seen that at high blowdown rate (e.g., Condition 1), the concentration of chemical constituent in the circulating water does not increase significantly with time for either the mass generation or loss scenario. At low blowdown rate (e.g., Condition 6), however, the concentration of chemical constituent in the circulating water increases significantly with time. After a long period, the concentration becomes nearly constant. As time increases, the term $e^{-(t-t_0)\left(\frac{Q_b}{V}\right)}$ tends to 0 and concentration tends to ($\frac{Q_m C_{m,i}}{Q_b} + \frac{k_0 V}{Q_b}$). There is not any significant difference observed for positive k_0 values (corrosion) and negative k_0 values (scaling). This can be explained from Equation 4.1.10, where it may be seen that there is no k_0 value in the exponential term. Hence, it cannot affect the concentration significantly with increase of time. For this reason, to get significant variation due to positive and negative k_0 values, the values of k_0 must be large.

Results of calculations of blowdown versus time for different cycles of concentration and zero order generation of chemical constituents are shown in Figure 4.1.7. It is found that blowdown rate is required to increase as time increases in order to maintain a particular cycle of concentration. Blowdown rate, however, tends to be constant as time increases for a particular cycle of concentration (Equation 4.1.13).

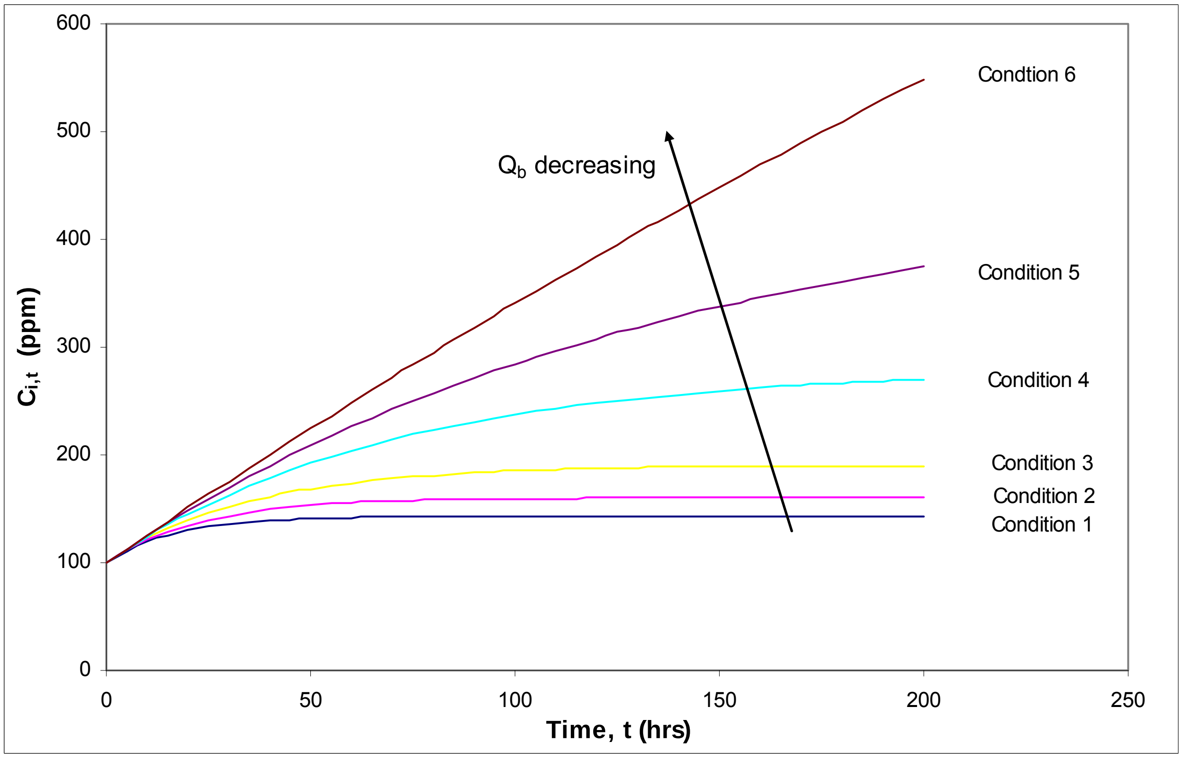

Figure 4.1.5 Concentration vs. time for k_0 = +0.01 ppm per hr in zero order generation model calculated with Equation 4.1.10 for six operational conditions shown in Table 4.1.2

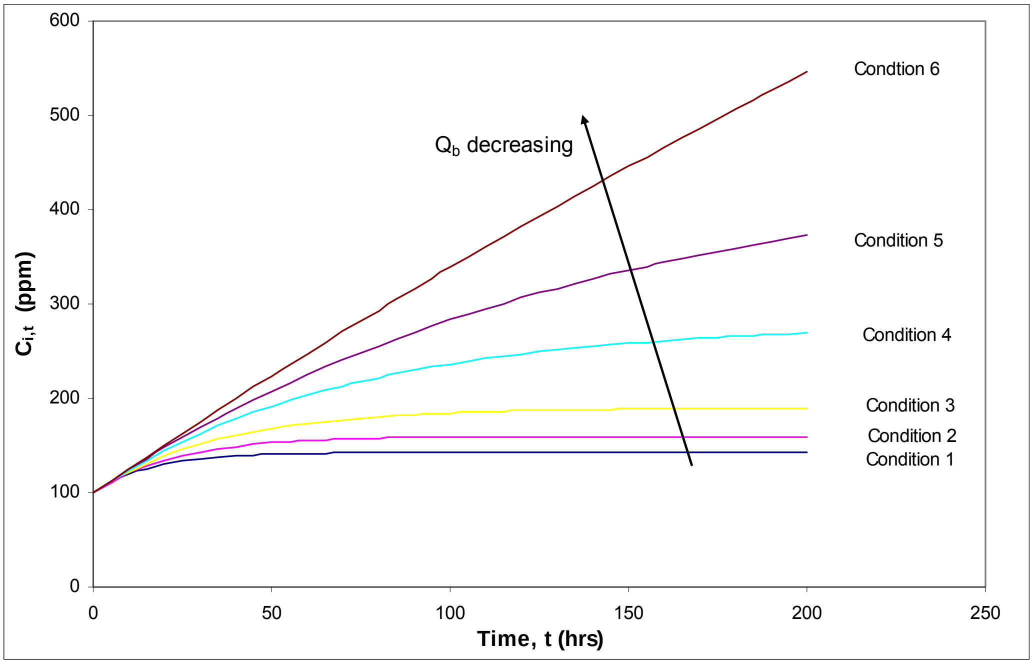

Figure 4.1.6 Concentration vs. time for k_o = -0.01 ppm per hr in zero order generation model calculated with Equation 4.1.10 for six operational conditions shown in Table 4.1.2

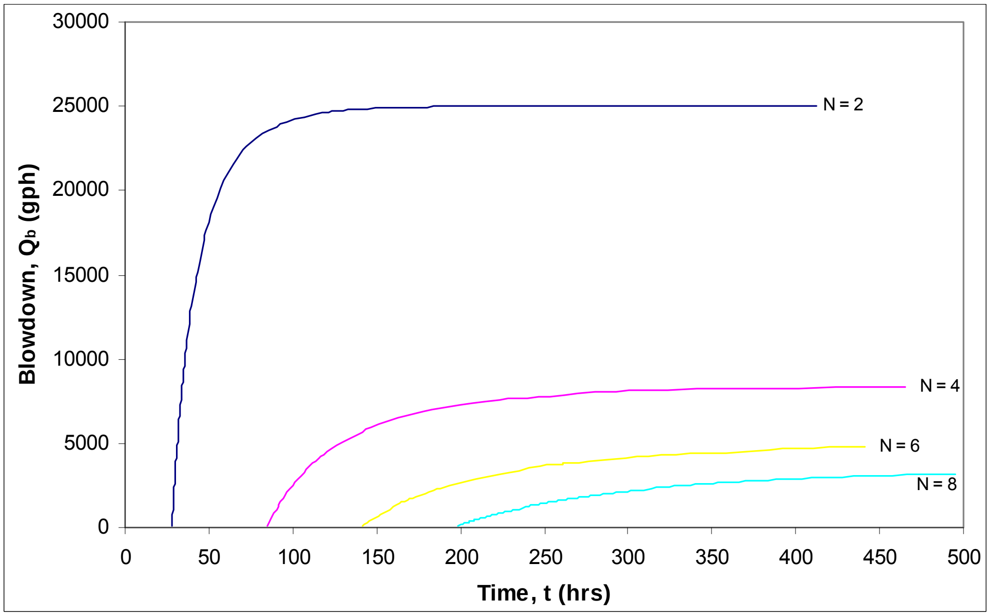

Figure 4.1.7 Blowdown vs. time for different cycles of concentration for k_o = +1 ppm per hr in zero order generation model calculated with Equation 4.1.11 for Q_e = 18000 gph, $C_{m,i} = C_{i,0}$ = 100 ppm

From Figure 4.1.8, where cycles of concentration are plotted versus time for different k_0 values with zero order mass generation/loss rate (Figure 4.1.8), it may be seen that cycles of concentration also increase with increase of time for positive k_0 values (corrosion) and decrease for negative k_0 values (scaling).

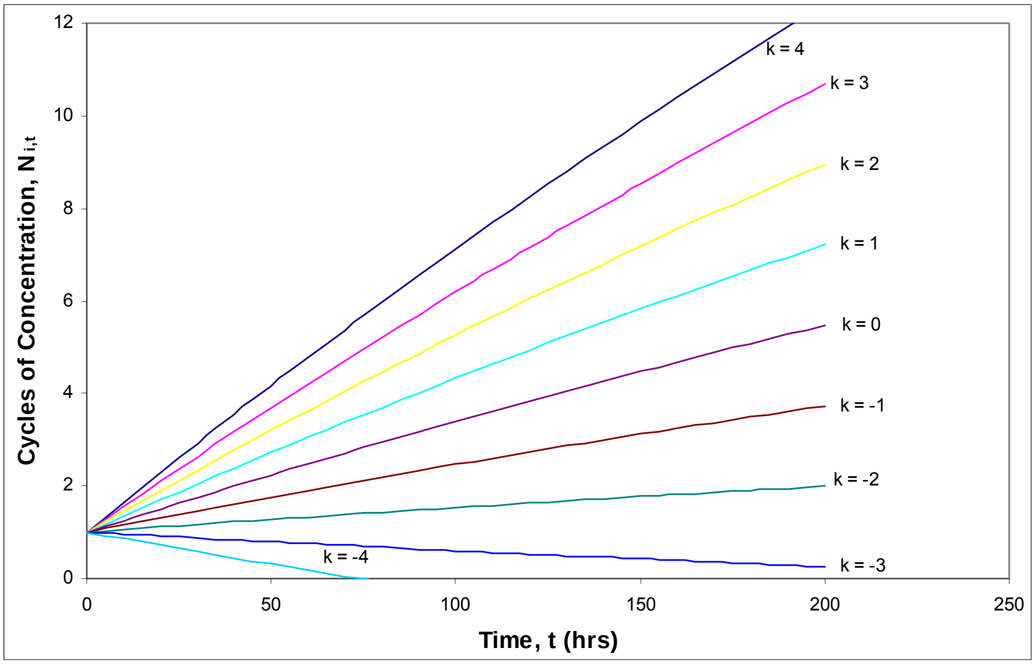

Figure 4.1.8 Cycles of concentration vs. time for different k_0 values for condition 6 in zero order generation model calculated with Equation 4.1.11 for Q_e= 18000 gph, $C_{m,i}$=$C_{i,0}$= 100 ppm.

First Order Generation Model

In the first order generation model, the rate of chemical generation or loss due to corrosion and scaling was assumed to be dependent on the concentration of the particular chemical in the cooling water. Thus,

$$r_{c,i} = k_1 C_i \tag{4.1.14}$$

where $r_{c,i}$ = mass rate of generation of chemical constituent "i" due to scaling or corrosion, $ML^{-3}T^{-1}$

C_i = concentration of chemical constituent "i" in circulating water, blowdown and drift, ML^{-3}

k_1 = rate constant, T^{-1}

Now, the mass balance of chemical constituent of “i” via Equation 4.1.1 yields

$$C_{i,t} = -\frac{Q_m C_{m,i}}{k_1 V - Q_b} + \left(C_{i,0} + \frac{Q_m C_{m,i}}{k_1 V - Q_b} \right) e^{(t-t_0)\left(k_1 - \frac{Q_b}{V}\right)} \tag{4.1.15}$$

$$N_{i,t} = -\frac{Q_m}{k_1 V - Q_b} + \left(\frac{C_{i,0}}{C_{m,i}} + \frac{Q_m}{k_1 V - Q_b} \right) e^{(t-t_0)\left(k_1 - \frac{Q_b}{V}\right)} \tag{4.1.16}$$

When time increases and if the term $\left(k_1 - \frac{Q_b}{V}\right)$ < 0, then

$$N_{i,t} = -\frac{Q_m}{k_1 V - Q_b}. \tag{4.1.17}$$

$$Q_b = \frac{Q_e + k_1 V N_{i,t}}{N_{i,t} - 1} \tag{4.1.18}$$

Simulations performed with Equation 4.1.15 for positive k_1 values in the first order generation model are presented in Figure 4.1.9 where it may be seen that the shape of the concentration versus time curve changes significantly from high blowdown rate to low blowdown rate. In the case of Conditions 1, 2, 3 and 4 (Table 4.1.2), concentration tends to be constant with increase of time. For Conditions 5 and 6, however, concentration tends to increase to infinity with time. At high blowdown, the value of $\left(k - \frac{Q_b}{V}\right)$ is negative which means that $e^{(t-t_0)\left(k - \frac{Q_b}{V}\right)}$ tends toward zero with the increase of time and $C_{i,t}$ tends to a constant value of $(-\frac{Q_m C_{m,i}}{kV - Q_b})$. At low Q_b, the value of $\left(k - \frac{Q_b}{V}\right)$ is positive which means that $e^{(t-t_0)\left(k - \frac{Q_b}{V}\right)}$ tends to be infinite with increase of time.

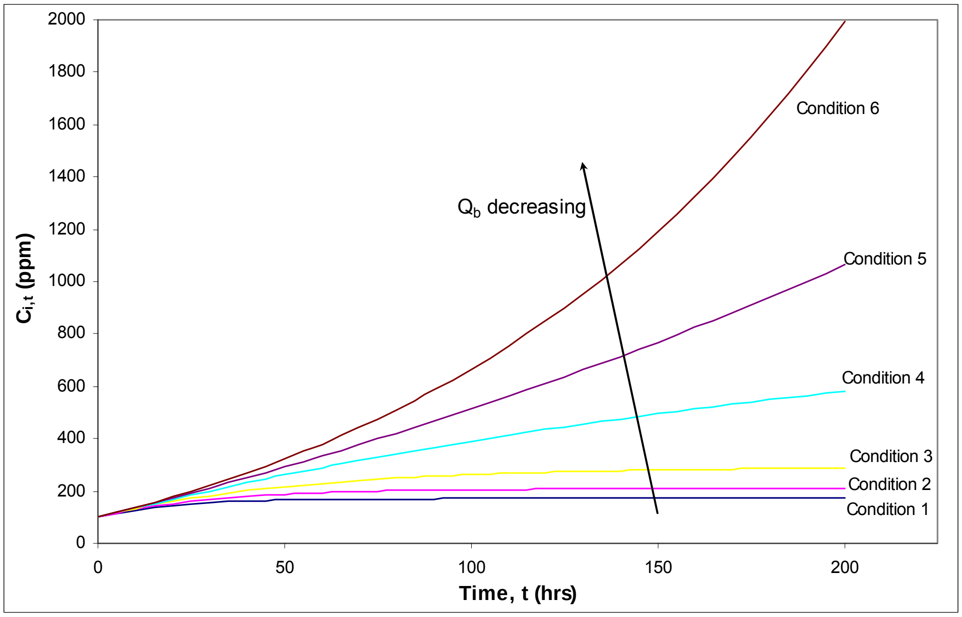

Figure 4.1.9 Concentration vs. time for k_1 = + 0.01 per hr in first generation model calculated with Equation 4.1.15 for six operational conditions shown in Table 4.1.2

In the case of negative k_1 value, reflecting mass loss, simulation results shown in Figure 4.1.10 reveal that the shape of the concentration versus time curve remains the same with increase of blowdown. In this case, $\left(k - \frac{Q_b}{V}\right)$ is negative irrespective of the value of $Q_{b,}$ so, concentration tends to a constant value of $(-\frac{Q_m C_{m,i}}{kV - Q_b})$ with increase of time irrespective of the value of Q_b.

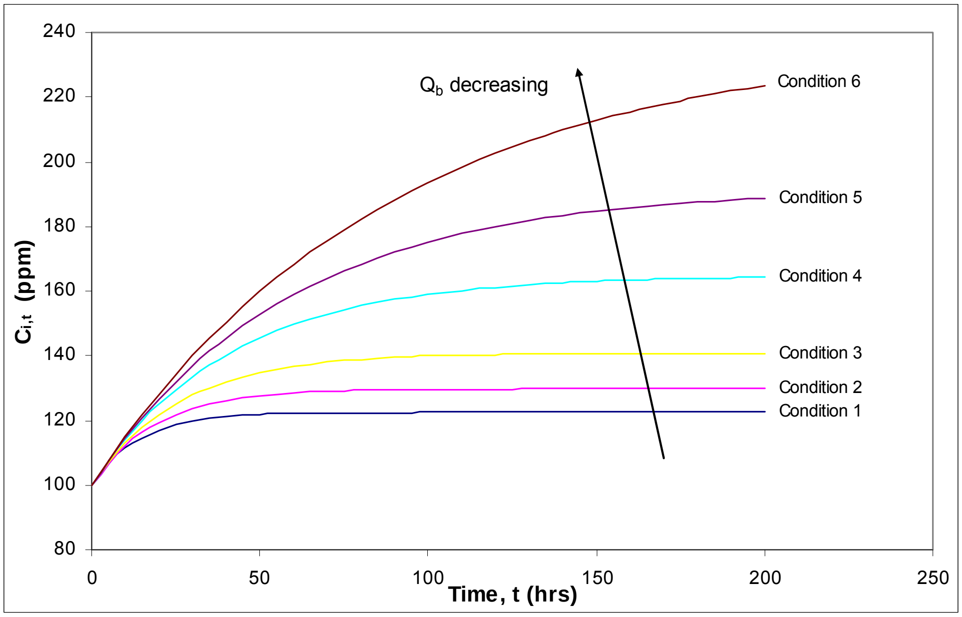

Figure 4.1.10 Concentration vs. time for k_1 = - 0.01 per hr in first generation model calculated with Equation 4.1.15 for six operational conditions shown in Table 4.1.2

Calculations of blowdown versus time for different cycles of concentration and first order generation (Figure 4.1.11) show that the blowdown rate is required to increase as time increases in order to maintain a particular cycle of concentration. The required blowdown rate, however, approaches a constant value as time increases for a particular cycle of concentration (Equation 4.1.18).

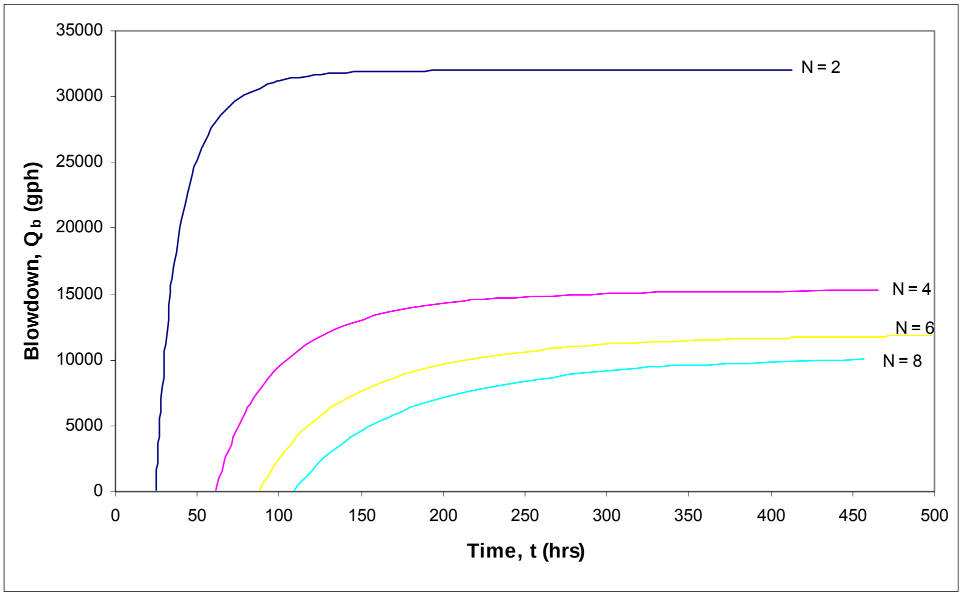

Figure 4.1.11 Blowdown vs. time for different cycles of concentration for k_1 = +0.01 per hr in first order generation model calculated with Equation 4.1.16 for Q_e = 18000 gph, $C_{m,i}$ = $C_{i,0}$ = 100 ppm

From the cycles of concentration versus time for different k_1 values in the case of the first order generation models (Figure 4.1.12), it may be seen that cycles of concentration also increase with increase of time for positive k_1 values (corrosion) and decrease for negative k_1 values (scaling).

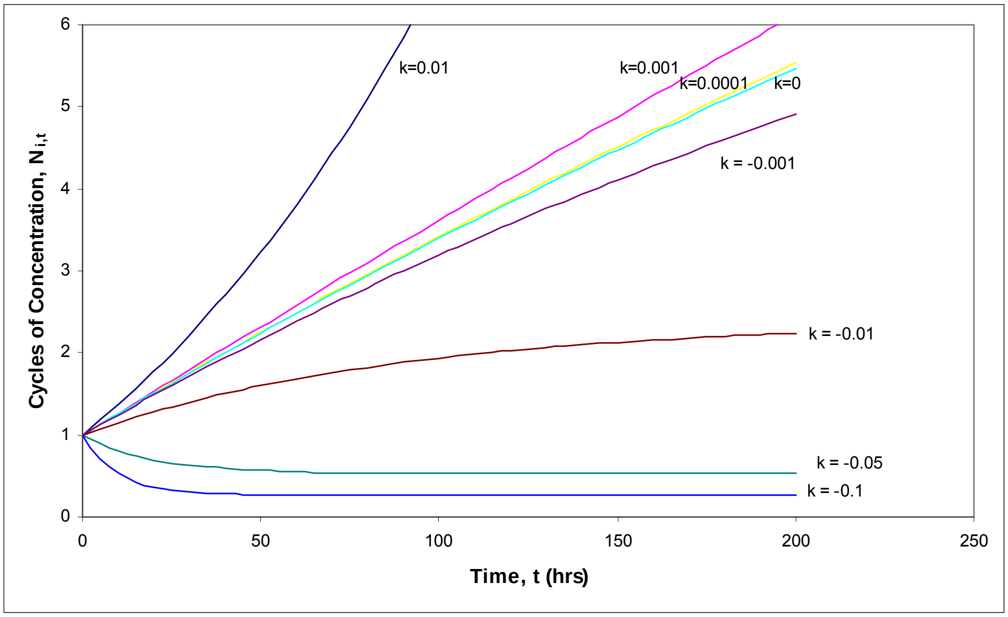

Figure 4.1.12 Cycles of concentration vs. time for condition 6 in first order generation model calculated with Equation 4.1.16 for Q_e= 18000 gph, $C_{m,i}$=$C_{i,0}$= 100 ppm

Combination of both Scaling Loss and Corrosion Generation Models

Another version of the chemical mass balance model was developed to investigate the combined effects of scaling and corrosion, and the effects of scaling and corrosion proceeding according to rate models not of the same order. Scaling mass loss was considered to be a first order process and corrosion mass generation was considered to be a zero order process. The chemical mass generation due to corrosion was expressed by:

$$(r_{c,i})_{Corrosion} = k_0 \qquad (4.1.19)$$

where k_0 = a rate constant, $ML^{-3}T^{-1}$

The chemical mass loss due to scaling was expressed by:

$$(r_{c,i})_{scaling} = k_1 C_i \qquad (4.1.20)$$

where k_1 = a rate constant, T^{-1}

C_i = Concentration of chemical constituent "i" in the circulating water

The net chemical mass generation is thus:

$$r_{c,\,i} = (r_{c,i})_{corrosion} + (r_{c,i})_{scaling} \qquad (4.1.21)$$

$$r_{c,i} = k_0 + k_1 C_i \tag{4.1.22}$$

The mass balance of chemical constituent "*i*" via Equation 4.1.1 yields

$$C_{i,t} = -\left(\frac{Q_m C_{m,i} + k_0 V}{k_1 V - Q_b}\right) + \left(C_{i,0} - \frac{Q_m C_{m,i} + k_0 V}{k_1 V - Q_b}\right) e^{(t-t_0)\left(k_1 - \frac{Q_b}{V}\right)} \tag{4.1.23}$$

$$N_{i,t} = -\left(\frac{Q_m C_{m,i} + k_0 V}{(k_1 V - Q_b) C_{m,i}}\right) + \left(\frac{C_{i,0}}{C_{m,i}} - \frac{Q_m C_{m,i} + k_0 V}{(k_1 V - Q_b) C_{m,i}}\right) e^{(t-t_0)\left(k_1 - \frac{Q_b}{V}\right)} \tag{4.1.24}$$

Equation 4.1.24 indicates that to maintain a particular cycle of concentration, the blowdown must be changed accordingly. When time increases, the term $e^{(t-t_0)\left(k_1 - \frac{Q_b}{V}\right)}$ tends to zero since $\left(k_1 - \frac{Q_b}{V}\right) < 0$ and

$$N_{i,t} = -\left(\frac{Q_m C_{m,i} + k_0 V}{(k_1 V - Q_b) C_{m,i}}\right) \tag{4.1.25}$$

$$Q_b = \frac{Q_e + k_1 V N_{i,t}}{N_{i,t} - 1} + \frac{k_0 V}{(N_{i,t} - 1) C_{m,i}} \tag{4.1.26}$$

Equation 4.1.23 represents the combined effect of both zero order corrosion and first order scaling on concentration of chemical constituent *i* in the circulating cooling water system. If we consider no first order generation, i.e. $k_1 = 0$, the result is the zero order generation model Equation 4.1.10 from Equation 4.1.23. Likewise, if we consider no zero order generation, i.e. $k_0 = 0$, the result is the first order generation model Equation 4.1.15 from Equation 4.1.23.

Equation 4.1.24 represents the combined effect of both zero order corrosion and first order scaling on blowdown requirements for particular cycles of concentration. If we consider no first order generation, i.e. $k_1 = 0$, the result is the zero order generation model Equation 4.1.10 from Equation 4.1.24. Likewise, if we consider no zero order generation, i.e. $k_0 = 0$, the result is the first order generation model Equation 4.1.16 from Equation 4.1.24**.**

4.1.4 Sensitivity Analysis of the Mass Balance Model

In this section, the sensitivity of the chemical mass balance model including zero order and first order generation/loss models has been analyzed with respect to different values of the rate constants k_o and k_1. The sensitivity of concentration with respect to rate constant has been calculated by using the following formula (Ramaswami et al., 2005):

$$S_1 = \left.\frac{\partial y}{\partial x_1}\right|_{x_1^*, x_2^*} \times \frac{x_1^*}{y^*} = \left.\frac{\partial \ln y}{\partial \ln x_1}\right|_{x_1^*, x_2^*} \tag{4.1.27}$$

where S_1 = dimensionless sensitivity

x_1= model inputs

nominal or base case scenario, $y^* = f(x_1^*, x_2^*)$

For both zero order and first order generation models, dimensionless sensitivity of concentration of chemical constituent in the circulating water with respect to rate constants has been evaluated. Equations 4.1.28 and 4.1.29 are the modified versions of Equation 4.1.27 for the zero order model and first order model:

$$S = \frac{\partial \ln C_{i,t}}{\partial \ln k_0} \tag{4.1.28}$$

$$S = \frac{\partial \ln C_{i,t}}{\partial \ln k_1} \tag{4.1.29}$$

where S = dimensionless sensitivity of concentration of chemical constituent with respect to rate constant, and $C_{i,t}$ = concentration of chemical constituent “i” in the circulating water after time t, calculated by Equation 4.1.10 for the zero order model and 4.1.15 for the first order model.

4.1.4.1 Sensitivity Analysis for Zero Order Generation Model

In calculating sensitivity, simulations for the six different conditions listed in Table 4.1.2 were used. It was determined from the sensitivity simulations that concentration increases linearly with increase of k_o value, which is evident from Equation 4.1.10 where there is a linear relationship between $C_{i,t}$ and k_o.

Figure 4.1.13 shows the variation of dimensionless sensitivity of concentration of chemical constituent “i” with respect to k_o with time for six different conditions in the zero order generation model. From this figure, it may be seen that dimensionless sensitivity of concentration for k_o increases with time for each condition, though the rate of increase of sensitivity decreases with time and tends to be constant. Also, proceeding from Condition 1 to Condition 6, i.e., low to high cycles of concentration, sensitivity increases with increase of cycles of concentration, though initial sensitivity seems nearly equal for all conditions.

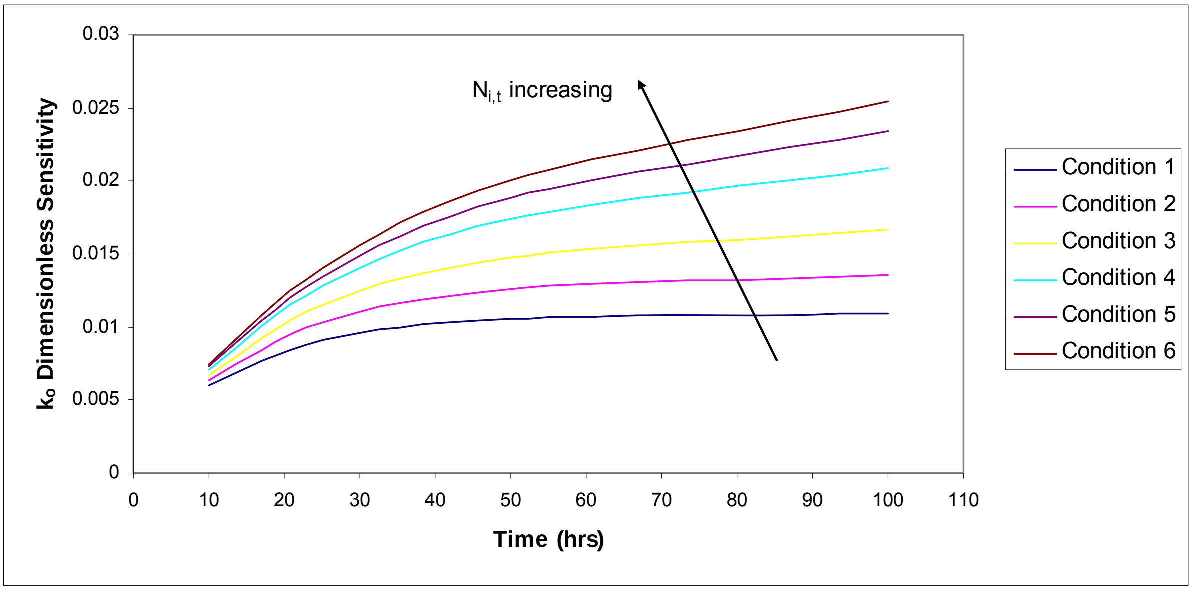

Figure 4.1.13 k_o dimensionless sensitivity vs. time for 6 different conditions in Table 4.1.2 for zero order generation model

4.1.4.2 Sensitivity Analysis for First Order Generation Model

Sensitivity analyses were also performed for the mass balance model with first order mass generation. It was determined from the sensitivity simulations that concentration increases with increase of k_1 values, but unlike the results with the zero order generation model, the increase is not linear. As time progresses, the rate of increase of concentration with time increases sharply. From the first order generation model, Equation 4.1.15, it may be seen that unlike the situation with the zero order generation model, k_1 is associated with time in the exponential term. Thus, as time increases, the rate of increase of concentration also increases.

Figure 4.1.14 shows the variation of dimensionless sensitivity of concentration of chemical constituent “i” with respect to k_1 with time for the six different conditions and the first order generation model. From this figure, it may be seen that dimensionless sensitivity with respect to k_1 increases linearly with time for each condition investigated. Also, from Condition 1 to Condition 6, i.e., low to high cycles of concentration, sensitivity of k_1 increases with increase of cycles of concentration.

Overall, it is seen that sensitivity of the first order generation model results to changes in rate constant k_1 is much higher than that of zero order generation model for rate constant k_o. It can therefore be concluded that the first order generation model is more sensitive than the zero order generation model with respect to the rate constant value.

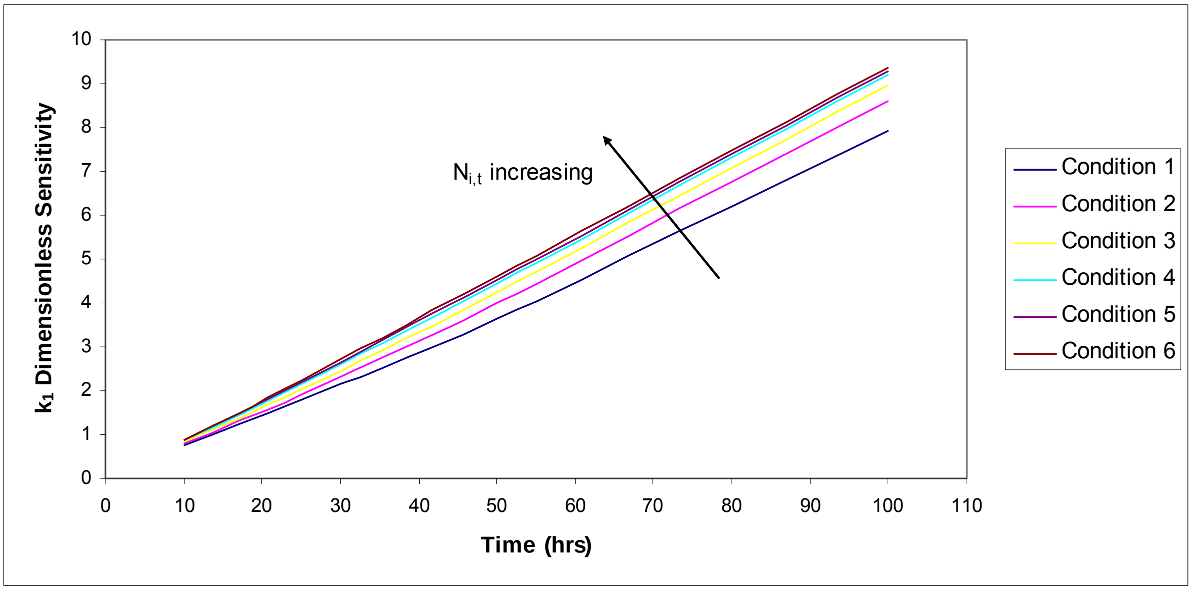

Figure 4.1.14 k_1 dimensionless sensitivity vs. time for 6 different conditions in Table 2 for first order generation model. Overall, it is seen that sensitivity of the first order generation model results to changes in rate constant k_1 is much higher than that of zero order generation model for rate constant k_o. It thus can be concluded that first order generation model is more sensitive than zero order generation model with respect to generation rate constant.

4.1.5 Application of Mass Balance Model for Pilot Scale Cooling Tower Simulation

In this section, the chemical mass balance model was applied to simulate the operation of a pilot scale cooling tower and to determine the effects of operating conditions, of particular interest were the operating parameter values needed to achieve a particular cycle of concentration. The following operating parameters were determined through simulation:

- Blowdown flow rate
- Makeup flow rate
- Time to start blowdown
- Time to achieve steady state condition

For simulation of field startup operations with a pilot-scale cooling tower, corrosion and scaling effects were not considered. Hence, for these simulations the model employed was Case 1: no chemical mass generation or loss due to corrosion or scaling.

4.1.5.1 Model Simulations

For the pilot scale cooling tower simulations, the following operating conditions were assumed: circulating water flow rate = Q_c= 3 gpm; and temperature drop in the cooling tower =

$\Delta T = 10^0$ F. From this, evaporation rate Q_e was estimated as 1.53 gph using Equation 4.1.30 from Perry (1997):

$$Q_e(gph) = 0.00085(\frac{1}{°F}) \times Q_c(gph) \times \Delta T(°F) \tag{4.1.30}$$

Estimated drift Q_d was 0.009 gph using Equation 4.1.31 from Tchobanoglous et al., (2003).

$$Q_d(gph) = 0.005 Q_c(gph)/100 \tag{4.1.31}$$

The estimated drift was 170 times less than evaporation rate. For this reason, drift was neglected in the model simulations. Total volume in the recirculating cooling tower was assumed as 22 gallons. These operating parameters were based on pilot-scale cooling towers employed in this study to investigate effectiveness of corrosion, scaling, and biofouling control in field tests with impaired waters.

For model simulations, two operational approaches for pilot cooling tower startup were considered:

- Approach 1: Apply the steady state required blowdown and makeup to achieve a certain cycle of concentration at the start of system operation.
- Approach 2: Apply the steady state required blowdown and makeup after a period of time is allowed until blowdown is initiated after a certain cycle of concentration is attained in the system.

Approach 1 for Pilot Cooling Tower Startup Simulation

In Approach 1, the following steps were followed to predict operational parameters using chemical mass balance model for the circulating cooling system:

- Calculate the steady state blowdown and makeup requirements to achieve a particular cycle of concentration from Equations 4.1.7 and 4.1.8.
- Apply the steady state blowdown and makeup water requirements at the starting of system operation.
- Use the calculated steady state blowdown and makeup in Equation 4.1.5 to plot cycles of concentration vs. time and determine the time to achieve steady state conditions from the plot.

Approach 2 for Pilot Cooling Tower Startup Simulation

In Approach 2, the following steps were followed to predict operational parameters using the chemical mass balance model for the circulating cooling system:

- To increase cycles of concentration, blowdown is not removed at the initial stage of operation. Makeup water is provided, but there is no blowdown until four cycles of concentration are achieved. Since there is no blowdown, makeup water flow rate should be equal to evaporation rate. Consequently, calculate the time when blowdown will be required to begin in order to maintain the desired cycle of concentration from Equation 4.1.30. Equation 4.1.30 is obtained by disregarding blowdown flow rate in the Equation 4.1.3.

$$t = t_0 + \frac{V}{Q_m}(N_{i,t} - \frac{C_{i,0}}{C_{m,i}}) \tag{4.1.30}$$

- After the initial time to build up concentrations in the system to the desired cycle of concentration, blowdown will be required. Then the steady state blowdown and makeup requirements will be applied to the system, and can be calculated by using same Equations 4.1.7 and 4.1.8 as in Approach 1.
- Use the calculated steady state blowdown and makeup in Equation 4.1.5.to plot cycles of concentration vs. time and determine steady state time from the plot.

4.1.5.2 Results and Discussion of the Mass Balance Model Simulations

From Equations 4.1.7 and 4.1.8, steady state blowdown and makeup flow rate requirements were calculated for the pilot scale cooling tower. Steady state blowdown and makeup flow rate requirements vs. cycles of concentration are plotted for the pilot scale cooling tower in Figure 4.1.15. From this plot, it may be seen that both steady state blowdown and makeup flow rate requirements decrease as cycles of concentration increases.

In Approach 1, steady state blowdown and makeup flow rate requirements were used for desired cycles of concentration 2, 4 and 6. Using Equation 4.1.5, cycles of concentration vs. time were calculated (Figure 4.1.16). Calculated operational parameters for the pilot scale cooling tower applying Approach 1 are summarized in Table 4.1.3. From Figure 4.1.16 and Table 4.1.3, it may be seen that the pilot scale cooling tower system was predicted to require approximately 34 hours, 117 hours and 216 hours to achieve 2, 4 and 6 cycles of concentration respectively if Approach 1 is followed in pilot-scale system startup.

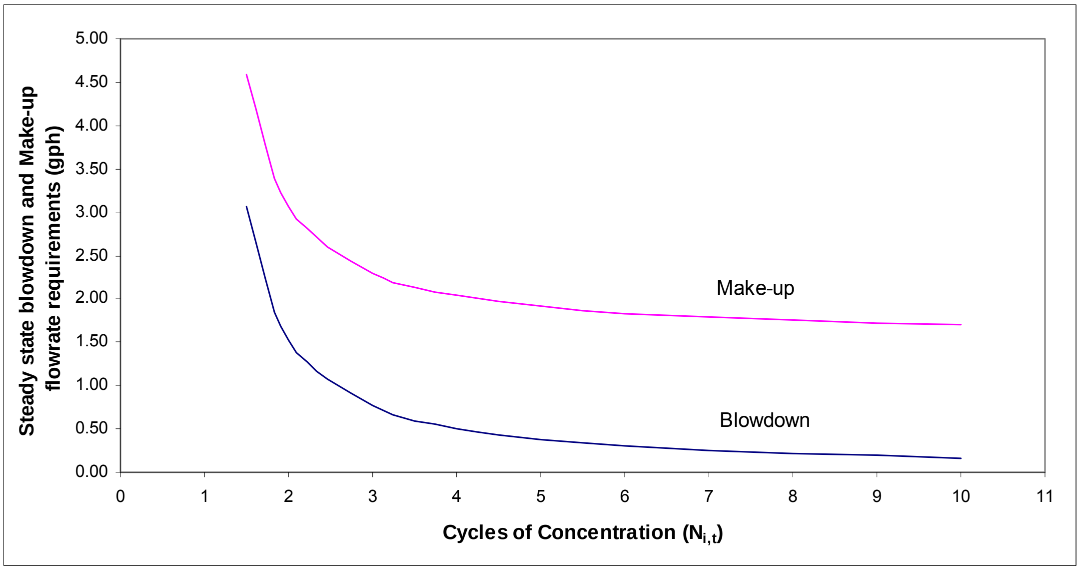

Figure 4.1.15 Steady state blowdown and makeup flow rate requirements vs. cycles of concentration considering no chemical generation or loss calculated with Equations 4.1.7 and 4.1.8 using pilot scale cooling tower system data.

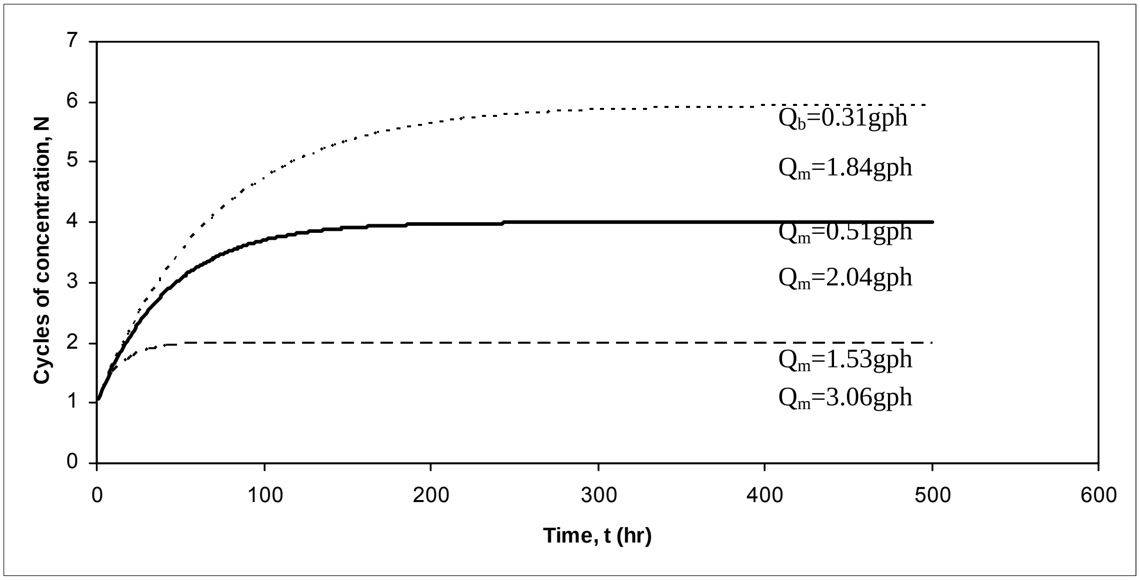

Figure 4.1.16 Cycles of concentration vs. time applying steady state blowdown and makeup at the start of the system calculated with Equation 4.1.5 using pilot scale cooling tower system data (Approach 1).

Table 4.1.3 Summary of operational parameters for pilot scale cooling tower applying Approach 1

		Cycles of Concentration ($N_{i,t}$) after											
Makeup, Q_m (gph)	**Blowdown, Q_b (gph)**	**50 hrs**	**100 hrs**	**150 hrs**	**200 hrs**	**250 hrs**	**300 hrs**	**350 hrs**	**400 hrs**	**450 hrs**	**500 hrs**	**550 hrs**	**600 hrs**
3.06	1.53	1.87	1.98	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00
2.04	0.51	2.49	3.24	3.62	3.81	3.90	3.95	3.98	3.99	4.00	4.00	4.00	4.00
1.84	0.31	2.69	3.80	4.53	5.01	5.33	5.54	5.67	5.76	5.82	5.86	5.89	5.90

In Approach 2, cycles of concentration vs. time to start blowdown were determined by using the pilot scale cooling tower system specifications in Equation 4.1.30. As shown in Figure 4.1.17, it was found that there is a linear relationship between cycles of concentration and the time to start blowdown. The slope of the line is Q_m/V.

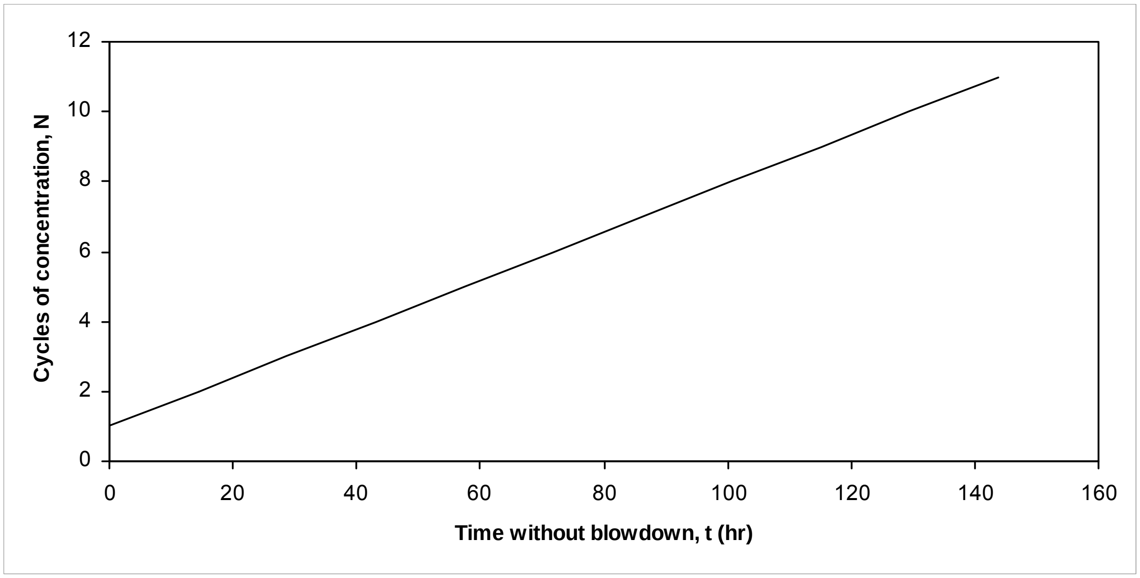

Figure 4.1.17 Cycles of concentration vs. time to start blowdown considering no chemical generation or loss calculated with Equation 4.1.28 using pilot scale cooling tower system data.

For Approach 2, which involves starting blowdown after the desired cycles of concentration are achieved, steady state blowdown and makeup flow rate requirements were determined for 2, 4, and 6 cycles of concentration using Equation 4.1.5. Calculated operational parameters for the pilot scale cooling tower applying Approach 2 are summarized in Table 4.1.4 and also shown in Figure 4.1.18. From Figure 4.1.18 and Table 4.1.4, it may be seen that the pilot scale cooling tower system was predicted to require about 14.4 hours, 43.1 hours and 71.9 hours to achieve 2, 4 and 6 cycles of concentration respectively if Approach 2 is followed in pilot-scale system startup.

Table 4.1.4 Summary of operational parameters for pilot scale cooling tower applying Approach 2.

Cycles of concentration ($N_{i,t}$)	Steady state required blowdown, Q_b (gph)	Steady state required makeup, Q_m (gph)	Time to start blowdown (hrs)	Time to achieve steady state condition (hrs)
2	1.53	3.06	24	24
4	0.51	2.04	73	73
6	0.31	1.84	121	121

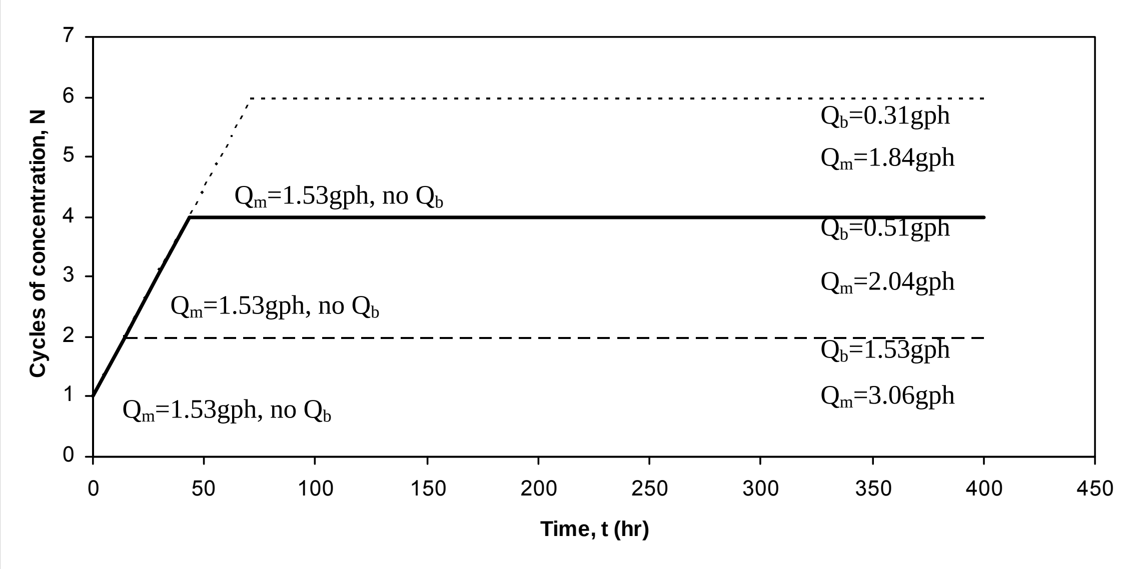

Figure 4.1.18 Cycles of concentration vs. time applying steady state blowdown and makeup after the time when blowdown will be required calculated with Equations 4.1.5, 4.1.7, 4.1.8 and 4.1.28 using pilot scale cooling tower system data (Approach 2)

If the steady state makeup and blowdown requirements are applied to achieve a particular cycle of concentration after allowing a desired concentration increase prior to starting blowdown (Approach 2), the steady state condition can be achieved quickly. However, this approach requires that monitoring be conducted to determine when the particular cycle of concentration is achieved.

If the system is started with the required steady-state makeup and blowdown initially (Approach 1), the main advantage is that it will not be necessary to change any intermediate system condition to achieve the desired cycle of concentration. The main shortcoming of this approach, however, is that it will take a longer time than Approach 2.

4.1.5.3 Examination of simulation results by the data of the pilot-scale field testing

Figure 4.1.19 shows a comparison of the cycles of concentration vs. time plots from chemical mass balance model simulation and results from pilot-scale field testing using secondary and tertiary treated municipal wastewater in Franklin Township Municipal Sanitary Authority in July – August, 2008. This testing and the results obtained are described in detail in Chapter 5. The field testing data are from total Mg concentration monitoring in three pilot scaling cooling towers (CTA, CTB, and CTC) operating under the conditions used in the model simulations but with different chemical treatments to control corrosion, scaling, and biofouling. Mg was chosen because it was found that Mg had negligible precipitation and behaved as a nonreactive, conservative constituent in the field testing. Cycles of concentration of Mg were calculated as $C_{Mg,b}/C_{Mg,m}$. Figure 4.1.19 shows good agreement between model simulation and the field testing. In model simulation, 4 cycles of concentration were reached in about two days, which was also the case in the field testing. In the field testing, there was no blowdown in the first two days for 4 cycles of concentration to be reached. After that, regular blowdown was initiated. This corresponded to Approach 2 used in the model simulations.

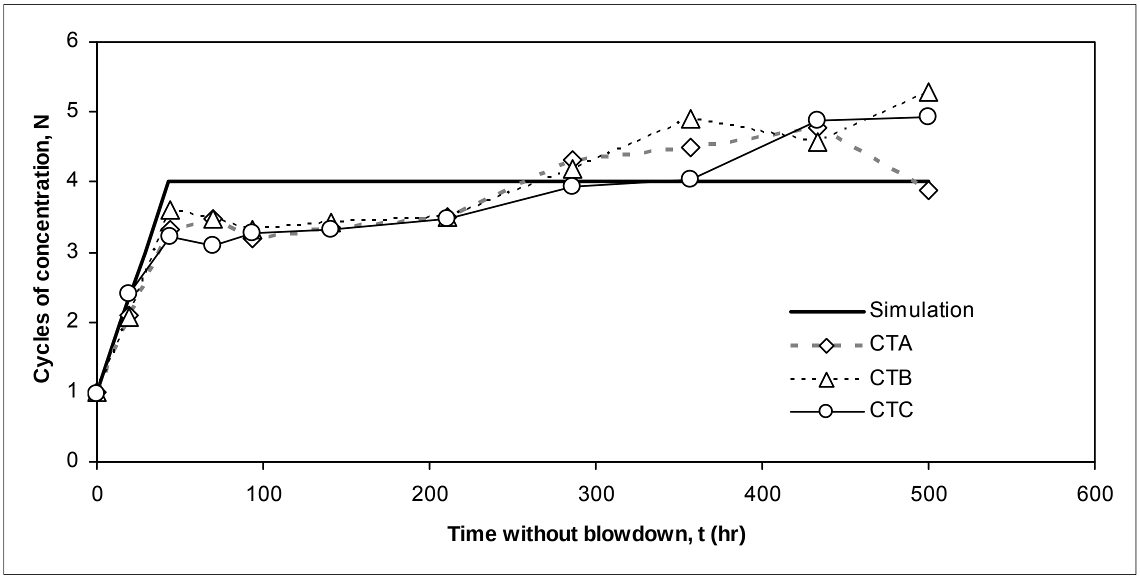

Figure 4.1.19 Comparison of the cycles of concentration vs. time results from chemical mass balance model simulation and results from pilot-scale field testing using secondary and tertiary treated municipal wastewater at the Franklin Township Municipal Sanitary Authority in July – August, 2008. The field testing data are from total Mg concentration monitoring in three pilot scaling cooling towers (CTA, CTB, and CTC) operating under conditions used in the model simulations. Mg was chosen because it was found that Mg had negligible precipitation and was conservative in the field testing

4.1.6 Limitations of Chemical Mass Balance Modeling for a Recirculating Cooling System

The chemical mass balance model was developed to simulate water chemistry evolution and control in a recirculating cooling system, and to determine appropriate conditions for pilot scale cooling tower operation. In the model, the volume of water in the cooling system was described as a completely stirred tank reactor (CSTR); effects of local chemical inputs and losses, and of transport were not considered. Effects of passage through the heat exchanger and cooling tower were not considered separately. One system consisting of a recirculating water loop that includes both the heat exchanger and the cooling tower was assumed. Chemical inputs from corrosion and chemical losses from scaling were modeled empirically.

4.1.7 Summary and Conclusions

A chemical mass balance model has been developed for a recirculating cooling system, including consideration of chemical mass loss by scaling and mass input by corrosion.

The chemical mass balance modeling has provided a number of useful insights into chemical behavior in a recirculating cooling water system, and has also enabled predictions of water chemistry evolution. The model demonstrates the well known relationship between blowdown rate and cycles of concentration, i.e., that blowdown rate required decreases with increase of cycles of concentration. Simulations with the model also indicate, however, that chemical mass generation by corrosion and loss by scaling can significantly affect the required blowdown. It usually will not be beneficial to operate above 10 cycles of concentration as additional reductions in blowdown volume are small at high cycles of concentration.

4.2 Chemical Equilibrium Modeling of Scaling Potentials

Abstract

Selection of appropriate cycles of concentration (CoC) is a prerequisite for successful operation of recirculating cooling towers that use impaired waters because solid precipitation and subsequent mineral scaling depend strongly on CoC. After evaluation of three chemical equilibrium models, MINEQL+ (Schecher and McAvoy, 1999, version 4.5) was used to study the potential for precipitation at different CoC levels. The chemistry and potential for precipitation of the four impaired waters studied in this project were modeled by MINEQL+ under conditions relevant to cooling tower operations. The modeling results revealed that the power plant ash pond effluent would produce the least amount of mass precipitation while the passively treated mine drainage would produce the greatest amount, particularly when the CoC was increased beyond 5. Solids production from the secondary treated municipal wastewater was relatively low. For both of the mine drainage waters evaluated, the ratio of total precipitated solids to total dissolved solids dramatically increased for CoC 5-7, indicating that excessive precipitates would result once the cycles of concentration exceeded 5. It was thus decided to conduct pilot-scale cooling tower tests at CoC < 5.

4.2.1 Introduction

Mineral precipitation and deposition in water-based cooling systems occur when water becomes supersaturated with regard to its mineral constituents. The supersaturation condition that leads to solid precipitation most commonly occurs due to changes in solution temperature, addition of chemicals, or loss of water to evaporation. The amount and type of solids that will precipitate from the solution can be calculated based on thermodynamic principles, assuming equilibrium conditions. Chemical equilibrium calculations were used as a predictive tool in this project to evaluate the potential for precipitation/scaling of four impaired waters considered for use as makeup water for recirculating cooling systems.

4.2.2 Equilibrium Model Selection of MINEQL+

In this project, three chemical equilibrium models were evaluated and compared for the ease of use and their ability to provide comprehensive assessment of the impaired water chemistries relevant for cooling tower use. The models investigated were MINEQL+ (version 4.5) (Schecher and McAvoy, 1992; 1999); Visual MINTEQ (version 2.52) (Gustafsson, 2007); and WinSEQUIL (version 2.0) (EPRI, 1998).

The MINEQL program was originally designed as a research tool in aquatic chemistry for inorganic chemical speciation (Morel and Morgan, 1972; Westall et al., 1976) and subsequently has been applied to study a wide range of engineered and natural systems. The original model was improved with the development of MINEQL+ (Schecher and McAvoy, 1992; 1999) by expanding the types and number of reactions considered, and incorporating a modern graphical user interface. Visual MINTEQ (Serkiz et al., 1996) is the MS Windows version of MINTEQA2 (Allison et al., 1991) that was originally developed by the US EPA for the calculation of metal speciation and solubility equilibria for natural waters. Both MINEQL+ and MINTEQ incorporate an extensive thermodynamic database that allows for the computation of chemical speciation, solubility, and equilibria of solid and dissolved phases of minerals in aqueous solutions. MINEQL+ employs the same thermodynamic database developed and maintained for MINTEQ. The thermodynamic database utilized by these two models is not only extensive, but also well documented. Further, the database can be modified by the user as desired, e.g., to alter equilibrium constants or add new reactions. Both models have been used in equilibrium and speciation calculations in the study of natural water chemistry as well as water chemistry in water and wastewater treatment and reuse systems (Twiss et al., 2001; Unsworth et al., 2006; Cloutier-Hurteau et al., 2007; Gallios and Vaclavikova, 2008).

While both MINTEQ and MINEQL+ are equally capable of modeling a broad range of species and chemical equilibria among different phases, a few functional differences exist. In MINEQL+, users can create a chemical system by adding tailor-made chemical components that are not readily available from the default list and by inputting new reaction data in a personalized thermodynamic database. In MINTEQ, such flexibility can only be achieved by direct modification of the incorporated thermodynamic database, which is cumbersome. In many situations precipitating solids of the same chemical composition may take several forms with varied degrees of hydration and crystallinity, not all of which are desired forms to be included in an equilibrium calculation that is intended to test solid formation under specific conditions. Moreover, under kinetically limited conditions, it is not uncommon that the thermodynamically most stable phases do not form in the time scale relevant to typical cooling tower operations. Turning off or deleting these solids tends to be a tedious endeavor within MINTEQ, while the Solids Mover function provided in MINEQL+ make solids/phases selection straightforward. In addition, the computation with MINTEQ does not always converge when the program is required to calculate pH based on mass balance and electroneutrality, and has more problems when required to take into account non-ideal effects based on ionic strength calculations.

WinSEQUIL (EPRI, 1998) was developed by the Electric Power Research Institute specifically to simulate the water chemistry in power plant cooling water systems. Its primary function is to predict the scaling (precipitation) tendency of cooling waters, based on the water composition, pH, and temperature. However, only a limited number of inorganic species are considered, including a total of six cations (Ca, Mg, Na, K, Fe, NH_3) and five anions (Cl, CO_3, NO_3, SO_4, PO_4) plus silicate (SiO_2). Further, only the oxidized Fe(III) form of iron is considered for modeling, and its associated equilibrium constants are not adjusted for temperature changes. Such a narrow scope of reactions and species greatly restricts its capacity for modeling waters that contain a broader range of chemicals or waters that contain Fe(II) such as abandoned mine drainage water. In addition, the model lacks the ability to calculate solution pH and alkalinity values independently. A predetermined pH has to be specified when an alkalinity value is given in order to run the model. WinSEQUIL does not support multi-run scenarios, such as repeated calculations for a broad range of pH values.

Critical assessment of the applicability of the three equilibrium models was performed under conditions relevant to a recirculating cooling system using impaired water. This assessment included evaluation of the pre-defined thermodynamic database supporting the computational engines of the models to determine if they were adequate for describing the chemistry of circulating cooling waters, and evaluation of the flexibility and ease of adjusting calculation parameters. Based on the evaluation, MINEQL+ stood out as a versatile and reliable program to satisfy the modeling needs, and was chosen for predicting the scaling potentials of the impaired waters studied in this project. The detailed modeling results presented in subsequent chapters of this report were derived from MINEQL+ simulations, unless stated otherwise.

4.2.3 Modeling Results

MINEQL+ modeling was used to calculate the scale forming potentials of the four impaired waters: Franklin Township municipal secondary treated wastewater effluent (MWW), passively treated Scrubgrass abandoned mine drainage (AMD), passively treated St. Vincent College abandoned mine drainage (AMD), and Reliant Energy ash sedimentation pond water effluent (APW). The water quality data used as inputs for the modeling of the four waters are summarized in Table 4.2.1.

The amount of solid precipitates formed at equilibrium for the four impaired waters operated at different cycles of concentration (CoC) is shown in Figure 4.2.1. Increased amount of solids is predicted to precipitate out of solution as the CoC increases due to greater supersaturation. Comparatively, the MWW generated the least amount of solids and the Scrubgrass AMD generated the most. Figure 4.2.2 shows the solution ionic strength (IS) at equilibrium after the precipitation reactions take place. The solution IS increased with increasing CoC for all the waters modeled. However, the extent of increase in IS for the same range of CoC varied noticeably for different waters as evidenced in Figure 4.2.2. The order of the calculated increase in IS for the four impaired waters, from the smallest to the greatest was as follows: Reliant Energy APW < Franklin Township MWW < St. Vincent AMD < Scrubgrass AMD. This ordering was consistent with experimental observations from bench-scale experiments (based on three waters- the Scrubgrass AMD water was not tested in lab). The ordering qualitatively reflects the “holding capacity” of the waters for dissolved solids. For the same range of CoC increase (from 1 to 11), the Reliant Energy APW was least capable while the Scrubgrass AMD was most capable.

Table 4.2.1. Summary of the chemical analysis data for the four impaired waters.

Analyte	Scrubgrass AMD[1]		St. Vincent AMD[1]		Franklin MWW[1]		Reliant Energy APW[1]		Analysis Limit[1]
	Filtered	Unfiltered	Filtered	Unfiltered	Filtered	Unfiltered	Filtered	Unfiltered	
Al	ND [2]	ND	ND	ND	ND	0.24	0.23	0.59	0.20
Ca	114.0	117.0	208.0	213.0	39.0	39.7	42.8	43.4	5.0
Fe [3]	61.2	68.0	ND	2.6	ND	0.72	ND	0.34	0.10
K	6.3	6.4	ND	ND	16.0	15.8	ND	ND	5.0
Mg	39.6	40.6	58.4	59.6	9.8	9.8	9.3	9.4	5.0
Mn	0.84	0.86	3.3	3.4	ND	0.3	ND	0.028	0.015
Na	330.0	334.0	90.2	92.0	79.2	78.0	21.6	21.6	5.0
SiO_2	16.1	15.8	14.3	16.6	6.8	7.0	2.7	3.3	1.0
Cl	270.0	275.0	51.1	52.5	96.3	96.3	28.6	30.4	1.07
SO_4	643.0	657.0	781.0	734.0	83.3	83.1	87.3	92.4	1.0
NH_3-N	ND	ND	ND	ND	ND	ND	ND	ND	0.1
NO_3-N	ND	ND	ND	ND	18.1	18.1	0.23	0.28	0.1
Total P	ND	ND	ND	ND	3.4	3.8	ND	ND	0.1
HCO_3 Alkalinity	128.0	119.0	119.0	116.0	23.7	25.4	56.6	56.3	5.0
Total Alkalinity	128.0	119.0	119.0	116.0	23.7	25.4	60.8	60.4	5.0
BOD	6.4	5.3	ND	ND	2.7	5.8	ND	ND	2.0
TOC	2.7	0.8	2.3	1.1	9.5	8.7	3.0	2.4	1.0
TDS	1610.0	1630.0	1320.0	1310.0	466.0	473.0	252.0	271.0	10.0
TSS	12.0	30.0	ND	4.0	ND	20.8	ND	20.8	4.0
SC	2470	2470	1620	1640	734	739	398	402	1.0
pH [4]	6.3	6.1	6.5	6.8	7.0	7.0	8.6	8.4	
pH [5]		6.2		6.4		7.1		8.6	
Acidity	ND	ND	ND	ND	ND	ND	ND	ND	5.0

Notes: 1 Units are in mg/L, except for Conductivity (SC), which is in µmhos/cm.
2. All ND, Not Detected (values below the listed Analysis Limit).
3.The amount of Fe in filtrant is soluble Fe(II).
4. Measured in lab; 5 measured in the field.

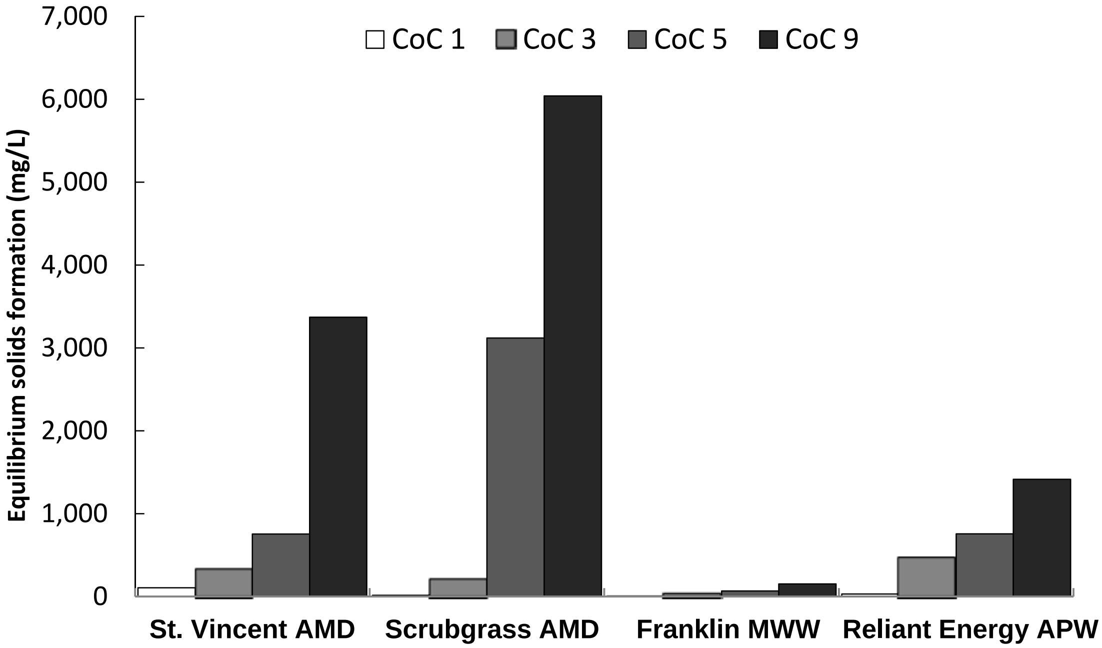

Figure 4.2.1. Modeling results of precipitates formation of the four impaired waters at different cycles of concentration. Modeling condition: open to atmosphere, T = 40 °C, pH calculated by MINEQL+.

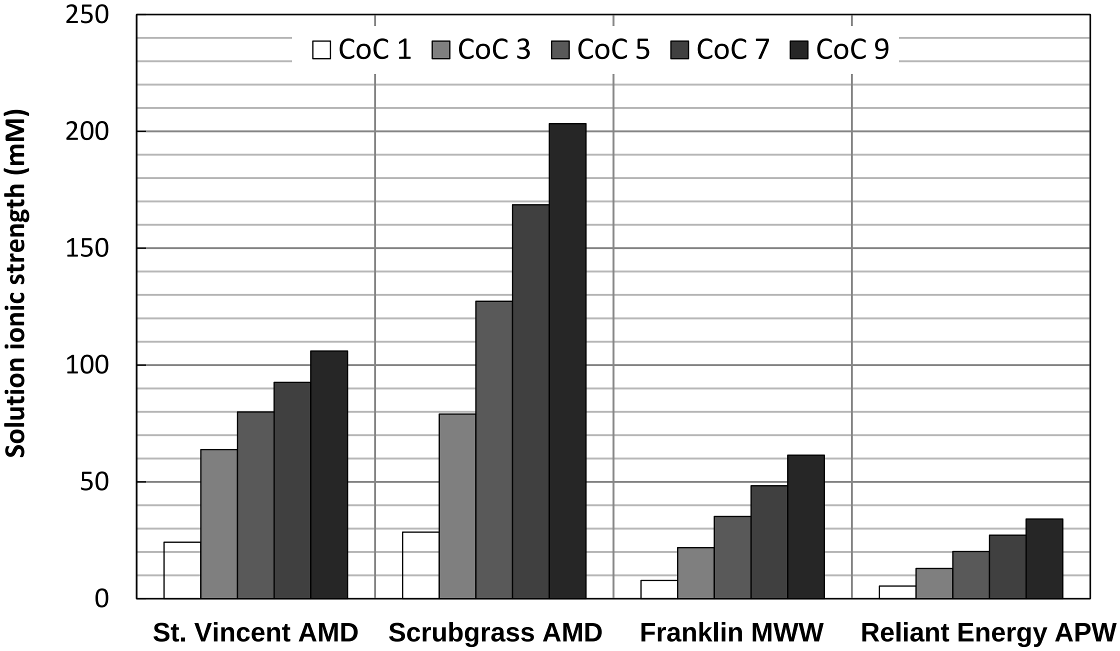

Figure 4.2.2. Modeling results of solution ionic strength of the four impaired waters at different cycles of concentration. Modeling condition: open to atmosphere, T = 40 °C, pH calculated by MINEQL+.

The ratio of total precipitated solids to total dissolved solids (TPS/TDS) at equilibrium was used as a direct measure of the scaling potentials for the impaired waters (Figure 4.2.3). This ratio varied markedly among the four impaired waters, thereby indicating different scaling potentials. The Franklin Township MWW demonstrated the lowest scaling potential. Even at CoC 11, more than 90% of the originally dissolved solids (salts) were predicted to remain in the aqueous phase. For the Reliant Energy APW, there was a significant jump in scaling potential as CoC increased from 1 to 3. The scaling potential stayed relatively stable at a TPS/TDS ratio of 22% when the CoC continued to increase to 11. The Scrubgrass AMD water was predicted to hold up to 90% of total solids in solution at CoC < 5. At higher CoC, however, the capacity dramatically decreased. The St. Vincent AMD water was predicted to have the greatest scale formation potential based on the TPS/TDS ratio. Presumably, the TPS/TDS ratio may be a better indicator of a water's scaling potential than the ionic strength when the water is subjected to increased CoC under cooling tower conditions, because the TPS/TDS ratio takes into account both the precipitated and dissolved solids while the IS measurements only consider TDS.

Based on the scaling potential modeling, it was decided to operate the pilot-scale cooling towers below CoC 5 to avoid excessive precipitation when testing the impaired waters.

Major solid precipitates to form in the impaired waters were predicted by MINEQL+ and details are provided in subsequent chapters of the report. The solid precipitate most commonly predicted to form upon concentration of the impaired waters was calcite, $CaCO_3(s)$, implying that it is important to control the amount of calcium and carbonate species.

The variations of solution pH were also calculated by MINEQL+. When the waters were open to the atmosphere to allow equilibrium with $CO_2(g)$, pH values tended to be reasonably stable with variations between 7.5 and 8.5, due to the buffering capacity provided by the $CO_2(g)$-carbonate system. Conversely, when the waters were closed to the atmosphere, pH tended to decrease with increasing cycles of concentration because of the loss of alkalinity to calcite formation.

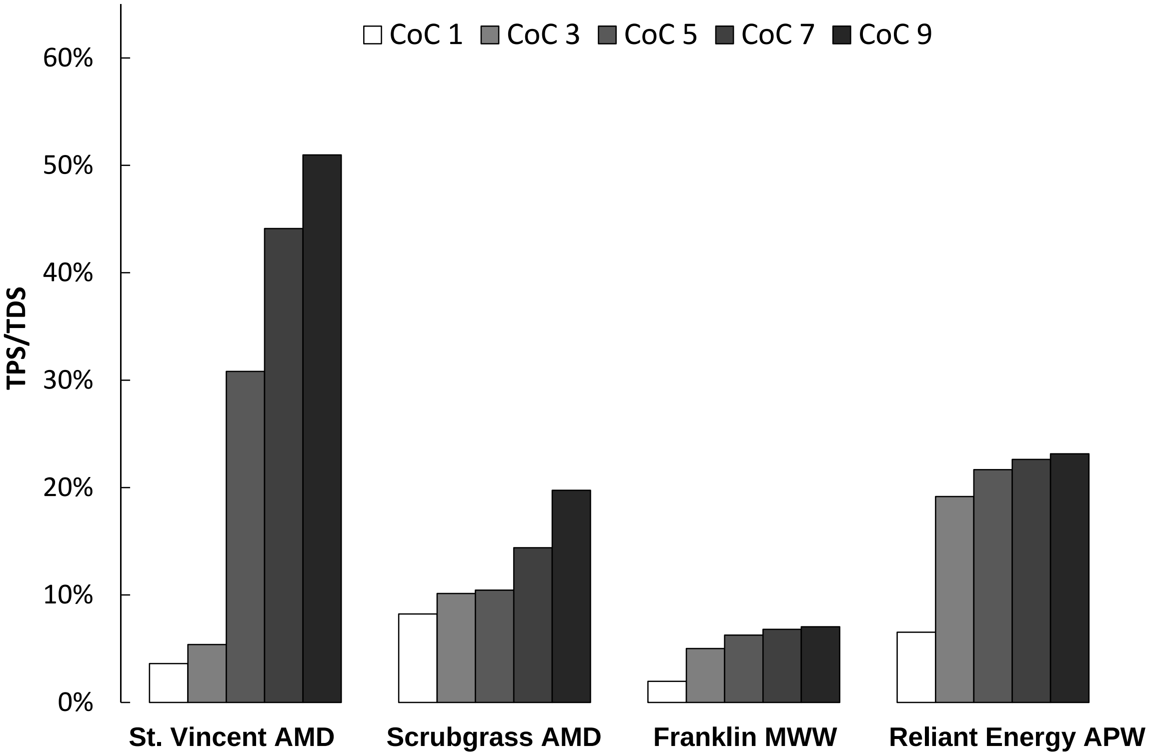

Figure 4.2.3. Ratio of total precipitated solids to total dissolved solids for the four impaired waters at different cycles of concentration. Modeling condition: open to atmosphere, T = 40 °C, pH calculated by MINEQL+.

4.2.4 Summary and Conclusions

Three chemical equilibrium models were evaluated and compared for their ability to provide comprehensive assessment of the scaling potentials of the impaired waters to be tested for use in recirculating cooling systems. MINEQL+ (version 4.5) was identified as a versatile and reliable program to meet the modeling needs in this study.

MINEQL+ modeling calculations were performed to analyze the scaling potentials of four impaired waters at equilibrium when the waters were subjected to different cycles of concentration (CoC), simulating cooling system operation conditions. The four impaired waters examined were secondary treated municipal wastewater, passively treated mine drainage from two sources, and effluent from an ash sedimentation pond at a power plant. Based on the predicted amount of solid precipitates, the solution ionic strength, and the ratio of total precipitated solids to total suspended solids, it was decided to conduct bench-scale and pilot-scale experiments at CoC levels below 5, to avoid the excessive amounts of precipitates predicted to form when the waters were operated beyond CoC 5. From the chemical equilibrium modeling performed at CoC < 5, it was determined that the impaired water with the lowest potential for precipitate formation was the ash sedimentation pond effluent while the two mine drainage waters exhibited the greatest potential for precipitate formation. The solid precipitate most commonly predicted to form upon concentration of the impaired waters was calcite, $CaCO_3$(s), implying the need to manage calcium and carbonate species concentrations in cooling systems employing impaired water.

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5.0 Reuse of Secondary Treated Municipal Wastewater as Alternative Makeup Water for Cooling Systems

Municipal wastewater collected and treated by utilities in the U.S represents a widely available, potential non-traditional source of cooling water. The main challenge when secondary treated municipal wastewater is reused in recirculating cooling water systems is more complicated control of corrosion, scaling, and biological fouling due to the lower quality of the water. When secondary treated municipal water is to be used, cooling water quality requirements may be more difficult to achieve, and extraordinary corrosion, scaling and biological fouling control programs may be required.

In this study, the feasibility of controlling corrosion, scaling, and biofouling when using secondary treated municipal wastewater in cooling water systems was investigated through laboratory and pilot-scale experiments. Bench-scale recirculating systems and three pilot-scale cooling towers were employed for testing of various chemical control schemes for corrosion, scaling, and biofouling in systems using secondary treated municipal wastewater. The testing was conducted with conditions of temperature, flow velocity, and water constituent concentration similar to those in a recirculating cooling water system. The effectiveness of chemical treatment strategies in inhibiting corrosion, scaling, and biomass growth was studied through exposure and monitoring specially designed coupons in extended duration tests.

5.1 Corrosion Control for Municipal Wastewater Used for Cooling

Abstract

Secondary treated municipal wastewater is a promising alternative to fresh water as power plant cooling water system makeup water especially in arid regions. This study conducted laboratory and field testing to evaluate corrosion potential of secondary treated municipal wastewater in cooling systems and different corrosion control strategies through chemical treatment. It was determined that orthophosphate, abundant in secondary treated municipal wastewater, contributed to scaling problem and to precipitative removal of phosphorous based corrosion/scaling inhibitors. The corrosion inhibitor tolyltriazole worked effectively to reduce corrosion rates of copper and cupronickel both in bench-scale and pilot-scale experiments. The biocide monochloramine was found to be less corrosive than more commonly used free chlorine. Although scaling was found to be a challenge when using wastewater for cooling, it also provided a certain degree of corrosion protection for the metal alloys tested in this study.

5.1.1 Introduction

Secondary treated municipal wastewater is of increasing interest as an alternative source of makeup water for thermoelectric power plant recirculating cooling water systems. In the U.S., 17 power plants reported employing treated municipal wastewater as makeup in 1986 (Ehrhardt et al., 1986), while a more recent survey identified 47 power plants using treated municipal wastewater in recirculating cooling water systems (Veil, 2007). Most of the 47 plants are in southwestern regions and Florida, corresponding to the regions susceptible to water supply constraints. Another analysis showed that secondary treated municipal wastewater represents the most widely available alternative cooling water source for existing and future power plants in terms of quantity and proximity to the ultimate use location (Chien et al., 2008).

The main challenges when secondary treated municipal wastewater is reused in recirculating cooling water systems are complicated corrosion, scaling, and biological fouling processes due to the degraded quality of the waters. For example, secondary treated sewage effluent usually has higher concentrations of organic matter, hardness, phosphate, ammonia, and total dissolved solids compared to freshwater sources (Williams, 1982; Weinberger, 1966). Organic matter, phosphate, and ammonia increase the growth of biomass; high hardness and phosphate increase scaling potential; ammonia is highly corrosive to copper, and total dissolved solids generally increase the corrosiveness of water to various metals by increasing the conductance of water (Breistein and Tucker, 1986; Selby and Helm, 1996; Goldstein, 1981). Thus, when secondary treated municipal water is to be used, cooling water quality requirements are more difficult to achieve, and extraordinary corrosion, scaling and biological fouling control programs are often required (EPRI, 2003).

Phosphate and ammonia are municipal wastewater effluent constituents of particular interest since the former is protective and the latter is corrosive to mild steel and copper alloys (Jones, 1996; Uhlig and Reive 1985). Ammonia is corrosive since it can form soluble complexes with copper (Stumm and Morgan, 1981) and iron (Uhlig and Revie, 1985). Orthophosphate behaves as a weak anodic inhibitor and can facilitate the formation of iron oxides or participate in protective film formation (McCoy, 1974; Saha and Kurmaih, 1986; Drogowska et al., 1992; Borras et al., 2000; Giacomelli et al., 2006; Benzakour and Derja, 1993). Although orthophosphate has corrosion inhibition ability, phosphate in impaired waters with high calcium and alkalinity has higher calcium phosphate scaling potential (Goldstein et al., 1981).

Higher microbial concentrations in secondary treated wastewater increase the potential of microbiologically influenced corrosion (Schumerth, 2006). The use of biocide to kill bacteria decreased mild steel corrosion rate (Gayosso et al., 2005; Ramesh et al., 2003). However, free chlorine residual for biocidal action is aggressive to copper (Harrison and Kennedy, 1986), reacts readily with metallic materials (Nalepa et al., 1996; Jones, 1996; Tuthill et al., 1998), and increases corrosion rate of carbon steel and cast iron significantly at concentrations higher than 0.5 ppm as Cl_2 (Boffardi, 1992). Further, large doses of chlorine increase corrosion rate of mild steel (Nalepa et al., 1999). Chlorine can also degrade some organic corrosion inhibitors such as tolyltriazole (Breske, 1983). It has been shown that using chloramine instead of free chlorine can reduce metal alloy corrosion in drinking water distribution systems (MacQuarrie et al., 1997). However, the influence of chloramine on metal alloy corrosion in recirculating cooling water system using impaired waters has not been studied.

The use of corrosion inhibitors is the most widely employed approach to control corrosion in recirculating cooling water system (Frayne, 1999). Corrosion inhibitors usually form barrier layers on the surface of a metal and thus decrease corrosion rate. Barrier forming inhibitors are categorized into three types: adsorbed layer formers, oxidizing inhibitors (passivators), and conversion layer formers (Dean et al., 1981). Briefly, adsorbed layer formers function by adsorbing to the metal surface; oxidizing inhibitors function by shifting the metal's electrochemical potential to a region where the metal oxide or hydroxide is stable (passivating); and conversion layer formers function by forming a low solubility deposition on the metal surface (Dean et al., 1981). Among the commonly used corrosion inhibitors, orthophosphate, polyphosphate and tolyltriazole were selected to be tested in this research based on review of the cooling water practice literature (McCoy, 1974; Frayne 1999; Jones, 1996; Harston, 2004), and by consulting with cooling water corrosion control experts (Scandolari, 2008; Christophersen and McDonald, 2008).

Polyphosphates, such as pyrophosphate, are the most common corrosion inhibitors used in cooling water treatment (Frayne, 1999) and other U.S. utility (McNiell and Edwards, 2002). Polyphosphates are identified as cathodic corrosion inhibitors (Saha and Kurmaih, 1986). Polyphosphate compounds in water gradually hydrolyze to orthophosphate (Frayne, 1999), which is an anodic inhibitor (Saha and Kurmaih, 1986). However, phosphate scaling potential increases when the aqueous solution has high hardness (Goldstein et al., 1981). Generally, the feasibility of employing phosphorous based inhibitors in cooling tower systems using impaired waters with high hardness and alkalinity has not been well documented.

Tolyltriazole (TTA) is an inhibitor specifically for copper alloys. Its NH group can adsorb onto the metal surface thus forming a barrier layer (Hollander and May, 1985). Copper corrosion inhibition by TTA can be reduced by free chlorine residual (Breske, 1983; Lu et al., 1994; Harrison and Kennedy, 1986), which is often maintained in cooling systems to prevent microbial growth and biofouling. On the other hand, chloramine has lower oxidizing power but studies of its influence on copper corrosion inhibition by TTA are limited.

The overall goal of this study was to investigate the feasibility of using secondary treated municipal wastewater in cooling water systems by metal alloy corrosion rate monitoring and comparison with general corrosion criteria (Table 5.1.1). Specifically, the objectives of this study were to 1) investigate the feasibility of using phosphorous-based inhibitors in bench-scale systems with synthetic secondary treated municipal wastewater, 2) design an experimental matrix and perform laboratory experiments to evaluate influence on metal alloy corrosion of ammonia and orthophosphate present in the wastewater, as well as polyphosphate, TTA, free chlorine, and monochloramine additives, and 3) apply the optimal corrosion control program identified from bench-scale experiments to pilot-scale cooling systems operated with secondary treated municipal wastewater in the field.

Table 5.1.1 Corrosion criteria for commonly used metal alloys in cooling tower systems.

Metal	Corrosion rate (mils per year, MPY)	Classification
Mild steel piping	< 1	Excellent
	> 1 to 3	Good
	> 3 to 5	Fair
	> 5 to 10	Poor
	> 10	Unacceptable
Mild steel heat exchanger tubing	< 0.2	Excellent
	> 0.2 to 0.5	Good
	> 0.5 to 1.0	Fair
	> 1.0 to 1.5	Poor
	> 1.5	Unacceptable
Copper and copper alloys	< 0.1	Excellent
	> 0.1 to 0.2	Good
	> 0.2 to 0.3	Fair
	> 0.3 to 0.5	Poor
	> 0.5	Unacceptable
Galvanized steel	< 2	Excellent
	> 2 to 4	Good
	> 4 to 8	Fair
	> 8 to 10	Poor
	> 10	Unacceptable
Stainless steel	< 0.1	Acceptable
	> 0.1	Unacceptable

Source: P. Puckorius. "Cooling water system corrosion guidelines," *Process Cooling*, July 1, 2003 (Available at http://ewr/pubs/IEP_Power_Plant_Water_R&D_Final_1.pdf, accessed: 10/17/2008)

5.1.2 Materials and Methods

5.1.2.1 Synthetic wastewater preparation, and secondary treated municipal wastewater characterization

Secondary treated municipal wastewater represents an abundant cooling water makeup alternative but the water quality varies with location and time. In order to accurately study water that could represent many of the available secondary treated waters, effluent characteristics from four municipal wastewater treatment plants (Tsai, 2006; EPRI 2003) was reviewed. A "universal composition" for secondary treated municipal wastewater quality was determined by averaging (shown in Table 5.1.2) and this generalized water quality was used to prepare synthetic municipal wastewater (SMW) for bench-scale experiments. Although SMW was prepared without considering organic matter, the influence of the organic matter of secondary treated municipal wastewater on metal alloy corrosion was studied, as presented in Appendix F.

Table 5.1.2 Characteristics of synthetic municipal wastewater

Analytes	Concentration
pH	8.3
Specific Conductivity (mS/cm)	1.4
Ca (mg/L)	76
Na (mg/L)	77
K (mg/L)	6.8
Mg (mg/L)	43.5
NH_3-N (mg/L)	25
Cl (mg/L)	276
SO_4 (mg/L)	68
PO_4 (mg/L)	6.5
Total Alkalinity (mg/L as $CaCO_3$)	336

A simplified synthetic municipal wastewater (simplified SMW) was prepared for scaling potential analysis of phosphorous based inhibitors in batch reactor experiments. The simplified SMW was prepared with 8 mM $CaCl_2$, 4 mM MgCl, 4 mM $MgSO_4$, and 14 mM $NaHCO_3$. The initial alkalinity and hardness of the simplified SMW were similar to those of SMW (Table 5.1.2) at four cycles of concentrations (CoC 4), where CoC is the concentration factor for the water, e.g., CoC 4 implies the water has four times total dissolved solids of raw water.

Actual secondary treated municipal wastewater from Franklin Township Municipal Sanitary Authority (Murrysville, PA) was chosen to be tested in the bench-scale recirculating system and the pilot-scale cooling towers in field. The characteristics of the actual wastewater (FTMW) sampled on September 3, 2008, are shown in Table 5.1.3. Water samples were collected with a 1-L polyethylene container and then transferred to appropriate polyethylene or glass sample containers provided by the commercial laboratory, TestAmerica (Pittsburgh, PA). Appropriate preservatives were added to the sample bottles prior to the sampling event by TestAmerica.

Portions of the FTMW sampled for the bench-scale experiments was concentrated in the laboratory by heated evaporation (35 – 40 °C) to reach CoC 4 as determined by 75 % water volume reduction.

Table 5.1.3 Characteristics of secondary treated municipal wastewater from Franklin Township Municipal Sanitary Authority (sampled on September 3, 2008).

Analytes	Unit	Result (unfiltered)	Reporting limit
Al	μg/L	200	200
Ca	μg/L	41500	5000
Cu		28.2	25
Fe	μg/L	504	100
K	μg/L	16300	5000
Mg	μg/L	10700	5000
Mn	μg/L	317	15
Na	μg/L	94200	5000
SiO_2	μg/L	8540	1070
Zn	μg/L	74.1	20
pH		7.1	
NH_3-N	mg/L	21.0,^{J}	0.50
Bicarbonate Alkalinity	mg/L	177,^{J}	5.0
BOD	mg/L	31.9	2.0
Cl	mg/L	106	10
NO_3-N	mg/L	3.6	0.05
SO_4	mg/L	86.0	1.0
Total P	mg/L	4.5	0.50
Total Alkalinity	mg/L	177,^{J}	5.0
TOC	mg/L	27.0	1.0

Notes: J: Method blank contamination. The associated method blank contains the target analyte at a reportable level

5.1.2.2 Metal alloy pre-exposure and post-exposure treatment

Metal alloys chosen for study were mild steel (UNS G10180), aluminum (UNS A91100), copper (UNS C10100), and cupronickel (UNS C70600). These are commonly used in cooling water systems (Herro and Port, 1993). The metal alloy specimens tested were cylinder-shaped with the diameter of 0.375 inch and length of 0.5 inch from Metal Samples Company (Munford, AL). The particular geometry was selected so that the specimens could be used directly for electrochemical measurements.

Prior to being exposed to SMW in bench-scale recirculating system or FTMW in pilot-scale cooling towers, the metal alloy samples were wet polished with SiC paper to a 600 grit surface finish, dried, degreased with acetone, rinsed in distilled water, weighed to 0.1 mg and then mounted to bench-scale recirculating system or pilot-scale cooling towers.

During the exposure in the bench-scale recirculating system, polarization resistance R_P of the metal alloy samples was semi-continuously monitored. The samples were removed at the end of third day, cleaned by following ASTM G1 (ASTM, 2005a), and then reweighed to 0.1 mg for determining weight loss, *WL,* during exposure.

In the pilot-scale cooling towers, only the weight loss method was applied and the post-exposure treatment of metal alloy specimens was the same as for the bench-scale experiments. For each tower, five mild steel specimens were removed from the exposure rack at different times. Aluminum, copper, and cupronickel specimens were also removed at the end of field testing. The testing period was three weeks.

5.1.2.3 Corrosion and scaling inhibitors

Inhibitors selected for testing in this study included tetra-potassium pyrophosphate (TKPP, a corrosion and scaling inhibitor), sodium polyphosphate glassy (SHMP, a corrosion and scaling inhibitor), 2-phosphonobutane-1,2,4-tricarboxylic acid, (PBTC, a scaling inhibitor), TTA (a copper corrosion inhibitor), and the commercial scaling inhibitor Aquatreat AR540 (a scaling inhibitor, Alco Chemical, Chattanooga, TN). TKPP, SHMP, PBTC, and TTA were from The National Colloid Company (Steubenville, OH). TKPP, SHMP, and PBTC are phosphorous-based inhibitors.

5.1.2.4 Bench-scale recirculating water system configuration

A bench-scale circulating water system was designed and constructed for exposure of metal alloys to conditions of temperature, flow velocity, and water quality similar to those in a recirculating cooling water system. The bench-scale circulating water system consisted of a centrifugal pump, a water bath on a hotplate to control the water’s temperature, and a pipe rack made of 0.75 inch PVC to hold metal alloy specimens (Figure 5.1.1A). The pipe rack consisted of several tee sections into which alloy specimen holders were mounted.

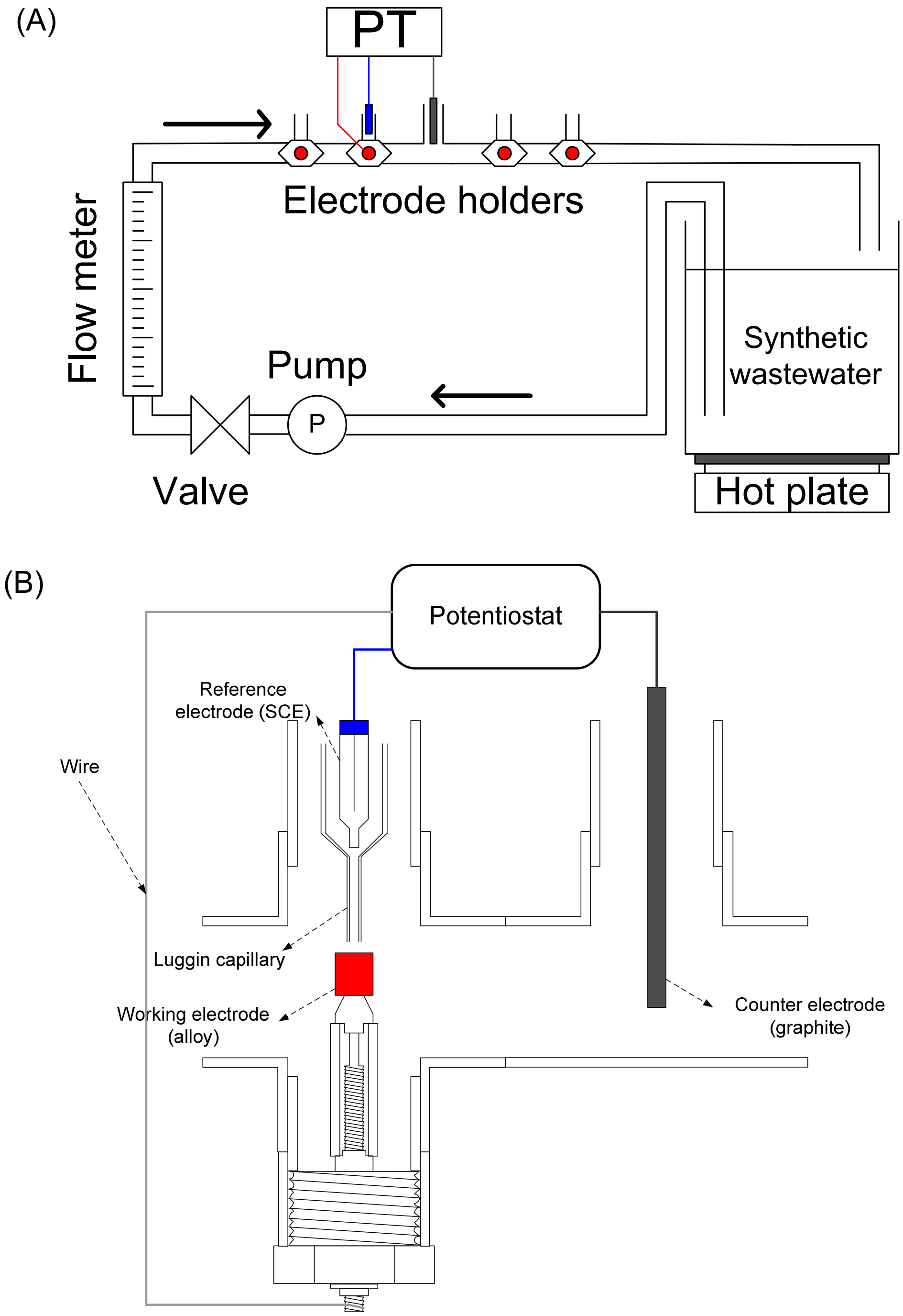


Figure 5.1.1 Schematics of (A) bench-scale recirculating system (B) detail of mild steel specimen holder and ports for counter electrode and reference electrode equipped in bench-scale recirculating system.

Corrosion measurements were performed using a combination of gravimetric weight loss and electrochemical polarization resistance measurements to determine average and instantaneous corrosion rates. For electrochemical measurement in the bench-scale circulating water system, the pipe rack was equipped to accommodate a saturated calomel reference electrode (RE) in a Luggin capillary, and a graphite counter electrode (CE). Each specimen holder was made of an end-cap plug containing a threaded stainless steel rod with an alloy specimen attached. The alloy specimen, RE, and CE were connected to a potentiostat for electrochemical corrosion analysis (Figure 5.1.1B). After exposure, each alloy specimen can be removed for gravimetric corrosion analysis.

5.1.2.5 Instrumentation for electrochemical polarization resistance measurement

Metal alloy specimens in the bench-scale recirculating system were also used for electrochemical polarization resistance (R_P) measurements. R_P was measured using a PGSTAT100 potentiostat (ECO CHEMIE, the Netherlands). A three electrode system was employed with the alloy specimen as a working electrode, graphite as a counter electrode, and saturated calomel electrode as a reference electrode in a Luggin capillary probe. Each polarization scan was performed from -30 mV to +30 mV with respect to the corrosion potential at a scan rate of 0.3 mV/s.

5.1.2.6 Pilot-scale cooling tower configuration

Three pilot-scale cooling towers were constructed to test the optimal chemical control methods identified from bench-scale experiments. A schematic of one tower is shown in Figure 5.1.2. The towers were transported to Franklin Township Municipal Sanitary Authority for side-by-side evaluation of different corrosion/scaling/biofouling control programs. The three towers were operated with following conditions: 1) CoC 4; 2) flow rate 3 GPM (passing through a 0.75 inch PVC coupon rack); 3) circulating water temperature of 105 °F at the top of the tower and 95 °F in the collection basin.

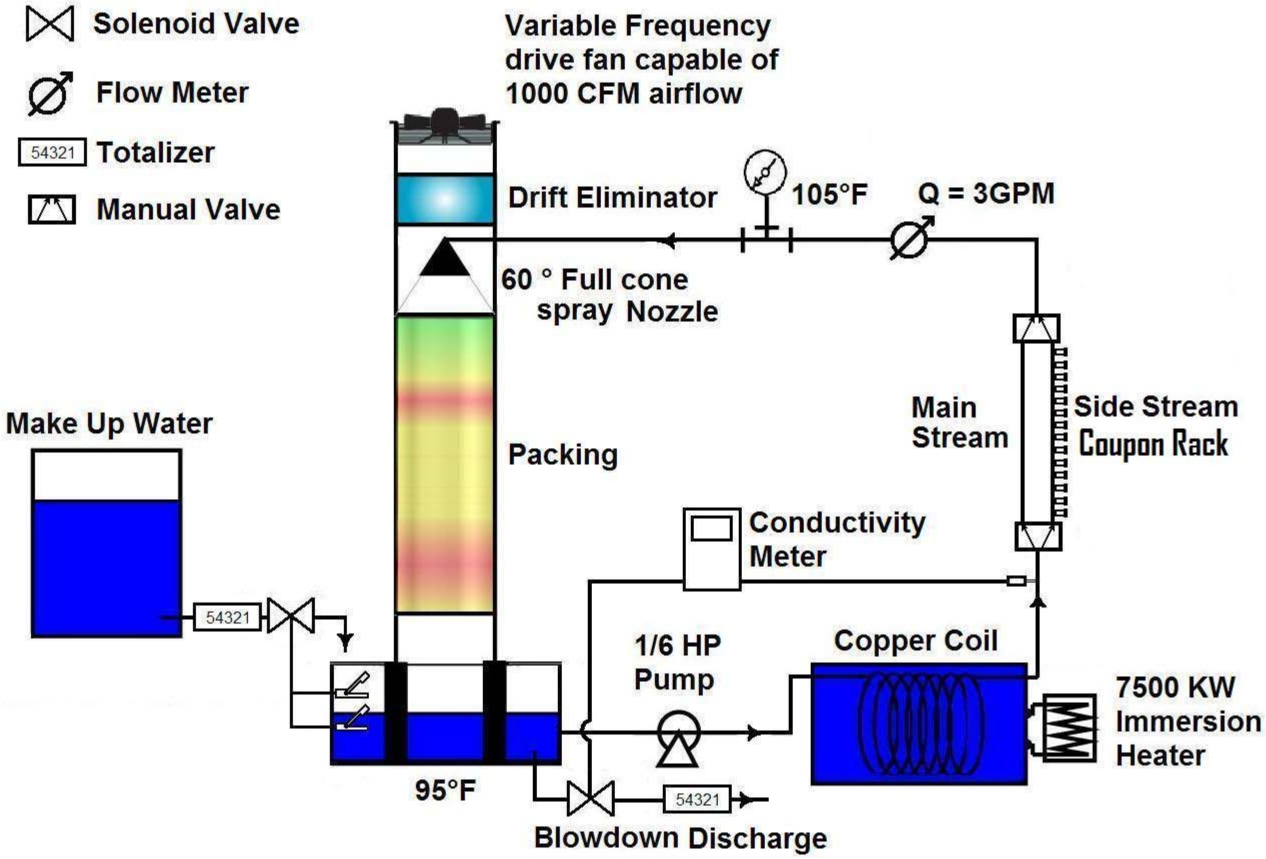


Figure 5.1.2 Schematic of pilot-scale cooling tower design. The coupon rack has similar design as Figure 5.1(b) except that there are no ports for counter and reference electrodes.

The side-stream coupon rack was used to study eight metal specimens simultaneously. The gravimetric weight loss method was used. Due to the inability to equip the coupon rack to accommodate reference and counter electrodes in the field, the electrochemical polarization resistance method was not used for the field testing.

5.1.2.7 Batch reactor study on precipitation of phosphorous-based inhibitors in simplified SMW

Batch reactor studies were conducted to investigate the precipitation potential of orthophosphate and phosphorous-based inhibitors in high hardness and high alkalinity simplified SMW. Series of batch reactors with simplified SMW were prepared with or without the addition of di-potassium orthophosphate (DKP), TKPP, SHMP, and PBTC. The water was stirred and aerated. Turbidity (absorbance at 520 nm by Spec 20) and pH were monitored with time. After one hour, the solution was filtered with a 0.45um cellulose membrane filter (Gelman Sciences Co., Ann Arbor, MI). The filtrate was analyzed for alkalinity, hardness, orthophosphorous, TKPP, SHMP, and PBTC, the last four by following APHA 4500-P. The weight of filtrand was also analyzed after being dried overnight. The results were used to show the potential for precipitation of phosphorous-based inhibitors in synthetic SMW.

5.1.2.8 Corrosion experiment matrix for bench-scale experiments with SMW

Preliminary studies revealed that the most important water quality parameters that distinguish secondary treated municipal wastewater from freshwater with respect to corrosion were ammonia and orthophosphate. In industrial settings, polyphosphate and TTA are widely applied as corrosion inhibitors in cooling tower systems. Combining these constituents with some commonly used scaling and biomass inhibitors, an experimental matrix was designed to study the influence of the following parameters: ammonia, orthophosphate, free chlorine, monochloramine, TKPP, TTA, PBTC, and AR540.

The experimental matrix for corrosion and scaling analysis of alloys in contact with SMW at CoC 4 is shown in Table 5.1.4. The matrix was designed to investigate a) the influence of orthophosphate and ammonia on corrosion and scaling, b) the influence and effect of inhibitors on corrosion and scaling, c) the necessity to remove orthophosphate and/or ammonia from raw waste water, d) the effect of biocide on corrosion and scaling, and e) the necessity of each inhibitor in terms of corrosion and scaling control. The temperature of the SMW was controlled at 40 ± 1 °C. The flow rate was controlled at 3 GPM, equal to a flow velocity of around 0.6 m/s in the 0.75-in diameter pipe. The pH of SMW at equilibrium was 8.8 ± 0.1.

Table 5.1.4 Experimental matrix for bench-scale corrosion study with synthetic municipal wastewater. Flow velocity 2 ft/s, temperature 40° C, and no pH adjustment (pH ~ 8.6 ± 0.15).

Synthetic wastewater composition tested	Objectives of experiments with different wastewater compositions				
	Influence of PO_4 and NH_4 in raw water	Effectiveness of inhibitors	Necessity to remove PO_4 and/or NH_4 in raw water	Effect of chlorine on corrosion	Necessity of each ingredient in Mix1
CoC 4	X	X			
CoC 4(noNH)	X				
CoC 4(noPO)	X				
CoC 4_Mix1(0.5x)		X			
CoC 4_Mix1		X	X	X	
CoC 4_Mix1_AR10		X			
CoC 4(noPO)_Mix1			X		X
CoC 4(noNH)_Mix1			X	X	
CoC 4(noNH)_Mix1_FC1				X	
CoC 4_Mix1_MCA1				X	
CoC 4(noPO)_Mix1(noTTA)					X
CoC 4(noPO)_Mix1(noTKPP)					X
CoC 4(noPO)_Mix1(noPBTC)					X

Notes: CoC: cycles of concentration; (CoC 4 has the water quality of Ca = 304.6 ppm; K = 27.3 ppm; Mg = 174.0 ppm; Na = 309.1 ppm; NH_4 = 126.2 ppm; Cl = 1104.9 ppm; CO_3 = 819.9 ppm; SO_4 = 272.7 ppm; HPO_4 = 20.2 ppm)
noPO: no orthophosphate
noNH: no ammonia
Mix1: PBTC (2-Phosphonobutane-1,2,4-Tricarboxylic Acid) 10 ppm, TTA (tolytriazole) 4ppm,TKPP (tetra-potassium pyrophosphate $K_2P_2O_7$) 10 ppm as PO_4
Mix1(0.5x): half concentration of Mix1
AR10: AR540 10 ppm (AR540 is commercial scaling inhibitor; marketing name: Aquatreat AR540; information about Aquatreat AR540 is available at: www.nicnas.gov.au/publications/car/new/na/nafullr/na0900fr/na921fr.pdf)
FC1 and MCA1: intermittently maintain 1 ppm total Cl_2 twice per day. FC represents free chlorine and MCA represent monochloramine.

For corrosion analysis, in each experiment, mild steel, aluminum, copper, and cupronickel specimens were exposed to SMW at CoC 4 in the bench-scale recirculating system for 3 days. The instantaneous corrosion rate was measured semi-continuously by electrochemical polarization resistance, and weight loss of each specimen was determined immediately after the 3-day exposure. The average corrosion rate was then calculated from the weight loss. In cases where the weight loss was not detectable, the average corrosion rate was then determined through the electrochemical polarization resistance method.

Visual observation was used for precipitation potential analysis. The water cloudiness was recorded during each test and the scaling on metal alloy specimens was documented with photographs.

5.1.2.9 Corrosion analysis of actual wastewater in bench-scale recirculating system.

Raw and CoC 4 FTMW were tested in the bench-scale recirculating system under different chemical treatments to investigate the effectiveness of inhibitors with FTMW and to verify the representativeness of the results from experiments with SMW. The FTMW and chemical treatment conditions included:

1) CoC 1, no chemical addition;
2) CoC 4, no chemical addition;
3) CoC 4, PBTC 10 ppm, TTA 4 ppm, and TKPP 10 ppm as PO_4;
4) CoC 4, PBTC 10 ppm, TTA 4 ppm, and TKPP 10 ppm as PO_4, and free chlorine 0.5 – 1 ppm as Cl_2;

Scaling analysis was not performed since during the preparation (sampling and concentrating process) of CoC 4 FTMW, the water had lost significant scaling potential through precipitation.

5.1.2.10 Corrosion experiment matrix for pilot-scale testing with actual wastewater

The experimental matrix for pilot-scale testing was based on results of bench-scale testing with respect to corrosion, scaling, and biomass studies. TKPP and TTA were chosen as corrosion inhibitors and PBTC and PMA (polymaleic acid, a scaling inhibitor identified to be effective in scaling control through other bench-scale experiments not reported here) were chosen as scaling inhibitors. Monochloramine was chosen as biomass control agent.

The three pilot-scale cooling towers were operated simultaneously for 21 days after CoC 4 had been reached. Then two of the three towers were operated for another 21-day run. Thus, in total the matrix included five different chemical treatment strategies as shown in Table 5.1.5. In the pilot-scale testing, corrosion inhibitors TKPP and PBTC concentrations were monitored by following APHA/AWWA/WEF Standard Method 4500-P (APHA/AWWA/WEF, 2005), TTA concentration was monitored by HACH® Method 8079 (HACH Company, 2008). Other water chemistry parameters (PMA, monochloramine, anions, alkalinity, pH, and conductivity) and cooling tower operational parameters (water flow rate, air flow velocity, temperature, makeup water flow rate, and blowdown water flow rate) were also monitored regularly.

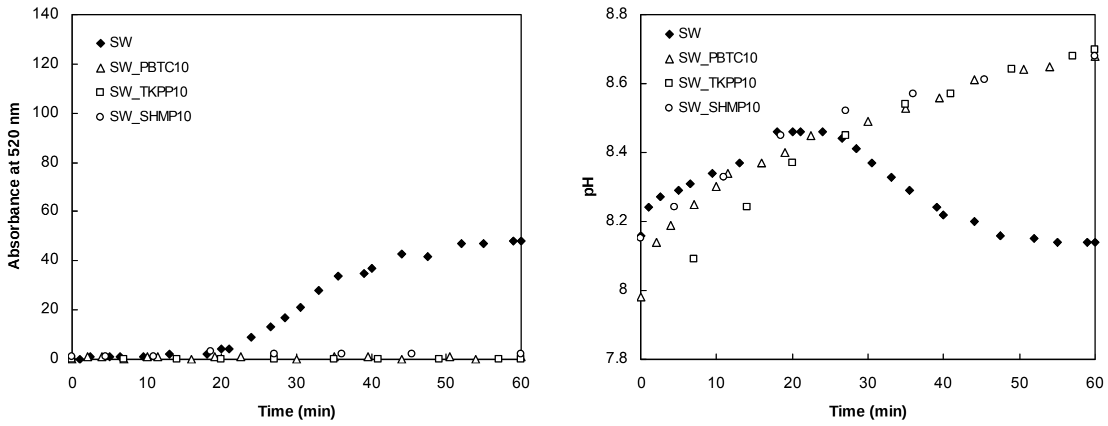
Table 5.1.5 Experimental matrix of pilot-scale cooling tower field testing with secondary treated municipal wastewater at Franklin Township Municipal Sanitary Authority. In parenthesis are actual monitored results from field testing. Samples for analysis were all filtered with 0.45 μm membrane.

Chemical	Unit	Chemical concentrations				
		Tower A1	Tower B1	Tower C1	Tower A2	Tower B2
TTA	ppm	2 (2.0±0.9)	1 (1.0±0.8)	2 (1.8±1.0)	2 (1.8±1.0)	0
TKPP	ppm as PO_4	10 (0.6±0.4)	0	10 (0.6±0.4)	0	0
PBTC	ppm	5 (0.8±0.3)	0	10 (0.9±0.7)	0	0
PMA	ppm	10 (4.3±1.3)	0	20 (9.7±2.1)	10 (4.5±1.3)	0
MCA	ppm as Cl_2	1-2 (1.0±0.7)	1-2 (1.2±0.9)	1-2 (1.5±0.8)	2-3 (3.6±2.2)	2-3 (3.2±1.3)

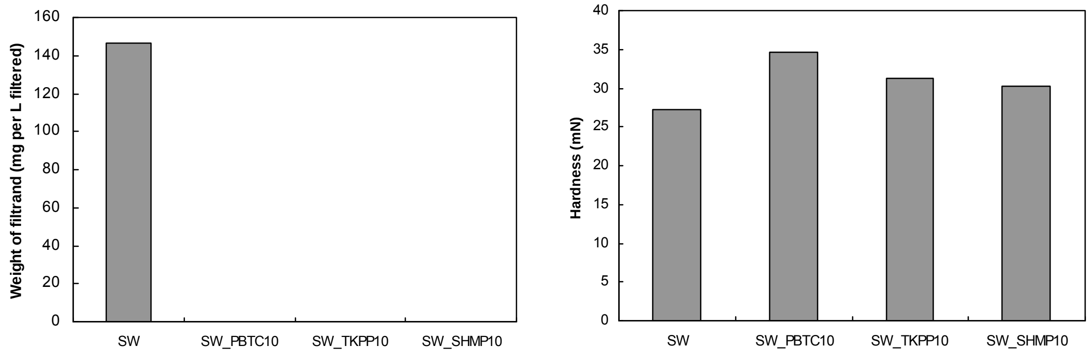
5.1.3 Results and Discussion

5.1.3.1 Batch reactor study on precipitation of phosphorous-based inhibitors in simplified SMW

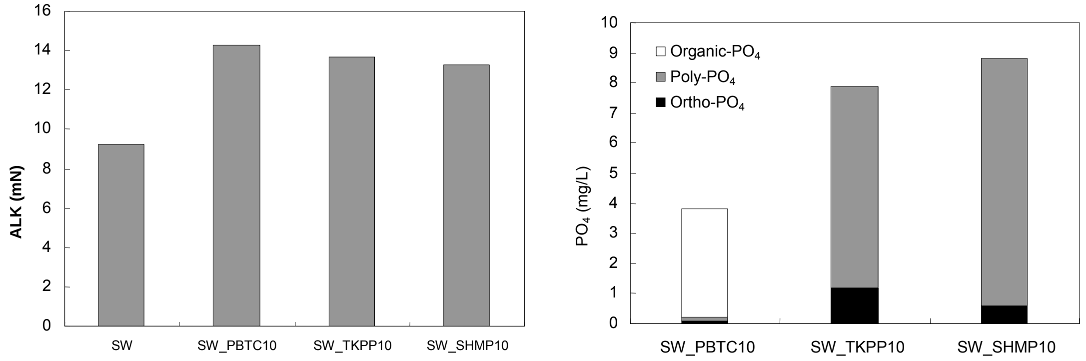
Results of the influence of PBTC, TKPP, and SHMP on precipitation potential are shown in Figure 5.1.3. Results of the influence of addition of tetra-potassium orthophosphate (DKP) on precipitation potential are shown in Figure 5.1.4. As can be seen in Figure 5.1.3a, the turbidity of the synthetic water increased with time during the experimental period, indicating the formation of suspended solids. However, with the addition of inhibitor PBTC, TKPP, or SHMP, the turbidity remained low, indicating the ability of PBTC, TKPP, or SHMP to control suspended solids formation, that is, to prevent precipitation potential of the synthetic water. In Figure 5.1.3b, it was found that the pH value of the synthetic water increased with time during the experimental period in every case. In the case where no inhibitor was added, the pH started to decrease at around 20 minutes, when the turbidity of the water also started to increase as indicated in Figure 5.1.3a. The data in Figure 5.1.3c show suspended solids formation in synthetic water without any inhibitor and the scaling inhibition effectiveness of all inhibitors tested. Figure 5.1.3d shows the hardness of the synthetic waters one hour after preparation and after being filtered. It can be seen that the hardness in the synthetic water without any inhibitor was significantly lower than the others, indicating the occurrence of precipitation.



(a) Turbidity vs. time (b) pH vs. time



(c) Weight of filtrand per L of water (d) Hardness concentration in filtrate



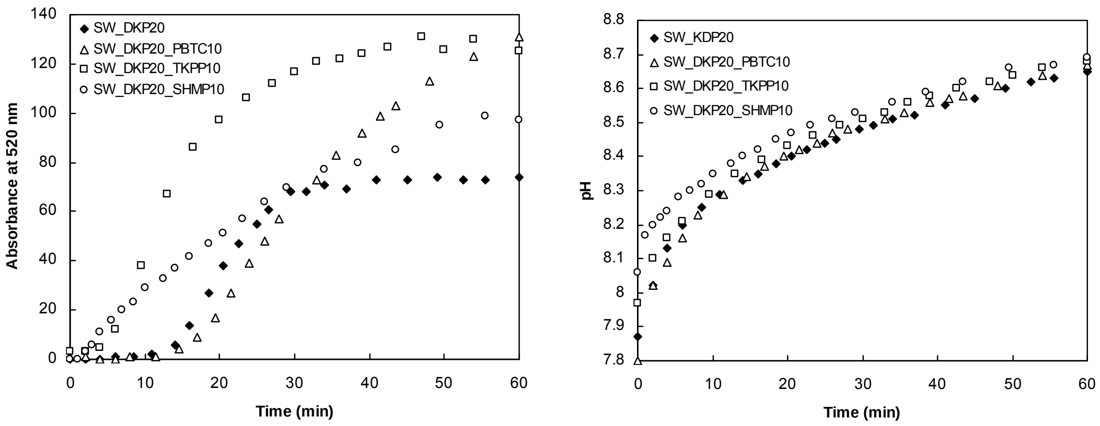
(e) Alkalinity in filtrate (f) Phosphate concentration in filtrate

Figure 5.1.3 The scaling potential of simplified synthetic municipal wastewater (SW) influenced by PBTC (10 ppm as PBTC or 3.5 ppm as PO_4), TKPP (10 ppm as PO_4), and SHMP (10 ppm as PO_4) addition. The temperature was at room temperature and the water was stirred in all tests. Recipes for SW were 8 mM $CaCl_2$, 4 mM $MgCl_2$, 4 mM $MgSO_4$, and 14 mM $NaHCO_3$. **(a)** In the absence of any inhibitor, turbidity started to build up after around 20 minutes. **(b)** In the absence of any inhibitor, pH started to descend after around 20 minute. **(c)** In the presence of any inhibitor, the weight of filtrand on 0.45 μm membrane was non-detectable. **(d)** Hardness of filtered SW decreased significantly. **(e)** Alkalinity of filtered SW decreased significantly. **(f)** Added inhibitors were mostly recovered in the tests.

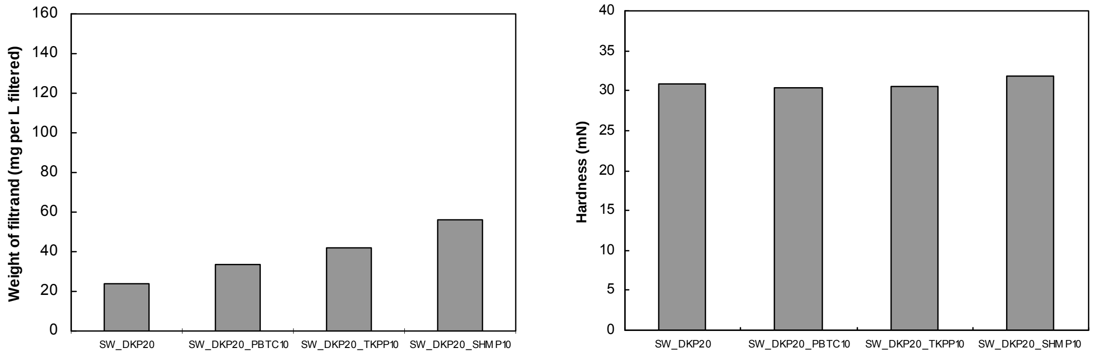
The alkalinity of synthetic water without any inhibitor was significantly lower than the tests with inhibitor one hour after preparation and after being filtered (Figure 5.1.3e). In the cases where inhibitors were added, those inhibitors mostly were recovered from the solution one hour after preparation and after being filtered (Figure 5.1.3f). Overall, data presented in Figure 5.1.3 suggests that PBTC, TKPP, or SHMP can effectively inhibit precipitate formation in the simplified SMW.

In all cases where DKP was added, turbidity (with inhibitors or not) increased with time, indicating suspended solids were formed (Figure 5.1.4a). In Figure 5.1.4b, pH increased with time in the same manner in every case, likely due to carbonate species exchange between solution and the atmosphere. The filtered mass data in Figure 5.1.4c confirm the formation of suspended solids in all cases. Figure 5.1.4d, and Figure 5.1.4e show that the hardness and alkalinity were slightly consumed in every case . Figure 5.1.4f shows that most of the added inhibitor and DKP mass was not recovered from the filtered solution.

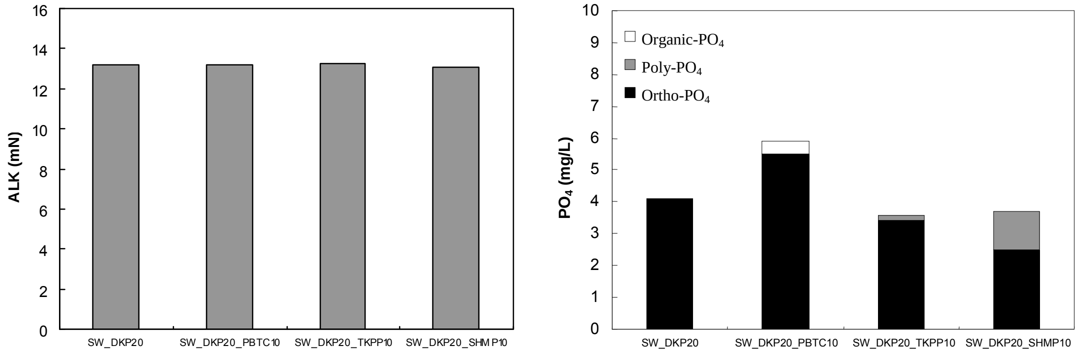
Overall, data presented in Figure 5.1.4 suggests that in the presence of DKP, none of PBTC, TKPP, and SHMP could inhibit precipitation. The pH, hardness, and alkalinity results indicate that calcium and/or magnesium carbonate precipitation was not as abundant as in the case where no DKP or inhibitors were added to SMW. However, the addition of DKP caused the co-removal of DKP and PBTC, TKPP, or SHMP. In a word, when using secondary treated municipal wastewater as cooling tower makeup water, due to the high alkalinity, hardness, and orthophosphate concentration, the addition of PBTC, TKPP, or SHMP might cause their precipitate with DKP and the simultaneous use of these chemicals need to be further examined.



(a) Turbidity vs. time (b) pH vs. time



(c) weight of filtrand per liter water (d) Hardness concentration in filtrate



(e) Alkalinity in filtrate (f) Phosphate concentration in filtrate

Figure 5.1.4 The scaling potential of synthetic municipal wastewater (SW) influenced by tetra-potassium orthophosphate (DKP, 20 ppm as PO_4), PBTC (10 ppm as PBTC, or 3.5 ppm as PO_4), TKPP (10 ppm as PO_4), and SHMP (10 ppm as PO_4) addition. The temperature was at room temperature and the water was stirred in all tests. Recipes for SW were 8 mM $CaCl_2$, 4 mM $MgCl_2$, 4 mM $MgSO_4$, and 14 mM $NaHCO_3$. **(a)** In all cases, turbidity built up with time. **(b)** In all cases, pH increased with time. **(c)** In all cases, detectable weight of filtrand was measured on 0.45 μm membrane. **(d)** In all cases, hardness of filtered SW consumed slightly (32 mN added). **(e)** In all cases, alkalinity of filtered SW consumed slightly (14 mN added). **(f)** In all cases, added DKP or inhibitors were largely not recovered.

5.1.3.2 Bench-scale recirculating system with SMW: corrosion and precipitation analysis

The average corrosion rate of each alloy in each test listed in Table 5.1.4 is shown in Table 5.1.6. Table 5.1.6 also shows the corrosion inhibition effectiveness of selected chemicals when compared to the case where no inhibitors were added and no removal of ammonia and orthophosphate was performed. Also, the occurrence of pitting corrosion is indicated. The precipitation potential was qualitatively recorded after visual observation of water turbidity.

The results summarized in Table 5.1.6 revealed the following:

1) Influence of ammonia and phosphate: The presence of ammonia in SMW significantly exacerbated the corrosion of mild steel, aluminum, and copper. On the other hand, the presence of phosphate inhibited the corrosion of all metal alloys tested except aluminum.

2) Influence of inhibitor mixture: The addition of TKPP (5 – 10 ppm as PO_4), TTA (2 – 4 ppm), and PBTC (5 – 10 ppm) significantly decreased the corrosion rate of mild steel, aluminum, and copper. The inhibition effectiveness reached more than 90% compared to the control with no inhibitors present.

3) Necessity of ammonia and phosphate removal in the presence of inhibitor_mixture: When TKPP 10 ppm (as PO_4), TTA 2 ppm, and PBTC 10 ppm were present, the removal of phosphate further enhanced the corrosion inhibition for all metal alloys, likely due to the absence of scaling. Although the removal of ammonia strongly enhanced copper corrosion inhibition, it actually deteriorated the corrosion inhibition of mild steel and aluminum.

Table 5.1.6 Average corrosion rate after 3 days of metal contact with synthetic municipal wastewater (SMW) and corrosion inhibition effectiveness

	Average corrosion rate, mils per year (MPY) (Corrosion inhibition effectiveness, %)			
	Mild steel	Aluminum	Copper	Cupronickel
Control: CoC 4	15.37 (---)	80.02 (P) (---)	0.835 (---)	0.099 (---)
Influence of NH_3/PO_4				
CoC 4(noNH)	2.92 (81.0 %)	**12.61** (84.2 %)	~ 0.27[c] (67.7 %)	0.202 (-104.0 %)
CoC 4(noPO)	45.35 (-195.1 %)	80.90 (P) (-1.1 %)	7.76 (-829.3 %)	3.364 (-3298.0 %)
Influence inhibitors mixture				
CoC 4_Mix1(0.5x)	1.20 (92.2 %)	**4.71** (94.1 %)	**0.038** (95.5 %)	0.121 (-22.2 %)
CoC 4_Mix1	**0.48 (N)** (96.9 %)	**6.31** (92.1 %)	**0.019** (97.7 %)	0.029 (70.7 %)
CoC 4_Mix1_AR10	1.12 (N) (92.7 %)	NA	**0.017** (98.0 %)	0.152 (-53.5 %)
Necessity of NH3/PO4 removal				
CoC 4(noPO)_Mix1	**0.20 (N)** (98.7 %)	**0.41** (99.5 %)	**0.011** (98.7 %)	0.011 (88.9 %)
CoC 4(noNH)_Mix1	1.03 (N) (93.3 %)	**6.75** (91.6 %)	**0.004** (99.5 %)	0.040 (59.6 %)
Influence of free Cl2 and chloramine				
CoC 4(noNH)_Mix1_FC1	3.28 (78.7 %)	**8.74** (89.1 %)	< 0.041[c] (P) (> 95.1 %)	< 0.077[b] (> 22.2 %)
CoC 4_Mix1_MCA1	2.17 (85.9 %)	14.70 (81.6 %)	**0.019** (97.7 %)	0.069 (30.3 %)
Influence of ingredients in Mix1				
CoC 4(noPO)_Mix1(noTTA)	2.57 (83.3 %)	NA	8.20 (-882.4 %)	0.076 (23.2 %)
CoC 4(noPO)_Mix1(noTKPP)	2.66 (82.7 %)	21.24 (P) (73.5 %)	**0.015** (98.2 %)	0.053 (46.5 %)
CoC 4(noPO)_Mix1(noPBTC)	**0.43 (N)** (97.2%)	2.98 (P) (96.3 %)	**0.012** (98. 6%)	0.034 (65.7 %)

Notes: a: not measured
b: Estimated value. Electrode only immersed for 40hrs
c: Intermittent free chlorine sudden increase made corrosion rate not stable
P: Pitting
N: For mild steel, non-corroded surface except threaded side
Mix1: PBTC 10 ppm, TTA 4ppm, TKPP 10 ppm as PO_4
noPO: no orthophosphate
noNH: no ammonia
AR10: AR540 10 ppm
Shaded: satisfactory results: no pitting and

- mild steel < 2 MPY and "N",
- aluminum < 2 MPY or estimated to decrease below 2 MPY,
- copper < 0.2 MPY,
- cupronickel <0.2 MPY

Bolded: Inhibition reached 95% and no pitting, or instantaneous corrosion rate of aluminum is predicted to drop below 2 MPY

4) Influence of free chlorine and monochloramine in the presence of inhibitor mixture: Copper and copper nickel were very sensitive to 1 ppm of free chlorine (as Cl_2) but the corrosion rates were still below 0.2 mils per year (MPY) when TTA 4 ppm was present. Mild steel corrosion was also exacerbated by the addition of free chlorine. In contrast, copper and cupronickel were not so sensitive to chloramine. The aggressiveness of monochloramine to mild steel was also less than that of free chlorine.

5) Influence of each ingredient in the inhibitor mixture: When TTA was not added, copper showed an extremely high corrosion rate, indicating TTA is a very effective inhibitor to overcome the aggressiveness of ammonia to copper. When TKPP was removed, mild steel corrosion rate increased more than 10 times. The removal of PBTC didn’t significantly deteriorate the corrosion inhibition of mild steel, copper, and cupronickel.

Visual observation showed that TKPP and PBTC inhibited precipitation in the absence but not in the presence of orthophosphate. The result is in agreement with batch reactor tests.

Overall, the presence of the mixture of inhibitors generally reduced corrosion rate of all alloys tested but precipitation potential remained. In the cases when orthophosphate was removed from the wastewater and TKPP, PBTC, and TTA were present, precipitation was inhibited and the corrosion of alloys was also significantly retarded, indicating that corrosion inhibition was even more effective when precipitation is controlled. TKPP or PBTC could inhibit precipitation only in the absence of orthophosphate. In summary, in the SMW, ammonia was corrosive to all metal alloys and orthophosphate caused the precipitation of TKPP and PBTC, as shown in batch reactor tests. Monochloramine biocide had lower corrosivity compared to free chlorine biocide. Thus, the challenges of using secondary treated municipal wastewater (ammonia and orthophosphate not removed) in cooling systems would be mainly scaling regardless of whether phosphorous-based inhibitors were used or not. Mild steel corrosion protection from orthophosphate present in the wastewater could be quite significant. Effective copper corrosion protection could be provided by TTA. Cupronickel would have the best corrosion resistance and might not need any corrosion inhibitor.

5.1.3.3 Bench-scale recirculating system with FTMW: corrosion analysis

The results in Table 5.1.7 show that CoC 4 FTMW had higher corrosivity to mild steel then CoC 1 FTMW and also caused the pitting of aluminum. CoC 1 FTMW and CoC 4 FTMW were both not very corrosive to copper and cupronickel. With the addition of the mixture of inhibitors, corrosion rates of all metal alloys decreased significantly. The addition of free chlorine in the presence of the inhibitor mixture (CoC 4 FTMW_Mix1_FC) caused mild steel and copper corrosion rates to increase but still remained very low. Free chlorine also caused pitting of aluminum.

Table 5.1.7 Results of corrosion rate after 7 days of metal contact with actual secondary treated municipal wastewater from Franklin Township Municipal Sanitary Authority with bench-scale recirculating system

	7-day average corrosion rate, mils per year (MPY)			
	Mild steel	**Aluminum**	**Copper**	**Cupronickel**
CoC 1 FTMW	2.24	2.66	0.23	0.22
CoC 4 FTMW	14.89	2.05 (P)	0.08	0.17
CoC 4 FTMW_Mix1	0.36	ND	ND	ND
CoC 4 FTMW_Mix1_FC	1.15	0.46 (P)	0.23	ND

MPY: mils per year
FT: Franklin Township secondary treated municipal wastewater
CoC#: # cycles of concentration
Mix1: PBTC 10 ppm, TTA 4ppm, TKPP 10 ppm as PO_4
FC: free chlorine 0.5 – 1 ppm as Cl_2
P: pitting corrosion
ND: not detectable (the lower detection limit for copper and cupronickel was 0.017 MPY)

Overall, the mixture of the inhibitors effectively inhibited the corrosivity of CoC 4 FTMW. However, free chlorine biocide was aggressive to most alloys except to cupronickel. These results generally agree with the corrosion results obtained with SMW using the bench-scale system.

Results of bench-scale experiments with SMW and FTMW indicated that in secondary treated municipal wastewater 1) TTA is a very effective copper corrosion inhibitor, 2) phosphorus based inhibitors (TKPP, PBTC, or SHMP) can mitigate metal alloy corrosion but are likely to be removed through precipitation together with orthophosphate present in the wastewater, 3) monochloramine biocide is less corrosive then free chlorine biocide, and 4) cupronickel is a satisfactory corrosion resistant metal alloy even in the absence of any inhibitors. These results were used for the design of pilot-scale experimental matrix shown in Table 5.1.5.

5.1.3.4 Pilot-scale experiments

The corrosion results obtained in the pilot-scale experiments (Table 5.1.5) are shown in Table 5.1.8 and Figure 5.1.5. Table 5.1.8 shows the average corrosion rates of metal alloys and Figure 5.1.5 shows the accumulated weight loss of mild steel with time during the 21-day field testing with FTMW.

Table 5.1.8 Average corrosion rates of metal alloys contacted with secondary-treated wastewater at 4 cycles of concentration in cooling tower for three weeks and their category according to general corrosion criteria for cooling systems

Metal alloys	Average corrosion rate (mils per year, MPY) and category[a]				
	Tower A1	Tower B1	Tower C1	Tower A2	Tower B2
Mild steel (21-day avg.)	3.35 (fair)	3.51 (fair)	3.28 (fair)	4.78 (fair)	8.21 (poor)
Mild steel (last 5 days avg.)	1.99 (good)	0.37 (excellent)	3.24 (good)	2.45 (good)	3.51 (fair)
Aluminum (21-day avg.)	2.3, pitting (unacceptable)	1.74, pitting (unacceptable)	1.18, pitting (unacceptable)	6.86, pitting (unacceptable)	13.7, pitting (unacceptable)
Copper (21-day avg.)	ND (excellent)	ND (excellent)	0.03 (excellent)	0.11 (good)	0.08 (excellent)
Copper-nickel (21-day avg.)	ND (excellent)	0.03 (excellent)	ND (excellent)	0.05 (excellent)	0.04 (excellent)

a Corrosion rate category is based on corrosion criteria shown in Table 5.1.1
ND: non-detectable (the lower detection limit for copper and cupronickel was 0.017 MPY)

The results of corrosion and scaling inhibitor (TTA, TKPP, PBTC, and PMA) concentrations monitoring are shown in Table 5.1.5. As can be seen for this table, TTA was easily maintained in the towers, but large portions of phosphorous based inhibitors were not detected and were likely removed through precipitation. Also, most orthophosphate from the makeup wastewater was not detected and was also likely removed through precipitation. These results are in agreement with the results from bench-scale tests in the laboratory: i) phosphorous based inhibitors can't be maintained in solution, and ii) orthophosphate can pose scaling potential in cooling tower systems when secondary treated municipal wastewater is used as makeup water.

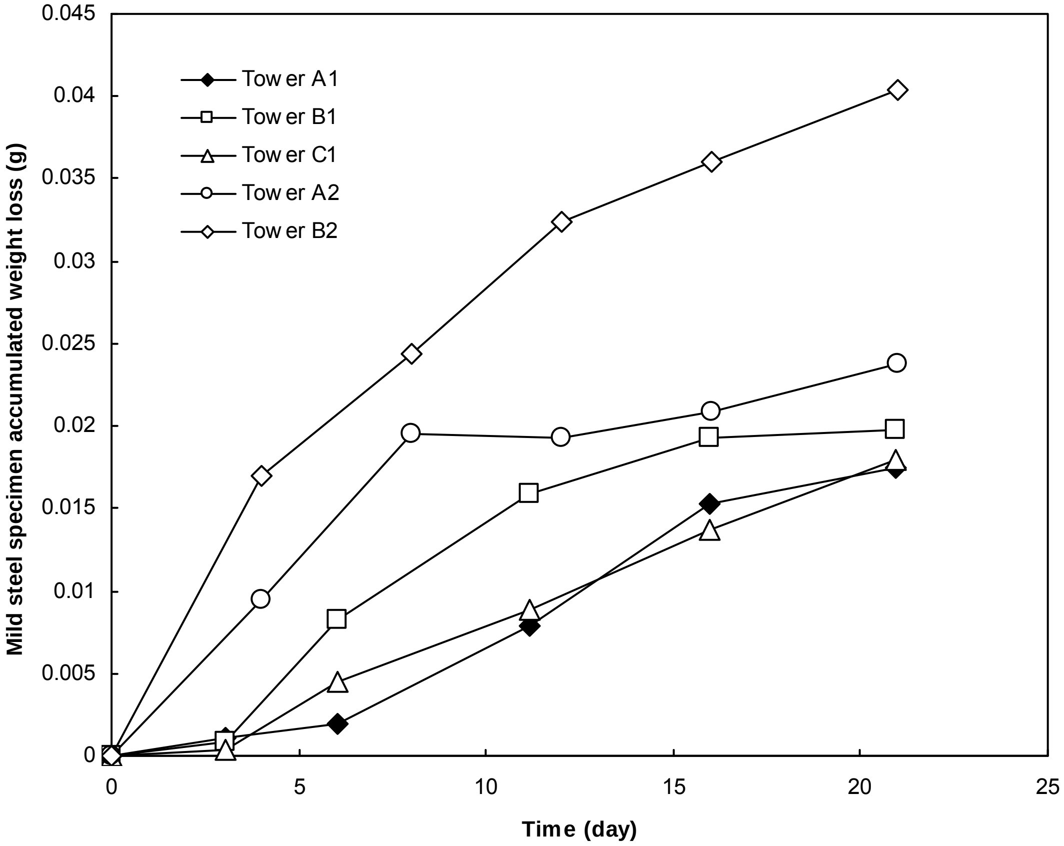


Figure 5.1.5 Accumulated weight loss of mild steel specimens with time in pilot-scale cooling tower field testing with the Franklin Township Municipal wastewater at CoC 4.

Copper and cupronickel showed very good corrosion resistance both in the absence and presence of corrosion inhibitors but especially in the presence TTA (see data in Table 5.1.8). Higher monochloramine made corrosion rates of copper and cupronickel higher but still lower than the general criteria of “good performance” (< 0.3 MPY). One expected major concern for copper in contact with concentrated secondary treated municipal wastewater is ammonia. However, the ammonia monitoring result indicated that in the cooling tower systems, the dissolved ammonia was less than 1 ppm as N. Thus, more than 98 % of ammonia had been removed from the system (probably through volatilization). This might be the reason why copper and cupronickel still had low corrosion rates in the absence of TTA.

In the absence of inhibitor and with higher monochloramine biocide dose, the average corrosion rates for aluminum were not acceptable and pitting corrosion occurred (data presented in Table 5.1.8). Although the average corrosion rates for aluminum were low in the presence of inhibitors and low monochloramine dose, pitting corrosion still occurred. Thus, pitting corrosion is the main concern for aluminum, making it inappropriate material in cooling tower systems with secondary treated municipal wastewater.

The 21-day average corrosion rates of mild steel were generally in the category of “fair” except in the case where no inhibitors were present (Tower B2), when the category was “poor” (see Table 5.1.8). Also, higher monochloramine biocide concentration posed higher 21-day average corrosion rates of mild steel. However, the last 5-day (days 16 – 21) average corrosion rates of mild steel were all lower than the relative 21-day average corrosion rates and had the category better than or equal to “fair”. Further, no significant difference was observed among the towers based on the average corrosion rates during the last 5 days of the field test. Data presented in Figure 5.1.5 show that the corrosion rates of mild steel in Tower A2 (which has higher monochloramine than A1, B1, and C1, and only has TTA as corrosion inhibitor) and in Tower B2 (which had higher monochloramine and no inhibitor) had higher initial corrosion rates but then had similar corrosion rates as others towards the end of the run. It was determined that the mild steel specimens in all towers after 21 day exposure were covered by a scale layer (Figure 5.1.6). Thus, it was concluded that the growth of the scale layer gradually inhibited the corrosion of mild steel specimens in all towers (the aggressive natures of monochloramine and protective nature of TTA and TKPP became negligible).


(A) Before cleaning (B) After cleaning

Figure 5.1.6 Mild steel specimen withdrawn from pilot-scale cooling tower system (Tower B2) after 21-day test with secondary treated municipal wastewater from Franklin Township Municipal Sanitary Authority. (A) Dried mild steel specimen before surface cleaning. (B) Mild steel specimen after acid surface cleaning.

5.1.4 Summary and Conclusions

In this study, the corrosion control of metal alloys in cooling tower systems using secondary treated municipal wastewater was evaluated. According to the results from all batch, bench-scale, and pilot-scale experiments performed in this study, it was determined that commonly used phosphorous based corrosion and scaling inhibitors are likely to be largely co-removed with orthophosphate present in the wastewater,. TTA showed very effective corrosion inhibition for copper alloys in the bench-scale and pilot scale experiments. Ammonia from the wastewater was largely removed in pilot-scale cooling tower systems through volatilization, and was not a concern for corrosion control in the pilot-scale testing. Monochloramine biocide was revealed to be less corrosive than free chlorine biocide. Although phosphorous based inhibitors cannot be kept freely dissolved to provide good corrosion protection and thus are not suitable for reuse of secondary treated municipal wastewater, corrosion in cooling water systems might still not be a concern since the wastewater has high scaling potential and the scaling layer can provide certain degree of protection to metal alloys.

Overall, for corrosion control of metal alloys contacted with CoC 4 municipal wastewater in cooling systems, 1) TTA can be employed for copper alloy corrosion inhibition, 2) monochloramine biocide can be used instead of free chlorine as biocide, and 3) phosphorous based corrosion or scaling inhibitors are not appropriate to be used due to their precipitation with orthophosphate.

5.2 Scaling Control for Municipal Wastewater Used for Cooling

Abstract

Secondary treated municipal wastewater (MWW) is a promising alternative to fresh water for power plant cooling tower makeup water, especially in arid regions. This study conducted theoretical, laboratory, and field testing to evaluate the scaling potentials of secondary treated municipal wastewater in cooling systems and test different scaling control strategies based on solution chemistry modifications. It was determined that orthophosphate, which is abundant in secondary treated municipal wastewater, contributed to scale formation and to phosphorous removal via precipitation. The scaling inhibitor polymaleic acid (PMA) worked effectively to reduce scaling in both bench-scale and pilot-scale experiments. The biocide monochloramine was found to be less aggressive than free chlorine in attacking PMA to reduce its effectiveness and longevity as antiscalant. In addition, although scaling was found be to a challenge in use of MWW for cooling, scale layers formed on metal surfaces provided a certain degree of corrosion protection for the metal alloys tested.

5.2.1 Introduction

Wastewater is now being recognized as a significant source of water, particularly for non-potable uses (Metcalf & Eddy (AECOM), 2007). Secondary treated municipal wastewater is of increasing interest as an alternative source of makeup water for thermoelectric power plant recirculating cooling water systems because of its abundance and wide availability. In the U.S., 17 power plants reported employing treated municipal wastewater as makeup in 1986 (Ehrhardt et al., 1986), while a more recent survey identified 47 power plants using treated municipal wastewater in recirculating cooling water systems (EPRI, 2008). Most of the 47 plants are in southwest regions and Florida, corresponding to the regions susceptible to water supply constraints. Another analysis determined that secondary treated municipal wastewater represents the most widely available alternative cooling water source for existing and future power plants in terms of quantity and proximity to the ultimate use location (Chien et al., 2008).

The main challenges with MWW reuse in recirculating cooling water systems arise from complicated corrosion, scaling, and biological fouling processes due to compromised quality of the water. For example, secondary treated sewage effluent usually has high concentrations of organic matter, hardness, phosphate, ammonia, and total dissolved solids compared to freshwater sources (Weinberger et al., 1966; Williams, 1982). The presence of organic matter, phosphate, and ammonia has been shown to increase the growth of biomass; high hardness and phosphate increases scaling potential; ammonia is undesirable because it is highly corrosive to copper, and elevated total dissolved solids levels lead to accelerated solid precipitation when water is concentrated due to evaporation. Thus, when secondary treated municipal water is to be used for cooling purposes, the water quality requirements are more difficult to achieve and extraordinary corrosion, scaling and biological fouling control programs are often required (EPRI, 2003).

Orthophosphate and ammonia are the constituents of particular interest in municipal wastewater effluent because phosphate can react with calcium and magnesium, resulting in a compound with high phosphate scaling potential (Goldstein et al., 1981). Ammonia is corrosive and is aggressively controlled since it can form complexes with copper and iron that are often present in cooling systems (Stumm and Morgan, 1996).

The use of oxidizing biocides to kill microorganisms could compromise the effectiveness of added scaling control chemicals. Free chlorine is aggressive to many organic compounds due to its outstanding oxidizing power. Further, large doses of chlorine increase the corrosion rate of mild steel (Nalepa et al., 1999), which in turn leads to excessive iron precipitation. Additionally, the ammonia existing in the wastewater may readily react with the free chlorine to form chloramines. It was determined that chloramine poses less risk for metal alloy corrosion in drinking water distribution systems (MacQuarrie et al., 1997). However, the influence of chloramine on scaling controls in recirculating cooling water system using MWW has not been studied to date.

Scaling inhibiting chemicals (antiscalants) are widely used to prevent mineral scaling in recirculating cooling water systems (Frayne, 1999). Scaling inhibitors usually interact with the mineral nuclei to disrupt the crystallization process and thus decrease the size of the precipitating colloids, making them less prone to sedimentation and surface deposition. Some antiscaling polymers adsorb onto surfaces, acting as a barrier to prevent mineral deposition. Another mechanism of scaling inhibition is through the formation of metal complexes with polymeric antiscalants to increase the operational solubility of precipitation metals, primarily Ca and Mg.

Presently, COOH-containing organic polymers like polyacrylic acid (PAA), polyacrylamide, polymaleic acid (PMA) and various phosphonates and polyphosphates are widely used in industry as efficient antiscalants. Phosphorous-bearing groups exhibit strong interactions with surfaces (Nowack, 2003). For this reason, these chemicals are also used as common corrosion inhibitors (McNiell and Edwards, 2002). However, the phosphorous compounds tend to gradually hydrolyze in water to orthophosphate (Saha and Kurmaih, 1986), resulting in an increased phosphate scaling potential, especially when the aqueous solution contains high hardness (Goldstein et al., 1981). The feasibility of using phosphate based inhibitors in cooling tower systems using impaired waters with high hardness and alkalinity has not been well documented.

Numerous polymer antiscalants are commercially available with varied structural features and effectiveness toward different waters. PMA was selected in this study as a principal antiscalant based on the review of the cooling water practice literature (DOE-NETL, 2007; Metcalf & Eddy (AECOM), 2007; EPRI, 2008), and via consultation with experts in cooling water design and operation (Scandolari 3/12/2008; Beardwood 3/17/2009; Christophersen 12/19/2007). PMA is believed to be effective as both a dispersant and crystal distorter, particularly for Ca precipitates.

The objective of this study was to determine the scaling characteristics of the secondary treated MWW in recirculating cooling systems and the feasibility of adding antiscaling chemicals to inhibit scale formation. Specifically, the objective was achieved by completing the following three tasks: 1) Modeling precipitation potentials of the MWW water under different conditions relevant to actual cooling tower operation; 2) design an experimental matrix and perform laboratory experiments to evaluate influence of ammonia, orthophosphate, polyphosphate, TTA, free chlorine, and monochloramine on scaling; and 3) apply the optimal scaling control program established in bench-scale experiments to pilot-scale cooling systems operated with a secondary treated MWW in the field.

5.2.2 Materials and methods

5.2.2.1 Secondary treated municipal wastewater characterization and synthetic wastewater preparation

The general characteristics and water qualities of secondary treated municipal wastewater (MWW) effluent reported in the literature were surveyed and compiled. The goal was to obtain data from several representative treatment plants in different U.S. geographical locations so that variations of water quality can be included. Data not available in the literature for some secondary effluents that are currently being used as makeup water for cooling systems were sought and included in this compilation.

In addition, water quality characteristics of the MWW from Franklin Township Municipal Sanitary Authority (FTMSA) treatment facility located in Murrysville, PA that was used in the pilot-scale testing were determined. This MWW is denoted FTMW in this study. Water samples (after secondary treatment but prior to nitrification, sand-filtration, and disinfection) were collected with 1-L polyethylene (PE) containers and analyzed for a range of water quality constituents. A portion of each sample was passed through a 0.45-μm filter prior to analysis. The filtered and unfiltered samples were transferred to different PE containers that were prepared with the addition of appropriate preservatives.

The FTMW was tested in the bench-scale recirculating system and the pilot-scale cooling towers. The characteristics of this secondary wastewater are provided in Section 5.1. For the bench-scale experiments, the actual wastewater was concentrated in the laboratory by heated evaporation at 35-40°C to reach CoC 4 as determined by 75 % water volume reduction, prior to be tested in the recirculating system. However, it was discovered that pre-concentrating the actual FTMW led to losses of its mineral content because of precipitation during pre-concentrating. To avoid this complication, a simplified synthetic MWW (denoted SMW), based on the average quality data for secondary treated MWW obtained from the literature survey, was prepared for detailed investigation at bench scale. The chemical composition of the SMW is provided in Table 5.2.1.

Table 5.2.1. Chemical composition of the SMW water (simulating CoC 4) used for MINEQL+ modeling calculations and bench-scale experiments.

Cation	Concentration		Anion	Concentration	
	mM	mg/L		mM	mg/L
Ca^{2+}	7.60	305	SO_4^{2-}	2.84	273
Mg^{2+}	7.16	174	HCO_3^-	13.44	820
Na^+	26.88	618	Cl^-	31.13	1105
K^+	0.70	27	PO_4^{3-}	0.21	20
NH_4^+ (as N)	7.01	98			

The initial level of TDS of the water, before any precipitation takes place, is 3455 mg/L.

5.2.2.2 Equilibrium modeling of MWW scaling potentials

The chemistry of MWW cooling water at different cycles of concentration (CoC) was modeled using MINEQL+ version 4.5 (Schecher and McAvoy, 1992; 1999) to gain insight into the effects of CoC. The primary objective for this effort was to estimate the amount and composition of mineral solids that would precipitate and the water chemical composition that would occur in the pilot cooling units as a function of CoC, as well as to interpret and understand the chemistries observed in the pilot tests. The major constituents and their chemical speciation were assessed and the dominant scale-producing reactions were identified.

The following four operational conditions were tested for the MWW water:

1) The aqueous system was open to the atmosphere ($PCO_2 = 10^{-3.5}$ atm) to allow the alkalinity to be in equilibrium with CO_2(g) and solids were allowed to precipitate.

2) The aqueous system was open to the atmosphere ($PCO_2 = 10^{-3.5}$ atm) to allow the alkalinity to be in equilibrium with CO_2(g) and solids were not allowed to precipitate (i.e., water can be super-saturated).

3) The aqueous system was closed to the atmosphere with total alkalinity fixed and solids were allowed to precipitate.

4) The aqueous system was closed to the atmosphere with total alkalinity fixed and solids were not allowed to precipitate.

The four conditions represent the extreme effects of atmospheric CO_2 and solution supersaturation. It is reasonable to expect that the actual conditions for field testing would fall within these boundary conditions.

5.2.2.3 Scaling inhibition in bench-scale tests

Methods for studying scaling in cooling tower systems were not readily available in the literature. A well-documented method to measure scaling deposition and kinetics *in-situ* was not found in the course of this research. Most established techniques pertaining to scaling phenomena confine themselves to means of static observations and analysis once solid scales have formed and have been collected (e.g., ASTM Method D1245-84, D2331-80, D933-84, D934-80, D887-82). Very limited effort has been devoted to the study of scaling dynamics and kinetics in terms of how scales form and at what rate(s) they form. In addition, there is no quantitative knowledge of conditions influencing and mechanisms dictating scale forming processes.

A method to study scale formation tendency and kinetics for MWW and other impaired waters was developed in this study. Bench-scale water circulating systems similar to those employed in the corrosion studies were constructed and dedicated to investigate scaling phenomena. Stainless steel circular discs were inserted through sampling ports into the recirculating water to provide collecting surfaces for scaling/deposition, as shown in Figure 5.2.1. A mass gain method, similar to the mass loss method for corrosion, was used as a straightforward means to record the scale forming quantities at different water chemistries and scaling control conditions. Scaling kinetics of the MWW was studied at varying cycles of concentration (CoC) in the bench-scale water recirculating systems. Water temperature was fixed at 104°F (40°C) and the flow rate was 3 GPM. The system was open to air so that the alkalinity may approach equilibrium with the atmospheric CO_2, a condition similar to actual cooling tower operation.

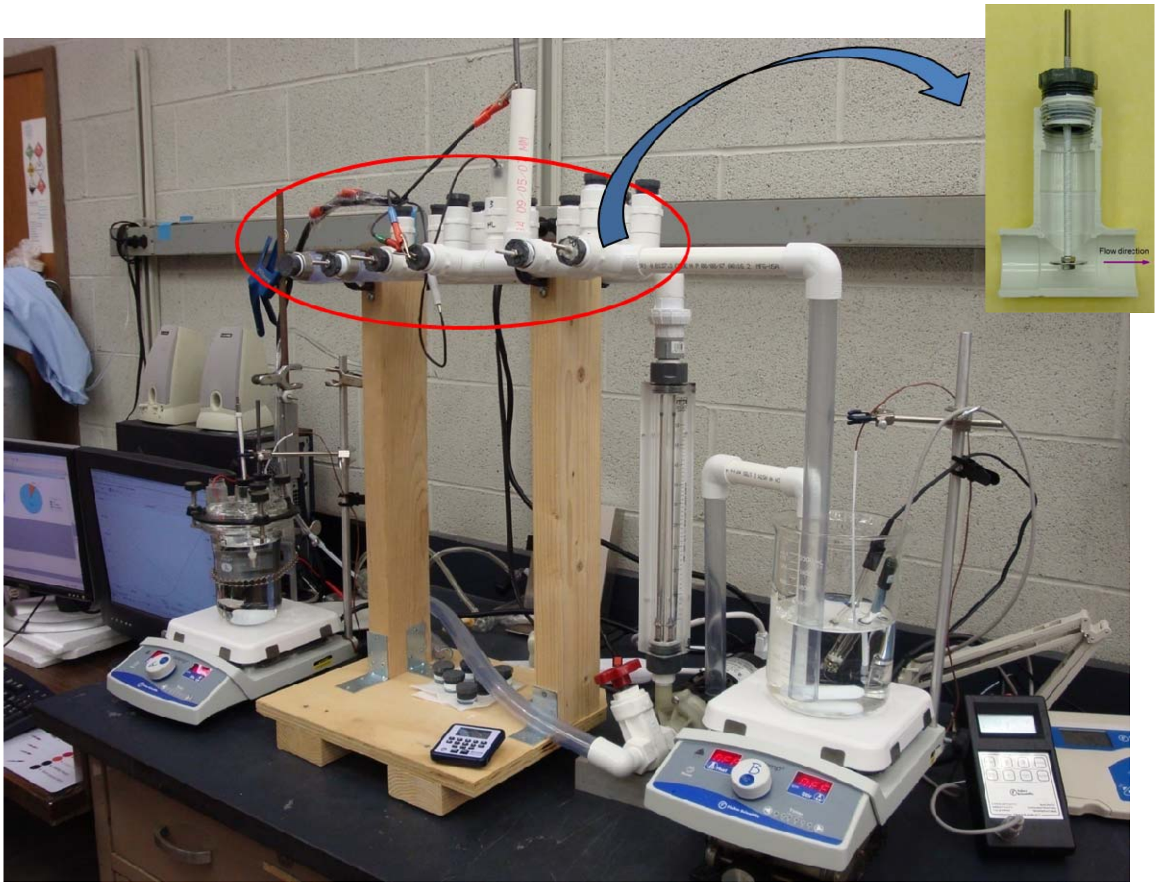


Figure 5.2.1. Bench-scale water recirculating system with inserted stainless steel circular discs for scale collection and subsequent mass gain measurement.

The scale samples collected on the test discs were air-dried and inspected using Scanning Electron Microscopy (SEM, FEI/Philips XL30), and the elemental composition was determined by energy dispersive X-ray spectroscopy (EDS, EDAX/AMETEK). Surface images were obtained by microphotography (Fisher Micromaster optical microscope coupled with a Sony digital camera) and SEM. These studies helped to identify connections between scaling kinetics and scale characteristics. Insights drawn from the connections facilitate the selection of most effective scaling control methods. For example, identification of the mineral deposits by SEM/EDS would instruct the selection of the appropriate antiscaling chemicals to inhibit formation of the specific minerals identified.

To obtain a good understanding of the influence of key cooling tower operational factors on scaling, bench recirculating tests were conducted with both actual and synthetic MWW under different conditions. The operational variables examined included CoC, flow rate, temperature, and scaling inhibitors. A synthetic MWW representative of typical treated municipal wastewaters concentrated at CoC 4 (SMW) was used together with an actual MWW from the FTMSA site that was pre-concentrated to CoC 4 by evaporation at room temperature (FTMW). The recirculating flow rate and water temperature were both controlled at the values to be used in pilot-scale testing, i.e., flowrate of 3 GPM and temperature of 40°C.

Inhibitors included for testing in this study were tetra-potassium pyrophosphate (TKPP, a corrosion and scaling inhibitor), 2-phosphonobutane-1,2,4-tricarboxylic acid, (PBTC, a scaling inhibitor), Polymaleic acid (PMA, scaling inhibitor), as well as Tolyltriazole (TTA, a copper corrosion inhibitor).

Important parameters governing scale deposition in a cooling water system are cycles of concentration, scaling inhibitors, phosphate, and chlorine. Experiments spanning a range of values for these parameters were conducted to study the following:

- effect of concentration cycles
- influence of important water constituents
- effectiveness of different antiscalants
- interference of bio-control chemicals

In addition to scaling and corrosion controls, another important consideration is the simultaneous control of biofilm growth for municipal wastewater effluent. Since chlorine was selected as our primary biocontrol chemical, its potential interference with the antiscalants had to be determined. PBTC and TKPP were tested intensively in the presence and absence of chlorine. A combination of PMA and PBTC, which was recommended by industrial practitioners, was tested with a simultaneous addition of chlorine to the water.

Ammonia and phosphate are major constituents found in municipal wastewaters after secondary treatment and their influence on the scaling control by PBTC and TKPP was also evaluated. Since ammonia was present in the municipal wastewater, it readily reacted with added chlorine (in the form of NaOCl) to form chloramines. Therefore, the chlorine interference with antiscaling agents in municipal wastewater can be more accurately expressed as the interference by chloramines. For the experiment particularly intended to study the effect of chlorine, the ammonia was removed from water before chlorine addition to prevent chloramine formation.

5.2.2.4 Pilot-scale cooling tower tests

Three pilot-scale cooling towers were constructed to test the optimal chemical control methods identified from the bench-scale experiments. The towers were transported to Franklin Township Municipal Sanitary Authority for side-by-side evaluation of different corrosion/scaling/biofouling control programs. The three towers were operated with the following conditions: 1) CoC 4; 2) flow rate 3 GPM (passing through a 0.75” ID PVC pipe); 3) circulating water temperature of 105 °F entering the tower and 95 °F in the collection basin.

The cooling towers were operated using secondary municipal wastewater effluent from the Franklin Township Municipal Sanity Association (FTMSA) for two consecutive 21-day periods. The towers were cleaned with acetic-acid solution and disinfected by free chlorine between the two tests. Detailed information on tower operations was recorded, including the temperature of water at specific locations, airflow rate inside the cooling tower, the conductivity of recirculating system, makeup water volume, blowdown volume, water flowrate, and ambient condition (weather, temperature, relative humidity). It was documented that the towers were able to perform according to design specifications and adequately simulate the operation of full-scale cooling towers in thermoelectric power plants. Appropriate methods for maintaining and cleaning pilot scale cooling towers were developed and the results indicate that these towers can be restored to proper operation with these cleaning procedures. Data that indicated stable performance during the second run illustrate that the cooling towers are durable and reliable even after exposure to severe scaling/biofouling problem. Solid (scale) deposition rates on stainless steel coupon surfaces were documented during all runs (along with corrosion weight loss of metal alloys, and heterotrophic planktonic/sessile bacteria). Water chemistry parameters were monitored to obtain detailed understanding of the cooling tower behavior.

5.2.3 Results and Discussion

5.2.3.1 Precipitation modeling with equilibrium calculations

MINEQL+ (version 4.5) was used in detailed evaluation of the cooling water chemistries, as noted in Section 4.2. Scaling potentials at different cycles of concentration, as measured by the two most commonly referenced practical saturation indexes and direct predictors of precipitation formation, were analyzed. The pH values with respect to cycles of concentration were also calculated.

Detailed modeling results consist of the following:

- The Langelier Saturation Index (LSI) and Ryznar Stability Index (RSI) under open/closed conditions (Figure 5.2.2);

- Amount and form of solid precipitates under open/closed conditions with increasing CoC (Figure 5.2.3); and
- Changes of aqueous pH with increasing CoC (Figure 5.2.4).

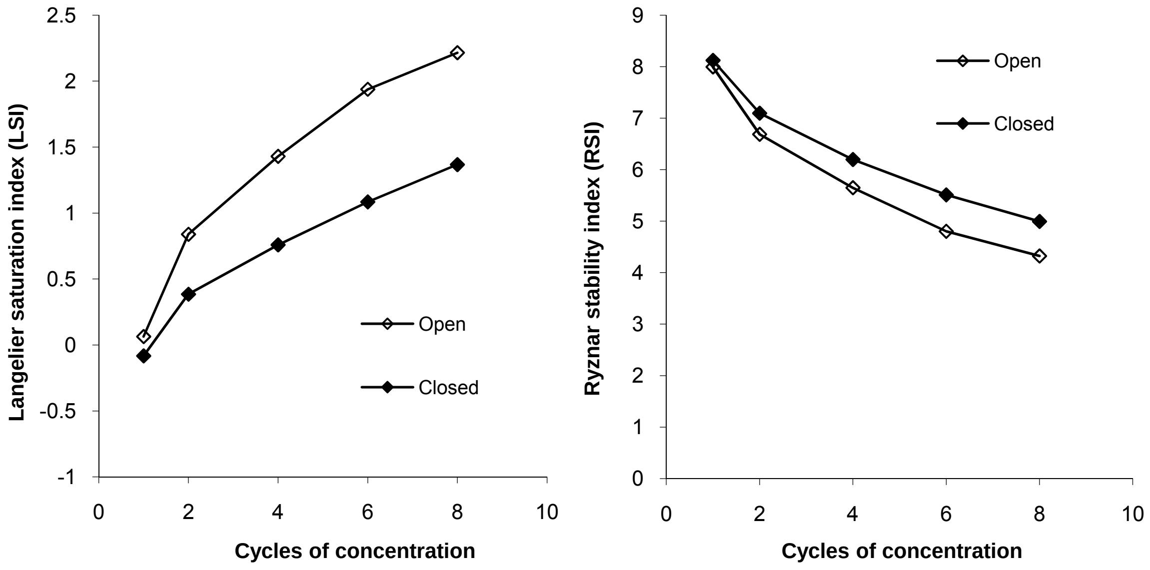
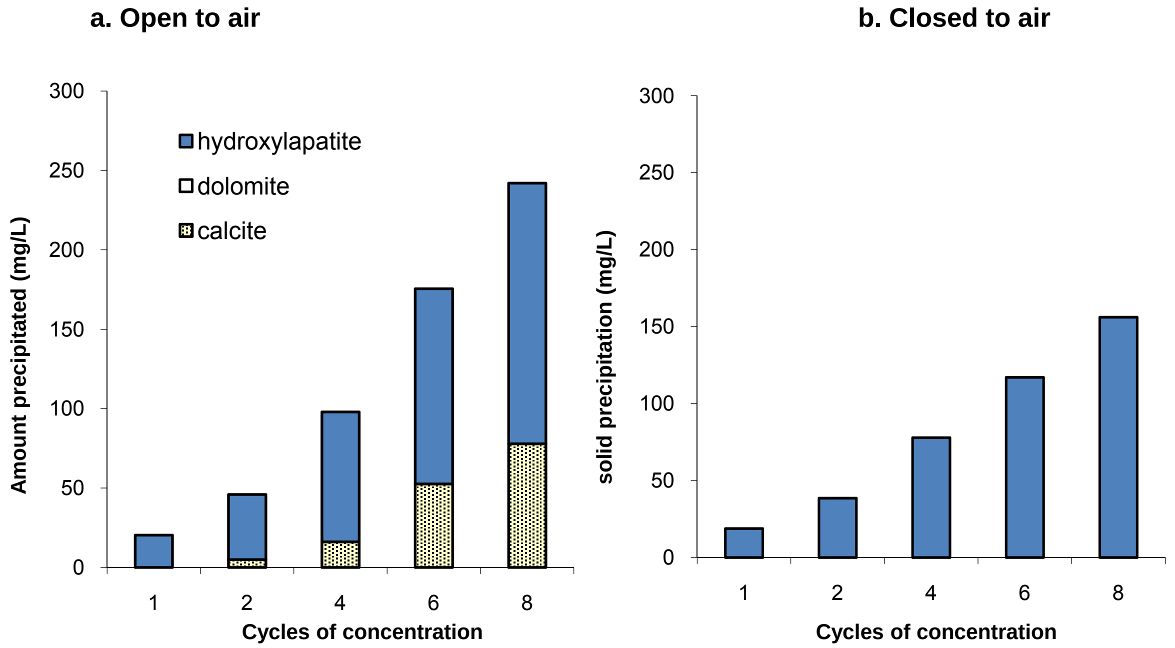


Figure 5.2.2. Modeling results of LSI (left) and RSI (right) for both open and close to air cases.


a. Open to air

b. Closed to air

Figure 5.2.3. Predicted solid precipitation from the Franklin Township Municipal Wastewater Effluent, calculated by MINEQL+.

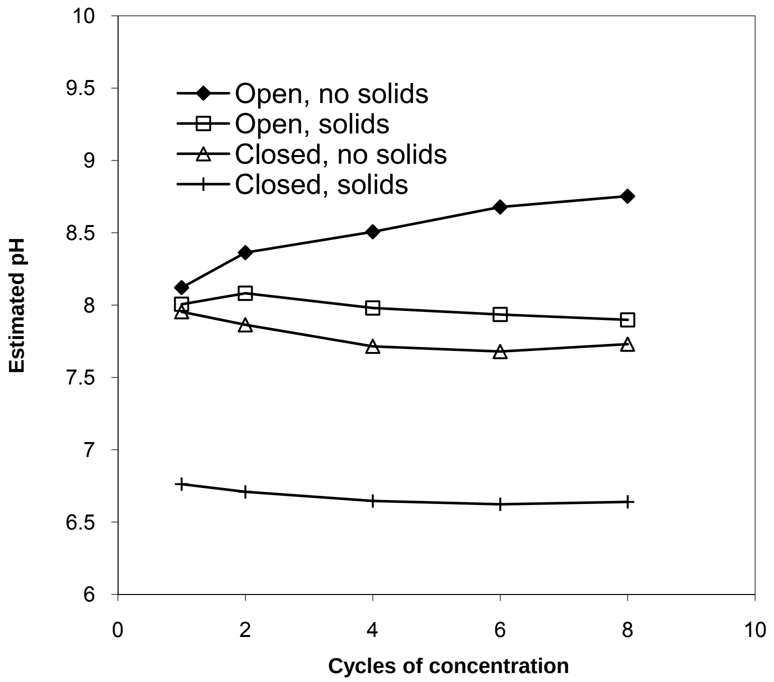


Figure 5.2.4. Predicted solution pH at different CoC under four different operation scenarios (open or closed to air; whether solid precipitation is allowed or not).

The Langelier Saturation Index (LSI) increased with cycles of concentration, as did the scaling potential. When the water was open to the atmosphere at any cycles of concentration, or when closed to the atmosphere but at a cycle of concentration greater than 2, the wastewater tended to form scale in terms of the calcite precipitation potential. Because the Ryznar Stability Index (RSI), by its definition, is calculated by a different formula and usually demonstrates an opposite trend compared to the LSI, the RSI values decreased with the cycles of concentration (as did the corrosion potential). Under most conditions, RSI values were below 6, indicating mild to severe corrosion potentials.

Hydroxylapatite and calcite are the major solid precipitates predicted to form in the Franklin Township municipal wastewater effluent under recirculating cooling tower conditions (open to air).

When the water was open to the atmosphere to allow equilibrium with CO_2(g), the pH values tended to be reasonably stable, with variations between 7.5 and 8.5. When the water was closed to the atmosphere, the water became more acidic with increasing cycles of concentration.

5.2.3.2 Bench-scale recirculating system experiments

Test results with concentrated actual municipal wastewater effluent

From preliminary studies, it was determined that actual waters concentrated by evaporation were not suitable for scaling studies because a significant amount of dissolved solids precipitated during the evaporation process. Nevertheless, actual municipal wastewater was tested in our lab to demonstrate the impact of cycles of concentration and the effectiveness of a dual antiscalants (PBTC and TKPP) in the presence and absence of chlorine. Although the results may not be directly comparable with those obtained with synthetic wastewaters, some conclusions could be drawn from the observed scaling of actual water under different treatment conditions.

As expected, more deposits were obtained at CoC 4 than at CoC 1 (Figure 5.2.5). PBTC and TKPP dosed at 10 ppm each effectively suppressed scale formation in the absence of chloramines (Figure 5.2.5). In the presence of chloramines (1 ppm), more deposits were collected within the first 5 days, indicating that the effectiveness of the antiscalants was reduced, probably due to reactions between the oxidizing biocide and the antiscalants. Study of the exact mechanisms of antiscaling interference by chlorine (chloramines) was beyond the scope of this project.

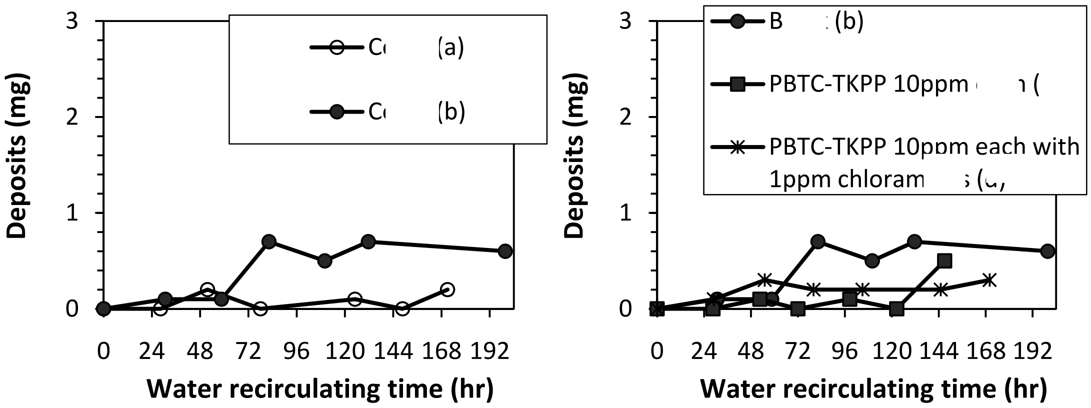


Figure 5.2.5. Scaling behavior of the Franklin Township municipal wastewater secondary effluent in bench-scale tests. Left: Effect of cycles of concentration. Right: Effectiveness of PBTC-TKPP dual antiscalants at CoC 4 with and without chloramine addition.

Test results with synthetic municipal wastewater effluent

The chemical composition of the synthetic municipal wastewater is listed in Table 5.2.1. A series of experiments were conducted to test the effectiveness of the three antiscalants, especially in the presence of chlorine (chloramines), ammonia, or phosphate.

Effect of CoC and antiscalant dosage. Like in the case of actual wastewater, deposition during recirculation of the synthetic wastewater was greater at CoC 4 than at CoC 1 (Figure 5.2.6). However, the amount of deposits collected from the synthetic wastewater at CoC 4 was much greater than that from the actual water concentrated to CoC 4. It is believed that solid precipitation occurred during the evaporative concentration stage for the actual wastewater and this precipitation was not captured by the coupon mass gain measurements but was correctly measured for the synthetic wastewater. Additionally, it was determined that PBTC and TKPP dosed at 10 ppm each were more effective than when dosed at 5 ppm each (Figure 5.2.5), suggesting that the municipal wastewater operated at CoC 4 demands high doses of antiscalants for satisfactory scaling controls.

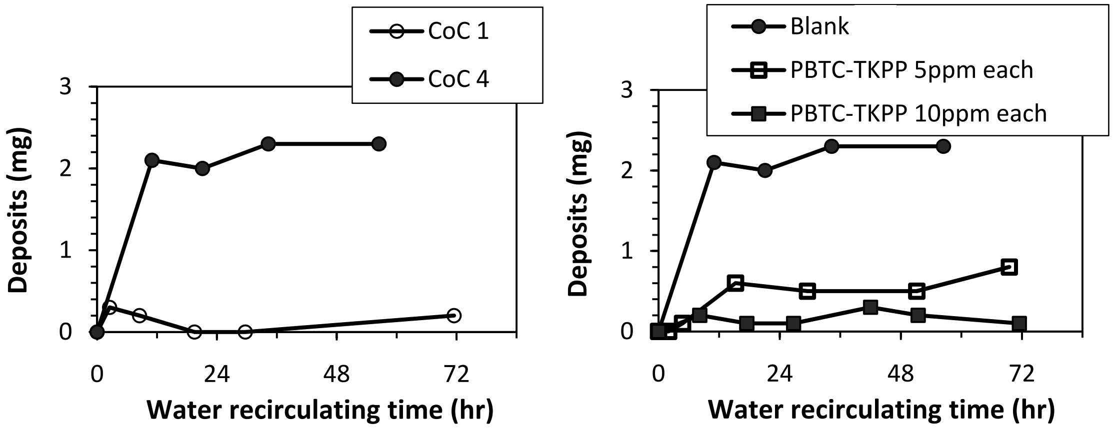


Figure 5.2.6. Scaling behavior of synthetic municipal wastewater effluent in the absence of chlorine in bench-scale tests. Left: Effect of cycles of concentration. Right: Effectiveness of PBTC-TKPP dual antiscalants dosed at 5 ppm each and 10 ppm each at CoC 4.

Influence of ammonia and phosphate. As can be seen from Figure 5.2.7, removal of ammonia (100 mg/L as N) caused more pronounced scale formation, while orthophosphate (20 mg/L) did not have a pronounced impact on scaling control at this concentration level by PBTC-TKPP (Figure 5.2.7). The beneficial impact of ammonia was likely due to the complex formation between ammonia and calcium and/or magnesium, which resulted in greater solubilities for these cations.

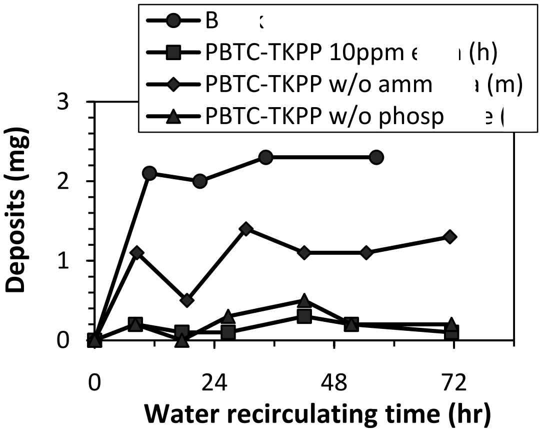


Figure 5.2.7. Influence of ammonia and phosphate on scaling control by PBTC-TKPP dual antiscalants dosed at 10 ppm each with synthetic municipal wastewater at CoC 4. Tests conducted in bench-scale recirculating system.

Interference of chlorine. As shown in Figures 5.2.8 and 5.2.9, addition of chlorine to control biogrowth significantly reduced scaling inhibition by PBTC-TKPP and PMA-PBTC antiscalants. The three antiscalants were profoundly impaired by the addition of the oxidizing biocide, both for their effectiveness and for their active life. It is noteworthy that chlorine is more aggressive than chloramines to impair the antiscaling effect of PBTC-TKPP (Figure 5.2.8). It is worth noting that in the absence of the biocides, the PMA-PBTC combination inhibited scaling almost completely throughout the course of experiment.

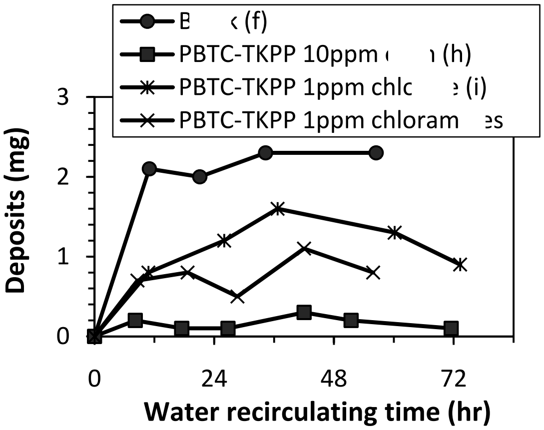


Figure 5.2.8. Interference of chlorine on scaling control by PBTC-TKPP dual antiscalants dosed at 10 ppm each with synthetic municipal wastewater at CoC 4. Tests were conducted in bench-scale recirculating system.

The interaction between the antiscalants and biocides is explained by the data shown in Figure 5.2.9. PMA-PBTC started to deplete after 3 days of interacting with scale forming chemicals and chloramines for both doses tested in the study. The total chlorine demand when high dose of PMA and PBTC (20 ppm and 10 ppm, respectively) were added to the water was much greater than in the case of normal dosage (i.e., 10 ppm PMA plus 5 ppm PBTC): 26 mg/L vs. 6 mg/L. This explains, at least in part, the sharp decrease in PMA after day 3: PMA was substantially consumed by the biocide after day 3. Correspondingly, the scaling inhibition effect started to vanish after the same time period.

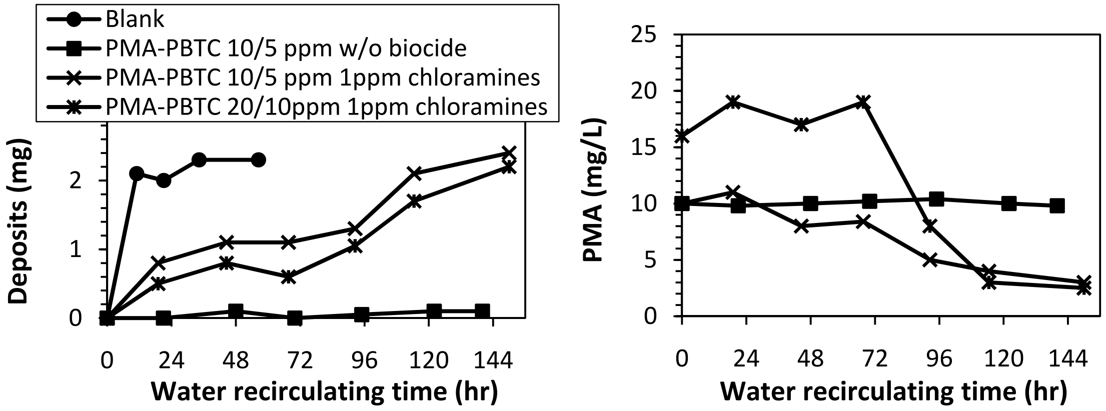


Figure 5.2.9. Interference of chloramine on scaling control by PMA-PBTC antiscalants dosed at 10/5 and 20/10 ppm with synthetic municipal wastewater at CoC 4. Left: Scaling behavior. Right: Depletion of PMA concentration in the aqueous solution. The total amount of NaOCl added to the 20/10 solution was 26 mg/L; whereas only 6 mg/L total chlorine was needed by the 10/5 solution. Tests conducted in bench-scale recirculating system.

From the bench-scale experimental results with the municipal wastewater, it can be concluded that:

- Sufficiently high doses of antiscalants PMA and PBTC applied in combination can be used to control scaling.
- The presence of ammonia in the secondary treated municipal wastewater could potentially help reduce the scaling tendency of this wastewater.
- Chlorine-based biocides significantly reduce the effectiveness of the antiscalants. Higher doses of antiscalants can increase the effectiveness of scaling inhibition, but not necessarily increase their active life time.

5.2.3.3 Pilot-scale study

The results of the bench-scale systems provided data on the effectiveness of PMA, PBTC, and TKPP in preventing scaling from the MWW water. Based on these results, a chemical dosing program was developed for the pilot-scale cooling tower tests (Table 5.2.2). PMA and PBTC were added as scaling inhibitors, TKPP and TTA were added as corrosion inhibitors, and free chlorine or monochloramine was added as biocide.

Table 5.2.2. Chemical treatment programs for pilot-scale tests with secondary treated municipal wastewater at Franklin Township, PA.

	Target concentration (ppm)				
Cooling Tower	**A1**	**B1**	**C1**	**A2**	**B2**
Reagent					
TTA	2	1	2	2	0
TKPP	10	0	10	0	0
PMA	10	0	20	10	0
PBTC	5	0	10	0	0
Free Cl_2	1~2	1~2	1~2	--	--
MCA	--	--	--	2~3	2~3

Bulk water chemistry in cooling tower system

Concentrations of aqueous species including anions (chloride, sulfate, and phosphate) and cations (calcium, magnesium, iron, and copper), total alkalinity, chemical treatment agents (pyrophosphate, tolyltriazole, PMA, and chloramine) in the recirculating water of the pilot-scale cooling towers were monitored and the results are provided in Table 5.2.3 (cationic species and PMA) and Table 5.2.4 (anionic species).

Table 5.2.3. Concentrations of cationic species and PMA (anti-scalant) in makeup water (secondary effluent) and recirculating water (CoC 4-5) in field testing with pilot-scale cooling towers. All units are in mg/L.

Species		Raw water	Tower A1	Tower B1	Tower C1	Tower A2	Tower B2
Ca	Total	35.2±1.5	112±8	97±7	111±10	113±7	105±3
	Filterable	34.5±1.1	100±9	91±7	102±11	103±6	98±4
Mg	Total	10±1	58±5	47±8	57±5	43±3	46±3
	Filterable	10±1	55±4	45±8	54±5	42±3	44±3
Fe	Total	0.37±0.11	0.81±0.25	0.59±0.23	0.68±0.25	0.86±0.28	0.74±0.24
	Filterable	0.12±0.03	0.05±0.04	0.06±0.02	0.07±0.03	0.08±0.05	0.06±0.03
Cu	Total	0.06±0.03	0.13±0.03	0.12±0.03	0.13±0.04	0.22±0.09	0.28±0.14
	Filterable	0.06±0.03	0.10±0.03	0.10±0.03	0.11±0.04	0.18±0.09	0.23±0.11
PMA	Total	--	6.8±1.9	--	14.6±2.6	6.9±1.6	--
	Filterable	--	4.3±1.3	--	9.7±2.1	4.5±1.3	--

Data are mean values with one standard deviation. Sample size for raw water n = 7. Samples for recirculating water in the cooling towers were from day 4 to day 24 during the tower operation (sample size for tower A: 10, tower B: 10, tower C: 11).

Table 5.2.4. Concentrations of anionic species and other chemical additives (for corrosion and biofouling control) in makeup water (secondary effluent) and recirculating water (CoC 4-5) in field testing with pilot-scale cooling towers.

	Concentrations (mg/L)[1]					
Species	**Raw water**	**Tower A1**	**Tower B1**	**Tower C1**	**Tower A2**	**Tower B2**
ALK	113±34	364±53	283±54	324±25	244±79	232±68
SO_4	75±7	388±49	357±39	378±76	356±27	323±30
Cl	142±22	937±74	955±135	917±152	1050±115	859±133
PO_4	11.5±1.8	4.1±1.0	5.9±1.1	5.2±0.6	8.1±3.3	7.5±2.7
TKPP	--	0.6±0.4	--	0.6±0.4	--	--
PBTC	--	0.8±0.3	--	0.9±0.7	--	--
TTA	--	2.0±0.9	1.0±0.8	1.8±1.0	1.8±1.0	--
Total Cl_2	--	1.0±0.7	1.2±0.9	1.5±0.8	3.6±2.2	3.2±1.3

[1] For ALK, units are mg/L as $CaCO_3$.

Water samples were obtained from the sump below each cooling tower. A summary of the results is as follows:

pH -- The pH value remained steady once it reached 8.5 in towers using the Franklin Township secondary effluent as makeup water source. As a comparison, the raw secondary effluent had an average pH of 7.2. The greater pH levels of the cooling tower recirculating water operated at CoC 4 was primarily due to an increase in solution alkalinity.

Chloride -- Concentrations in the towers were generally 6-7 times higher than in the makeup water. This ratio of chloride concentration in the recirculating water to chloride concentration in the makeup water was higher than the volume-based cycles of concentration (4-5) due to the input of chloride from the biocide (i.e., monochloramine).

Sulfate -- Concentrations in the towers were generally 4-5 times higher than in the makeup water. This ratio was close to the volume-based cycles of concentration since there was no additional sink or source for sulfate.

Phosphate -- Although the water was concentrated four to five times in the towers, phosphate concentration in the recirculating water of the towers was actually much lower than that in the makeup water. This was due to the very low solubility of phosphate in the concentrated recirculating water causing most of the phosphate to precipitate.

Alkalinity -- The alkalinity in the recirculating water was generally 2-4 times higher than in the makeup water. This ratio was lower than the volume-based cycles of concentration because alkalinity might be consumed through the precipitation of carbonate species, such as calcite and/or dolomite.

Pyrophosphate (TKPP) -- TKPP was added in Towers A1 and C1 as a corrosion inhibitor but most of it precipitated so that the dissolved concentration was extremely low. The feasibility of using TKPP as corrosion inhibitor in secondary treated municipal wastewater is questionable and it only increased the challenge of scaling control.

Tolyltriazole (TTA) -- TTA was added in all towers as a corrosion inhibitor for copper. It was well maintained at the target concentration levels in the towers.

Total Cl_2 -- Total chlorine, a surrogate measure for the biocide chloramine, was maintained around 1-2 ppm in Towers A1, B1, C1 and 3-4 ppm in Towers A2 and B2.

Calcium -- The amount of calcium in the recirculating water accounted for 60-70% of the amount fed with the makeup water, i.e., 30-40% of the calcium precipitated. Tower B, which received no PMA or PBTC as scaling inhibitors in both runs, precipitated the most calcium, while Towers A and C retained higher amount of calcium in the recirculating water due to the presence of PMA and PBTC. About 10% of calcium present in the water phase as suspended solids (those unfilterable by a 0.22-μm membrane) probably acted as the precursor species for mineral deposition.

Magnesium -- Concentrations in the recirculating waters were 4-5 times more than that in the makeup water, suggesting that magnesium precipitation was minimal. This was confirmed by EDS analysis of the collected solids, which revealed very low (detectable) amounts of magnesium.

Iron -- Iron concentrations were very low in all runs (below 1 ppm). About 70% of iron in the makeup water was unfilterable, whereas 90% of iron in the recirculating water was unfilterable. Such behavior suggests that iron oxidation and precipitation occurred in the recirculating water where dissolved oxygen remained at high levels given the fact that the water was in constant contact with air.

Copper -- Copper levels were monitored to obtain information on possible copper dissolution from the copper coils used in the heating bath of each cooling tower. Because the copper concentrations in the recirculating waters were not higher than 4-5 times of that in the makeup water, it appeared unlikely that the copper coil had been corroded or dissolved by the recirculating water. This indicates that the TTA added as the corrosion inhibitor for copper worked well.

Polymaleic Acid (PMA) -- PMA was added to Towers A and C to control scaling. The added amounts in Tower A for both runs were 10 mg/L (based on the volume of recirculating water), and in Tower C for the first run was 20 mg/L. The detectable PMA in Tower A, however, was reduced to 7 mg/L in both runs, suggesting that about 30% of the polymer antiscalant was quickly coprecipitated and settled out of the liquid phase (the time delay between PMA addition and measurement was only half to one hour). Further, free PMA (the filterable fraction) accounted for about 60% of total aqueous PMA, indicating that 40% was bound to suspended solids to prevent the solids from deposition.

Mass deposition measurement over time

Figure 5.2.10 depicts the time course of scale mass deposited on stainless steel coupon discs from the cooling towers during the two pilot-scale runs. For the first run, PMA and PBTC dosed at 10 and 5 ppm respectively in Tower A1 had the least scaling among the three towers. When the dosage was doubled in Tower C1, anticipated better scaling control was not observed. After day 6, an accelerated mass gain of solids on the coupon discs in all three towers was obvious. Analysis of the composition of the solids collected revealed that biomass accounted for more than 1/3 of the solid deposits, indicating that the biogrowth control was not very effective. However, biosolids alone cannot be used to fully explain the acceleration of solids accumulation on the coupon discs. Possible reasons for the accelerated scaling include that the biomaterials helped accelerate mineral deposition. During the second run, the mass gains in Towers A2 and B2 were similar to those observed during the first run in Towers A1 and B1, indicating a good reproducibility of the tower performance.

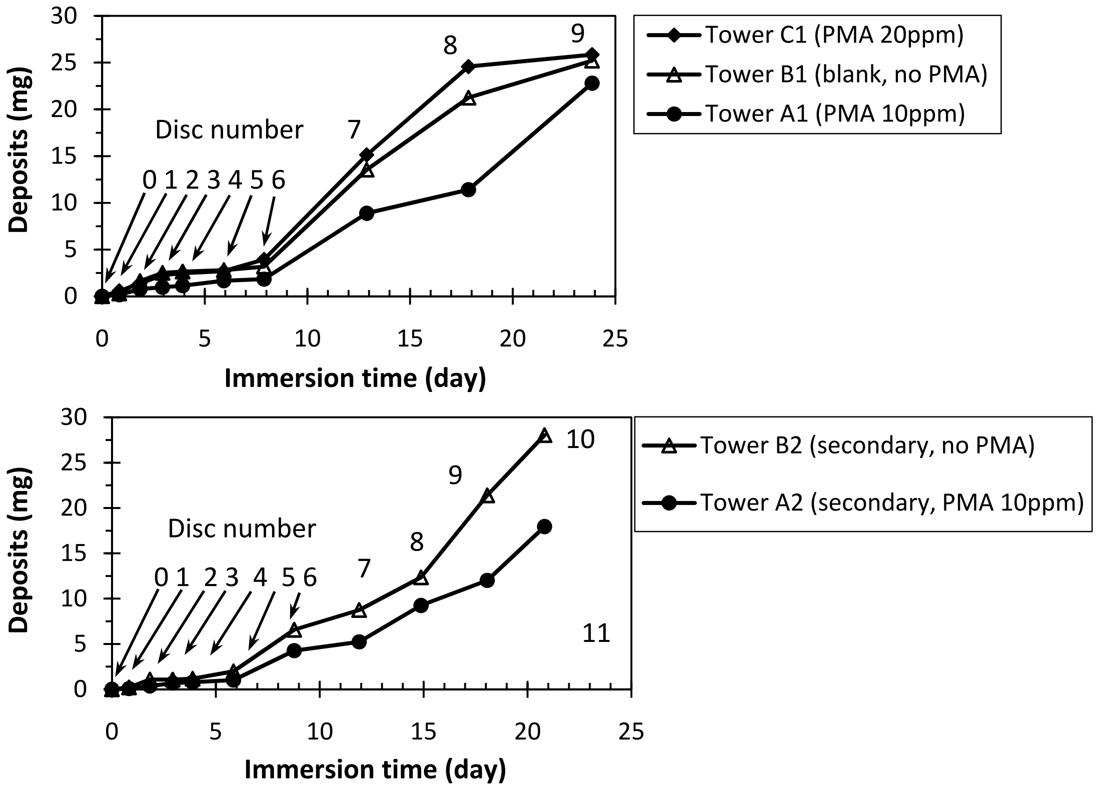


Figure 5.2.10. Mass gain measurement in pilot-scale cooling tower tests with Franklin Township municipal wastewater effluent. Top: run 1, Bottom: run 2. Deposits were collected on stainless steel coupon discs immersed in the pipe flow. Effective collection area 5.61 cm^2, flow velocity 1.9 ft/sec (3 GPM in 3/4" pipe), water temperature 104 ± 2°F, pH 8.5 ± 0.3 (open to air).

<u>Organic deposition</u>

In terms of the organic content of the cooling water, 40% of the organic matter was determined to be particulate bound (Figure 5.2.11). This was correlated to the relatively high levels of suspended growth in the wastewater. Concentrations and fate of PMA in Towers A and C are also shown in Figure 5.2.11. Measured total PMA was lower than the amount added for both towers, indicating fast coprecipitation of PMA with solids deposition. Free PMA accounted for about 60% of total PMA remaining in water. The rest (i.e., 40%) was associated with suspended solids as PMA adsorbed to mineral particles to prevent settling through electrostatic and steric stabilization. Additionally, since the added PBTC was not detected after addition during the first run, it was decided that PBTC would not be used during the second run. To accommodate this decision, the PMA dosage was maintained at the same level in Tower A2 to study the effect of monochloramine.

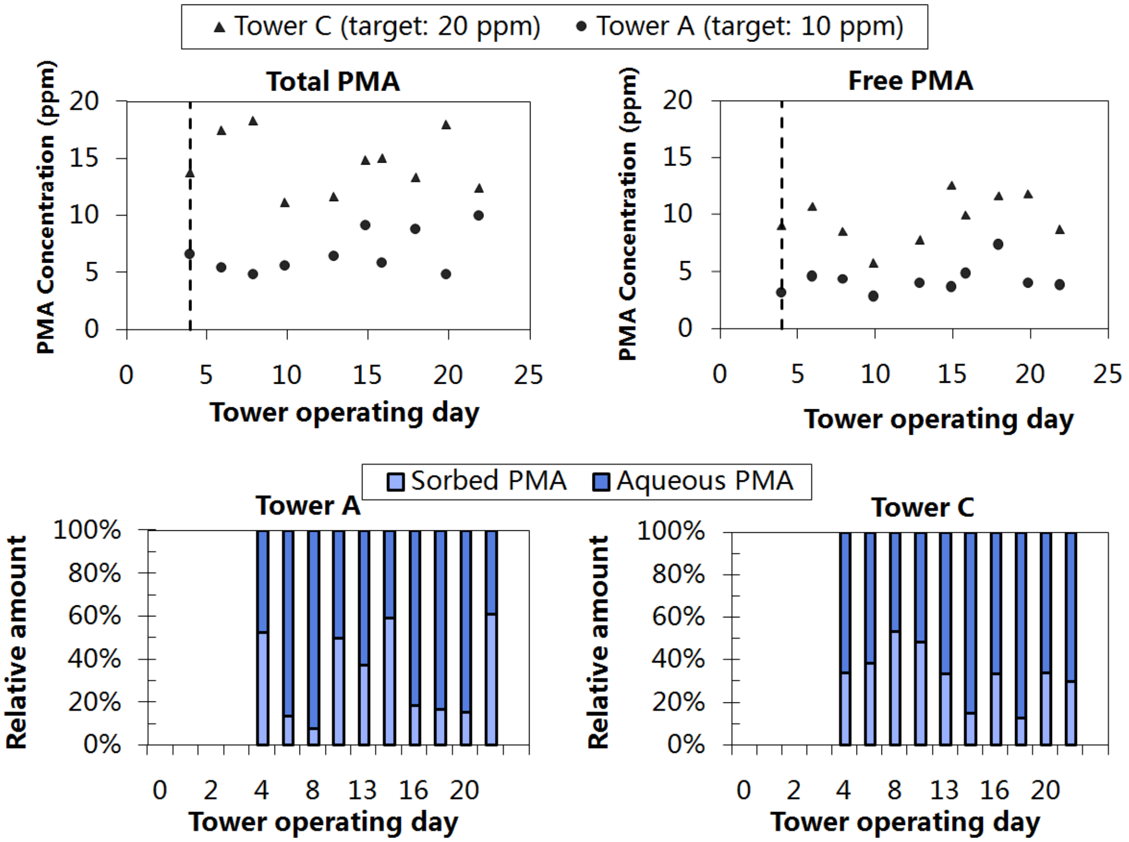


Figure 5.2.11. ***Top:*** total PMA (left) and aqueous PMA (right) concentrations in the recirculating water of Towers A1 and C1 as measured after daily addition of PMA whose dose was based on blowdown volume. Aqueous concentrations were obtained by filtering the water samples through a 0.22-μm filter and measuring the PMA concentration in the filtrates. ***Bottom:*** the distribution of PMA between the aqueous phase and suspended solid phase in the recirculating water of Towers A1 and C1 as measured after daily addition of PMA whose dose was based on blowdown volume. Sorbed PMA was calculated by subtracting the aqueous PMA from total PMA.

5.2.3.4 Comparison of experimental observations and equilibrium predictions

The MINEQL+ modeling provided estimates of the chemical composition of precipitated solids at equilibrium as well as their relative abundance. Forms of precipitates predicted by MINEQL+ were compared with the species of actual deposits collected from experiments conducted at both bench-scale employing water recirculating systems and pilot-scale with cooling towers. These solids deposits were inspected and imaged using Scanning Electron Microscopy and the elemental composition determined by Energy Dispersive X-ray Spectroscopy (SEM/EDS) analysis. The total mass of the solids collected was also compared with the amount predicted from modeling efforts.

Information obtained from these comparisons was used to test the usefulness of the equilibrium modeling as a predictive tool in assessing the cooling water scaling behavior. Possible explanation for discrepancies between modeling prediction and experimental observation were offered in the following discussion, together with suggestions for future improvements of mathematical modeling for cooling water quality characteristics.

Based on the chemical composition of the WMW provided in Table 5.2.1, MINEQL+ predicted that hydroxyapatite (HAP) and dolomite (ordered) would precipitate (modeling condition: ionic strength corrected, 40°C, and closed system) with the following amounts:

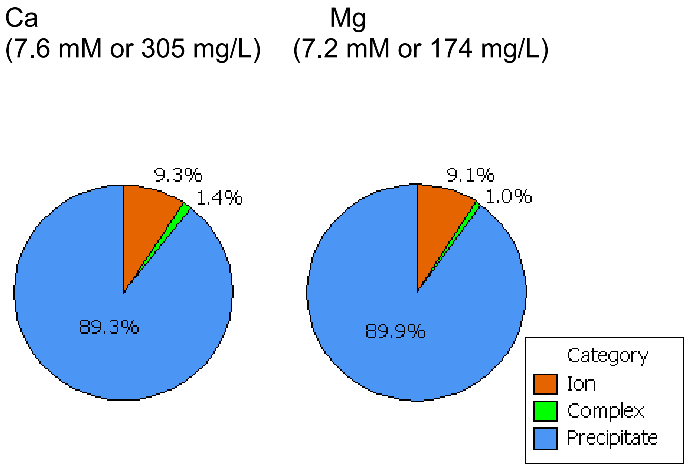
HAP [$Ca_5(PO_4)_3OH$]:	0.07 mM (35.2 mg/L)
Dolomite [$CaMg(CO_3)_2$]:	6.44 mM (1187.5 mg/L)

The elemental composition of the predicted precipitation solids is shown in the Table 5.2.5.

Table 5.2.5. Elemental composition of precipitates from SMW predicted by MINEQL+.

Element	Ca	Mg	P	C	O	H
% (molar)	10.3	9.8	0.3	19.5	60.0	0.1
% (wt)	22.3	12.8	0.5	12.7	51.8	0.0

The initial TDS in the SMW (CoC 4) was 3,455 mg/L, and 1,223 mg/L of solids were predicted to precipitate at equilibrium. The TDS of the solution at equilibrium should therefore be 2,233 mg/L, which is 65% of the initial TDS level. Of particular interest is the distribution of Ca and Mg at equilibrium: precipitated, complexed, and free ions. Figure 5.2.12 illustrates the predicted distribution and indicates that almost 90% of the initial Ca and Mg should precipitate out of solution at equilibrium.


Ca
(7.6 mM or 305 mg/L)

Mg
(7.2 mM or 174 mg/L)

Figure 5.2.12. Distribution of Ca and Mg at equilibrium predicted by MINEQL+ (40°C, closed system; solution intrinsic pH = 8.4 as calculated by the model). Complexes consist of mainly ion-pairs with carbonate and sulfate.

Experimentally, stainless steel circular coupon discs immersed in the bench-scale water recirculating system operated with the synthetic MWW were allowed to collect deposits for 6 days. After 6 days, the discs were removed from the recirculating system and air-dried prior to SEM/EDS analysis. Figure 5.2.13 shows the SEM/EDS results for the deposits collected on the disc. The SEM image shows well-shaped crystalline morphologies. Based on the EDS analysis, the average abundance of the elements in the collected solids is listed in Table 5.2.6.

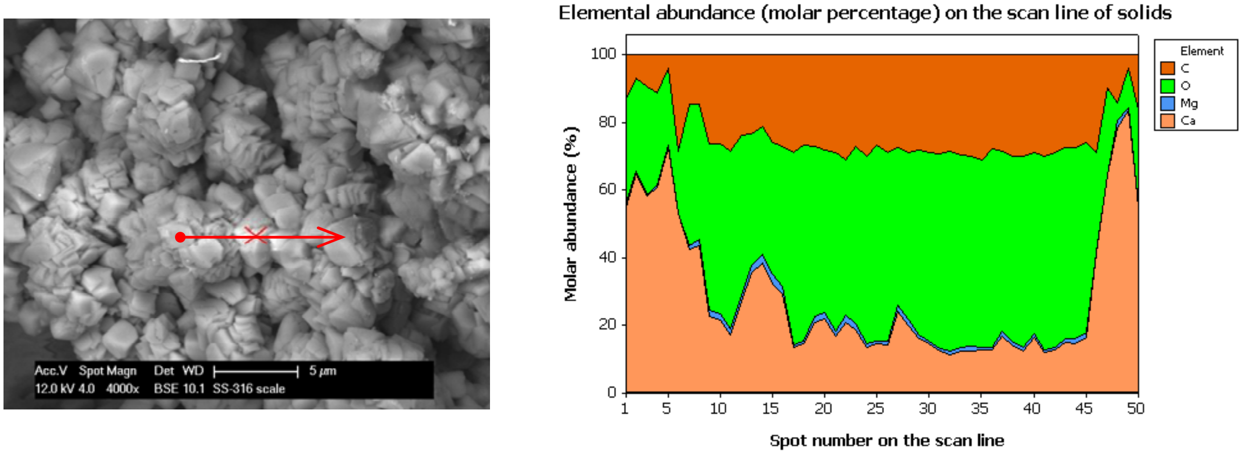


Figure 5.2.13. SEM image and quantitative 1D EDS analysis of the deposits collected on a stainless steel disc that is immersed in the precipitating solution. The red line (10 μm in length) indicates the scan line for the EDS analysis of elemental abundance. P and H are not detected by EDS.

Table 5.2.6. Elemental composition of precipitates from SMW observed in bench-scale experiments.

Element	Ca	Mg	C	O
% (molar)	28.7	1.3	24.2	45.8
% (wt)	52.2	1.4	13.2	33.2

Compared to the model prediction (Table 5.2.5), the actual solids collected contained excess Ca but was deficient in Mg content. Such observation that Mg did not participate in the solids formation was confirmed by monitoring aqueous Mg concentration. The Mg concentration was essentially unchanged over the course of experiment (Figure 5.2.14). What the model predicts may be the most stable crystalline phases under equilibrium conditions. Deposits formation from the actual water, while ultimately ought to be driven by thermodynamics, can experience different pathways of formation patterns due to kinetic constraints and/or inhibitory factors imposed by the metal surface-solution interactions.

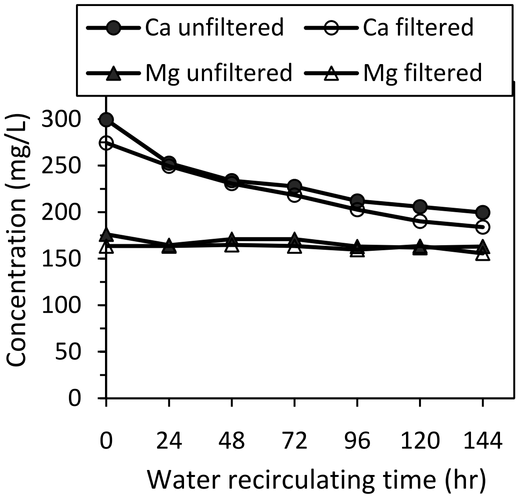


Figure 5.2.14. Changes in the aqueous concentrations of Ca and Mg in bench-scale water recirculating system operated with synthetic MWW. Closed data points represent concentrations of unfiltered water samples while open points filtered samples. The filtration is carried out using 0.45 µm HA type membrane filters (Millipore) to remove suspended solids.

Since Mg was marginally observed in the collected deposits, a second set of modeling calculations were performed under the constraint that Mg-containing solids (e.g., dolomite, huntite, artinite, brusite, and magnesite) were not allowed to form, and calcium carbonate takes the form of aragonite, a fast-forming phase of $CaCO_3$. Under these conditions, a total of 759 mg/L of precipitates in the form of HAP and aragonite were predicted to form, resulting in a 22% decrease in solution TDS.

HAP [$Ca_5(PO_4)_3OH$]:	0.07 mM (35.2 mg/L)
Aragonite [$CaCO_3$]:	7.23 mM (723.6 mg/L)

The elemental composition of the solids predicted to precipitate under these conditions is shown in Table 5.2.7:

Table 5.2.7 Elemental composition of precipitates from SMW predicted by MINEQL+ under kinetic constraints.

Element	Ca	Mg	P	C	O	H
% (molar)	20.1	0	0.6	19.2	60.0	0.2
% (wt)	40.0	0	0.9	11.4	47.7	0.0

These results are in a closer agreement with the experimental observation with regard to the elemental composition of the deposits. However, the total solids actually precipitated in the experiment were estimated to be 150-200 mg/L, which is significantly less than the equilibrium model prediction (759 mg/L).

The concentration of Ca was determined over the course of the experiment. The data shown in Figure 5.2.14 suggests that 35% of Ca precipitated during 6 days. This magnitude of Ca precipitation was also observed in pilot-scale cooling tower tests (section 5.2.3.3).[1] Tower B, which received no polymaleic acid (PMA) as the scaling inhibitor, precipitated the largest amount of Ca, while Towers A and C retained higher amount of Ca in the recirculating water due to the presence of PMA. This suggests that PMA retarded Ca precipitation, resulting in higher Ca concentrations than predicted remaining in solution during the course of tower operation. Therefore it is clear that kinetic constraints of precipitation arising from PMA addition are not captured by the equilibrium modeling that is entirely based on thermodynamic calculations, such as MINEQL+.

For pilot-scale cooling tower experiments, SEM/EDS analysis was performed on deposits collected from Tower B1 after 6 d of operation at CoC 4. The EDS spectra (Figure 5.2.15) revealed almost undetectable amounts of Mg, thereby confirming the results shown in Figures 5.2.13 and 5.2.14. The SEM image displays solids of more amorphous character as opposed to those depicted on Figure 5.2.13. Alvarez et al. (2004) observed that the Ca-P complex preferentially precipitates as amorphous forms in the presence of soil organic matter. In addition, amorphous $CaCO_3$ were collected on steel surfaces when organic additives are present in solution (Kjellin et al., 2001; Kjellin, 2003; Wei et al., 2004; Wei et al., 2005). These observed interactions with organic matter suggest that there is more complex chemistry occurring in pilot-scale cooling tower water using actual secondary treated MWW concentrated 4 times as compared to bench-scale water recirculating system using synthetic MWW simulating only the inorganic constituents.

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[1] Details regarding the setup and operation of pilot testing are not discussed here but are available in other sections of this report.

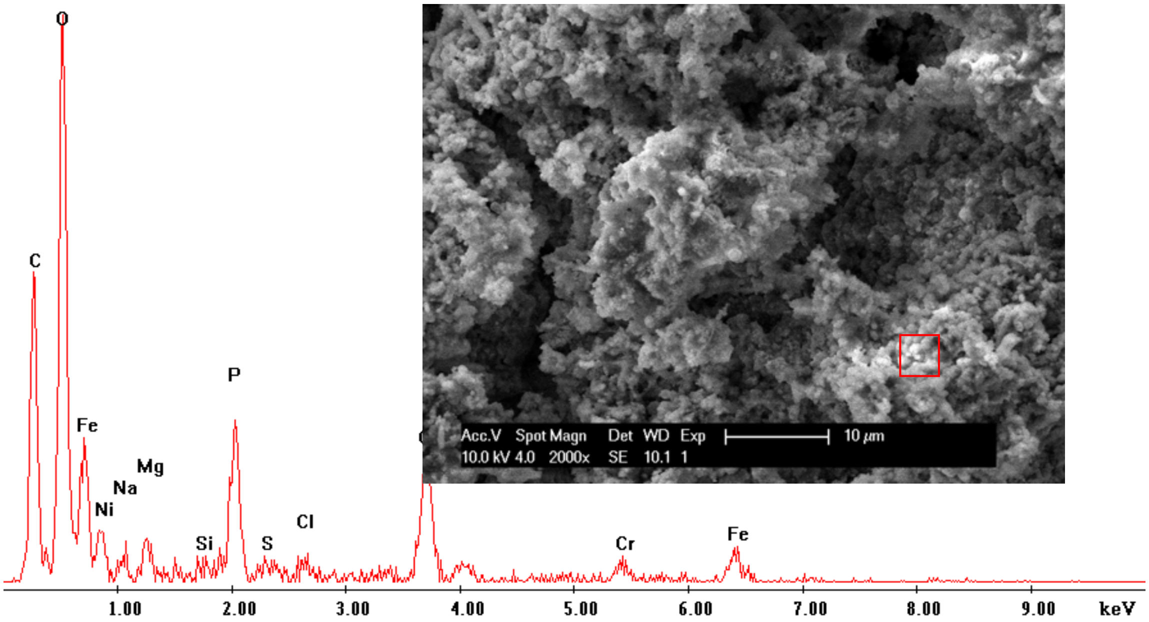

Figure 5.2.15. SEM image and the elemental composition of the solid deposits collected on a stainless steel disc immersed in the actual MWW of the pilot-scale cooling tower operated at CoC 4 (Tower B2). EDS scan was performed on the area outlined by the square box on the SEM image.

The EDS analysis conducted on these solids indicated that the deposits consist primarily of calcium carbonates and phosphates, which is in qualitative agreement with the revised model predictions. However, the quantity of phosphate present in the solids collected from the pilot-scale tests appears to be greatly enriched when compared to that in the deposits collected from the bench-sale studies using synthetic MWW. This is likely because of the higher P concentration in the raw Franklin Township MWW (i.e., 12 ppm vs. 5 ppm in the synthetic water). In addition, P-containing chemicals, in the form of 10 ppm of pyrophosphate (TKPP) and 5 ppm of 2-phosphonobutane-1,2,4-tricarboxylic acid (PBTC), were added to the cooling tower as corrosion inhibitors. Chemical analyses indicated that these added phosphates quickly became undetectable in the liquid phase, suggesting a fast precipitation that further contributed to the relatively high P signal in the EDS spectra (Figure 5.2.15).

5.2.4 Conclusions for Scaling Control in Reused Municipal Wastewater

The scaling behavior and control of secondary treated MWW in recirculating cooling systems was evaluated. Based on the results from both bench- and pilot-scale experiments performed in this study, it was determined that commonly used polymer-based scaling inhibitors can be effective in controlling potentially severe scaling when using this impaired water as makeup in recirculating cooling towers. PMA was very effective at scaling inhibition in the absence of free chlorine. Ammonia present in the wastewater suppressed the aggressiveness of the free chlorine on PMA in bench tests. However, ammonia was significantly removed from the cooling tower systems in pilot tests due to volatilization. Monochloramine biocide was applied in the pilot tests and was found to be less aggressive than free chlorine, while still being an effective biocide.

Overall, for scaling control of MWW concentrated to CoC 4 in recirculating cooling systems, 1) PMA can be applied at 10-20 ppm level for mineral scaling inhibition, 2) monochloramine is better suited to replace free chlorine in such applications, and 3) phosphorous based corrosion inhibitors are not appropriate due to their reversion to orthophosphate and subsequent precipitation with Ca and Mg.

5.3 Biofouling Control for Municipal Wastewater Used for Cooling

Abstract

Water shortages in some parts of the U.S., competition between major water uses, and increasingly stringent regulations on fresh water withdrawals have made the search for alternative water sources for power plant operation of significant interest. Among potential alternative water sources, treated municipal wastewater is one of the most abundant and widely distributed. Biofouling is one of the major problems in the use of treated municipal wastewater for cooling system makeup. In this study, the feasibility of using chloramination to control biofouling when secondary treated municipal wastewater was used in cooling systems was investigated through batch, bench-scale and pilot-scale studies. Both preformed monochloramine and chloramine formed by utilizing the ammonia in the wastewater were tested in this study. This study revealed that maintaining monochloramine concentration above 1 ppm as Cl_2 was necessary to control bioactivity in the cooling water. Pre-formed monochloramine yielded better biocidal activity than monochloramine formed by utilizing the ammonia in the secondary treated municipal wastewater because of the variations in ammonia concentration in the cooling systems.

5.3.1 Introduction

Biofouling caused by a wide variety microorganisms, such as bacteria, fungi, and algae, is one of the most common and significant problems in cooling systems (Frayne, 1999). Biofilm growth in cooling systems causes heat transfer resistance and microbiological induced corrosion under the biofilm can cause failure of the cooling system (Ludensky, 2005). Typical operating conditions maintained in a cooling system, such as temperature range, pH, continuous airflow and sunlight, can make this system a favorable place for biological growth. Along with the favorable growth conditions available in the cooling system, organic matter and nutrients in the makeup water can make biomass control a challenging task.

The main source of microbiological contamination is usually from the makeup water. Using fresh water with lower organic matter and nutrient concentrations as makeup water in cooling systems has lower biomass growth potential compared to using treated municipal wastewater with higher organic matter and nutrient concentrations. In addition to the microorganisms in the makeup water, airborne microorganisms can aid the bacterial growth as they move through a cooling tower (Ludensky, 2005).

Chlorination is often used to inhibit biomass growth in cooling systems (Frayne, 1999). However, in order to maintain a certain level of free residual chlorine, a large amount of chlorine will be required to satisfy the chlorine demand of organic matter and ammonia. This is especially true in the case where treated municipal wastewater is used as cooling system makeup. Thus, maintaining residual free chlorine may be a challenging option for the control of biofouling when secondary treated municipal wastewater is used as cooling system makeup. Secondary treated municipal wastewater usually has a significant amount of ammonia, which can react with free chlorine to form chloramines. Chloramines include monochloramine (NH_2Cl), dichloramine ($NHCl_2$), and trichloramine (NCl_3). Monochloramine has the highest disinfecting power among these chloramines (Wolfe et. al., 1984) but it is generally a weaker disinfectant than free chlorine (Wolfe et. al., 1984).

Chloramination may be an option for biofouling control when secondary treated municipal wastewater is used in cooling systems, especially when considering the high chlorine demand of this impaired water. Turetgen (2004) observed that monochloramine was significantly more effective than free chlorine against cooling tower biofilms. Rao et al. (1998) demonstrated that monochloramine and free chlorine showed similar biocidal activity in controlling biofilms and that monochloramine formed in situ in the cooling circuit could be as effective as free chlorine. Hence, chloramination that relies on the availability of ammonia in wastewater may be an effective biomass control option in cooling systems using secondary treated municipal wastewater as makeup.

The objective of this study was to determine the feasibility of using chloramination to control biomass growth in cooling systems using secondary treated municipal wastewater as makeup water. First, the appropriate residual chlorine range to control biofouling in the cooling system was determined by conducting experiments in batch and recirculating bench-scale systems. Effects of ammonia concentration in the wastewater and cycles of concentration on the biocidal efficacy of monochloramine were also explored in batch tests. Based on the batch and bench-scale tests, field tests were conducted at Franklin Township Municipal Sanitary Authority, Murrysville, PA for two consecutive 21-day periods to observe the effectiveness of biofouling control under the conditions that are representative of full scale cooling systems.

5.3.2 Materials and methods

5.3.2.1 Impaired Water Acquisition, Characterization, and Concentration

Actual secondary treated municipal wastewater was used in all experiments conducted in this study. This wastewater was collected at Franklin Township Municipal Sanitary Authority near Murrysville, PA. Samples of this water were refrigerated at 5 °C in 5-gallon carboys for a maximum of two weeks. The characteristics of this water are presented in Table 5.3.1. Raw wastewater was considered as Franklin Township wastewater at one cycle of concentration (FTMW CoC 1). This water was concentrated to CoC 4 by heating to 40 °C until the volume of water sample was reduced to one-fourth of its initial volume. Throughout the evaporation process, almost all ammonia was volatilized and it was compensated by adding ammonium chloride (NH_4Cl).

Table 5.3.1. Results of analysis of Franklin Township Municipal Sanitary Authority (Murrysville, PA) secondary treated effluent (Sampled on: March 14, 2008)

Parameters	Secondary treated	
	Filtered	Unfiltered
Conductivity (μs)		810
pH		7.31
TSS (mg/L)		24.5
TDS (mg/L)		593
COD (mg/L)	83.4 ± 2	96.5 ± 3
TOC (mg/L)	23.91 ± 0.07	25.43 ± 0.21
NH_3-N (mg/L)	19.66 ± 0.14	19.65 ± 0.82

5.3.2.2 Batch Experiments

Batch tests to evaluate the effectiveness of chlorine and chloramine were performed in 1-L glass beakers. Temperature of the water was maintained between 95 and 105 °F (35 – 41 °C) and the beakers were open to atmosphere and continuously stirred. Most of the batch tests lasted from 12 - 24 hours and some were extended for 3 days. The batch tests with chloramine were conducted at total chlorine levels of 0.2 - 0.5 ppm, 0.5-1 ppm, 1-2 ppm, 2-3 ppm, and 3-4 ppm as Cl_2 in both FTMW CoC 1 and FTMW CoC 4. In the batch tests, planktonic heterotrophic bacteria were measured by spread plate method (Method 9215 C, APHA, 1998). Plate count agar was used as the culture medium and the plates were incubated for 48h at 35°C. pH was measured by a pH meter (Accumet, Model 15). DPD colorimetric method (Method 4500-Cl G, APHA, 1998) was used to measure free chlorine, total chlorine and monochloramine. A field portable chlorine pocket photometer (HF Scientific, Inc, Florida) was used for DPD colorimetric analysis. This photometer was calibrated by CARY 300 Bio UV-visible spectrophotometer (Varian Inc., Palo Alto, CA). Ammonia was measured by Phenate Method (Method 4500-NH_3 F, APHA, 1998) and by HACH nitrogen test kit (Model NI-8, color disc; Method 4500-NH_3 B&C, APHA, 1998).

5.3.2.3 Bench-Scale Recirculating System

The effectiveness of chloramine to control biofilm growth was also tested in a recirculating system that was designed to simulate temperature, flow velocity and water quality similar to those in a real recirculating cooling tower systems. The system included a centrifugal pump, a water bath on a hotplate to control water temperature, and a pipe rack made of ¾ inch PVC to hold coupons for biofilm monitoring (Figure 5.3.1.). Temperature was controlled at approximately 40°C and flow rate was maintained at 3 gpm. Circular stainless steel coupons were used for biofilm sampling. Removal of biofilm from the coupons was done following the ASTM E 1427 method (ASTM, 2000). After withdrawing coupons aseptically from the coupon rack, water was drained (Bradshaw et. al., 1996) and the coupons were immersed in 50 mL phosphate buffered saline solution (Prosser et. al., 1987). The solution was sonicated for 5 minutes to dislodge the biofilm from the coupon and vortexed for 30 seconds to make it homogeneous (Prosser et. al., 1987). Planktonic heterotrophic plate count was measured for this solution and converted to CFU per cm^2 of coupon area.

Planktonic heterotrophic bacteria, total residual chlorine and monochloramine were monitored throughout the experiments in this system.

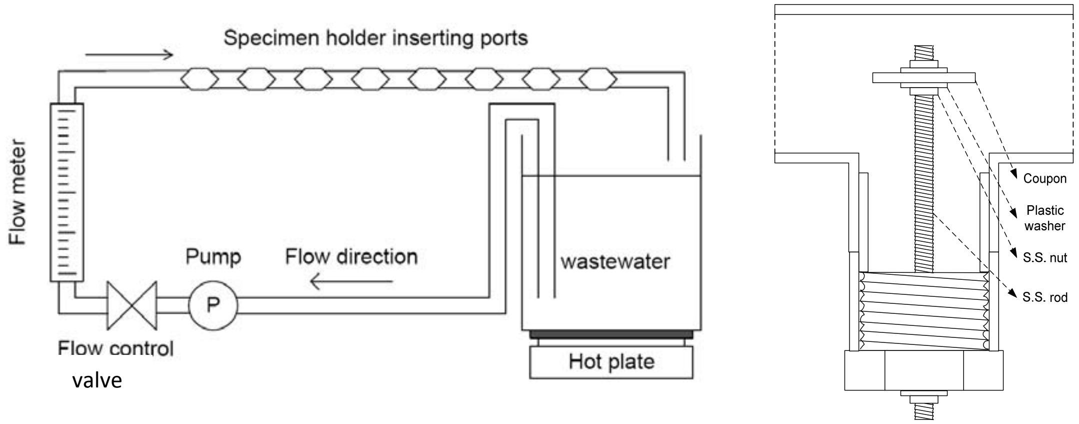

Figure 5.3.1. Schematic diagram of bench scale circulating system (left) and circular coupon with coupon holder for biofilm sampling (right)

5.3.2.4 Pilot-Scale Cooling System

To examine the effectiveness of biofouling control under the conditions similar to those in full-scale cooling systems, pilot-scale cooling towers we constructed and deployed in the field (Appendix D).These pilot-scale cooling towers were operated in the field for two 21-day test periods (total test time was 24 days but it took 3 days to reach CoC 4). The first test was conducted by operating three cooling towers in parallel and all three towers were monitored for biological activity. Only two towers were monitored in the second test. During the first test (July 11, 2008 to August 4, 2008), sodium hypochlorite solution was applied continuously to form monochloramine *in-situ* utilizing the ammonia already available in the secondary treated municipal wastewater. Secondary treated municipal wastewater was used as makeup water for all three towers during this run. Pre-formed monochloramine was applied to all three towers during the second run that was performed from August 11, 2008 to September 4, 2008. Monochloramine was pre-formed in the field by mixing sodium hypochlorite and ammonium chloride at 4:1 Cl_2:NH_3 weight ratio at pH 9.0 (EPA, 1999; Palin, 1950; Kirmeyer et al., 1993). Sodium hydroxide was used to control the pH.

Both planktonic and sessile heterotrophic bacteria were monitored during the 21-day pilot scale tests. Sessile bacteria were monitored by immersing circular stainless steel coupons in circulating cooling water. Coupons were inserted after achieving CoC 4. Coupons were pretreated with ethanol solution for sterilization (Obuekwe et al., 1981). Coupons were withdrawn from the coupon rack after 4, 7, 14 and 21 days. Removal and analysis of biofilm from the coupons was done in the same way as for the bench-scale recirculating system (Section 5.3.2.3).

5.3.3 Results and Discussion

5.3.3.1 Batch Experiments

Preliminary tests were conducted to determine the dosage of biocide, monochloramine, needed to control biogrowth in CoC 4 FTMW. The initial planktonic Heterotrophic Plate Count (HPC) in FTMW at CoC 4, was 4.5×10^4 CFU/mL. As indicated in Figure 5.3.2., total chlorine was maintained between 0.2 ~ 0.5 ppm as Cl_2 and monochloramine was between 0.11~0.28 ppm as Cl_2 since the initial ammonia concentration in this water was 50 ppm as N. By maintaining total chlorine and monochloramine in this range through periodic addition of sodium hypochlorite, planktonic HPC decreased from 4.5×10^4 CFU/mL to 1.1×10^3 CFU/mL after 9 hours of contact. However, the total HPC increased to 3.1×10^5 CFU/mL after 24 hours. In comparison, planktonic HPC in the control reactor receiving no disinfectant increased from 3.1 x

10^4 CFU/mL to 5.6 x 10^6 CFU/mL after 24 hours. Apparently, the efficacy of biocide at this dosage was not sufficient to achieve target HPC concentration of 10^4 CFU/mL. (CTI, 2006; Ludensky, 2005). However, maintaining total chlorine between 0.5-1 ppm as Cl_2 was found to control planktonic HPC in FTMW at CoC 4 extremely well (Figure 5.3.3). Just after adding 1 ppm total chlorine dose, total residual chlorine and monochloramine were measured as 0.79 and 0.61 ppm as Cl_2, respectively, and the planktonic HPC decreased from 6.5 x 10^4 CFU/mL to non-detectable levels. The total planktonic HPC remained at non-detectable levels for 9 hours and the last sample taken after 24 hours showed HPC at 3.1x10^4 CFU/mL.

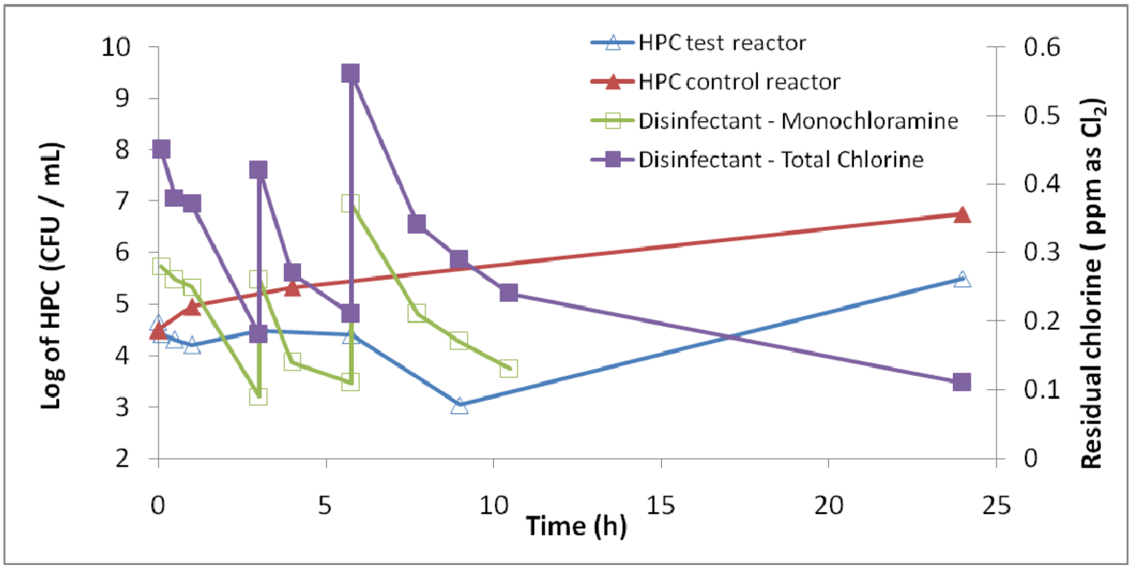

Figure 5.3.2. Effects of 0.2-0.5 ppm as Cl_2 of total chlorine on planktonic HPC in FTMW CoC 4 containing 50 ppm NH_3-N

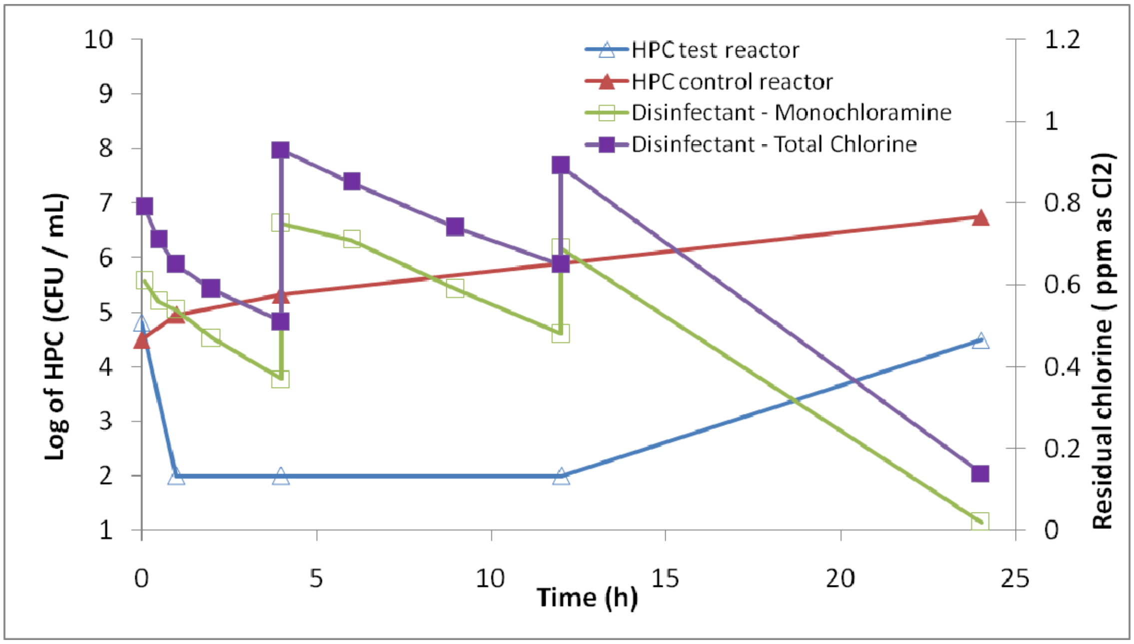

Figure 5.3.3. Effects of 0.5-1 ppm as Cl_2 of total chlorine on planktonic HPC in FTMW at CoC 4 containing 50 ppm NH_3-N

Further batch experiments were conducted to investigate the effects of ammonia concentration and cycles of concentration on the effectiveness of the disinfection process. In all cases, total chlorine was maintained between 0.5-1 ppm as Cl_2. As can be seen in Figure 5.3.4, maintaining total chlorine between 0.5-1 ppm as Cl_2 in FTMW at CoC 1 with 1 ppm NH_3-N reduced planktonic heterotrophic bacteria by about 3 orders of magnitude. However, adding between 0.5-1 ppm of total chlorine to FTMW at CoC 4 containing just 1 ppm NH_3-N could not reduce planktonic HPC at all. Such behavior is most likely due to extremely high free chlorine demand in FTMW at CoC 4 so that the entire chlorine dose was consumed by side reactions instead of HPC inactivation. Once the initial ammonia concentration in CoC 4 FTMW was increased to 100 ppm, planktonic HPC decreased by about 2 orders of magnitude within 1 hour. The abundance of ammonia in this test ensured adequate *in situ* chloramine formation, which was a lot less reactive with organic and inorganic constituents in CoC 4 FTMW and a lot more effective in HPC inactivation.

Similarly, when pre-formed monochloramine at 0.5-1 ppm as Cl_2 was added to FTMW at CoC 4 containing just 1 ppm ammonia, planktonic HPC decreased by about 3 orders of magnitude in one hour. Similar findings were reported by Wolf et al. (1985) who demonstrated that the biocidal efficacy of preformed monochloramine is significantly better than monochloramine formed *in-situ* by if the water has high organic nitrogen compounds.

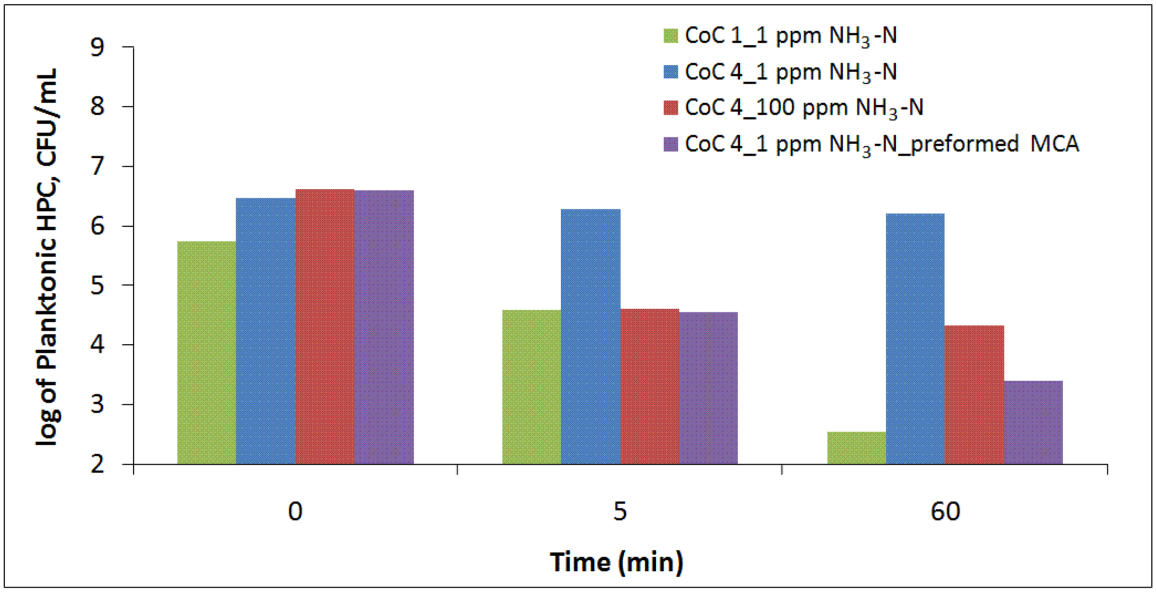

Figure 5.3.4. Effects of ammonia concentration and cycles of concentration on biocidal efficacy of chlorine in batch tests

5.3.3.1 Bench-Scale Experiments in a Recirculating System

The effectiveness of total chlorine and chloramine doses identified in the batch experiments were evaluated further in bench-scale recirculating system. As shown in Table 5.3.2., before applying sodium hypochlorite solution to CoC 4 FTMW in the bench-scale recirculating system, planktonic HPC was 1.2 x 10^5 CFU/mL. After adding 1 ppm of chlorine, the total chlorine was 0.79 ppm as Cl_2 and was predominantly in the form of monochloramine. The HPC immediately decreased below the target criterion of 10^4 CFU/mL. Subsequently, maintaining total chlorine between 0.5 - 1 ppm as Cl_2 and monochloramine between 0.31 - 0.77 ppm as Cl_2 for 10 hours kept planktonic HPC under the detection limit, i.e. below 300 CFU/mL. Last chlorine addition occurred after 10 hours and the planktonic HPC increased to 4.5 x 10^3 CFU/mL after 24 hours while monochloramine was not detectable. Based on these results, it can be concluded that maintaining total chlorine between 0.5-1 ppm as Cl_2 can control biofouling in FTMW at CoC 4. Similar results were observed when the total chlorine in FTMW at CoC 4 was maintained between 1-2 ppm as Cl_2 (data not shown). However, bench scale system does not have continuous makeup water addition and excludes exterior influence, such as sunlight, wind, temperature variances, humidity, etc. and may underestimate biocide demand. Further experiments were conducted in pilot scale cooling towers to simulate realistic process conditions and verify preliminary findings from laboratory studies relative to biofouling control.

Table 5.3.2. Disinfection efficiency of total chlorine at 0.5-1 ppm as Cl_2 in CoC 4 FTMW containing 100 ppm NH_3-N in bench-scale recirculating system

Chlorine addition	Time (h)	Total chlorine (ppm as Cl_2)	Monochloramine (ppm as Cl_2)	Planktonic HPC (CFU/ mL)
	0.00	-	-	1.2E+05
add 1 ppm Cl_2	0.08	0.79	0.71	2.3E+03
add 0.5 ppm Cl_2	0.50	0.54 (B) / 0.85 (A)	0.42 (B) / 0.71 (A)	-
	1.00	0.75	0.66	ND
	1.50	0.66	0.57	-
add 0.33 ppm Cl_2	2.00	0.62 (B) / 0.88 (A)	0.53 (B) / 0.72 (A)	ND (B)
add 0.33 ppm Cl_2	4.50	0.57 (B) / 0.83 (A)	0.51 (B) / 0.69 (A)	ND (B) / ND (A)
add 0.33 ppm Cl_2	6.00	0.61 (B) / 0.90 (A)	0.52 (B) / 0.77 (A)	ND (B)
	8.00	0.69	0.57	ND
add 0.5 ppm Cl_2	10.00	0.43 (B) / 0.89 (A)	0.31 (B) / 0.76 (A)	ND (B) / ND (A)
	24.00	0.09	ND	4.5E+03

Notes: "HPC" = Heterotrophic Plate Count; "ND" = non-detectable (detection limit for chlorine is 0.01 ppm as Cl_2 and for HPC is 300 CFU /mL; "B" = Before the Cl_2 addition; "A" = After the Cl_2 addition; "-" = Not measured

5.3.3.2 Pilot-Scale Testing

Two 21-day tests with pilot-scale cooling systems (design and operation of the pilot-scale cooling towers is described in Appendix D) were conducted to evaluate the effectiveness of chloramine in controlling biomass growth when secondary treated municipal wastewater was used as cooling system makeup. Both pilot-scale cooling towers had similar operating conditions in both tests. In the first test, monochloramine was formed *in-situ* through the reactions between free chlorine that was added and ammonia already present in the wastewater. Free chlorine was added to the bottom sump from the 500 mg/L as Cl_2 stock hypochlorite solution using a peristaltic pump operated on a timer at a preset feeding schedule. In the second run, pre-formed monochloramine was used to control biofouling in both towers. Monochloramine stock solution at 1,000 mg/L as $Cl_2$was also added to the bottom sump using a peristaltic pump.

Effectiveness of *in-situ* formed monochloramine

Total average chlorine in Cooling Tower A was maintained at 0.90±0.67 ppm as Cl_2 for 21 days of the first test (Figure 5.3.5.). Monochloramine comprised most of the total chlorine and it averaged at 0.82±0.55 ppm as Cl_2 throughout the test. During the first day, total chlorine and monochloramine were above 1.0 ppm as Cl_2 and the planktonic HPC were below the target criterion of 10^4 CFU/mL. However, as the total chlorine slowly decreased below 0.5 ppm as Cl_2 from Day 2 to Day 5, planktonic HPC started to increase to 10^6 CFU/mL. From day 6 to day 8, the total chlorine again increased above 1.0 ppm as Cl_2 and planktonic HPC decreased below 10^4 CFU/mL. From day 9 to day 11, total chlorine and monochloramine again gradually decreased below 0.5 ppm and planktonic HPC bounced back to 10^6 CFU /mL. Similar scenario was observed from day 12 to day 21; when total chlorine and monochloramine were below 0.5 ppm as Cl_2, planktonic HPC was higher than the target criterion of 10^4 CFU/mL and when total chlorine and monochloramine were above 1 ppm as Cl_2, HPC was controlled below 10^4 CFU /mL. The average planktonic heterotrophic plate counts (HPC) throughout the entire test was $4.1 \pm 6.5 \times 10^5$ CFU/mL, which is 40 times higher than the target of 10^4 CFU/mL.

The average sessile HPC for Cooling Tower A in this test was $9.9 \pm 9.7 \times 10^4$ CFU/cm^2. Similar to the trend shown by planktonic HPC, sessile HPC in Tower A decreased from day 4 to day 7 (Figure 5.3.5). Sessile bacterial count in Tower A was below the target criterion of 10^4 CFU/cm^2 only at day 7. From day 14 to day 21, sessile HPC in tower A remained virtually unchanged.

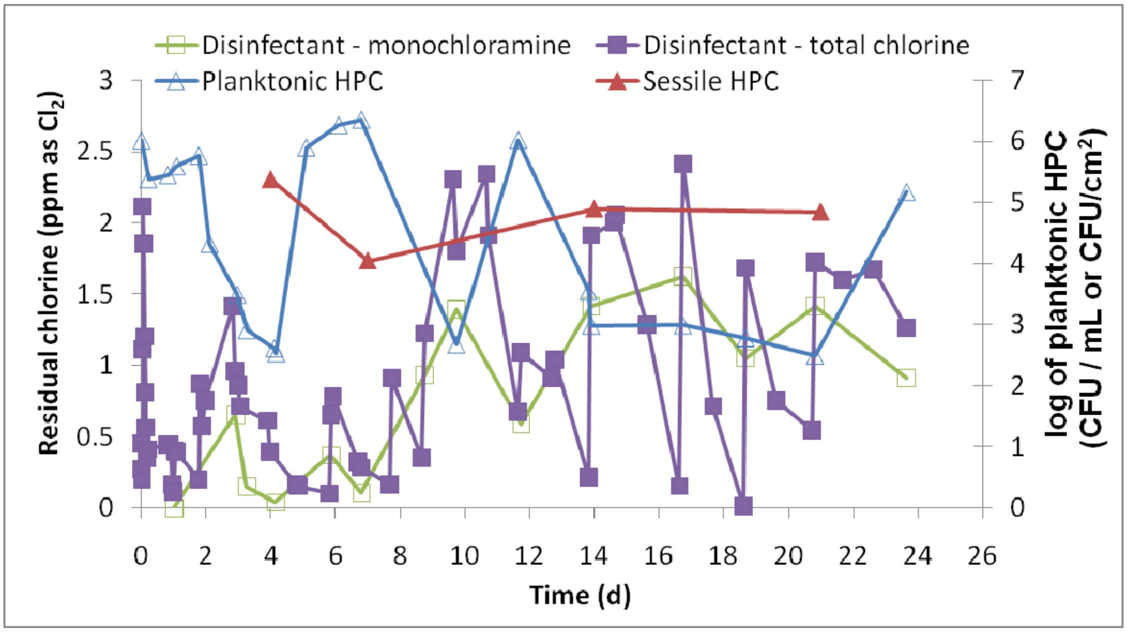

Figure 5.3.5. Total chlorine, monochloramine and planktonic and sessile HPC in Cooling Tower A during the first pilot-scale test at Franklin Township Municipal Sanitary Authority, Murrysville, PA from July-August, 2008

Similar behavior was observed in cooling towers B and C. Over a 24 day period, the total average chlorine in cooling tower B was 1.05 ± 0.9 ppm as Cl_2 and monochloramine was 0.83±0.68 ppm as Cl_2 (Figure 5.3.6). Average planktonic heterotrophic bacteria (HPC) during this period were at 5.77±10.3 x 10^5 CFU/mL. For the first 3 days, total chlorine varied from 0.2 - 1.5 ppm as Cl_2. When total chlorine was above 1 ppm as Cl_2, planktonic HPC decreased below target criterion of 10^4 CFU /mL and when total chlorine decreased below 0.5 ppm as Cl_2, planktonic HPC increased sharply. From day 3 to day 6, total chlorine and monochloramine levels decreased to non-detectable levels, thereby allowing biogrowth to establish itself so that it took several days to reverse this behavior. Results of sessile bacterial counts revealed that biofilm growth was always greater than the target criterion of 10^4 CFU/cm^2 and the average sessile HPC in cooling tower B was 4.13±7.26 x 10^6 CFU/mL during the 24 days test.

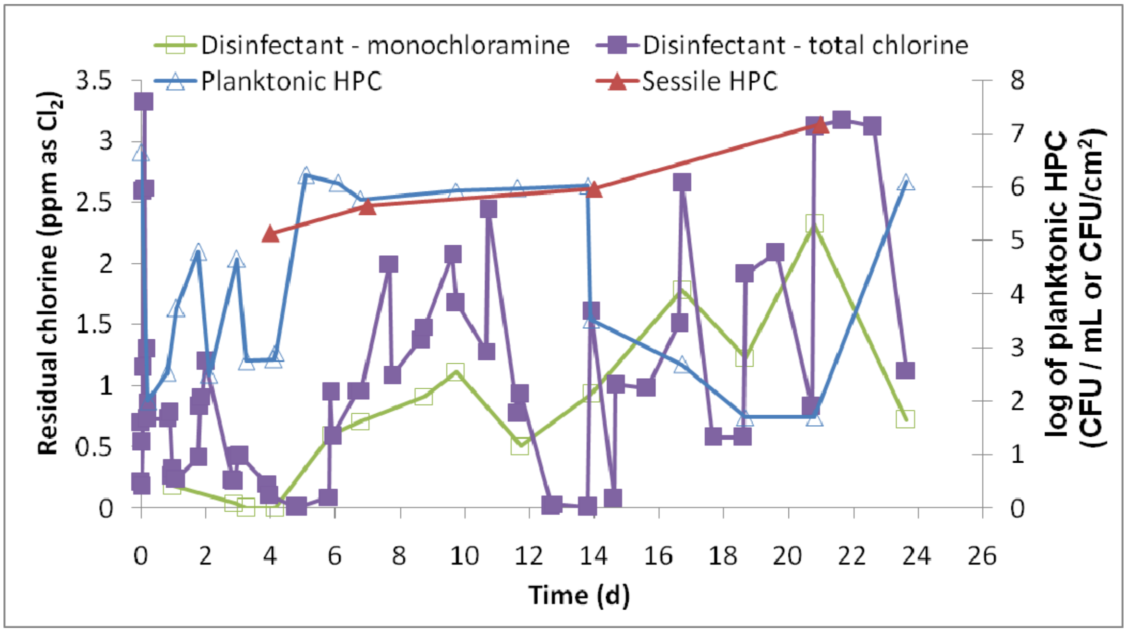

Figure 5.3.6. Total chlorine, monochloramine and planktonic HPC in Cooling Tower B during the first pilot-scale test at Franklin Township Municipal Sanitary Authority, Murrysville, PA from July-August, 2008

As can be seen in Figure 5.3.7 the total chlorine in cooling tower C was maintained at 1.27 ±0.78 ppm as Cl_2 for 21 days. Monochloramine averaged at 0.80±0.54 ppm as Cl_2 during this period. Average planktonic heterotrophic plate counts (HPC) were 3.0±5.7 x 10^5 CFU/mL, which exceeded the target criteria for biofouling control. Figure 5.3.7 illustrates that when total chlorine and monochloramine were initially greater than 1 ppm as Cl_2, planktonic HPC decreased from 10^6 CFU/mL to below 10^4 CFU/mL. However, when total chlorine residual decreased below 1 ppm as Cl_2, planktonic HPC returned to levels above 10^4 CFU/mL. From day 9 to day 11, total chlorine and monochloramine were below 0.5 ppm as Cl_2 and planktonic HPC increased to almost 10^6 CFU/mL. However, from day 11 to day 14, total chlorine and monochloramine were greater than 1 ppm as Cl_2, but planktonic HPC remained above 10^4 CFU/mL. From day 14 to day 17, residual chlorine decreased again and planktonic HPC increased above 10^5 CFU/mL. At day 17, planktonic HPC again decreased to 10^4 CFU/mL when total residual chlorine increased above 2 ppm as Cl_2. At day 24, planktonic HPC increased again above 10^5 CFU / mL due to the drop of total residual chlorine as well as monochloramine dropped below 1 ppm as Cl_2.

Biofilm samples collected from Tower C revealed that HPC were below the 10^4 CFU/cm^2 target only on day 4 (Figure 5.3.7). Sessile HPC were between 10^5 - 10^6 CFU/cm^2 on day 7, 14 and 21. The results on Figure 5.3.7 indicate that when total chlorine and monochloramine levels decrease to low levels (e.g., 1 ppm total chlorine), biogrowth becomes well-established and it is difficult to reverse.

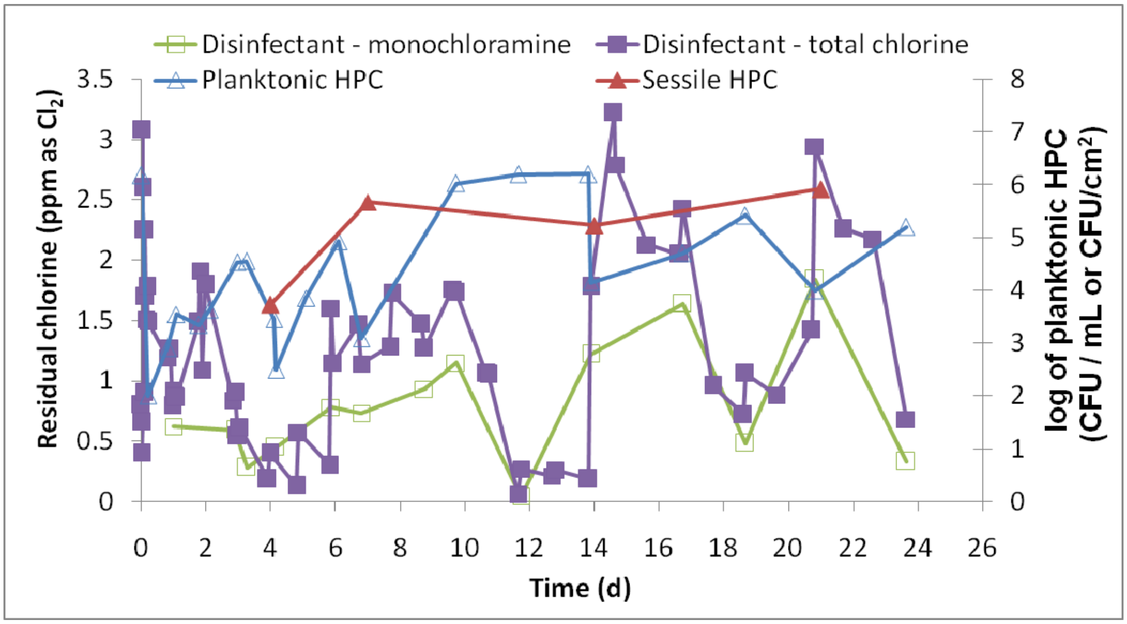

Figure 5.3.7. Total chlorine, monochloramine and planktonic HPC in Cooling Tower C during the first pilot-scale test at Franklin Township Municipal Sanitary Authority, Murrysville, PA from July-August, 2008

Effectiveness of pre-formed monochloramine

In the second test, preformed monochloramine was added to all three towers by feeding the monochloramine solution directly to the bottom sump of each tower using the peristaltic pump. However, the results from cooling tower C are excluded from this study because it received makeup water from a different source (tertiary treated wastewater). The average planktonic HPC in the makeup water (secondary treated wastewater) was 9.4±1.2 x 10^6 CFU/mL, which was almost 3 orders of magnitude greater than the target criterion of 10^4 CFU/mL.

The total average residual chlorine in Tower A during the 21 days of continuous tower operation was 3.64±2.17 ppm as Cl_2 and it was predominantly present as monochloramine with an average concentration of 2.35±1.35 ppm as Cl_2. Planktonic HPC varied from 1.4 x 10^1 CFU/mL to 9.2 x 10^6 CFU /mL with an average of 9.68±27.5 x 10^5 CFU/mL. At Day 1, the average total chlorine was 4.2 ppm as Cl_2 and planktonic HPC was far below the target criteria of 10^4 CFU/mL (Figure 5.3.8.). At Day 2, the total chlorine as well as monochloramine decreased to 1 ppm as Cl_2 and planktonic HPC increased above the target criteria. From Day 2 to Day 7, total chlorine as well as monochloramine was maintained between 2-6 ppm as Cl_2 which effectively controlled the biogrowth below the target criteria. Between Day 9 and 11, the total chlorine was below 2 ppm as Cl_2 and consequently planktonic HPC increased sharply. After that, whenever the total chlorine as well as monochloramine increased above 2 ppm as Cl_2, planktonic HPC decreased below the target criteria.

The average sessile HPC in Tower A during the entire run was 6.8±7.6 x 10^3 CFU/cm^2. Although sessile HPC samples collected at days 8 and 14 revealed slightly greater bacterial density than the target criteria of 10^4 CFU/cm^2, the overall sessile bacteria for 21-day were well controlled.

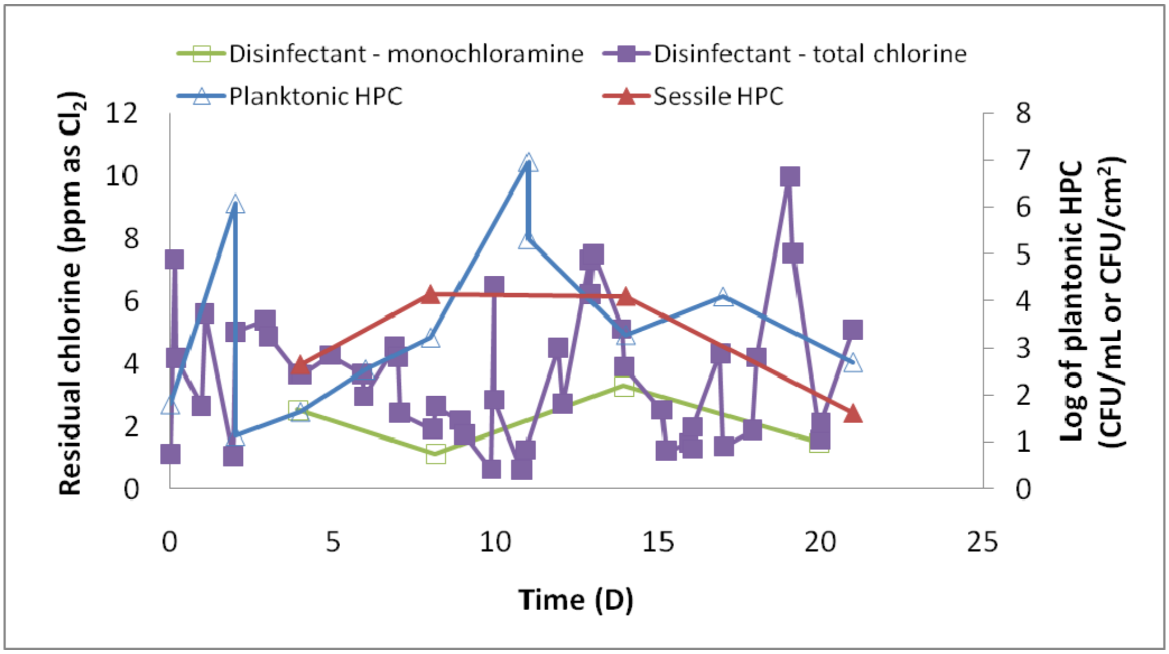

Figure 5.3.8. Total chlorine, monochloramine and planktonic HPC in Cooling Tower A during the second pilot-scale test at Franklin Township Municipal Sanitary Authority, Murrysville, PA from August-September, 2008

The average total residual chlorine in Tower B was maintained at 3.24±1.34 ppm as Cl_2, which was also dominated by monochloramine at an average concentration of 3.54±1.01 ppm as Cl_2. The average planktonic HPC was at 8.4±8.7 x 10^3 CFU/mL (Figure 5.3.9.). Similar to Tower A, when the total chlorine and monochloramine were above 2 ppm as Cl_2, planktonic HPC was well below the target criteria of 10^4 CFU/mL and whenever the total chlorine level decreased below 1 ppm as Cl_2, planktonic HPC increased sharply.

Biofilm samples collected form Tower B at days 4, 8 and 21 revealed bacterial densities that were well below the target criteria of 10^4 CFU/cm^2, while the sample collected on day 14 contained HPC far above the target criteria. Overall sessile HPC in Tower B averaged 2.4±4.1 x 10^4 CFU/cm^2.

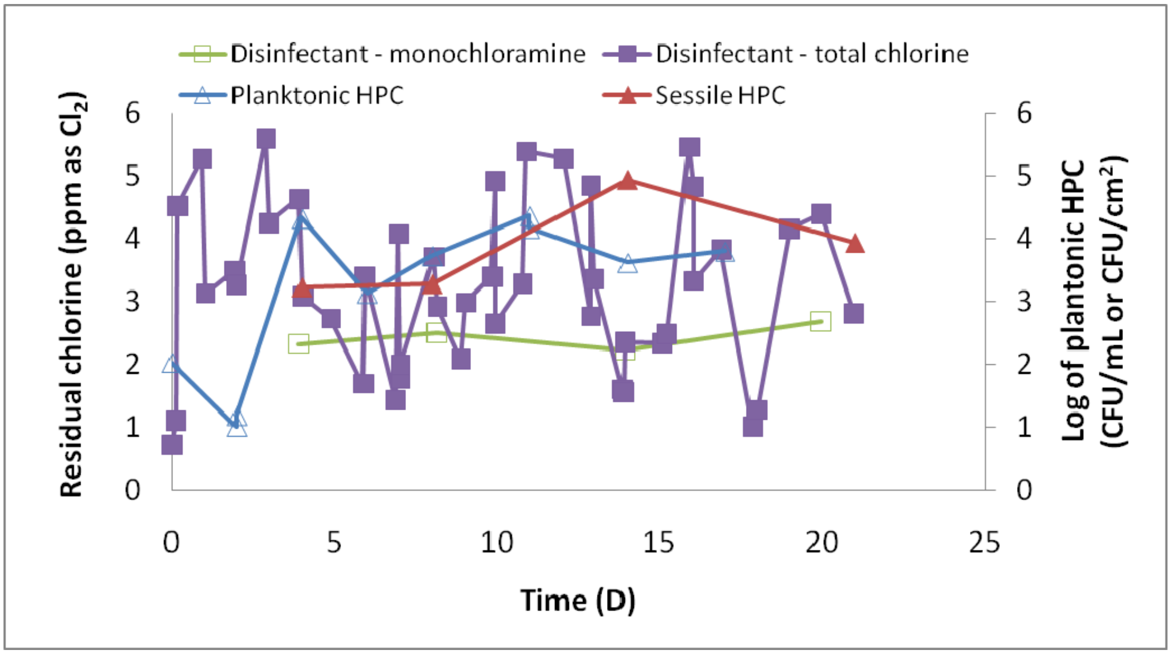

Figure 5.3.9. Total chlorine, monochloramine and planktonic HPC in Cooling Tower B during the second pilot-scale test at Franklin Township Municipal Sanitary Authority, Murrysville, PA from August-September, 2008

Comparing the results from two pilot-scale tests reveals that biofouling control during the second test with preformed chloramination was more successful than the first run with chloramines formed *in-situ*. One reason for this behavior may be the low ammonia concentration in the recirculating water during the first test. The average ammonia concentration in the makeup water was 18.4±6.8 ppm NH_3-N. However, ammonia concentration in recirculating water decreased sharply and reached a steady-state concentration within 3-4 days. At steady state, the average ammonia concentration under the chloramination in cooling towers A and B were only 3.4±1.6 ppm NH_3-N, and 3.4±1.9 ppm NH_3-N, respectively. Batch tests showed that low ammonia concentration could significantly affect the biocidal efficacy of added chlorine due to the competition of ammonia and other organic compounds in the wastewater to react with chlorine. Batch tests also demonstrated that pre-formed chloramination offered better biocidal efficacy even at low ammonia concentration. The results from the second test with pilot-scale towers with pre-formed monochloramine also supported this observation from the batch tests.

Biocide usages during the 21-day test for both runs are shown in Table 5.3.3. Dosage factor was derived by dividing daily biocide consumption, which was converted to 5% sodium hypochlorite solution, with mean total chlorine concentration. Results revealed that using monochloramine formed in-situ required approximately 10 % more sodium hypochlorite per unit total chlorine concentration then when preformed monochloramine was used. This implies that in-situ chloramine formation requires greater free chlorine addition to maintain the same biocide residual level. As indicated before, such behavior indicates that the added free chlorine was partially consumed by organic compounds due to low ammonia concentration in recirculating water. Due to lower reactivity, preformed monochloramine did not exhibit such behavior and was more effective in controlling biological growth in the cooling tower.

Table 5.3.3. Amount of 5% sodium hypochlorite solution required to maintain 1 mg/L total chlorine concentration in pilot scale experiments using secondary treated wastewater.

	Experiment	A	B	C	Average
Dosage factor (mL/ ppm/day)	First test	1647	2054	1190	1630
	Second test	1610	1346	-	1478

5.3.4 Summary and Conclusions

The use of chlorine as a biocide in recirculating cooling tower systems employing secondary treated municipal wastewater as makeup water can be effective provided that the proper concentration and speciation of the disinfectant is maintained during the tower operation. Due to the high concentration of organic matter and inorganic constituents typically present in this impaired water, it is difficult to achieve residual free chlorine without very high doses of chlorine. A total free chlorine residual in the recirculating water of 1-3 ppm as Cl_2 may be able to control biofouling in the cooling tower. In comparison, a total monochloramine concentration of at least 1 ppm as Cl_2 is necessary to control bioactivity in the recirculating cooling water. However, maintaining a total monochloramine concentration of 1 ppm as Cl_2 cannot efficiently suppress the development of the biofilm.

If the ammonia concentration in the cooling water is low, batch studies and pilot scale tests demonstrated that it is difficult to achieve requisite biocidal efficacy of monochloramine formed *in-situ* by the addition of sodium hypochlorite. This can be explained by the competing reactions between free chlorine and organic and inorganic constituent in secondary municipal wastewater. Additional batch studies revealed that the biocidal efficacy of chloramination in the secondary waste water can be significantly increased by using pre-formed monochloramine instead of *in situ* chloramination. Pilot-scale studies also indicated that disinfection with pre-formed monochloramine can achieve biocidal efficacy required to maintain HPC in planktonic and sessile phase below 10^4 CFU/ml or 10^4 CFU/cm^2, respectively. Further pilot-scale studies revealed that maintaining pre-formed monochloramine level between 1-3 ppm as Cl_2 can control the biofouling in the pilot scale cooling system.

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6.0 Reuse of Passively Treated Abandoned Mine Drainage as Alternative Makeup Water for Cooling Systems

In coal mining regions, where substantial coal-based power generation takes place, significant quantities of abandoned mine water that exist in mine voids represent a potential for use as a stable, large volume supply of cooling water. Reusing passively treated abandoned mine drainage (AMD) can avoid the contamination of surface water caused by discharge of mine pool water, which is usually acidic and contains high concentrations of metals, especially iron. However, since using AMD as cooling tower makeup is not widely practiced, knowledge about the potential for control of corrosion, scaling, and biomass growth issues in cooling systems with acid mine drainage is limited.

In this study, the feasibility of controlling corrosion, scaling, and biofouling when using passively treated AMD in cooling water systems was investigated through laboratory and pilot-scale experiments. Bench-scale recirculating systems and three pilot-scale cooling towers were employed for testing of various chemical control schemes for corrosion, scaling, and biofouling in systems using passively treated AMD. The testing was conducted with conditions of temperature, flow velocity, and water constituent concentration similar to those in a recirculating cooling water system. The effectiveness of chemical treatment strategies in inhibiting corrosion, scaling, and biomass growth was studied through exposure and monitoring of specially designed coupons in extended experimental tests.

6.1 Corrosion Control for Reuse of Passively Treated Abandoned Mine Drainage

Abstract

Passively treated abandoned mine drainage (AMD) is a promising alternative to fresh water as power plant cooling water system makeup water in mining regions where such water is abundant. Reusing passively treated AMD can avoid the contamination of surface water caused by discharge of mine pool water, which is usually acidic and contains high concentrations of metals, especially iron. The purpose of this study was to evaluate the feasibility of reusing passively treated AMD with respect to corrosion control through laboratory experiments and pilot-scale field testing. Results showed that with the addition of the inhibitor mixture, orthophosphate, tolyltriazole, and polymaleic acid, mild steel and copper corrosion rates were reduced to acceptable levels. Aluminum had pitting corrosion problems in every condition tested, while cupronickel showed that even in the absence of any inhibitor and in the presence of monochloramine, its corrosion rate was still very low.

6.1.1 Introduction

Abandoned mine drainage (AMD) is the contaminated water produced by dissolution of pyrite ($FeS_{2(s)}$) and other metal sulfides commonly found in the rocks adjacent to coal seams. This water accumulates in the voids left in abandoned mines, and discharges to surface water from the filled voids. AMD contaminates surface water through its low pH and mineral precipitation, especially ferric hydroxide. The major impacts are endangerment of aquatic and benthic life. Because of the iron precipitation, streams impacted by AMD have different sediment color ranging from red to orange or yellow.

Coal mining is a major source of AMD, especially in Pennsylvania, where more than 25 percent of the nation’s total coal output was produced during the past 200 years (USGS, 2008). Thus, AMD has been a major water-pollution problem in Pennsylvania, where over 3,000 miles of streams and associated ground waters have been contaminated (USGS, 2008). Other areas in the U.S. with large volumes of AMD include the other Appalachian coal-producing states and the Illinois-Indiana coal mining region (EPA, 1995). AMD is also generated in the hard-rock mining areas of the western U.S., although such water was not examined in this study.

In the U.S., local, regional, and statewide freshwater shortages occur frequently (USGAO, 2003; Roy and Summers, 2003). The consumptive use of freshwater in thermoelectric power generation cooling water systems can contribute significantly to the water shortage problem in some areas. In the U.S., thermoelectric power generation consumed 3.3 BGD of freshwater in 1995 (USGS, 1998).

Impaired waters are of increasing interest as alternative sources of makeup water for thermoelectric power plant recirculating cooling water systems. Water in and discharging from abandoned coal mines represents significant quantities of possible cooling water in coal mining regions where substantial coal-based power generation takes place (Veil et al., 2003a; 2003b). It was estimated that there is approximately 250 billion gallons of mine pool volume in West Virginia and Pennsylvania (Veil et al., 2003a). In addition to avoiding withdrawal of surface water for cooling, other benefits of reusing mine pool water in power plants are avoidance of surface water contamination caused by AMD discharges, and additional flexibility in siting of new power plants. Although pretreatment might be necessary due to the degraded quality of mine pool water (low pH, high metal concentration, and high total dissolved solids), the development of passive treatment systems for abandoned mine drainage makes it promising to access mine pool water with better quality: neutralized, iron removed, precipitated, and settled (Hedin et al., 1994; Fish and Fish, 1999). Furthermore, many older mine drainage discharges have evolved in chemical composition over time to become much less acidic and even near neutral in pH, with lower dissolved solids loads (Lambert et al., 2004). Thus, such discharges can be treated just with temporary retention in ponds to allow oxidation and precipitation of iron as $Fe(OH)_{3(s)}$. Passively treated, near-neutral pH mine discharge waters are good candidates for use in power plant cooling systems. There is already some experience with operating their cooling systems totally or partially with treated mine pool water in Pennsylvania (Veil, 2006).

One of the main challenges when AMD is reused in recirculating cooling water systems is the potential for enhanced corrosion due to the degraded quality of the water. Since using AMD as cooling tower makeup is not widely practiced, literature concerning corrosion of metal alloys in contact with AMD as cooling water is limited. A pilot-scale experiment demonstrated that, with appropriate corrosion inhibitor addition, the corrosion rate of mild steel in contact with concentrated AMD was very low (Harriram and Nieuwenhuis, 2006; Swart and Engelbrecht, 2004). Details of the chemical treatment technique were not provided, however.

The overall goal of this study was to study the feasibility of reusing AMD water in power plant cooling tower systems. Specifically, the objectives of this study were to 1) evaluate the effectiveness of different chemical treatment programs on corrosion inhibition for mild steel in contact with 4 times concentrated (to simulate 4 cycles of concentration (CoC) in a cooling tower) AMD from a specific site, and 2) evaluate the effectiveness for corrosion control of three selected chemical treatment programs identified from laboratory experiments in pilot-scale cooling towers operated with CoC 4 AMD.

6.1.2 Materials and Methods

6.1.2.1 Passively treated AMD characterization and preparation for laboratory and field testing

Passively treated AMD from the St. Vincent College (SVAMD) mine drainage site (Latrobe, PA) was chosen for testing in laboratory experiments and in pilot-scale cooling towers. Passive treatment at the St. Vincent site involves a system of constructed wetlands to reduce iron content. A 7,000-gallon of SVAMD was collected with a steel tanker truck on September 30, 2008 for use in tests with pilot-scale cooling towers. For pilot-scale testing, the SVAMD was transported to the Franklin Township Municipal Sanitary Authority (Murrysville, PA) where it was transferred to a covered, lined steel roll-off container stored outside at ambient temperature. The SVAMD in the roll-off steel tank served as makeup water for the field testing.

Characterization samples were removed from the tank. Water samples were collected with a 1-L polyethylene sampler and then transferred to appropriate polyethylene or glass sample containers provided by the commercial laboratory, TestAmerica (Pittsburgh, PA). Appropriate preservatives were added to the sample bottles prior to the sampling event by TestAmerica. Analyses performed are listed in Table 6.1.1.

Table 6.1.1 Characteristics of the passively treated acid mine drainage from St. Vincent College mine drainage site (sampled on November 4, 2008).

Analytes	Unit	Result (unfiltered)	Reporting limit
Al	μg/L	ND	400
Ca	μg/L	228000	10000
Cu	μg/L	ND	50
Fe	μg/L	ND	200
K	μg/L	5210 B	10000
Mg	μg/L	61800	10000
Mn	μg/L	172	30
Na	μg/L	96400	10000
SiO_2	μg/L	14900	2140
Zn	μg/L	28.1 B	40
pH		7.8	
NH_3-N	mg/L	0.34 J	0.1
Bicarbonate Alkalinity	mg/L	117 J	5
BOD	mg/L	ND	2
Cl	mg/L	56.1	1
NO_3-N	mg/L	0.32	0.05
SO_4	mg/L	656 J	25
Total P	mg/L	0.056 B	0.1
Total Alkalinity	mg/L	117 J	5
TOC	mg/L	1.7	1
TDS	mg/L	991	10
TSS	mg/L	ND	4

Notes: J: Method blank contamination. The associated method blank contains the target analyte at a reportable level
B: Estimated result. Result is less than reporting limit.

Samples of SVAMD were also collected for laboratory experiments. The SVAMD was concentrated in the laboratory by evaporation at 35 – 40 °C to reach 4 cycles of concentration (CoC) as determined by 75 % water volume reduction.

6.1.2.2 Metal alloy pre-exposure and post-exposure treatment

Metal alloys chosen for study were mild steel (UNS G10180), aluminum (UNS A91100), copper (UNS C10100), and cupronickel (UNS C70600). These are commonly used in cooling water systems (Herro and Port, 1993). Only mild steel was tested in laboratory experiments, while all four alloys were tested in the pilot-scale experiments. The metal alloy specimens tested were cylinder-shaped with the diameter of 0.375 inch and length of 0.5 inch from Metal Samples Company (Munford, AL)

The pre-exposure treatment procedures for metal alloys tested in the laboratory and the pilot-scale testing were the same. Prior to being exposed to SVAMD in the laboratory experiments or in the pilot-scale cooling towers, the metal alloy specimens were wet polished with SiC paper to a 600 grit surface finish, dried, degreased with acetone, rinsed in distilled water, and then mounted in the laboratory apparatus or in the pilot-scale cooling towers. Metal alloy specimens for the pilot-scale testing were also weighed to 0.1 mg prior to being tested since weight loss measurement was performed, while they were not weighed for laboratory experiments since only electrochemical measurements were employed for these tests.

In the pilot-scale cooling towers, only the weight loss method was applied and the post-exposure treatment of metal alloy specimens was the same as for the bench-scale experiments. For each tower, five mild steel specimens were removed from the exposure rack at different times. Aluminum, copper, and cupronickel specimens were also removed at the end of field testing. The testing period was three weeks. After withdrawal, the specimens were cleaned by following ASTM G1 (2005) and then reweighed to 0.1 mg for determining weight loss.

6.1.2.3 Chemicals: corrosion and scaling inhibitors, biomass control agent

Inhibitors tested in this study included di-potassium phosphate (DKP, a corrosion inhibitor), tetra-potassium polyphosphate (TKPP, a corrosion and scaling inhibitor), tolyltriazole (TTA, a corrosion inhibitor), polymaleic acid (PMA, a scaling inhibitor), and commercial scaling inhibitor Aquatreat AR540 (AR540, Chattanooga, TN). DKP, TKPP, TTA, and PMA were from The National Colloid Company (Steubenville, OH). Monochloramine, prepared by mixing sodium hypochlorite and ammonium chloride (Fisher Scientific Inc.) at 4:1 wt. ratio (Cl_2: NH_3-N), was used as a biomass control agent in the pilot-scale testing.

6.1.2.4 Bench-scale experiments

In the laboratory experiments, a corrosion cell with a volume of 1 L was used, as shown in Figure 6.1.1. A three-electrode system was employed with a mild steel specimen as a working electrode, graphite as a counter electrode, and saturated calomel electrode as a reference electrode in a Luggin capillary probe. The cylinder-shaped mild steel specimen was embedded in a PVC tube filled with epoxy and only the bottom side of the specimen with a surface area of 0.66 cm^2 was exposed to the CoC 4 SVAMD which was aerated by purging air into the solution, stirred, and heated to 40 °C in the 1 L corrosion cell during testing.

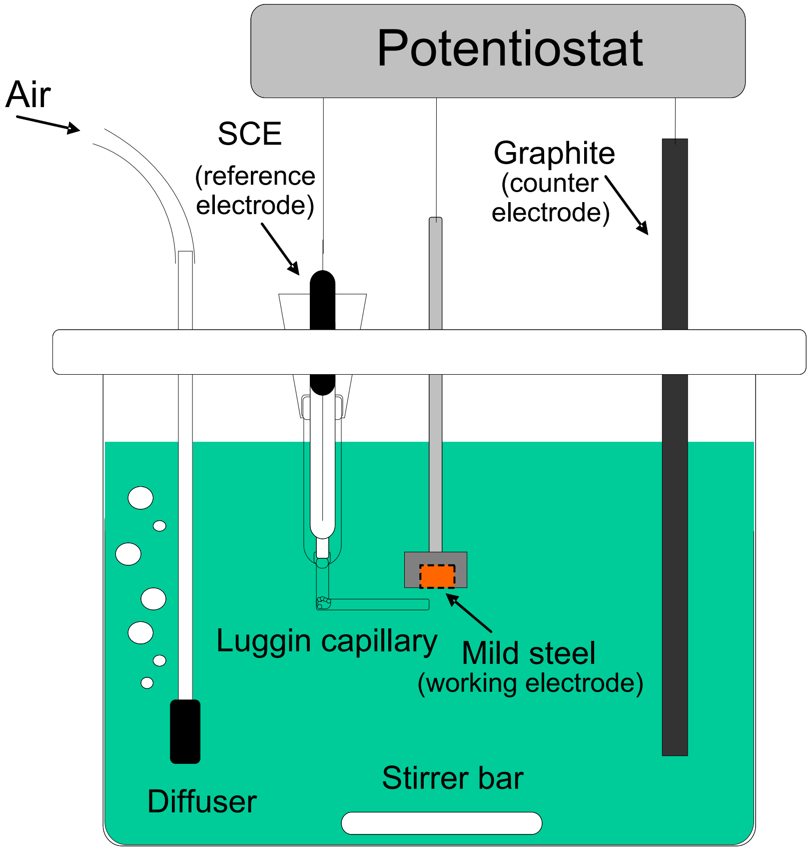

Figure 6.1.1 Schematic of laboratory experimental apparatus. A 1 L corrosion cell was used for the electrochemical polarization resistance measurement of a mild steel specimen, which was served as a working electrode.

6.1.2.5 Instrumentation for electrochemical polarization resistance measurement

Electrochemical polarization resistance (R_P) of mild steel specimens was measured in the laboratory experiments to assess corrosion rates under different exposure conditions. R_P measurements, which reflect corrosion resistance, were used to evaluate the corrosion of mild steel in contact with CoC 4 SVAMD in the laboratory experiments. R_P is defined as the slope of an E_{app} vs. I plot resulting from a linear potentiodynamic scan at E_{app} = 0, where E_{app} is applied potential (V) and I is the induced current (A). The linear potentiodynamic scan was conducted using a PGSTAT100 potentiostat (ECO CHEMIE, the Netherlands). The linear potentiodynamic scan was performed from -30 mV to +30 mV with respect to the corrosion potential at a scan rate of 0.3 mV/s.

6.1.2.6 Pilot-scale cooling tower configuration

Three pilot-scale cooling towers were constructed to test the effectiveness of different chemical treatment programs identified from the laboratory experiments. A schematic of one tower is shown in Figure 6.1.2. The towers were transported to Franklin Township Municipal Sanitary Authority (Murrysville, PA) for side-by-side evaluation of different corrosion, scaling, and biofouling control programs. The three towers were operated with following conditions: 1) CoC 4; 2) flow rate 3 GPM (passing through a 0.75 inch PVC coupon rack); 3) recirculating water temperature of 105 °F entering the tower and 95 °F in the collection basin.

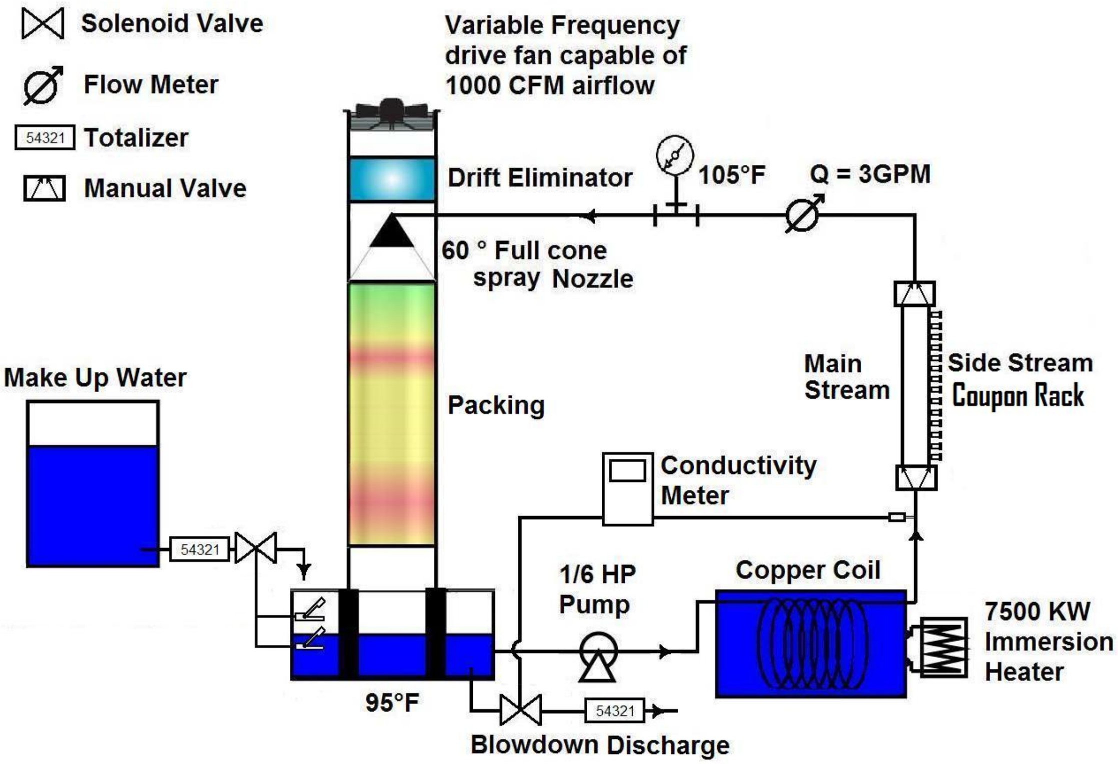

Figure 6.1.2 Schematic of pilot-scale cooling tower design. The coupon rack had similar design as Fig. 3-1(b) except that there were no ports for counter and reference electrodes.

The side-stream coupon rack was used to study eight metal specimens simultaneously. The gravimetric weight loss method was used. Due to the inability to equip the coupon rack to accommodate reference and counter electrodes in the field, the electrochemical polarization resistance method was not used in the field testing.

6.1.2.7 Corrosion experiment matrix for the bench-scale experiments with SVAMD

The bench-scale laboratory experiments were focused on mild steel corrosion analysis, based on previous experiments (Chapter 5) that had shown mild steel corrosion behavior to be sensitive to changing solution conditions. Although aluminum, copper, and cupronickel were included along with mild steel in the pilot-scale testing, experience from previous studies with secondary treated municipal wastewater showed that: aluminum exhibited pitting corrosion across a wide range of conditions, copper corrosion could be strongly retarded by TTA, and cupronickel is very corrosion resistant. Thus, the bench-scale study was focused on mild steel, which showed more variable corrosion rates sensitive to cooling water chemistry.

In the laboratory experiments, the influence of the widely used corrosion inhibitors, DKP, TKPP, and TTA, and scaling inhibitors, TKPP, AR540 and PMA, on corrosion of mild steel were examined. Since previous work (Chapter 5) showed that phosphorous-based inhibitors had the potential to precipitate in cooling tower systems with impaired waters, the concentrations of dissolved phosphorous based inhibitors (TKPP and DKP) were measured in this laboratory study to evaluate their precipitation potential.

The matrix of experiments conducted is shown in Table 6.1.3. The matrix was designed to 1) study the influence of different inhibitors on mild steel corrosion, 2) evaluate the effectiveness of inhibitor mixtures, and 3) investigate the influence of pH on mild steel corrosion and phosphorous-based inhibitor precipitation. In each test, a mild steel specimen as a working electrode was immersed in CoC 4 SVAMD (with and without inhibitor addition and pH adjustment) which was maintained at 40 °C, aerated, and stirred. After one hour, R_P of the mild steel specimen was measured. Then, if TKPP or DKP was added, part of the CoC 4 SVAMD was filtered with a 0.45 µm cellulose membrane (Gelman Sciences Co., Ann Arbor, MI) for dissolved TKPP or DKP measurement, which was used to evaluate the precipitation potential of TKPP or DKP in CoC 4 SVAMD.

6.1.2.8 Corrosion experiment matrix for the pilot-scale testing with SVAMD

The experimental matrix for the pilot-scale testing was based on the results of the laboratory experiments with respect to corrosion, scaling, and biofouling studies (scaling and biofouling control studies are not covered in this section). DKP and TTA were chosen as corrosion inhibitors and PMA (a scaling inhibitor identified to be effective in scaling control through the laboratory experiments in another study) as a scaling inhibitor. Monochloramine was chosen as the biofouling control agent. The three pilot-scale cooling towers were operated together for 21 days after CoC 4 had been reached. The matrix included three different chemical treatment strategies as shown in Table 6.1.3. In the pilot-scale testing, the corrosion inhibitor DKP concentration was monitored using the Standard Method 4500-P (APHA/AWWA/WEF, 2005), and TTA concentration was monitored by HACH® Method 8079 (HACH Company, 2008). Other water chemistry parameters (PMA, monochloramine, anions, alkalinity, pH, and conductivity) and cooling tower operational parameters (water flow rate, air flow velocity, temperature, makeup water flow rate, and blowdown water flow rate) were also monitored. The inhibitors tested were added once per day.

6.1.3 Results and Discussion

6.1.3.1 Laboratory study with CoC 4 SVAMD: mild steel R_P analysis and phosphorous-based inhibitor precipitation potential

The results of R_P measurements of mild steel in CoC 4 SVAMD with different inhibitor addition conditions and different pH in the 1 L corrosion cell are shown in Table 6.1.2, which also shows the concentrations of dissolved DKP and TKPP.

Table 6.1.2 Experimental matrix for bench-scale experiments with a 1 L corrosion cell with the passively treated acid mine drainage from St. Vincent College mine drainage site. Mild steel corrosion was studied in these experiments. As shown, some tests were repeated but with pH adjusted to 7.0 (pH adjusted by H_2SO_4).

	pH unadjusted (pH = 8.25 ± 0.15)		**pH adjusted to 7.0**	
	Polarization resistance (ohm)	**DKP/TKPP (ppm as PO_4)**	**Polarization resistance (ohm)**	**DKP/TKPP (ppm as PO_4)**
Control				
CoC 4_Control	470	---	430	---
Influence of different inhibitors				
CoC 4_DKP10	540	3.3 / ---	---	---
CoC 4_DKP20	1300	6.2 / ---	12000	21.2 / ---
CoC 4_TKPP10	560	3.6 / 0.9	---	---
CoC 4_TTA10	500	---	---	---
CoC 4_AR10	380	---	---	---
CoC 4_PMA15	420	---	---	---
Influence of inhibitor mixture				
CoC 4_DKP10_TKPP10	830	3.1 / 0.2	---	--- / ---
CoC 4_DKP20_TKPP20	960	6.6 / 1.8	16000	20.6 / 9.3
CoC 4_PMA15_DKP20	3500	10.62 / ---	---	---

Notes: CoC: cycles of concentration
DKP#: di-potassium phosphate # ppm as PO_4
TKPP#: tetra-potassium polyphosphate # ppm as PO_4
TTA10: tolyltriazole 10 ppm
AR10: Aquatreat AR540 10 ppm
PMA15: Polymaleic acid 15 ppm

The results reveal varying influence of different specific inhibitors. In CoC 4 SVAMD, the addition of scaling inhibitors, such as AR540 and PMA, didn't retard the corrosion of mild steel. TTA, which is a copper alloy corrosion inhibitor, didn't increase the R_P (corrosion resistance) of mild steel significantly in this laboratory study. The addition of DKP or TKPP at 10 ppm (as PO_4) increased R_P only slightly, but the addition of DKP at 20 ppm (as PO_4) increased R_P by a factor of three. Measurements of dissolved DKP showed that only a small portion (around 30%) of DKP was still in the dissolved phase, indicating that most of DKP added subsequently precipitated. Similarly, only 45% of TKPP added was still in the dissolved phase and 80% of it in the dissolved phase had transformed to orthophosphate.

The influence of inhibitor mixtures on corrosion rate was also studied. The combined addition of DKP and TKPP at 10 ppm (as PO_4) each or at 20 ppm (as PO_4) each increased R_P to about two fold. The combined addition of PMA at 15 ppm and DKP at 20 ppm (as PO_4) significantly increased R_P by a factor of 7 – 8. DKP and TKPP analysis showed that in the combination of DKP and TKPP, less than 20 % of DKP and TKPP added was still in the freely dissolved phase, indicating that most DKP and TKPP added had precipitated. For the combined addition of PMA at 15 ppm and DKP at 20 ppm (as PO_4), more than 50 % of DKP was still measured in the water, indicating that PMA helped in enhancing the solubility of DKP in the water, which likely yielded the significant increase of R_P.

The results also indicate the influence of pH on mild steel corrosion and phosphorous-based inhibitors precipitation. Table 6.1.2 shows that the adjustment of pH didn't significantly influence R_P of mild steel in CoC 4 SVAMD, but it dramatically increased the R_P of mild steel in CoC 4_DKP20 and CoC 4_DKP20_TKPP20 tests by factors of 25 and 34, respectively. The adjustment of pH also significantly increased the solubility of DKP and TKPP. Table 6.1.2 shows that for the 4CoC_DKP20 test, DKP was fully recovered and for the CoC 4_DKP20_TKPP20 test, about 75 % of DKP and TKPP were recovered.

Overall, the results of the laboratory experiments showed that the addition of AR540, PMA, or TTA didn't significantly influence R_P of mild steel in CoC 4 SVAMD, while the addition of DKP and/or TKPP enhanced the corrosion resistance but not strongly. Also, most of DKP and TKPP added precipitated one hour after the addition. Although PMA didn't directly influence the R_P of mild steel, it increased the solubility of DKP. The increase of DKP concentration thus resulted in the increase of R_P. The adjustment of pH to 7.0 didn't influence R_P significantly in the absence DKP and TKPP, but it increased the solubility of DKP and TKPP when they were added. The large increase of dissolved DKP and TKPP enhanced corrosion resistance. In the pH range tested (7.0 – 8.4) with SVAMD in the laboratory, pH didn't play an important role in corrosion chemistry, but lower pH significantly increased the solubility of phosphorous based inhibitors and enhanced the corrosion resistance of mild steel significantly. The relationship between the total dissolved concentration of phosphorous-based inhibitors and polarization resistance in the pH range studied with SVAMD is shown in Figure 6.1.3. It can be seen in this figure that the polarization resistance increased with the increase of the concentration of dissolved phosphorous based inhibitors.

Overall, the results indicated that when passively treated abandoned mine drainage is used as cooling water makeup without pH adjustment, DKP no more than 5 ppm can be used for mind steel corrosion and the addition of PMA 15 ppm can increase the solubility of DKP.

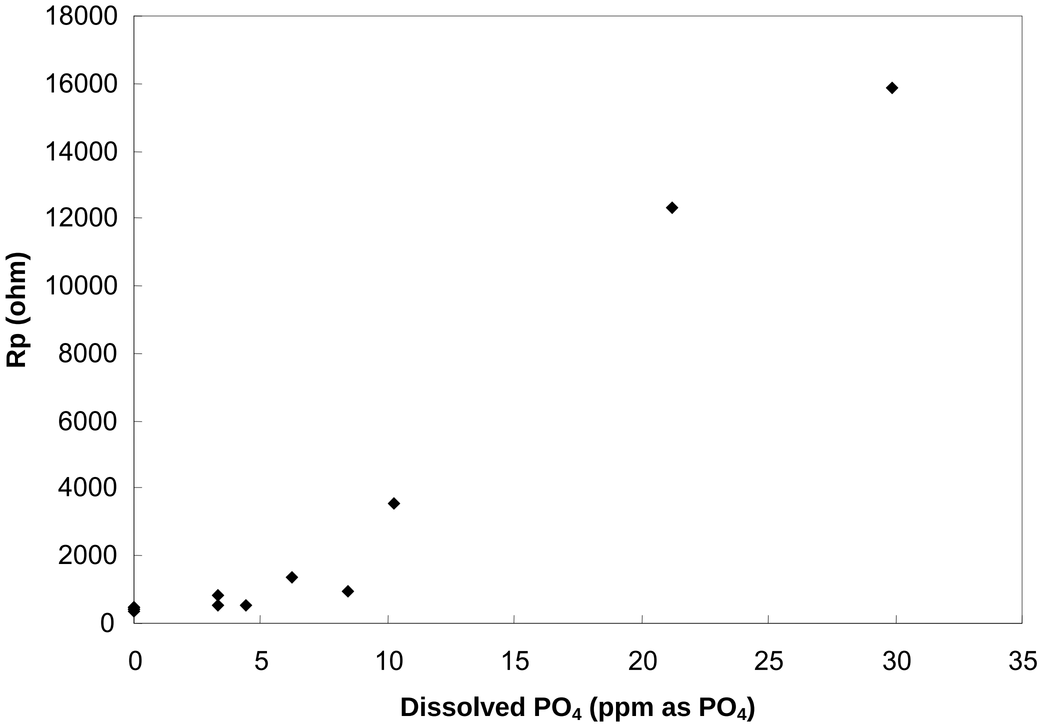

Figure 6.1.3 Relationship between dissolved PO4 and polarization resistance of mild steel in contact with CoC 4 passively treated AMD from St. Vincent College. It can be seen that polarization resistance increase with the increase of total dissolved PO_4 concentration in the pH range studied (7 – 8.4).

6.1.3.2 Pilot-scale experiments

The results of the laboratory experiments suggested that in order to effectively reduce mild steel corrosion the pH of SVAMD might need to be adjusted down to keep phosphorous-based inhibitors in solution. However, pH adjustment practice was not desired for the pilot-scale experiments in order to evaluate the ability to control corrosion, scaling, and biofouling in the SVAMD as received. Also, since the laboratory experiments were short-term, the necessity of using DKP and TKPP and conducting pH adjustment for long-term mild steel corrosion protection was not certain. The pilot-scale experiments were designed to study the corrosion of metal alloys for a relatively long-term period with no pH adjustment. Due to the low solubility of DKP and TKPP, only 5 ppm DKP was added in two of the three towers. The effectiveness of TTA at 2 ppm to protect copper and cupronickel from corrosion was also studied. The effectiveness of PMA and MCA on scaling and biofouling control, respectively, was studied and the results are presented in Chapters 6.2 and 6.3, respectively).

The average pH values of recirculating CoC 4 SVAMD water in the three towers were 8.7, 8.2, and 8.8 for Tower A, Tower B, and Tower C. The higher pH values in Tower A and

Tower C were due to the addition of PMA, which has scaling inhibition ability and thus influenced the water chemistry significantly, as indicated by the results of alkalinity and calcium (Ca^{2+}) measurements. Both alkalinity and calcium in Tower B were significantly lower than those in Tower A and Tower C, indicating that, calcium and alkalinity were removed from solution in Tower B through precipitation. For Tower A and Tower C, in contrast, PMA enhanced the solubility of calcium and carbonate species.

The results of metal alloy corrosion analysis are shown in Table 6.1.4 and Figure 6.1.4. Table 6.1.4 shows the 21-day overall average corrosion rate analysis for each metal alloy during the testing period. Figure 6.1.4 shows the accumulated weight loss of mild steel specimens with time in each tower.

Table 6.1.4 Average corrosion rates of metal alloys contacted with St. Vincent College passively treated acid mine drainage at 4 cycles of concentration in cooling tower for three weeks and their corrosion categories according to general corrosion criteria for cooling systems.

Metal alloys	**Average corrosion rate (MPY) and corrosion category**		
	Tower A	**Tower B**	**Tower C**
Mild steel	4.78 (fair)	7.25 (poor)	4.66 (fair)
Aluminum	2.12, pitting (unacceptable)	0.69, pitting (unacceptable)	0.11, pitting (unacceptable)
Copper	0.11 (good)	1.06 (unacceptable)	0.15 (good)
Copper-nickel	ND, < 0.01 (excellent)	0.07 (excellent)	0.02 (excellent)

Notes: [1] Corrosion criteria (Table 5.1.1)
Mild steel piping: 0-1 (MPY) excellent; 1-3 good; 3-5 fair; 5-10 poor; >10 unacceptable.
Copper alloys in heat exchanger: 0-0.1 excellent; 0.1-0.2 good; 0.2-0.3 fair; 0.3-0.5 poor; >0.5 unacceptable.
Pitting is not acceptable for all alloys
[2] ND: non-detectable

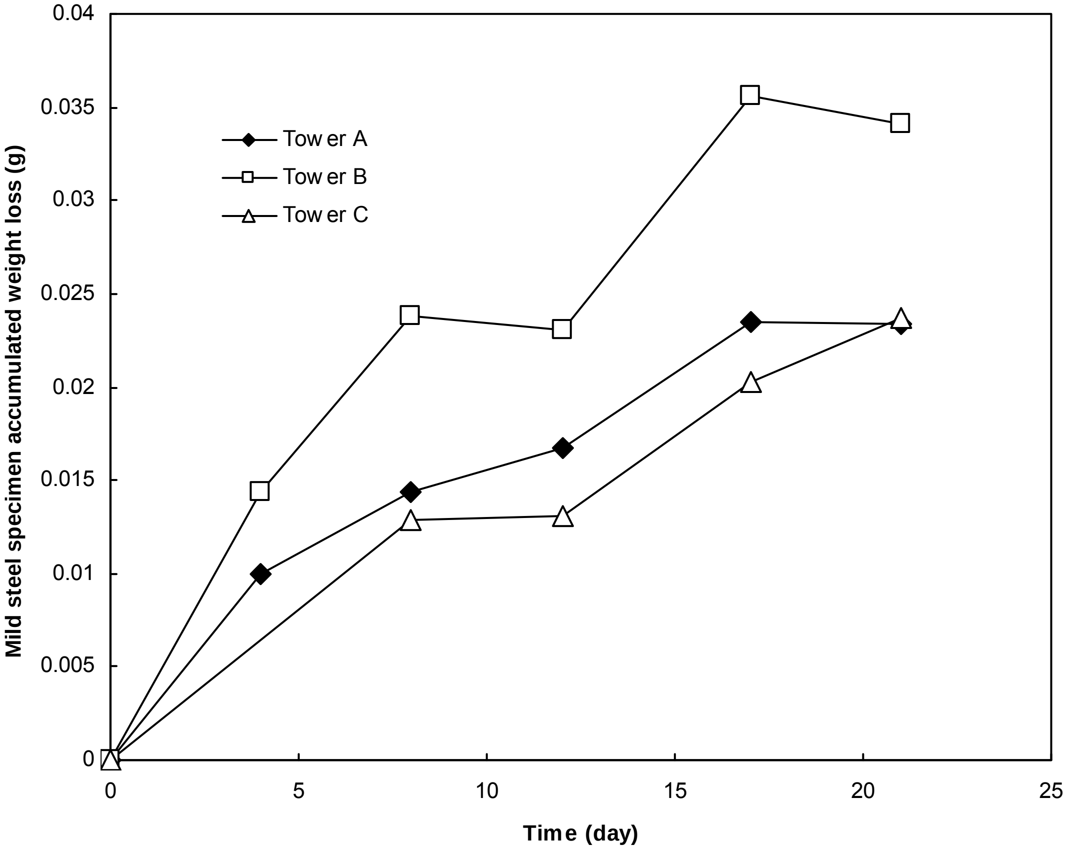

Figure 6.1.4 Accumulated weight loss of mild steel with time in contact with passively treated AMD at CoC 4 in field testing with the pilot-scale cooling towers. Each point was from a mild steel specimen withdrawn at a certain time from the specimen rack in the pilot-scale cooling system.

As shown in Table 6.1.4, 21-day average corrosion rates of mild steel in contact with CoC 4 SVAMD in Tower A and Tower C were 4.78 MPY and 4.66 MPY, which are in the category of “fair” (3 – 5 MPY) according to general corrosion rate criteria described in Table 6.1.4. In Tower B, the 21-day mild steel corrosion rate was 7.25 MPY, which was in the category of “poor”. Since corrosion and scaling inhibitors (DKP, TTA, and PMA) were applied in Towers A and C, it was evident that the addition of the inhibitor mixture helped in reducing mild steel corrosion rate. Figure 6.1.4 also suggests that corrosion rates of mild steel in all towers decreased slightly with time. The decrease of corrosion rates may have been caused by protection from the formation of a scaling layer observed on the mild steel specimens. Figure 6.1.4 also indicates that the initial corrosion rate of mild steel in Tower B, where no corrosion and scaling inhibitors were added, was significantly higher than that in Tower A and Tower C. Thus, the chemical additive mixture inhibited mild steel corrosion. The corrosion inhibition results in the pilot-scale experiments with the inhibitors mixtures were in agreement with these obtained in the laboratory experiments.

The average corrosion rates of aluminum in the three towers were significantly different, with highest rate in Tower A and lowest in Tower C. However, different degrees of pitting corrosion were observed on all aluminum specimens. Tower A and Tower B had higher average corrosion rates and Tower B had less severe pitting corrosion. Thus, average corrosion rate was not a useful indicator for aluminum corrosion evaluation. Pitting corrosion is not acceptable under any circumstances. Thus, aluminum does not appear to be feasible for use in cooling tower systems using passively treated AMD. The more severe pitting corrosion observed in Tower A and Tower C might be due to phosphate, since phosphate was found to cause aluminum pitting corrosion in bench-scale experiments (Chapter 5).

The average corrosion rates of copper in Towers A and C were 0.11 MPY and 0.15 MPY, respectively, which were in the category of “good” (0.1 – 0.2 MPY), while in Tower B the corrosion rate was 1.06 MPY, in the category of “unacceptable” (> 0.5 MPY). Since Tower A and Tower C had TTA addition, the low corrosion rate of copper was mainly due to the protection of TTA adsorption film on copper. In Tower B where TTA was not present, monochloramine biocide attacked copper and caused unacceptable copper corrosion, which was evident from visual observation of tarnishing. In contrast, the copper specimens in Tower A and Tower C were not tarnished as severely as that in Tower B.

The average corrosion rates of the cupronickel specimens in all three towers were in the category of “excellent” (< 0.1 MPY). Although in Tower B where TTA was not present, cupronickel had a slightly higher corrosion rate of 0.07 MPY; it was still in the category of “excellent.” Thus, the results indicated that cupronickel exhibited very strong corrosion resistance against CoC 4 SVAMD and against monochloramine at 1 – 2 ppm. With further addition of TTA to 2 ppm, the corrosion of cupronickel was inhibited to a very low value (< 0.02 MPY). Visual observation showed that no cupronickel specimens were tarnished.

The results of DKP and TTA concentration monitoring are shown in Table 6.1.3. As can be seen, TTA concentrations in Tower A and Tower C were maintained around 2 ppm. The fluctuation of the concentration of TTA (reflected through standard deviation of monitored TTA concentration) was due to the intermittent daily addition of inhibitors, and also the intermittent makeup water addition and intermittent blowdown discharge from the cooling tower systems. Although the goal was to maintain DKP at 5 ppm (as PO_4) in Tower A and Tower C, the actual DKP concentrations were generally lower than 1 ppm (as PO_4). It is worth mentioning that in the preliminary laboratory experiments on the corrosion of mild steel in contact with CoC 4 SVAMD, a DKP concentration of 5 ppm (as PO_4) could be maintained. However, in the field testing, although phosphate was added daily to target a concentration of 5 ppm, the actual dissolved DKP in water was generally below 1 ppm. The precipitation of DKP apparently occurred when the recirculating water passed through high temperature copper coil heater.

Table 6.1.3 Experimental matrix for field testing with the pilot-scale cooling towers and the passively treated acid mine drainage from St. Vincent College mine drainage site. In parenthesis are actual monitored results from field testing. The samples for analysis were all filtered with 0.45 μm cellulose membranes.

Chemical	**Unit**	**Chemical concentrations**		
		Tower A	**Tower B**	**Tower C**
TTA	ppm	2 (1.8±0.8)	0	2 (1.6±0.8)
DKP	ppm as PO_4	5 (0.5±0.5)	0	5 (0.4±0.3)
PMA	ppm	15	0	25
MCA	ppm as Cl_2	1-2	1-2	1-2

Overall, mild steel corrosion was inhibited by the presence of the inhibitors mixture. Copper corrosion was strongly inhibited in the presence of TTA or otherwise, copper corrosion was not acceptable. Cupronickel had excellent corrosion resistance even in the absence of TTA when its corrosion rate was still very low, in the category of “excellent”. DKP had very low solubility in the pilot-scale cooling tower systems with CoC 4 SVAMD, while TTA was easily maintained at a desired concentration. Aluminum was found to be an unsuitable material to be used in a cooling water system using passively treated SVAMD as makeup and operated at CoC 4 due to pitting corrosion.

Since it was found that DKP was actually not maintained at the target concentration (5 ppm as PO_4) in Tower A and Tower C, the observed corrosion resistance for the mild steel specimens might be due to phosphate scaling, TTA adsorption onto mild steel, or higher pH caused by PMA addition. The inhibition also could be the combinative effect of these factors. Previous laboratory work (Chapter 5) with synthetic municipal wastewater demonstrated that both phosphate scaling and TTA addition helped in mild steel corrosion protection.

6.1.4 Summary and Conclusions for Corrosion Control for Reuse of Passively Treated Abandoned Mine Drainage

The corrosion control of metal alloys in cooling tower systems using passively treated AMD was evaluated in this study. It was found that phosphorous-based inhibitors had very low solubility in CoC 4 AMD unless pH was adjusted to 7.0. The effectiveness of mild steel corrosion inhibition by phosphorous-based inhibitors was found to be positively related to the concentration of dissolved phosphorous-based inhibitors in the pH range studied (pH 7 – 8.4). The solubility of phosphorous-based inhibitors was enhanced by PMA addition in the laboratory experiments; however, it was still very low in the pilot-scale cooling towers, probably due to the high temperature in the heat exchanger. The inhibitors mixture (DKP, TTA, and PMA) successfully reduced mild steel corrosion rate to the acceptable range in field testing. TTA very effectively retarded the corrosion rate of copper in contact with CoC 4 SVAMD. Cupronickel was the most corrosion resistant material and the results showed that its corrosion rates were in the category of “excellent” even in the absence of any inhibitor and in the presence of monochloramine biocide. Aluminum exhibited pitting corrosion and is not a feasible material to be used in cooling tower systems when reusing passively treated AMD.

When using passively treated AMD for power plant cooling system makeup, cupronickel doesn’t need any chemical treatment for corrosion control and the addition of TTA, PMA and DKP can control effectively the corrosion of mild steel and copper.

6.2 Scaling Control for Reuse of Passively Treated Abandoned Mine Drainage

Abstract

Abandoned mine drainage (AMD) is a promising alternative to freshwater for thermoelectric power plant cooling needs in regions where such water is abundant and accessible. The use of AMD is predicated on being passively treated to remove Fe/Mn and a significant portion of suspended solids. Use of such passively treated AMD may help avoid surface water contamination that occurs through the overflow of the AMD from mine pools. This study evaluated the feasibility of using passively treated AMD in thermoelectric power plant cooling systems with respect to scaling control by chemical addition. Laboratory experiments and pilot-scale field testing showed that polymaleic acid (PMA) effectively decreased the settling of suspended solids and rendered the solids less prone to deposition onto the surfaces immersed in the pipe flow sections. In the absence of PMA, significant amount of solids settled in the tower sump where flow velocity was minimal. The PVC and stainless steel surfaces exhibited different affinities for scaling; PVC was determined to yield increased deposition in bench-scale recirculation systems. This observation implies that different degrees of scaling would take place in the sections made of different materials, which was also observed in the pilot-scale cooling towers using passively treated AMD.

6.2.1 Introduction

Abandoned mine drainage (AMD) refers to the release of the contaminated groundwater produced by dissolution of sulfide minerals (especially pyrite--FeS_2) and commonly found in the areas adjacent to abandoned mine sites (Akcil and Koldas, 2006). AMD is characterized by low pH, high content of iron hydroxides, as well as elevated levels of heavy metals (Rios et al., 2008). These characteristics are manifested in streams impacted by AMD through sediment color ranging from red to orange or yellow due to iron precipitation, and significant endangerment of aquatic and benthic life (Hustwit et al., 1992).

Coal mining produces bulk of AMD. This is especially true in Pennsylvania where more than 25 percent of the nation’s total coal output was produced over the past 200 years (USGS, 2008). As such, AMD has been a major water-pollution problem in Pennsylvania where over 3,000 miles of streams and associated ground waters have been contaminated (USGS, 2008). Other areas in the U.S. with large volumes of AMD include the other Appalachian coal-producing states and the Illinois-Indiana coal mining region (EPA, 1995). AMD is also generated in the hard-rock mining areas of the western U.S., although such water was not examined in this study.

Given the large quantity of AMD available, it may be possible to use it for cooling purposes in areas of the U.S. where freshwater shortages occur frequently (USGAO, 2003; Roy and Summers, 2003). This practice may significantly impact water conservation as consumptive withdrawal of freshwater by thermoelectric power generation cooling water systems can contribute significantly to the water shortage problem in some areas. In the U.S., thermoelectric power generation consumed 3.3 BGD of freshwater in 1995, mainly through evaporative loss from cooling towers (USGS, 1998).

Waters of impaired quality, such as AMD, are of increasing interest as alternative sources to freshwater for thermoelectric power plant recirculating cooling water systems. The AMD represents significant quantities of possible cooling system makeup water in coal mining regions where substantial coal-based power generation takes place (Veil et al., 2003a; 2003b). It was estimated that there is approximately 250 billion gallons of mine pool volume in West Virginia and Pennsylvania (Veil et al., 2003a). In addition to supplementing withdrawal of surface water for cooling, other benefits of reusing mine pool water in power plants are the prevention of AMD-related surface water contamination, and additional flexibility in siting new power plants. Although active pretreatment might be necessary to raise the water quality of AMD to allow reuse (treatments typically raise pH, reduce metal concentration and total dissolved solids), the development and successful implementation of passive treatment systems makes it promising to access AMD with better quality (Hedin et al., 1994; Fish and Fish, 1999). Further, AMD chemical compositions often evolve over time to become less acidic and can approach neutral pH in many cases, as well as have lower loads of dissolved solids over time (Lambert et al., 2004). Such AMD can be treated with temporary retention in ponds to allow oxidation and iron precipitation. Passively treated, near-neutral pH AMD waters are good candidates for use in power plant cooling systems. Indeed, there is already some experience with operating their cooling systems totally or partially with treated AMD in Pennsylvania (Veil, 2006).

However, mineral precipitation and subsequent surface scaling remains one of the main challenges for AMD reuse in recirculating cooling water systems. Up to date, knowledge in the literature concerning mineral scaling in cooling systems caused by AMD is limited due to the fact that using AMD as cooling tower makeup is not widely practiced.

The goal of this study was to evaluate the technical feasibility of reusing AMD in power plant cooling tower systems. Specifically, the objectives of this study were to 1) simulate scale formation under cooling tower operation conditions at different cycles of concentration via chemical equilibrium modeling, 2) test the effectiveness of different chemical treatment programs on scaling inhibition in bench-scale water recirculating systems, and 3) determine the viability of using AMD as cooling water makeup through testing in a pilot-scale cooling tower system.

6.2.2 Materials and methods

6.2.2.1 Passively treated AMD characterization and preparation for laboratory and field testing

Passively treated AMD from the St. Vincent College mine drainage site (Latrobe, PA) was chosen for testing in laboratory experiments and in pilot-scale cooling towers. Passive treatment at the St. Vincent site is accomplished through a system of constructed wetlands to reduce iron content. A total of 7,000 gallon of the AMD for use as makeup water in tests with pilot-scale cooling towers was collected and transported to our test site at the Franklin Township Municipal Sanitary Authority (Murrysville, PA) by a steel tanker truck on September 30, 2008. The AMD was transferred to a covered and lined steel roll-off container stored outside at ambient temperature and was used as needed.

Water samples were taken from the roll-off container before testing and intermittently during testing to serve as baselines for comparison purposes. These samples were collected with 1-L polyethylene sample bottles and transferred to appropriate polyethylene or glass sample containers provided by the commercial laboratory, TestAmerica (Pittsburgh, PA). Appropriate preservatives were added to the sample bottles prior to sampling. Results from the analysis are reported in Table 6.1.1.

Samples of the AMD were collected for laboratory experiments. The AMD was concentrated in the laboratory by evaporation at 35-40°C to reach 4 cycles of concentration (CoC 4) as determined by 75 % water volume reduction.

6.2.2.2 Equilibrium modeling of AMD scaling potentials

The chemistry of AMD cooling water at different CoC was modeled using MINEQL+ version 4.5 (Schecher and McAvoy, 1992; 1999) to predict the effects of CoC on scaling. The primary objective for this effort was to estimate the amount and composition of mineral solids that would precipitate from the solution in the pilot cooling units as a function of CoC, and to understand and interpret the chemistries observed in the pilot tests. In addition, the major constituents and their chemical speciation in solution were assessed and the dominant scale-producing reactions were identified.

The following four operational conditions were tested for the AMD water:

1) The aqueous system was open to the atmosphere ($PCO_2 = 10^{-3.5}$ atm) to allow the alkalinity to be in equilibrium with $CO_2(g)$ and solids were allowed to precipitate.

2) The aqueous system was open to the atmosphere ($PCO_2 = 10^{-3.5}$ atm) to allow the alkalinity to be in equilibrium with $CO_2(g)$ and solids were not allowed to precipitate (i.e., water can be super-saturated).

3) The aqueous system was closed to the atmosphere with total alkalinity fixed and solids were allowed to precipitate.

4) The aqueous system was closed to the atmosphere with total alkalinity fixed and solids were not allowed to precipitate.

The four conditions represent the extreme effects of atmospheric CO_2 and solution supersaturation. It is reasonable to expect that the actual conditions for field testing would fall within these boundary conditions.

6.2.2.3 Scaling inhibition in bench-scale tests

Methods for studying scaling in cooling tower systems were not readily available in the literature. A well-documented method to measure scaling deposition and kinetics *in-situ* was not found in the course of this research. Most established techniques pertaining to scaling phenomena confine themselves to means of static observations and analysis once solid scales have formed and have been collected (e.g., ASTM Method D1245-84, D2331-80, D933-84, D934-80, D887-82). Very limited effort has been devoted to the study of scaling dynamics and kinetics in terms of how scales form and at what rate(s) they form. In addition, there is no quantitative knowledge of conditions influencing and mechanisms dictating scale forming processes.

A method to study scale formation tendency and kinetics for AMD and other impaired waters was developed in this study. Bench-scale water circulating systems similar to those employed in the corrosion studies were constructed and were dedicated to investigate scaling. Stainless steel circular coupon discs were inserted through sampling ports into the recirculating water to provide collecting surfaces for scaling/deposition, as shown in Figure 6.2.1. A mass gain method, similar to the mass loss method for corrosion, was used as a straightforward means to record the scale forming quantities at different water chemistries and scaling control conditions. Scaling kinetics of the AMD was studied at varying cycles of concentration (CoC) in the bench-scale water recirculating systems. Water temperature was fixed at 104°F (40°C) and the flow rate was adjusted at 3 GPM. The system was open to air so that the alkalinity may approach equilibrium with the atmospheric CO_2, which is similar to conditions in actual cooling tower operation.

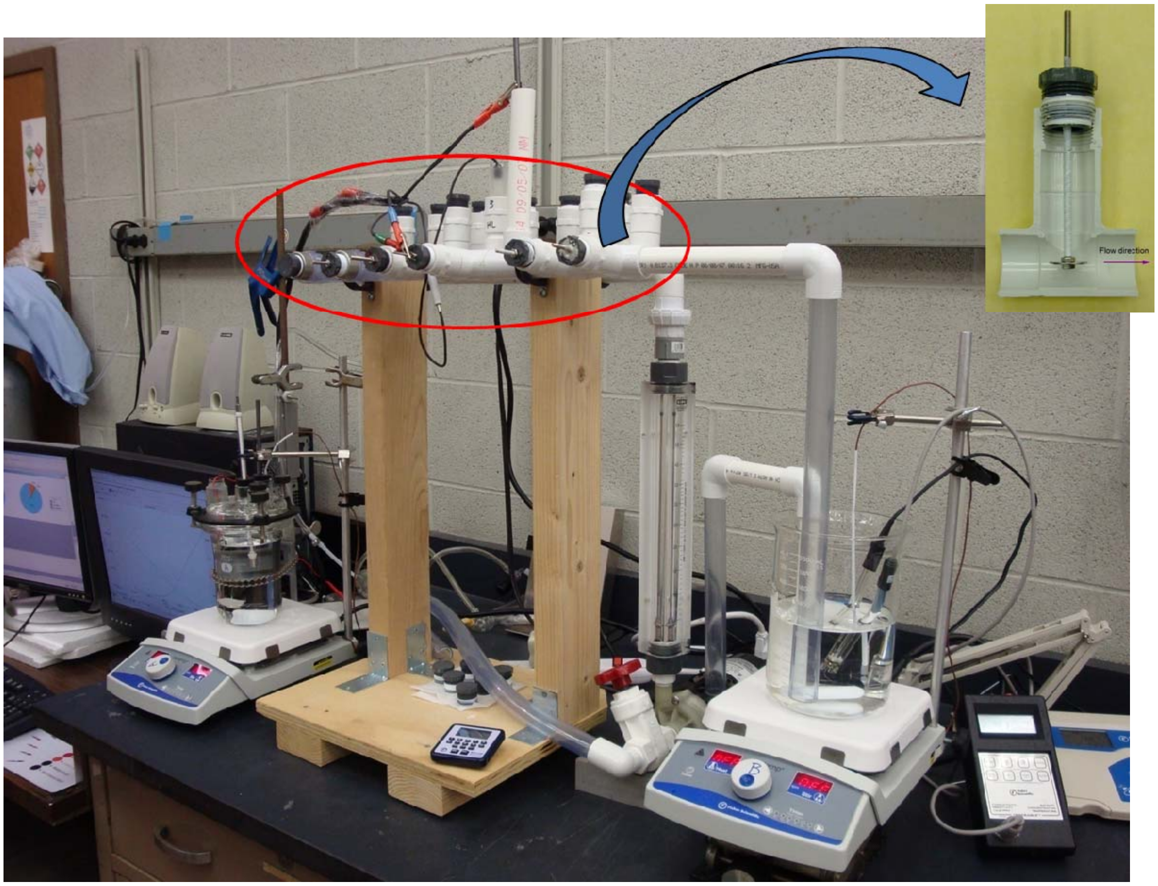

Figure 6.2.1. Bench-scale water recirculating system with inserted stainless steel circular discs for scale collection and subsequent mass gain measurement.

The scale samples collected on the test discs over time were air-dried and weighed with analytical balance to obtain mass data.

Scaling inhibitors tested in this study included tetra-potassium polyphosphate (TKPP, also a corrosion inhibitor), polymaleic acid (PMA), Aquatreat AR540 and AR 545 (terpolymers manufactured by Alco Chemicals, Chattanooga, TN), and Acumer 2100 (a carboxylic acid/sulonic acid copolymer manufactured by Rohm & Haas, Philadelphia, PA). TKPP and PMA were obtained from The National Colloid Company (Steubenville, OH). Monochloramine was prepared by mixing sodium hypochlorite (5% stock solution) and ammonium chloride (Fisher) at

Cl_2:NH_3-N of 4:1 wt. ratio and was used as a biomass control agent in the pilot-scale testing. In addition to TKPP, dedicated corrosion inhibitors in the form of tolyltriazole (TTA) and di-potassium phosphate (DKP) (The National Colloid Company, Steubenville, OH) were tested in this study.

Varied amounts of adsorption and adhesion of solids were observed on different materials in the pilot scale cooling towers. It was hypothesized that surfaces have different degrees of affinity toward suspended solids and thus lead to varied amounts of adsorption and adhesion of these solids. To test this hypothesis, both stainless steel and plastic coupon discs were used as collecting surfaces in bench-scale water recirculating systems. The plastic material selected for the experiment was the PVC that was used in the manufacture of the packing material used in the pilot-scale cooling towers, so that the information obtained from the bench-scale testing can be applied to the pilot-scale experiments.

6.2.2.4 Pilot-scale cooling tower tests

Three pilot-scale cooling towers were constructed to test the optimal chemical control methods identified from the bench-scale experiments. The towers were transported to Franklin Township Municipal Sanitary Authority for side-by-side evaluation of different corrosion/scaling/biofouling control programs. The three towers were operated with the following conditions: 1) CoC 4; 2) flow rate 3 GPM (passing through a 0.75” ID PVC pipe); 3) temperature 105°F of recirculating water entering the tower and 95°F in the collection basin.

The cooling towers were operated using passively treated abandoned mine drainage collected from the St. Vincent College wetland site. The preliminary AMD run started on October 8, 2008 and ended on October 17, 2008. The final AMD run started on October 18, 2008 and ended on November 9, 2008. In both runs, all towers were using passively treated abandoned mine drainage as makeup water and the target cycles of concentration (CoC) was 4. The objective of the initial 12 day run was to evaluate the influence of high alkalinity and high conductivity of makeup water on the operation of pilot scale cooling towers. It was found that solids deposition at the end of this run was excessively high (the scaling coupons immersed in water were completely covered by a thick layer of deposits), primarily because of the malfunctioning of the conductivity-based blowdown control. It was concluded that the in-line conductivity meter was not a reliable indicator of the actual CoC in the towers for AMD waters. Instead, the blowdown volume was fixed at 10 gallons per day to achieve CoC of 4.5 as the total daily makeup water addition averaged 45 gallons.

Prior to the final run, the towers were cleaned with acetic-acid solution and disinfected by free chlorine. Detailed information on tower operations, including the temperature of water at specific locations, airflow rate inside the cooling tower, the conductivity of recirculating system, makeup water volume, blowdown volume, water flowrate, and ambient condition (weather, temperature, relative humidity), was recorded throughout the run. It was documented that the towers were able to perform according to design specifications and adequately simulate the operation of full-scale cooling towers in thermoelectric power plants.

Different levels of polymaleic acid (PMA) were added to each tower to determine its effect on controlling scale formation. Towers A and C were dosed at 15 and 25 ppm levels, respectively, while Tower B was used as a study control and received no PMA treatment. Scaling behavior as monitored with the mass gain of stainless steel coupon discs was analyzed by using a mass balance approach for the entire cooling tower recirculating system. Solid (scale) deposition rates on the stainless steel coupon surfaces were documented during all runs (along with corrosion weight loss of metal alloys, and heterotrophic planktonic/sessile bacteria). Water chemistry parameters were monitored to obtain detailed understanding of the cooling tower behavior.

6.2.3 Results and discussion

6.2.3.1 Precipitation modeling with equilibrium calculations

MINEQL+ (version 4.5) was used as described in Section 6.2.2.2 to evaluate the scaling potentials of the AMD at different cycles of concentration. In addition, two most commonly referenced practical saturation indexes (Langelier Saturation Index and Ryznar Stability Index) were calculated as direct predictors of precipitation formation. The pH values with respect to cycles of concentration were also calculated.

Detailed modeling results, as a function of increasing CoC, consist of the following:

- The Langelier Saturation Index (LSI) and Ryznar Stability Index (RSI) under open/closed conditions (Figure 6.2.2);
- Amount and form of solid precipitates under open/closed conditions (Figure 6.2.3);
- Changes of aqueous pH (Figure 6.2.4).

The Langelier Saturation Index (LSI) increased with cycles of concentration, as did the scaling potential. Ryznar Stability Index (RSI) is calculated by a different formula and usual demonstrates an opposite trend compared to the LSI. The RSI values in Figure 6.2.2 decreased with the cycles of concentration and were below 6 under all conditions, which indicate mild to severe scaling potentials.

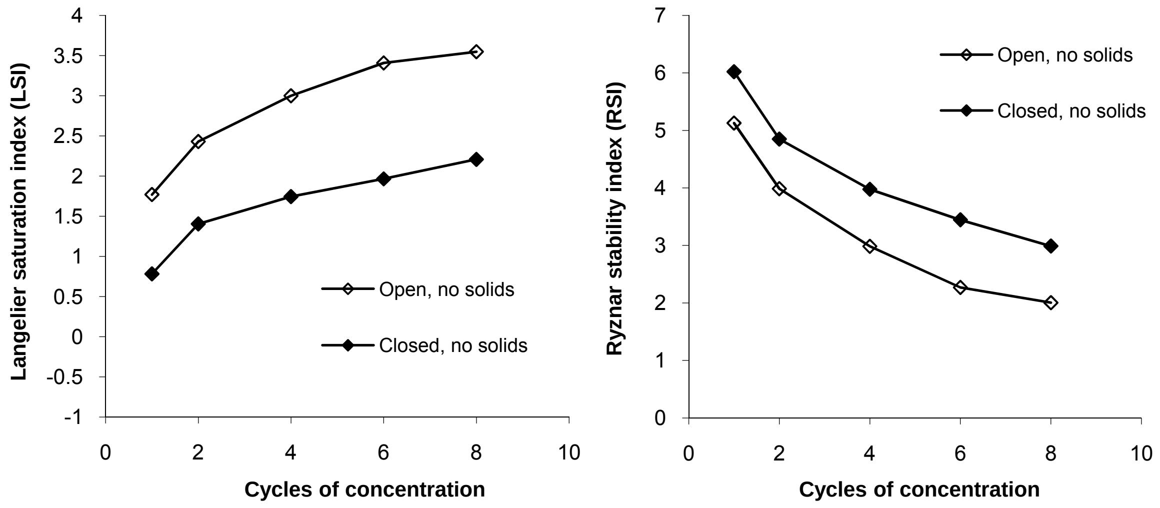

Figure 6.2.2. Modeling results of LSI (left) and RSI (right) for both open and closed to air cases without solids precipitation.

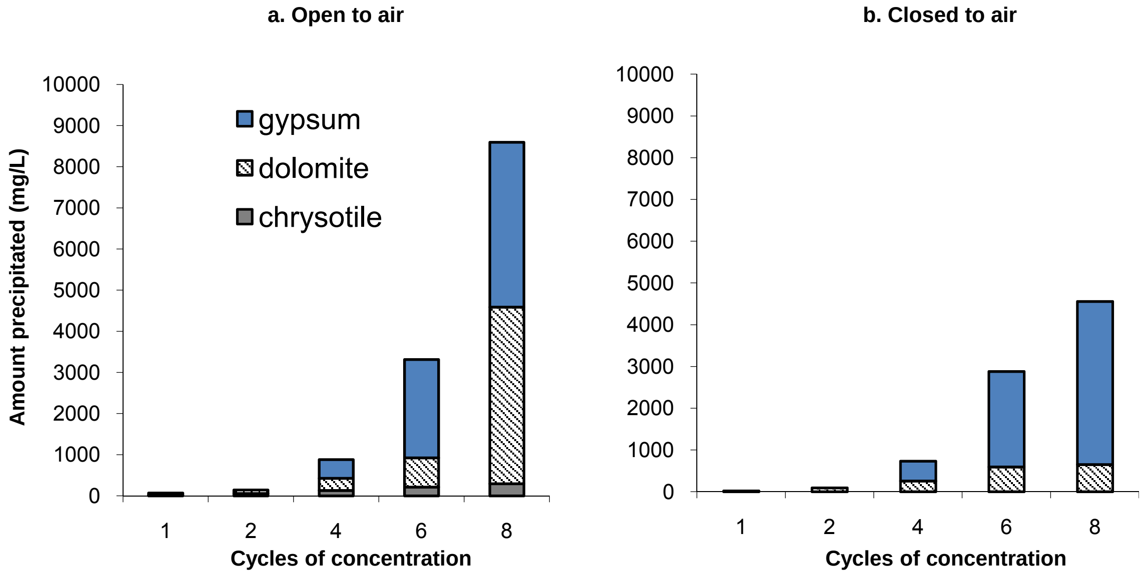

Figure 6.2.3. Predicted solid precipitation from the St. Vincent College Abandoned Mine Drainage calculated by MINEQL+.

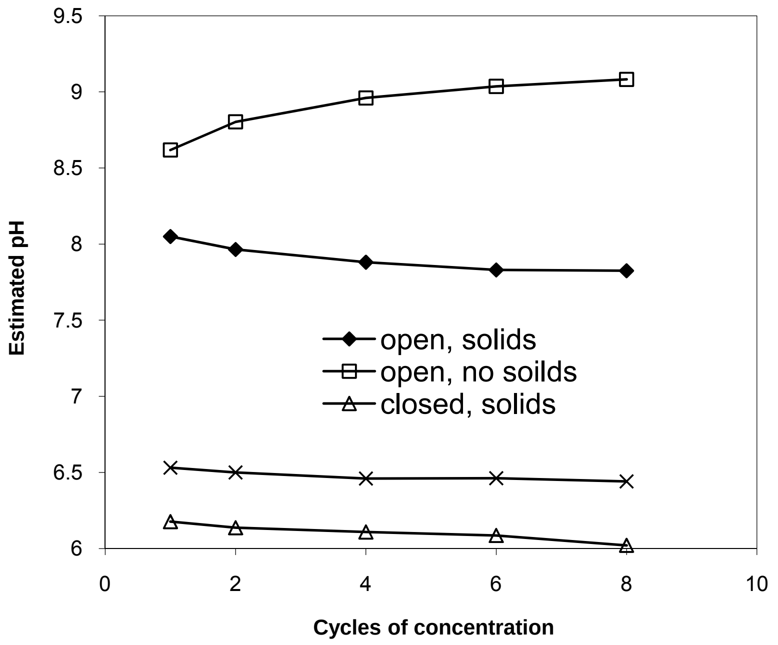

Figure 6.2.4. Predicted solution pH at different CoC under four different operation scenarios (open or closed to air; with and without solid precipitation).

MINEQL$^+$ modeling results suggest that gypsum and dolomite are the major solid precipitates to form from the St. Vincent College abandoned mine drainage under recirculating cooling tower conditions. More solids were predicted to precipitate under open-to-air condition because of the abundant supply of carbonation. As shown in Figure 6.2.3, a significant amount of otherwise dissolved solids could precipitate and contribute to solids accumulation when the towers operate at high cycles of concentration. The amount of solids precipitation at equilibrium was predicted to be 7-10 times more at CoC 8 than at CoC 4.

When the calculations allowed water to be open to the atmosphere and to equilibrate with CO_2(g), the pH values ranged between 8 and 9. When the calculations were performed in the absence of exposure to the atmosphere, the water was predicted to become acidic. Under the open condition, the calculated pH tended to increase with increasing CoC, when no solids were allowed to form. Such behavior was due to the accumulation of alkalinity with CoC. On the other hand, the pH tended to decrease with increasing CoC when solids formation was allowed to take place because the alkalinity was consumed through dolomite formation.

6.2.3.2 Bench-scale recirculating system experiments

Two bench-scale water recirculating systems were used to determine the scaling behavior of the actual SVAMD water at CoC 4 when inhibitors (i.e., PMA or AR-545) were added. The SVAMD water in both systems was treated with 15 ppm anti-scalant: System A with AR-545 and System B with PMA. SVAMD samples were added to the two water recirculating system and the water volume was reduced by 75% to CoC 4 with a heat source in about 5 days.

Concentration cycles, as determined by solution conductivity (which was the approach for field testing), took a longer time to reach CoC 4 than that based on water volume reduction (Figure 6.2.5). This suggests that the dissolved solids that precipitated during the concentrating process do not contribute to the conductivity measurements. The 1:1 trend line defines an ideal behavior by which all dissolved solids remain in solution during evaporative concentration. A deviation from the 1:1 line indicates that part of the dissolved solids has precipitated out of the solution during concentration. In the presence of anti-scalants, the degree of deviation from the ideal line indicates the effectiveness of the added antiscalants to hold the solids in solution. Using this criterion, it was determined that PMA was more effective.

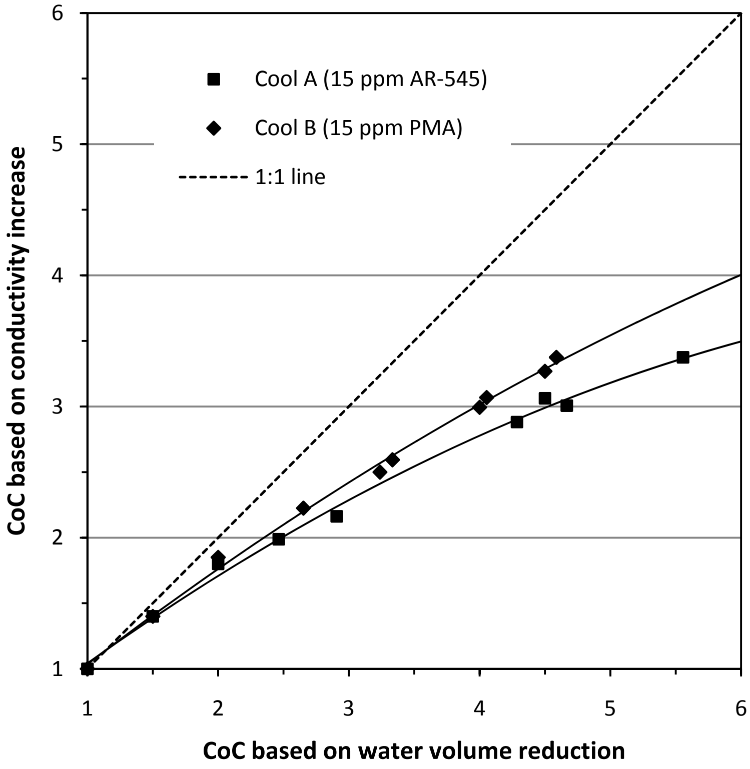

Figure 6.2.5. Correlation of concentration cycles determined by water volume reduction and conductivity measurements.

Coupon discs immersed in the SVAMD water treated with 15 ppm of AR-545 collected more solids after 8 days than those immersed in the SVAMD water treated with 15 ppm of PMA, suggesting that PMA performed better in such water (Figure 6.2.6). In addition, the turbidity of the AR-545-treated SVAMD water started to increase from ca. 2 NTU to greater than 10 NTU after 5 days, while the PMA-treated water remained relatively clear (< 4 NTU). By day 10, the difference in turbidity between these two waters grew to more than 35 NTU.

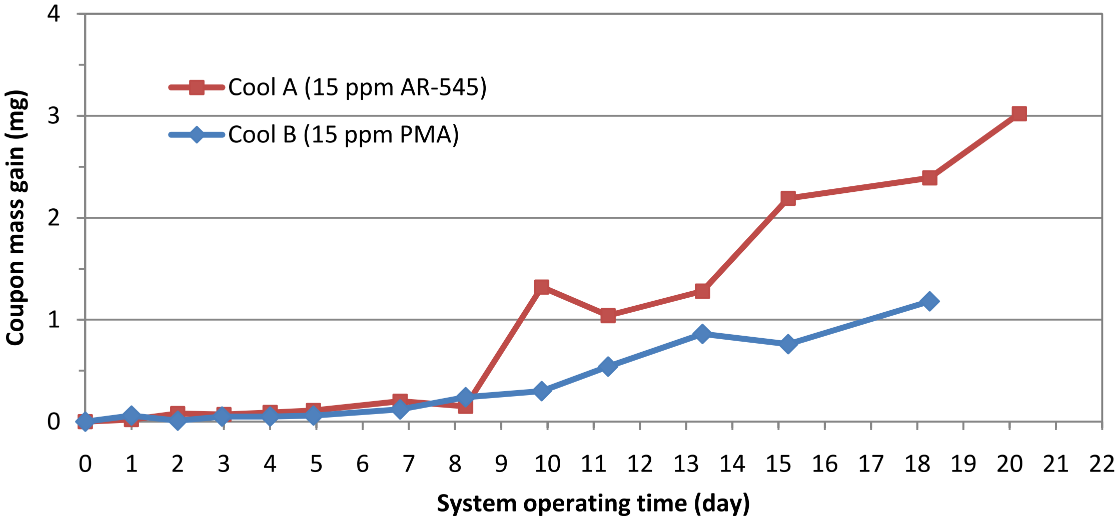

Figure 6.2.6. Coupon mass gain measurements for bench-scale water recirculating systems operated with the SVAMD (the water was stored in lab for a week prior to test). Recirculation conditions: 3 GPM, 40°C, pH 8.5.

Beaker tests with other anti-scalants (Acumer 2100 and AR-540) did not generate significantly better scaling inhibition performance than that of PMA (Figure 6.2.7) since the TDS of all solutions was approximately the same after reaching 75% volume reduction. These results suggest that PMA should be an effective scaling inhibitor for SVAMD water at 15-25 ppm dosage level. The effectiveness of PMA at both 15 ppm and 25 ppm concentrations were tested in pilot-scale experiments.

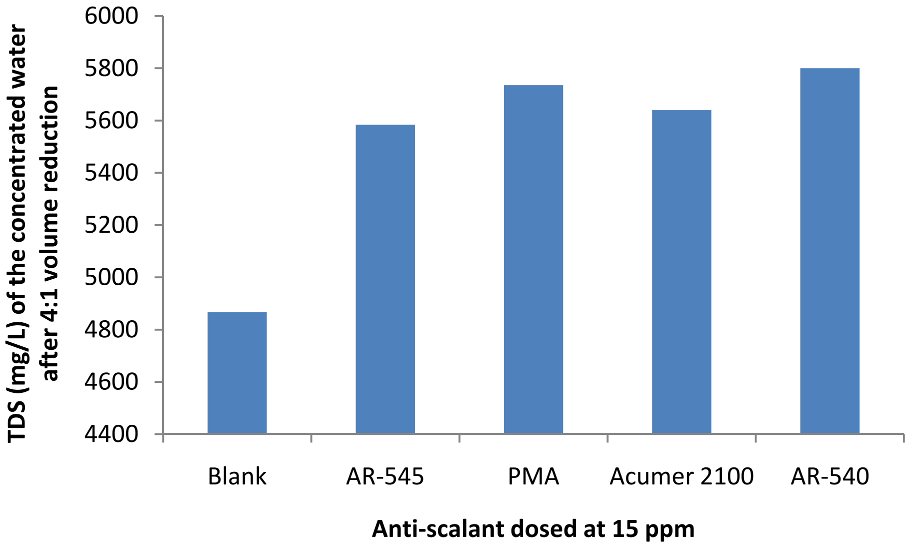

Figure 6.2.7. Beaker tests at 40-45°C. Initial water volume was 1.00 L, final volume for TDS measurements was 0.25 L. Water was heated in a water bath and bubbled with air to facilitate evaporation. It took 1-1.5 days for the water to reach CoC 4 (i.e., water volume reduction from 1.00 L to 0.25 L).

Figure 6.2.8 shows that the PVC discs collected more solids from water, especially in the absence of PMA, than the stainless steel coupons. On average, 3-4 times more solids were collected on the PVC than on the stainless steel.

The bench-scale experiments led to two basic conclusions: a) PMA performed satisfactorily well for scaling inhibition under the operating conditions employed; and b) Conductivity-based control of concentration cycles could deviate significantly from the concentration cycles determined based on water volume reduction.

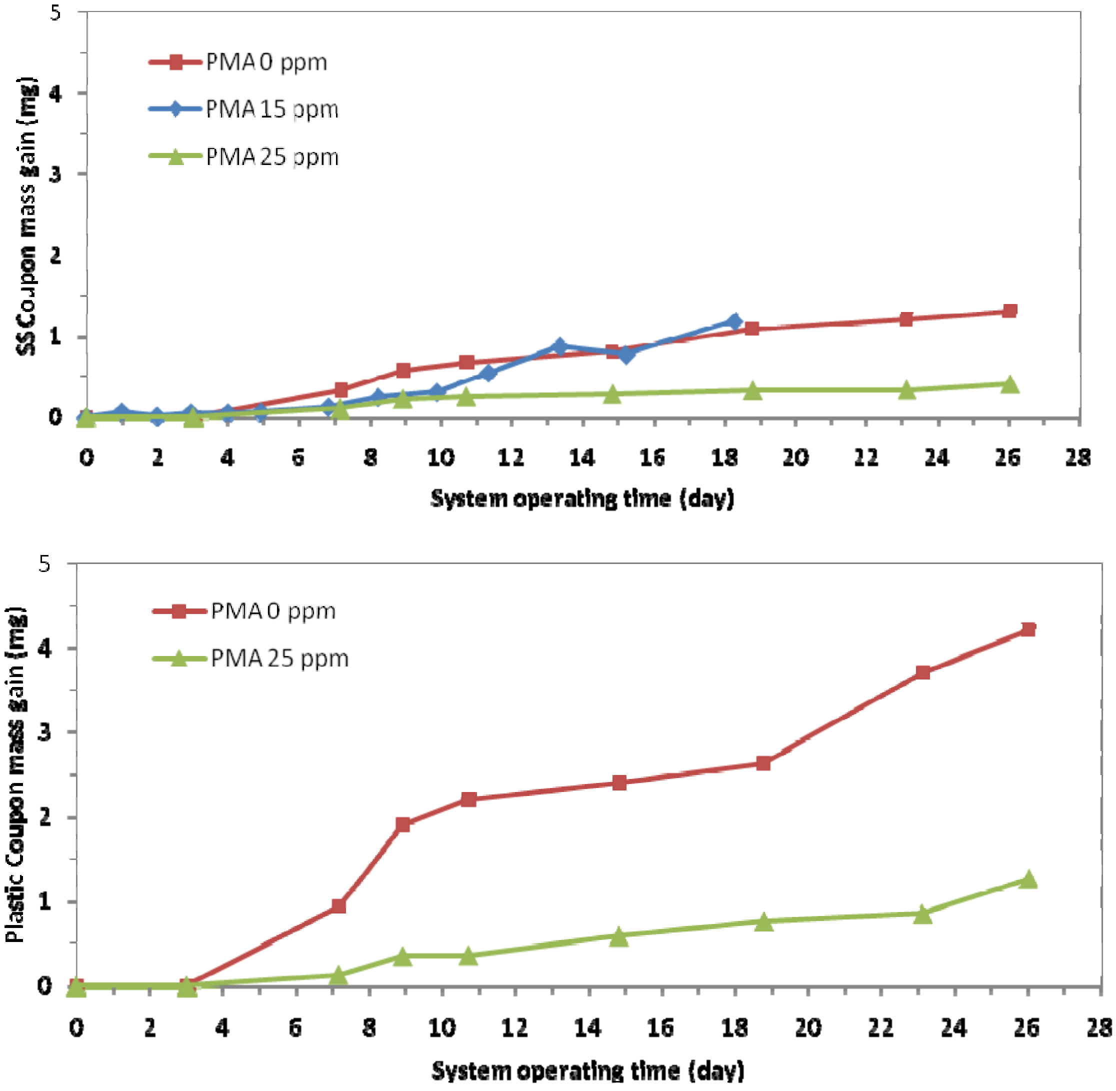

Figure 6.2.8. Coupon mass gain measurement for bench-scale water recirculating systems fed with the SVAMD water operated at 3 GPM, 40°C, and CoC 4. Upper panel: measured with stainless steel coupon discs. Lower panel: measured with PVC coupon discs.

6.2.3.3 Pilot-scale study

Bulk water chemistry in cooling tower system

Data from detailed water chemistry evaluations for the three cooling towers are summarized in Table 6.2.2. Selected data are discussed in detail below.

pH -- The pH values in towers treated for scaling inhibition by PMA (along with other chemical additives for simultaneous corrosion and bio-control) were different than those in the control tower. The control tower (Tower B) that had no PMA addition had an average pH of 8.2 whereas the two towers that received antiscaling and anticorrosion treatment had higher average pH of 8.7 for Tower A and 8.8 for Tower C. Raw SVAMD had an average pH of 7.8. The comparatively higher pH in the treated towers is attributed to the higher levels of solution alkalinity that was retained by PMA.

Chloride – Chloride concentrations in the recirculating water were generally 6-8 times higher than those in the makeup water (i.e., 400 mg/L in recirculating vs. 60 mg/L in makeup). As such, the values of CoC based on the chloride concentration were higher than the volume-based values of CoC 4~5 due to a significant input of chloride from the chlorine-based biocide (i.e., in the form of monochloramine).

Sulfate – Sulfate concentrations in the towers were generally 4-5 times higher than those in the makeup water. This ratio was close to the volume-based CoC since there was no additional sink or source of sulfate (gypsum was not found in solid deposits).

Phosphate -- Orthophosphate was added as a corrosion inhibitor. The target phosphate concentration was 5 ppm as PO_4^{3-} but it was not strictly maintained due to its low solubility in the presence of high concentration of calcium. Consequently, phosphate concentrations in the bulk water remained below 1 ppm. Corrosion studies showed that the added phosphate (in the form of pyrophosphate) was ineffective to prevent corrosion. Rather, the addition of phosphate produced more phosphate-containing scales.

Alkalinity -- Alkalinities in Towers A and C were around 4 times higher than those in the makeup water, close to the volume-based CoC. However, in Tower B, the alkalinity was close to makeup water. The significant difference in alkalinities between the test towers and the control tower is attributed to the addition of PMA. Without PMA addition in Tower B, alkalinity was consumed by the formation of calcium carbonate precipitates. In Towers A and C, PMA successfully inhibited the formation of calcium carbonates and as a result, most of the alkalinity remained in the aqueous phase.

Table 6.2.2. Cooling tower water quality in the field testing of the passively treated AMD from St. Vincent College mine drainage site. The recirculating tower water analyzed was operated at CoC 4 (the run from October 18, 2008 to November 9, 2008).

Tower A

Analyses	Unit	Result (unfiltered)	Reporting limit
Al	µg/L	ND	400
Ca	µg/L	825000	10000
Cu	µg/L	62.9	50
Fe	µg/L	ND	500
K	µg/L	29300	10000
Mg	µg/L	254000	10000
Mn	µg/L	578	30
Na	µg/L	446000	10000
SiO_2	µg/L	59100	2140
Zn	µg/L	56.7	40
NH_3-N	mg/L	0.57 J	0.1
Bicarbonate Alkalinity	mg/L	276 J	5
BOD	mg/L	ND	2
Cl	mg/L	216	50
NO_3-N	mg/L	1.1	0.05
SO_4	mg/L	2930 J	50
Total P	mg/L	0.64	0.1
Total Alkalinity	mg/L	407	5
TOC	mg/L	13.8	1

Tower B

Analyses	Unit	Result (unfiltered)	Reporting limit
Al	µg/L	ND	400
Ca	µg/L	674000	10000
Cu	µg/L	30.3 B	50
Fe	µg/L	ND	500
K	µg/L	23400	10000
Mg	µg/L	251000	10000
Mn	µg/L	109	30
Na	µg/L	450000	10000
SiO_2	µg/L	57900	2140
Zn	µg/L	101	40
NH_3-N	mg/L	0.74 J	0.1
Bicarbonate Alkalinity	mg/L	92.3 J	5
BOD	mg/L	ND	2
Cl	mg/L	239	50
NO_3-N	mg/L	1.1	0.05
SO_4	mg/L	2910 J	50
Total P	mg/L	0.032 B	0.1
Total Alkalinity	mg/L	92.3 J	5
TOC	mg/L	6	1

Tower C

Analyses	Unit	Result (unfiltered)	Reporting limit
Al	µg/L	ND	400
Ca	µg/L	796000	10000
Cu	µg/L	34.4 ^{B}	50
Fe	µg/L	ND	500
K	µg/L	26300	10000
Mg	µg/L	235000	10000
Mn	µg/L	595	30
Na	µg/L	418000	10000
SiO_2	µg/L	54900	2140
Zn	µg/L	53.1	40
NH_3-N	mg/L	0.64	0.1
Bicarbonate Alkalinity	mg/L	257 ^{J}	5
BOD	mg/L	ND	2
Cl	mg/L	223	50
NO_3-N	mg/L	1.1	0.05
SO_4	mg/L	2850 ^{J}	50
Total P	mg/L	0.65	0.1
Total Alkalinity	mg/L	400 ^{J}	5
TOC	mg/L	17	1

Notes: J: Method blank contamination. The associated method blank contains the target analyte at a reportable level
B: Estimated result. Result is less than reporting limit.

Mass deposition over time

During the pilot-scale testing with the SVAMD water, a preliminary run was conducted for a period of 12 days as a test run to obtain critical data for cooling tower performance. Figure 6.2.9 (upper panel) depicts the time course of scale mass deposited on stainless steel coupon discs in the three towers during the preliminary run. The scale accumulation on the coupon discs was excessive- the entire coupon surface was covered by a thick layer of deposits (ca. 2 mm thick). The excessive solids deposition was caused by the towers operating at much higher cycles of concentration than originally planned. The towers were operated at higher CoC because the conductivity probes in each tower that were used to monitor the conductivity of the recirculating water and to trigger blowdown at preset values failed to function properly. The experiment was designed to operate with raw SVAMD with an average conductivity of 1.91 mS/cm, which means that the recirculating water in each tower should have conductivity between 7.5~9.5 mS/cm to maintain a target of CoC 4~5. However, tower blowdown was not successfully triggered at these predetermined conductivity levels and the water volume balance indicated that the towers were actually operating at CoC 8~10 (more detailed description about the malfunctioned blowdown control is available in the tower performance section). Such excessive mass deposition was also expected based on the modeling predictions as revealed in Figure 6.2.3.

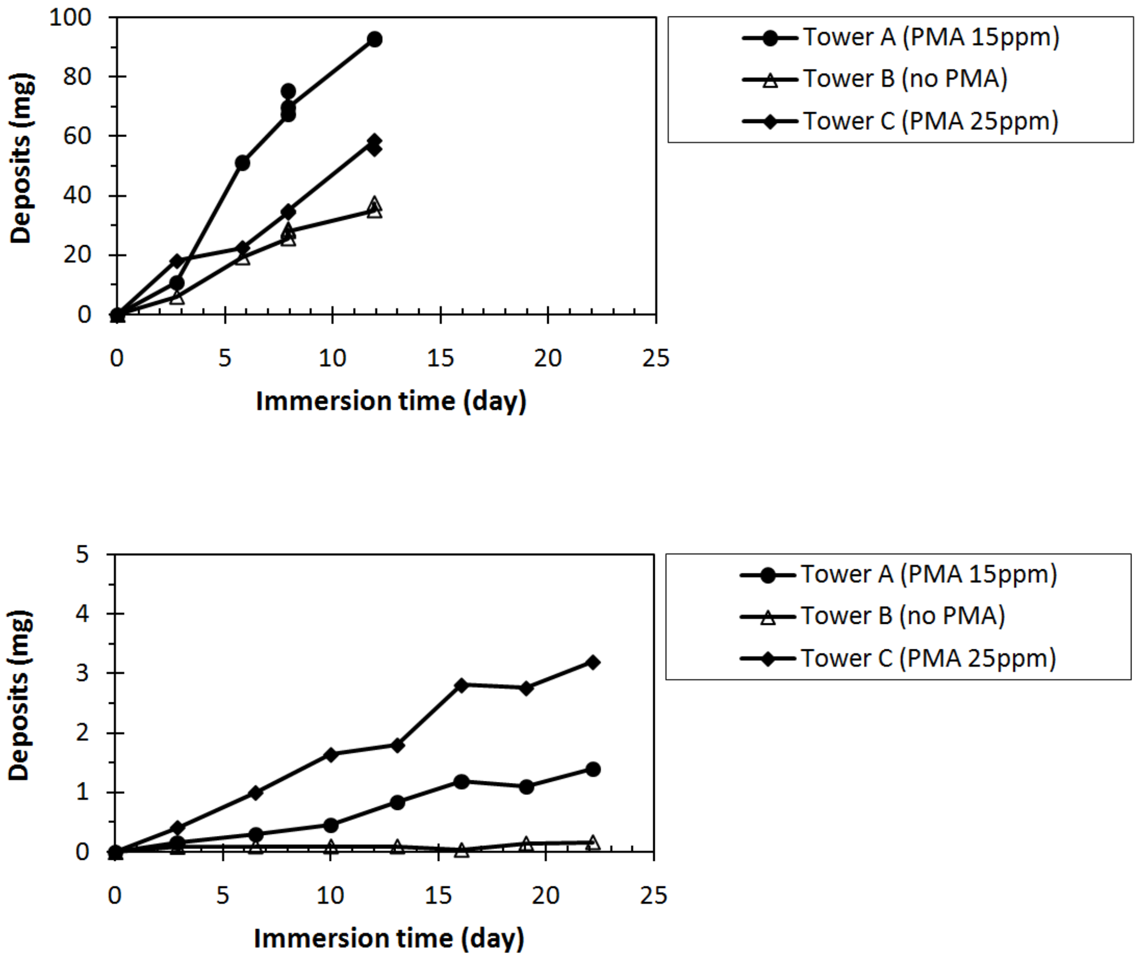

Figure 6.2.9. Mass gain measurement in the pilot-scale cooling towers operated with SVAMD water at FTMSA site. Upper: preliminary run; Lower: final run. Deposits were collected on stainless steel coupon discs immersed in pipe flow. Effective collection area 5.61 cm^2, flow velocity 1.9 ft/sec (3 GPM in 3/4" pipe), water temperature 104 ± 2°F, open recirculating system.

Upon completion of the preliminary run, the conductivity probes were either calibrated or replaced to ensure proper function prior to the final run. To guarantee proper blowdown when the towers reached CoC 4, daily check up on the blowdown volume was performed throughout the run. When the volume of blowdown based on the conductivity measurements was less than a quarter of the makeup water volume, manual blowdown was executed to maintain CoC 4 in each tower. The time course of scale mass deposited for the three towers during the final run is shown in Figure 6.2.9 (lower panel). Comparing with data from the preliminary run where CoC 4 was not maintained (Figure 6.2.9 upper panel), scale deposition was significantly reduced when CoC was maintained around 4.

However, the coupon mass gain measurements showed that the most scale formed on discs in water treated with the highest dosage of PMA, which is contrary to expectation. According to the data for scale build up over time (Figure 6.2.9), coupon discs immersed in Tower B that was not dosed with PMA collected the smallest amount of scale whereas the coupon discs in Tower C with 25 ppm PMA addition collected the largest amount. This outcome of scaling behavior is exactly the opposite of the intuitive expectation that addition of PMA would inhibit scaling and that higher PMA dosing would perform better. To understand these observations in the coupon mass gain measurements, a series of experiments were carried out at the pilot-scale and bench-scale and the results are discussed below.

Effectiveness of PMA to control scaling

The residual PMA concentration in the recirculating water was measured and compared to the amount added and then correlated to scale formation to determine the effectiveness of the PMA treatment. As shown in Figure 6.2.10, total measureable PMA in both Towers A and C was lower than the added concentration, suggesting that a fraction of the added PMA was removed from the aqueous phase. This removal was most likely through coprecipitation with solids. The dissolved (aqueous) PMA in water accounted for about 50-60% of total PMA in both towers. The remaining 40-50% was associated with suspended solids, thereby exerting repulsive forces between suspended particles to discourage solids settling (PMA molecules are generally negatively charged due to dissociation of carboxylic groups).

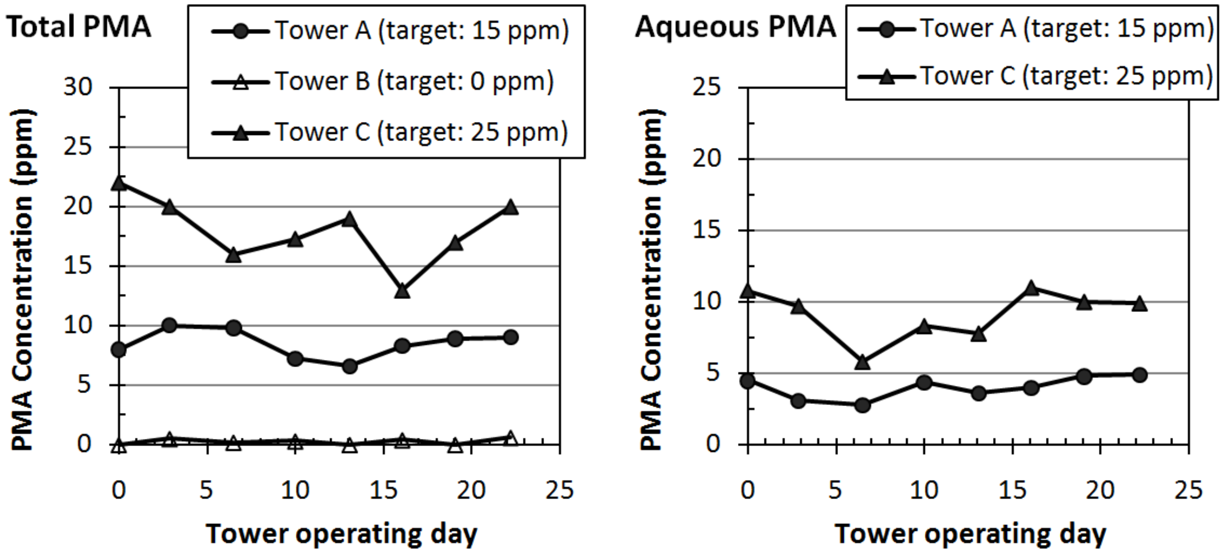

Figure 6.2.10. Total PMA (left panel) and dissolved (aqueous) PMA (right panel) concentrations in the recirculating water of the cooling towers as measured after daily addition of PMA (with 0.5 hr delay). PMA dose was based on water blowdown volume. The aqueous PMA concentration was obtained by filtering the water sample through a 0.22-μm filter. Background readings were corrected using water sampled from Tower B where no PMA was added.

The effect of PMA as an antiscalant was contrary to the original hypothesis that PMA would reduce scale formation; higher concentrations of PMA in the recirculating water resulted in more scale deposition on the steel coupons. Additional experiments determined that a significant amount of solids were precipitated on the packing in Tower B, which did not receive any antiscalant (the PVC surface exhibited significant affinity for the SVAMD solids) and that the turbidity of the recirculating water in Tower B was close to that of the makeup water (Figure 6.2.11). The large error bars (one standard deviation) of the turbidity measurements (Figure 6.2.11) with waters in Towers A and C suggest that the differences in turbidity of the two waters are statistically insignificant: both waters contained appreciable amount of suspended solids. Such findings suggest that the solids formed in Tower B were easily separated from the liquid phase and removed from the system. This was evidenced by the mass balance on four main sections of the recirculating cooling tower system (Table 6.2.3). At the bottom sumps of the towers, significant amounts of solids were accumulated under slow flow condition. For Tower B without PMA treatment, solids buildup became the most serious in the tower packing section where evaporative concentration led to precipitation-induced deposition. In Towers A and C, the influence of flow rate in the bottom sump and the evaporation on the tower packing were mitigated by the presence of PMA, which impeded solids deposition. Higher levels of suspended solids in Towers A and C resulted in higher water turbidities and a greater chance for the suspended solids to deposit on the pipe and coil sections. It is noteworthy that the ranking order of the solids deposition at the pipe and coil section of the three cooling towers calculated based on the mass balance analysis (i.e., C > A > B) is in agreement with the scaling trends measured by the coupon mass gain (Figure 6.2.9).

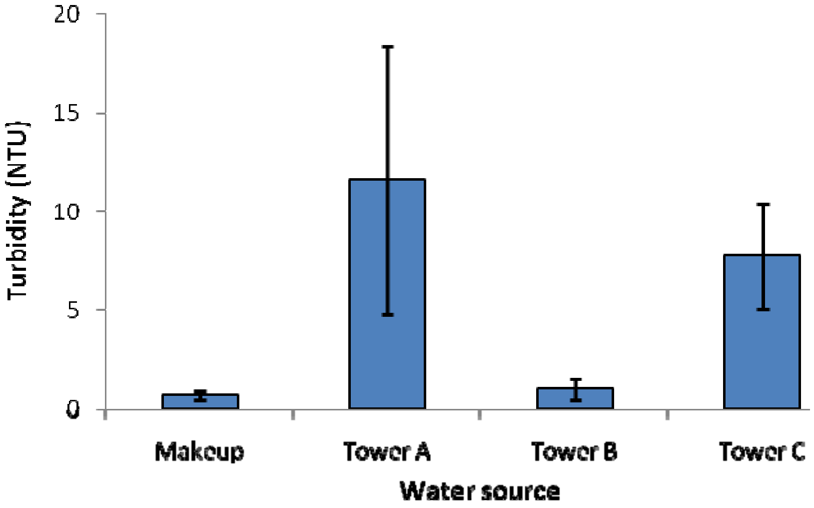

Figure 6.2.11. Turbidity of the makeup water and the recirculating water in the cooling towers during the CoC 4 operation. The column represents mean values of seven measurements over the course of tower operation; error bars represent 1 standard deviation of the seven measurements for each tower.

Table 6.2.3. Mass balance analysis of solids deposition in different sections of the cooling towers operated with SVAMD water at CoC 4 for 25 days (the final run). All units are in grams.

Cooling Tower	**A**	**B**	**C**
Solids input with makeup water (1)	6183	6126	6488
Solids output with blowdown (2)	4939	4574	5301
Net solids input to tower system (3) = (1) – (2)	**1244**	**1552**	**1187**
Solids accumulated in bottom sump (4)	491	557	469
Solids accumulated on tower packing (5)	506	936	220
Solids accumulated in the pipe and coil sections (6) = (3) – (4) – (5)	**247**	**59**	**498**

Overall, PMA was not very effective at keeping high levels of dissolved solids present in SVAMD in solution under the pilot testing conditions and the doses applied. The solids content of the SVAMD water at four cycles of concentration was extremely high and inhibition of precipitation by PMA was not effective.

6.2.4 Summary and Conclusion for Reuse of Passively Treated Abandoned Mine Drainage

The scaling behavior and control of wetland-treated abandoned mine drainage in recirculating cooling systems was evaluated in this study. Results from the pilot-scale experiments determined that the addition of commonly used polymer-based scaling inhibitors alone was ineffective for scaling control. The high concentration of total dissolved solids requires more comprehensive pretreatment and scaling controls. Nevertheless, the added PMA, at concentrations of 15 to 25 ppm, lent some stability to suspended mineral solids (high water turbidities) and there was less deposition in the pipe flow sections of the cooling towers.

Deposits from the SVAMD concentrated to CoC 4 in recirculating cooling systems exhibited varied affinities to different surfaces. More deposits were collected on the PVC surfaces that were used as the tower packing material. Hydrodynamics also played a role in deposition. Low flow velocities encountered in the plastic packing and bottom sump sections of cooling tower resulted in greater sedimentation. Indeed, significant amount of deposits were observed at the bottom of the tower sump, especially in the tower receiving no PMA treatment. The finding suggests that scaling took place in a nonuniform manner throughout the cooling tower system. Therefore, it is suggested that scaling measurements should be performed at tower sections where deposition is of concern. Also, similar materials of test coupon should be used for scale deposition to provide substrate surfaces representative of the building materials of cooling tower.

6.3 Biofouling Control for Reuse of Passively Treated Abandoned Mine Drainage

Abstract

Construction of new thermoelectric power plants in the U.S has frequently been under pressure because water resources that are required to meet their cooling needs are often not readily available. At the same time, it is expected that water demand for energy generation will increase by 50% by 2030. In eastern U.S., abundant mine drainage is stored in aged excavations with a total volume of approximately 250 billion gallons. This study incorporated laboratory and field experiments to investigate biofouling potential and biofouling control strategies when using abandoned mine drainage (AMD) in cooling systems. It was determined that both chlorination and chloramination can adequately control the biomass growth in passively treated AMD. This study also revealed that the chloramine concentration of 1~2 ppm as Cl_2 can achieve strict control of both planktonic and sessile heterotrophic bacteria in cooling towers using passively treated AMD as makeup water.

6.3.1 Introduction

Abandoned mine drainage (AMD), a potential alternative water resource, is found in areas where most of the mining legacy issues are still of concern: western Pennsylvania, almost all of West Virginia, and western Maryland. AMD is the product of the reaction between mineral pyrite ($FeS_{2(s)}$), water, and oxygen (Stumm and Morgan, 1996). It changes the appearance of receiving surface waters and endangers the aquatic and benthic life. Because of the oxidized iron precipitation, streams impacted by AMD will have different color sediments ranging from red to orange and yellow. The acidic discharge containing heavy metals, such as copper, lead, and mercury might dissolve into ground or surface water, thus affecting their relative speciation and toxicity. In the eastern U.S., about 20,000 km of streams and rivers have been contaminated by AMD (EPA, 1995; Ziemkiewicz et al., 2003).

Passive treatment system that does not require continuous chemical addition has been developed for the treatment of AMD (Hedin et al. 1994). Based on natural chemical and biological reactions, these AMDs can be reclaimed and could serve as alternative water resources due to the large amount of storage volume (estimated at 250 billion gallons) in the eastern U.S. (Veil et al., 2003).

The freshwater usage in the U.S has increased from 341 to 378 billion gallons per day between 1995 and 2000 (USGS, 2000). The major freshwater users are irrigation (39%) and thermoelectric power generation (38%). Thermoelectric power generation, which represents about 91% of electrical power produced in the U.S. (USEIA, 2007), requires an abundance of water for cooling. Fierce competition for water resources is inevitable and will force difficult decisions about allocation priorities and water availability for electric power production. Therefore, impaired water sources, such as the AMD, could become a valuable solution to water shortage problem.

Although the amount of AMD seems to be promising for the cooling application in power plants, the effectiveness of using this impaired water is still unknown. Biofouling is one of the challenges for modern cooling towers. In order to inhibit the formation of biofilm, oxidizing agents are commonly used in cooling towers. Chlorination by free chlorine is often used to inhibit the biomass growth in cooling systems (Frayne, 1999). Monochloramine is another effective biocide (Wolfe et al., 1984), but it has not been commonly used in cooling towers.

Turetgen (2004) observed that monochloramine was significantly more effective than free chlorine against cooling tower biofilms. Rao et al. (1998) demonstrated that monochloramine and free chlorine showed similar biocidal activity in controlling biofilms and that monochloramine formed in situ in the cooling circuit could be as effective as free chlorine. In cooling towers utilizing impaired waters, biofilm formation is one of the main concerns for effective tower operation. Hence, chloramination by preformed monochloramine at high pH may be an effective oxidizing biocide option for the control of biofouling in such cooling systems. The objective of this study was to determine a feasible disinfection strategy to control biofouling in a recirculating cooling system using passively treated acid mine drainage as makeup water. The appropriate residual disinfectant to control biofouling in the cooling system was determined from laboratory scale batch tests. Both chlorination and chloramination of the AMD water were conducted to establish the best biofouling control strategy. Based on results of the batch tests, a field test was conducted with passively treated acid mine drainage. The field-scale experiment with pilot-scale cooling towers was conducted for 21 days to observe the effectiveness of selected biofouling control strategies under the conditions similar to those in full scale cooling systems.

6.3.2 Materials and Methods

6.3.2.1 Impaired Water Acquisition and Characterization

Water samples of St. Vincent passively treated acid mine drainage (SVAMD) were used for both laboratory and pilot-scale experiments. SVAMD was collected from Cell # 5, St. Vincent College Wetland #3 (Latrobe, PA) without disturbing the bottom sediments. A total of 7000 gallons of SVAMD was transported and stored in a clean metal roll-off steel tank with tarpaulin cover at Franklin Township Municipal Sanitary Authority on September 30th 2008. This water served as makeup water for pilot-scale cooling towers after it was allowed to settle for 3 days prior to use. Settled SVAMD was pumped from the upper portion of the metal roll-off steel tank to three 60-gallon makeup tanks daily.

Characterization of the SVAMD was done by a commercial laboratory (TestAmerica, Pittsburgh, PA) and the results are shown in Table 6.1.1. Preliminary study of biofouling control was completed in a batch system to simulate the real situation in field test. Water samples used for laboratory experiments were stored at room temperature in a 5 gallon carboy. All experiments were conducted hours after collecting the water sample from the site to avoid the changes in bioactivity.

6.3.2.2 Batch Disinfection Experiments

Batch tests to evaluate the effectiveness of chlorine and chloramine were performed in 200 mL glass beakers. The beakers were open and exposed to light and air to simulate the outdoor conditions. Water temperature was maintained between 95-105 °F (35–41 °C) by a hotplate and most of the batch tests were performed over a period of 4 hours. The total chlorine concentration and heterotrophic plate counts (HPC) were measured every 10 minutes in the first hour and then hourly after that.

Batch tests for determining efficacy of chlorine and chloramine against heterotrophic bacteria in SVAMD were conducted using a total chlorine level at 0.5, 1, 2, 4, and 8 ppm as Cl_2. Total chlorine dose of up to 8 ppm was chosen based on the results of previous experiments with secondary treated wastewater (Chapter 5). Chlorine and chloramine were added to 200-mL beakers containing SVAMD with continuous stirring. At predetermined time intervals, three 2.5 mL water samples were taken to determine the free/total chlorine concentration and the background interference caused by chemical or biological compounds in the water. Chlorine and chloramine doses were determined following Method 2350 B Chlorine Demand/Requirement (APHA, 1998).

Commercial 5.25% sodium hypochlorite solution (NC9617752, Fischer Scientific, Inc.) was used to prepare a stock solution containing 1000 ppm of free chlorine. Chloramine stock solution was prepared by adding sodium hypochlorite and ammonium chloride in a mass ratio of 4:1 (Cl_2: NH_3-N). Total available chlorine and free available chlorine residual were measured using Method 4500-Cl G. DPD colorimetric method (APHA, 1998). Oxidizing chemicals, such as permanganate, iodate, chromate, and MnO_2 will interfere and magnify the chlorine residual measurement in the sample (APHA, 1998; Nollet, 2007). This phenomenon is referred to as background interference. The interference correction was determined by dechlorinating the water sample with 5 ppm sodium arsenite, then adding DPD reagent, and recording the amount of chlorine in the blank sample. The actual chlorine/chloramine residual concentrations were determined by deducting the interference correction from the original reading.

In the batch tests, planktonic heterotrophic bacteria were measured using Method 9215 C. Spread Plate Method (APHA, 1998). Plate count agar was used as the culture medium and plates were incubated for 48h at 35°C. Each water sample was diluted to 10^{-2} in order to estimate bacteria in the range of 30~300,000 and each diluted sample was cultured on duplicate plates.

6.3.2.3 Experiments with Pilot-Scale Cooling System

To determine the effectiveness of biofouling control under conditions similar to those in full-scale cooling systems, tests were conducted in pilot scale cooling towers described in Section 6.1.2.6.

Both planktonic and sessile heterotrophic bacteria were monitored in the system during the 21-day pilot-scale test. Sessile bacteria were monitored by immersing circular stainless steel coupons in the recirculating cooling water. . Coupons were pretreated with ethanol solution for sterilization (Obuekwe et al. 1981) and were inserted in the system after it has achieved four cycles of concentration (it took three days to achieve CoC 4 in all three towers). Stainless steel coupons were withdrawn from the coupon rack after 10, 15, and 23 days. Removal of biofilm from the coupons was performed following the ASTM Method E 1427 (ASTM, 2000). After the coupons were withdrawn aseptically from the coupon rack, water was drained off (Bradshaw et al., 1996) and the coupons were immersed in 50 mL phosphate buffered saline in a 200 mL bottle (Prosser et al., 1987). The bottles were sonicated gently for 5 minutes to dislodge the biofilm from the coupon (Prosser et al., 1987), and were vortexed for 30 seconds to make the solution homogeneous (Prosser et al., 1987). Planktonic heterotrophic plate counts were performed for these solutions and converted to CFU per cm^2 of coupon surface area.

Pre-formed chloramine solution was used for biofouling control instead of simultaneously feeding ammonia and hypochlorite. Chloramine stock solution was prepared by adding hypochlorite and ammonia in a mass ratio of 4:1 (Cl_2: NH_3-N). A biocide stock solution of 250 ppm chloramine as Cl_2 was kept in a storage tank and was continuously injected into the recirculating system using a variable speed peristaltic pump. The pump rate was adjusted based on the volume of makeup water fed into the tower daily.

6.3.3 Results and Discussion

6.3.3.1 Bacterial growth in raw SVAMD

Two 1-L samples of St. Vincent passively treated AMD water sample were well stirred and stored at room temperature. The jars were open and exposed to light/air to simulate the outdoor conditions. Heterotrophic plate count was performed on these raw SVAMD samples after 1, 6, 7, 8, 10, 15 and 20 days and the results of planktonic heterotrophic bacterial counts (HPC) are shown in Figure 6.3.1. The average planktonic HPC in the first sample during 20 days is $10^{3.9}$. The HPC decreased dramatically after Day 1 from $10^{4.54}$ to $10^{3.80}$ and became steady after that. Results from culturing another SVAMD water sample show similar low bacteria activity in a batch system. These results suggest a rather limited biofouling potential of this type of impaired water.

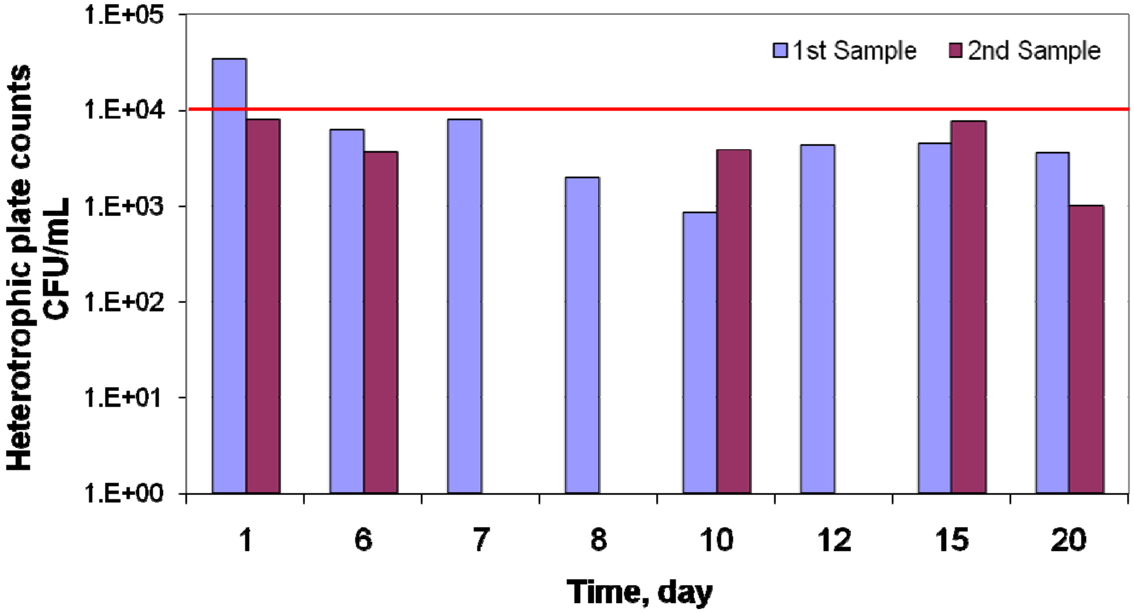

Figure 6.3.1. Heterotrophic plate counts in SVAMD stored in a batch system. The solid line indicates empirical biofouling control criteria of 10^4 CFU/cm^2 (Ludensky, 2005).

6.3.3.2 Laboratory-scale disinfection tests

The results of chlorination experiments with SVAMD with different initial concentrations of total chlorine in a batch reactor are shown in Figure 6.3.2.

The raw SVAMD has a background interference of as much as 1.3 ppm of total chlorine concentration at the beginning of the experiment. However, the background interference became less significant within an hour into the experiment and there was no need to account for it. Heterotrophic bacteria counts were analyzed 10 minutes and 3 hours after adding chlorine.

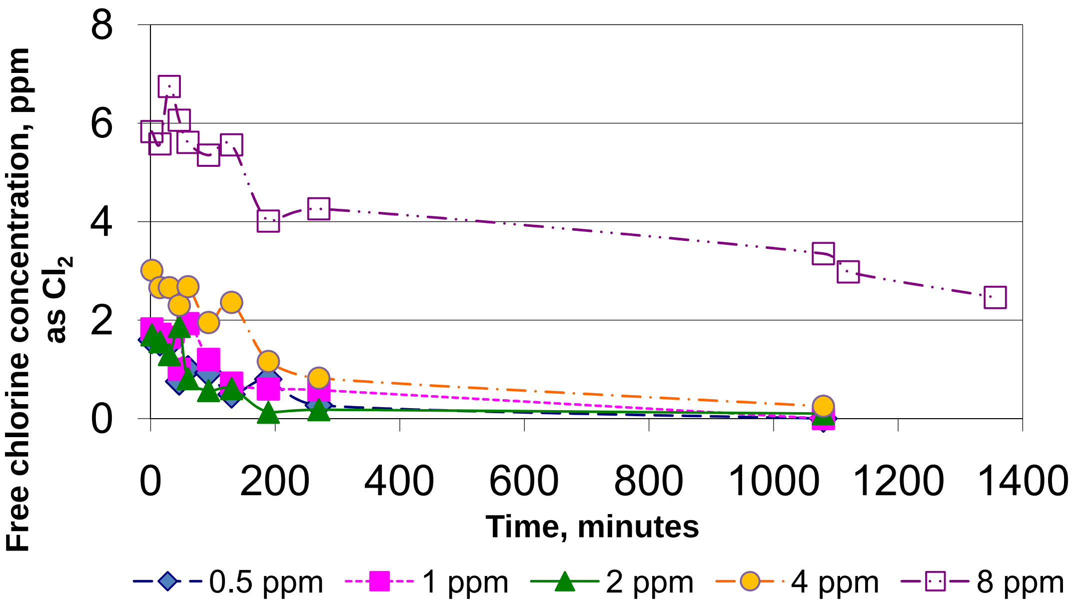

Figure 6.3.2. Chlorine demand of raw SVAMD.

Initial heterotrophic plate count in the raw SVAMD was $10^{3.9}$ CFU/mL. The results shown in Figure 6.3.4 indicate that chlorine could suppress heterotrophic bacteria below general biofouling control criteria of 10,000 CFU/mL within 3 hours of contact under most circumstances. The minimal chlorine dosage for effective biofouling control was 0.5 ppm. Dosage concentration higher than 2 ppm can decrease the heterotrophic bacteria colonies to non-detectable levels within 3 hours (Figure 6.3.3).

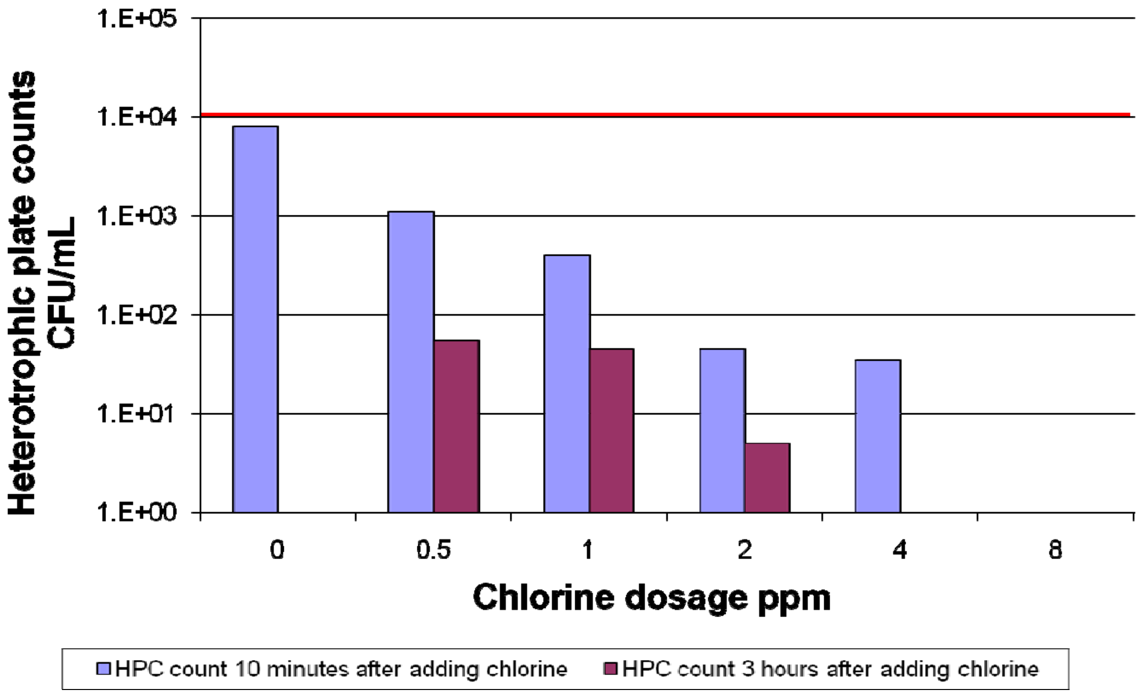

Figure 6.3.3. HPC of SVAMD exposed to different free chlorine dosage

Raw SVAMD exhibited background interference as 0.22 ppm with respect to monochloramine measurement and this value was used to modify the measurements collected in batch experiments. The pH of raw SVAMD changed from the initial value of 7.6 to about 8.2. This increase in pH ensured the high percentage of monochloramine formation in the batch system and may also contribute to the extended presence of monochloramine in the batch system as shown on Figure 6.3.4. Figure 6.3.4 shows that all of the monochloramine dosages tested in this study were maintained close to their initial levels even after 30 hours of contact with raw SVAMD.

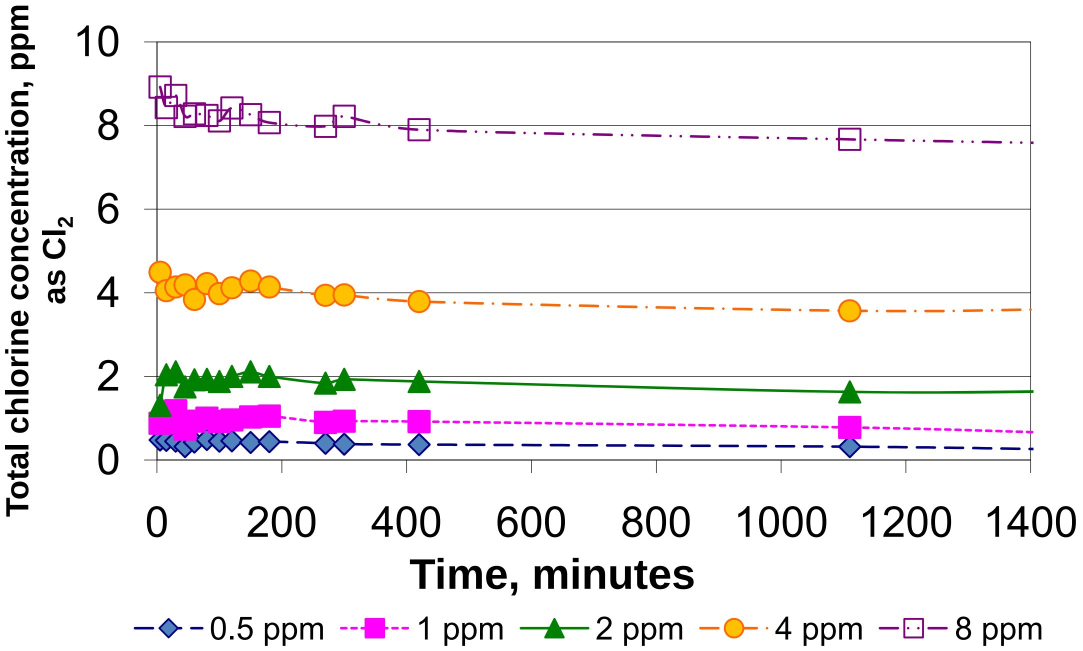

Figure 6.3.4. Chloramine demand of raw SVAMD.

The initial HPC was $10^{3.29}$ CFU/mL, which was comparatively low when compared to other impaired waters evaluated in this study. The results of disinfection experiments with monochloramine in raw SVAMD are shown in Figure 6.3.5. Because the raw water had relatively low bacterial counts, none of the batches had bacterial counts above 10^3 CFU/mL for any monochloramine concentrations tested in this study. All dosages above 0.5 ppm can efficiently decrease the heterotrophic bacterial counts to non-detectable levels within 10 minutes. Chloramination was capable of providing adequate disinfection efficiency and had more stable disinfection residual in passively treated acid mine drainage when compared to free chlorine. Therefore, chloramination was chosen as a disinfection modality for pilot-scale experiment.

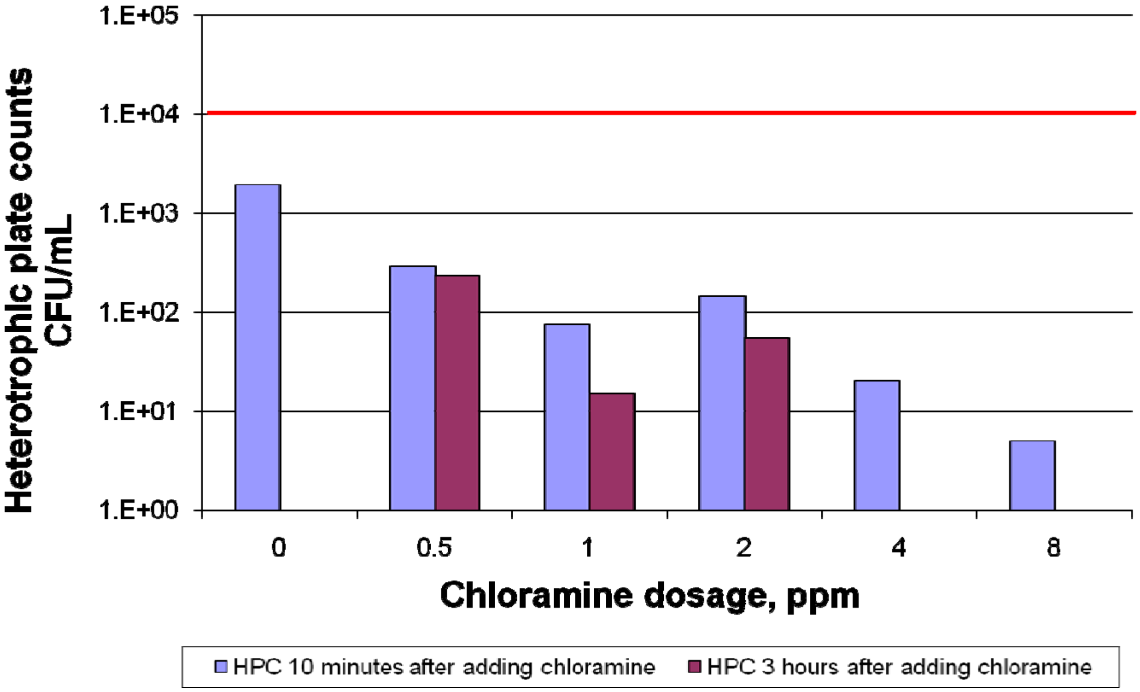

Figure 6.3.5. Heterotrophic plate counts of acid mine drainage with different chloramine dosage. With chloramine dosage higher than 4 ppm, bioactivity was undetectable after 3 hour.

6.3.3.2 Results of Pilot-Scale Experiments for Biofouling Control by Chloramination

The amount of bacteria in the raw SVAMD that was used as makeup water for the pilot-scale testing was recorded through the entire testing period and is displayed in Figure 6.3.6. After Day 10, the population of heterotrophic bacteria reached a stationary phase and remained at about $10^{4.3}$ for the rest of the testing period.

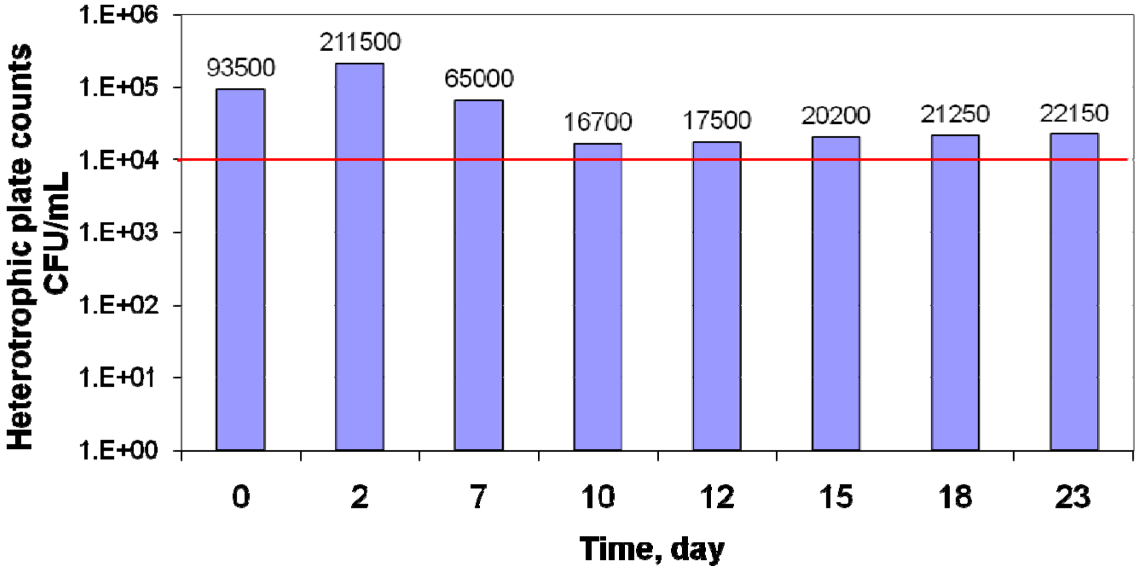

Figure 6.3.6. HPC in SVAMD (raw water). The solid line indicates the target criterion for biofouling control in cooling tower system.

Throughout the pilot testing with SVAMD, 1~2 ppm monochloramine as Cl_2 was added to each tower to suppress the microbial activity because of the low initial bacterial population in the makeup water. The dosage rate of biocide was adjusted to match possible maximum variation of evaporation rate and blowdown volume.

Figure 6.3.7 shows total daily chloramine residuals and the heterotrophic plate counts during the 21 days (plus 3 days of preliminary operation required to achieve CoC 4) of pilot-scale testing. The chloramine residual was well controlled in the range of 1~2 ppm as Cl_2. For Cooling Towers A, B and C, the total monochlorine was maintained at 1.11 ± 0.61, 1.28 ± 0.57 and 1.37 ± 0.60 ppm as Cl_2, respectively. The only exceptions occurred on days 3, 17 and 20 when excessive blowdown and occasional separation of the chloramine feed pipe caused significant excursions in monochlormaine concentration outside the desired range. However, the bioactivity in all three towers was completely suppressed during the entire testing period as evidenced by the total heterotrophic bacteria counts significantly below 10^4 CFU/mL. Results of sessile bacteria counts shown in Figure 6.3.8 revealed rather small amount of bacteria that was attached to the sampling surfaces.

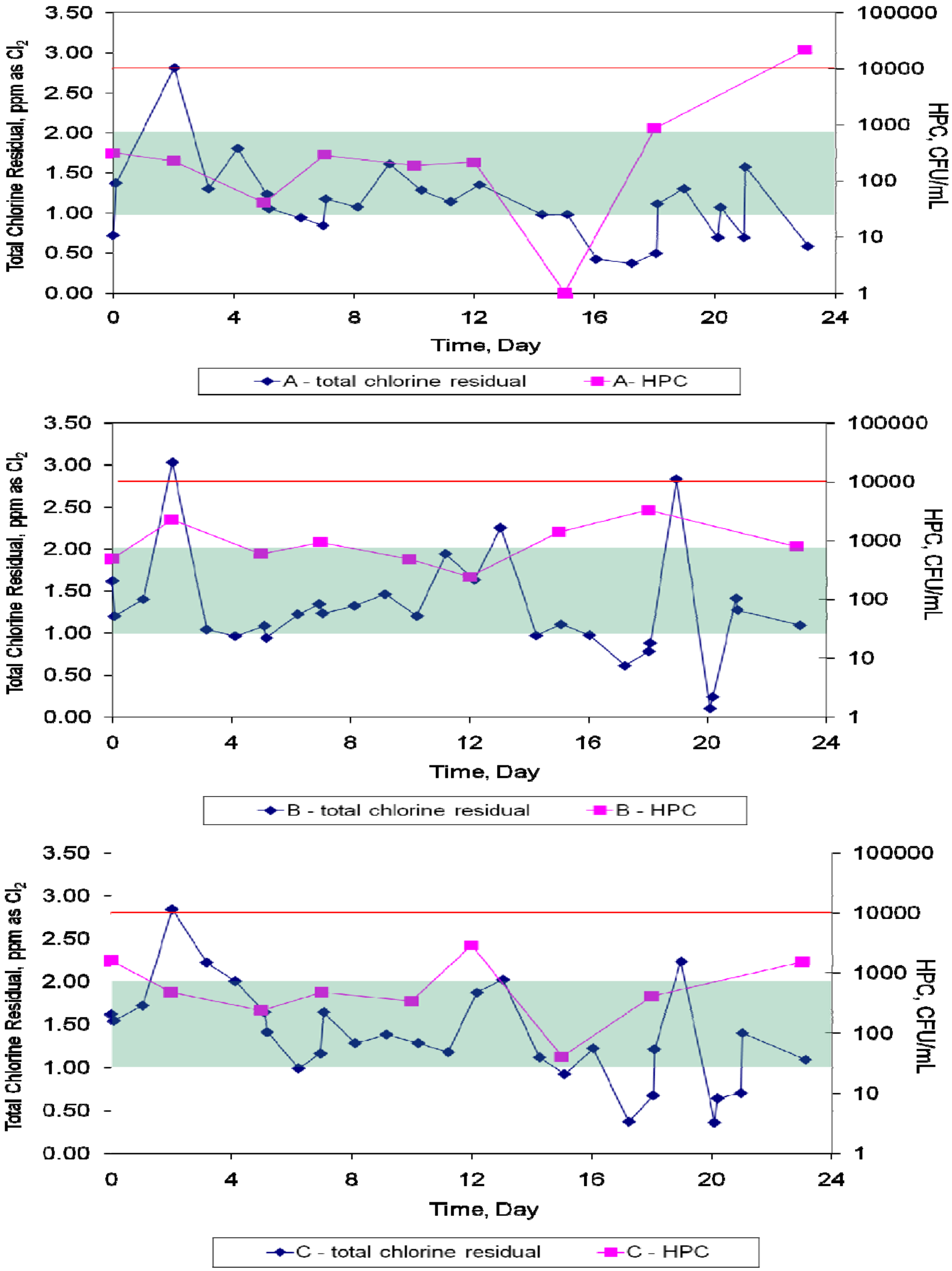

Figure 6.3.7. Total chlorine residual and HPC in a) Tower A, b) Tower B and c) Tower C operated with treated SVAMD. Shaded area indicates the target concentration of 1~2 ppm as Cl_2 and red solid line indicates the general control criteria for HPC of 10^4 CFU/mL (Ludensky, 2005)

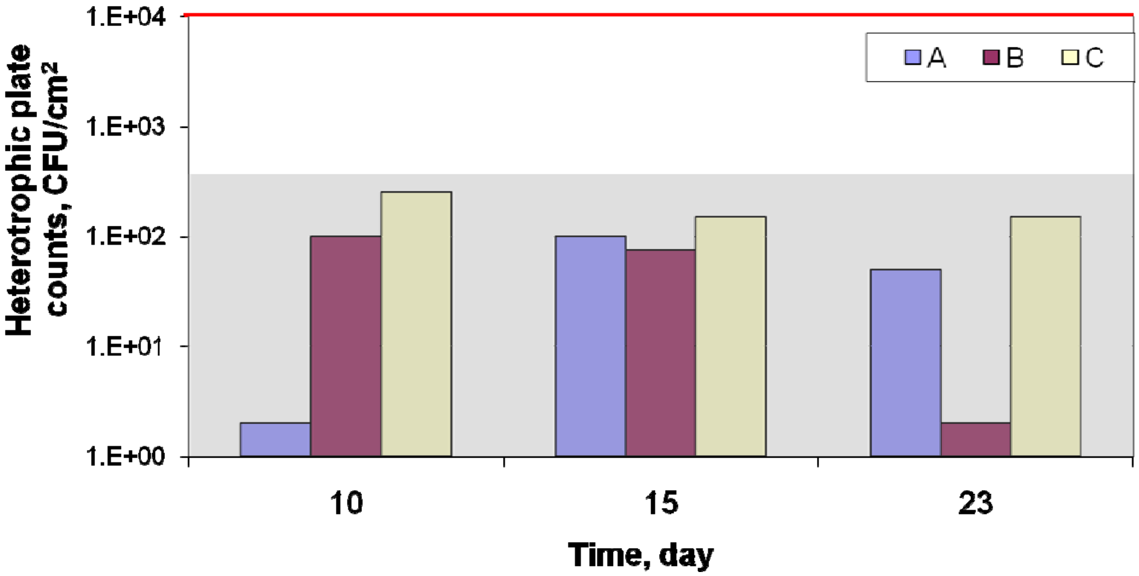

Figure 6.3.8. Sessile HPC vs. time in three towers. Shaded area denotes the detection limit of the method and the solid horizontal line reflects empirical biofouling control criteria of 10^4 CFU/cm^2.

6.3.4 Summary and Conclusions for Reuse of Passively Treated Abandoned Mine Drainage

Microbial activity in raw acid mine drainage selected for this study was rather limited and was decreasing with time (it was consistently below common biofouling control goal of 10^4 CFU/mL) in a batch system. Laboratory-scale studies with chlorine showed that it was effective in suppressing biological activity. Minimal chlorine dosage for effective disinfection was determined to be just 0.5 ppm since the raw water had relatively low bacterial counts. Dosages above 2 ppm were observed to effectively suppress the bioactivity within 3 hours. Batch studies also indicated that the chloramine was more stable in SVAMD and that lower dosage was required to reach the target level of biological activity (4 log of HPC CFU/mL) when compared to chlorination.

Because of the low initial bacteria counts, bioactivity was not much of a problem during the pilot–scale cooling tower testing and could be easily controlled. Planktonic HPC was maintained below the empirical criterion for biofouling control goal (10^4 CFU/mL) even when the total chloramine residual occasionally fell below 0.5 ppm as Cl_2. Results also indicated that biofilm could not successful grow on the stainless steel coupon when using acid mine drainage as cooling tower makeup water at an average monochloramine concentration between 1 and 2 ppm as Cl_2.

In general, it can be concluded that the chloramine concentration of 1~2 ppm as Cl_2 can achieve effective control of both planktonic and sessile heterotrophic bacteria in the system and that the desired control criteria for biofouling (10^4 CFU/mL, CFU/cm^2) can be easily accomplished if AMD water is used as makeup water in cooling towers.

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7.0 Reuse of Ash Transport Water as Alternative Makeup Water for Cooling Systems

Sluicing systems are commonly used at coal-fired electric power plants to remove combustion residues, i.e., fly ash and bottom ash, from the plant. The water is used to transport the ash to sedimentation ponds where the ash is settled. Ash transport water is a promising alternative to freshwater as coal-fired power plant cooling water system makeup water, as it is internally available at many plants. The amount of ash transport water available at a coal-fired power plant generally can satisfy the cooling water makeup needs of the recirculating system in the power plant. Reusing ash transport water, which contains soluble chemical species from leaching of the ash, can avoid its direct discharge to receiving waters.

In this study, the feasibility of controlling corrosion, scaling, and biofouling when using ash transport water in cooling water systems was investigated through laboratory experiments. Bench-scale recirculating systems were employed for testing chemical control schemes for corrosion, scaling, and biofouling in systems using ash transport water after the sedimentation pond. The testing was conducted at temperature, flow velocity conditions as well as water constituent concentrations similar to those in a recirculating cooling water system. The effectiveness of chemical treatment strategies in inhibiting corrosion, scaling, and biomass growth were studied through exposure and monitoring of specially designed coupons in extended duration tests.

7.1 Corrosion Control for Ash Transport Water Used for Cooling

Abstract

Ash transport water is a promising alternative to fresh water as coal-fired power plant cooling water system makeup water, as it is internally available at many plants. Reusing ash transport water, which contains soluble chemical species from ash leaching, can avoid its direct discharge to receiving waters. The purpose of this study was to evaluate the feasibility of using clarified ash transport water with respect to corrosion control through laboratory experiments. Results showed that tetra-potassium pyrophosphate (TKPP) is necessary for mild steel corrosion inhibition and tolyltriazole (TTA) is necessary for copper corrosion inhibition. Aluminum was determined not to be a suitable material for use in cooling systems with ash transport water because of pitting corrosion. Cupronickel is very corrosion resistant and doesn't need any inhibitor for corrosion control.

7.1.1 Introduction

Ash transport water is typically regarded as expendable waste because after sedimentation, the sluicing water effluent from the sedimentation pondsis usually discharged into receiving waters. A variety of soluble chemical species are present in ash transport water as a result of leaching from the fly bottom ashes and in some cases from addition of plant liquid wastes to the sluice water. Fly ash and bottom ash generally contain little organic matter. The chemical constituents of most concern in ash transport water with respect to discharge are inorganic, in particular metals (Suloway et al., 1983; Roy et al., 1984). These are derived from leaching of ash particles, which consist primarily of oxides of silicon, aluminum, and iron, but also contain a number of other metals at lower levels.

The consumptive use of freshwater in thermoelectric power generation cooling water systems can contribute significantly to freshwater shortage problems in some areas of the U.S. (USGAO, 2003; Roy and Summers, 2003). In the U.S., thermoelectric power generation consumed 3.3 BGD of freshwater in 1995, through evaporation (USGS, 1998).

Impaired waters are of increasing interest as alternative sources of makeup water for thermoelectric power plant recirculating cooling water systems. Ash transport water has the potential for use in cooling systems at coal-based power plants. The large amounts of water involved in these processes represent a substantial opportunity for internal water reuse in cooling systems at electric power plants. In most case the ash transport slurries are directed into sedimentation ponds in which settling of the ash particles takes place. There is potential to reuse a portion or all of the ash pond effluent, as has been investigated periodically in the past (e.g., Litherland et al., 1983).

The amount of ash transport water available at a coal-fired power plant generally can satisfy the cooling water need for the recirculating system in the power plant. The mean value of bottom ash pond overflow is 3,881 GPD/MW (Nemerow and Agardy, 1998), which can contribute 27% of the mean value of makeup water needs, in recirculating cooling system, which averages 14,400 GPD/MW (NETL, 2005).

The objective of this study was to investigate the corrosivity of ash transport water to metal alloys commonly used in cooling water systems and study the effectiveness of some commonly used corrosion inhibitors. Specifically, the corrosion of mild steel, aluminum, copper, and cupronickel was studied in bench-scale experiments with trial of various corrosion inhibitor concentrations.

7.1.2 Materials and Methods

7.1.2.1 Ash Pond Water Characterization and Preparation for Laboratory Testing

Ash pond water from the Reliant Energy (REAPW) coal-based thermoelectric power plant at Cheswick, PA, was used for testing in laboratory experiments. Water samples were collected on October 2, 2007, and analyzed for a range of water quality constituents. The water samples were collected with a 1-L polyethylene sampler and then transferred to appropriate polyethylene or glass sample containers provided by the commercial laboratory, TestAmerica (Pittsburgh, PA). Appropriate preservatives were added to the sample bottles prior to the sampling event by TestAmerica. Analyses performed are listed in Table 7.1.1.

Samples of REAPW were also collected for laboratory experiments. The REAPW sample was concentrated in the laboratory by heated evaporation at 35 – 40 °C to reach 4 cycles of concentration (CoC) as determined by 75 % water volume reduction.

Table 7.1.1 Characteristics of the ash pond water from Reliant Energy coal-based thermoelectric power plant, Cheswick, PA (sampled on October 2, 2007).

Analytes	Unit	Result Unfiltered	Reporting limit
Al	µg/L	588	200
Ca	µg/L	43400	5000
Fe	µg/L	344	100
K	µg/L	2560 B	5000
Mg	µg/L	9380	5000
Mn	µg/L	28.1	15
Na	µg/L	21600	5000
SiO_2	µg/L	3290	1070
pH		8.4	--
Acidity	mg/L	ND	5.0
NH_3-N	mg/L	0.068 B,J	0.10
Bicarbonate Alkalinity	mg/L	56.3	5.0
BOD	mg/L	ND	2.0
Cl	mg/L	30.4	1.0
NO_3-N	mg/L	0.28	0.05
Specific Conductance	µmhos/cm	402	1.0
SO_4	mg/L	92.4	1.0
Total P	mg/L	0.033 B	0.1
Total Alkalinity	mg/L	60.4	5.0
TDS	mg/L	271	10.0
TSS	mg/L	20.8	4.0
TOC	mg/L	2.4 J	1.0

Notes: J: Method blank contamination. The associated method blank contains the target analyte at a reportable level
B: Estimated result. Result is less than reporting limit.

7.1.2.2 Metal Alloy Pre-exposure and Post-exposure Treatment

Metal alloys chosen for study were mild steel (UNS G10180), aluminum (UNS A91100), copper (UNS C10100), and cupronickel (UNS C70600). These are commonly used in cooling water systems (Herro and Port, 1993). The metal alloy specimens tested were cylinder-shaped with the diameter of 0.375 inch and length of 0.5 inch from Metal Samples Company (Munford, AL).

Prior to being exposed to REAPW in the bench-scale recirculating system, the metal alloy samples were wet polished with SiC paper to a 600 grit surface finish, dried, weighed to 0.1 mg, degreased with acetone, rinsed in distilled water, and then mounted to the bench-scale recirculating system.

The samples were removed at the end of tests, cleaned by following ASTM G1 (ASTM, 2005a), and then reweighed to 0.1 mg for determining weight loss, *WL,* during exposure.

7.1.2.3 Corrosion and Scaling Inhibitors

Inhibitors selected for testing in this study included tetra-potassium pyrophosphate (TKPP), a corrosion and scaling inhibitor, 2-phosphonobutane-1,2,4-tricarboxylic acid, (PBTC), a scaling inhibitor, and tolyltriazole (TTA), a copper corrosion inhibitor. TKPP, PBTC, and TTA were from The National Colloid Company (Steubenville, OH).

7.1.2.4 Bench-scale Recirculating Water System Configuration

A bench-scale circulating water system described in Section 5.1 was designed and constructed for exposure of metal alloys to conditions of temperature, flow velocity, and water quality similar to those in a recirculating cooling water system. The bench-scale circulating water system consisted of a centrifugal pump, a water bath on a hotplate to control the water's temperature, and a pipe rack made of 0.75 inch PVC to hold metal alloy specimens (Figure 7.1.1). The pipe rack consisted of several tee sections into which alloy specimen holders were mounted. A gravimetric weight loss method was employed to determine average rates.

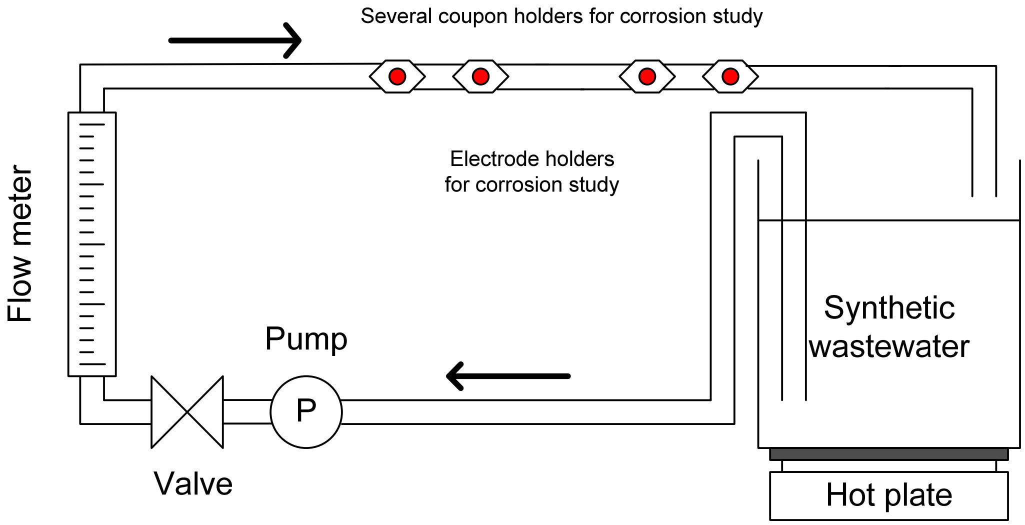

Figure 7.1.1 Schematic of bench-scale recirculating system

7.1.2.5 Corrosion Experimental Matrix for Bench-scale Experiments with REAPW

Corrosion control of metal alloys in contact with CoC 4 REAPW by using chemical additives was examined in this study. TKPP was used as corrosion and scaling inhibitor and PBTC as scaling inhibitor. Three tests were performed:

1) CoC 4 REAPW (7-day exposure)
2) CoC 4 REAPW, TKPP 15 ppm (as PO_4) and PBTC 10 ppm (7-day exposure)
3) CoC 4 REAPW, TKPP 20 ppm (as PO_4) and TTA 2 ppm (3-day exposure)

The effectiveness of TKPP, PBTC, and TTA on corrosion and scaling control were then determined using the approaches described in Section 5.1 of this report. Only corrosion results are shown and discussed in this section. Results for scaling control are reported in Section 7.2.

7.1.3 Results and Discussion

The results in Table 7.1.2 show that mild steel average corrosion rate in CoC 4 REAPW without inhibitors was in the category of "unacceptable". Aluminum had pitting corrosion in CoC 4 REAPW, while copper had "poor" average corrosion rate. Cupronickel had non-detectable weight loss and thus had "excellent" corrosion category in CoC 4 REAPW.

Table 7.1.2 Corrosion rate measurements for various metals contacted with ash pond water from the Reliant Energy coal-based thermoelectric power plant in the bench-scale recirculating system

	Average corrosion rate -- mils per year (MPY) (corrosion category)			
	Mild steel	**Aluminum**	**Copper**	**Cupronickel**
CoC 4 REAPW	10.03 (unacceptable)	3.66, pitting (unacceptable)	0.33 (poor)	0.12 (excellent)
CoC 4 REAPW, TKPP 15 ppm as PO_4 PBTC 10 ppm	3.77 (fair)	1.63, pitting (unacceptable)	0.41 (poor)	ND (excellent)
CoC 4 REAPW TKPP 20 ppm as PO_4 TTA 2 ppm	1.49 (good)	1.61	ND (excellent)	ND (excellent)

Notes: Corrosion rate category is based on corrosion criteria shown in Table 5.1.1
MPY: mils per year
REAPW:Ash pond water from Reliant Energy coal-fired thermoelectric power plant, Cheswick, PA
CoC#: # cycles of concentration
ND: not detectable (the lower detection limit for copper and cupronickel was 0.017 MPY)

With the addition of 15 ppm TKPP (as PO_4) and 10 ppm PBTC in CoC 4 REAPW, mild steel corrosion rate decreased significantly to the category of "fair", indicating the ability of TKPP to inhibit mild steel corrosion in CoC 4 REAPW. The corrosion rate of aluminum also decreased but pitting corrosion was still observed. Copper corrosion rate was still in the category of “poor”, indicating that TKPP is not a strong inhibitor for copper corrosion. Cupronickel corrosion rate was not detectable and in the category of “excellent”.

With the addition of 20 ppm TKPP (as PO_4) and 2 ppm TTA in CoC 4 REAPW, mild steel corrosion rate decreased further to the “good” category. Aluminum had no pitting corrosion. Copper and cupronickel both had non-detectable weight loss, indicating strong effectiveness of TTA as a copper corrosion inhibitor.

7.1.4 Summary and Conclusions for Corrosion Control in Reused Ash Pond Water

When using CoC 4 REAPW as cooling system makeup water, cupronickel was found to be the most corrosion resistant material, even in the absence of corrosion inhibitor. Copper in CoC 4 REAPW requires corrosion inhibitor, such as tolyltriazole (TTA), to inhibit its corrosion. The occurrence of pitting corrosion for aluminum even in the presence of corrosion inhibitor limits its usefulness as a cooling system material. Mild steel will need phosphorous-based corrosion inhibitor, such as TKPP, to inhibit its corrosion.

Overall, for corrosion control of metal alloys in contact with concentrated REAPW, TTA and phosphorous-based corrosion inhibitor (such as TKPP) are recommended for use in cooling tower systems operating using ash pond water as makeup water.

7.2 Scaling Control for Ash Transport Water Used for Cooling

Abstract

Ash sluicing/transport pond effluent in a coal-fired power plant is a promising alternative to fresh water as the cooling system makeup water because it is internally available at many plants. Reusing ash pond water (APW) not only saves fresh water, but helps avoid its direct discharge to receiving waters, which can be potentially contaminated by APW since it contains soluble chemical species from leaching of the sluiced ashes. The purpose of this study was to evaluate the feasibility of using clarified APW with respect to scaling control through modeling calculations and laboratory experiments. Results showed that scaling resulting from the use of the APW was much less severe than from the previously tested two impaired waters (i.e., secondary treated municipal wastewater and passively treated abandoned mine drainage). The addition of PMA (10 ppm) inhibited scale formation, which was mostly comprised of calcium solids when formed. In addition, this study demonstrated that corrosion products from metallic components of cooling towers could potentially lead to much more scaling due to the re-deposition of the solids, especially under the condition where the metallic surface in contract with cooling water is large.

7.2.1 Introduction

Background information regarding the general characteristics and significance of reusing ash pond water (APW) in coal-fired power plants for recirculating cooling towers is provided in Section 7.1. The objective of this study was to investigate the scaling potential of APW under the conditions commonly encountered in recirculating cooling water systems and study the effectiveness of some commonly used scaling inhibitors. Specifically, scale formation of the APW was calculated at different cycles of concentration (CoC) under relevant cooling tower operation conditions using the chemical equilibrium model MINEQL+. The actual APW taken from Reliant Energy Power Plant ash settling pond effluent was tested in a bench-scale water recirculating system to examine its scaling behavior under CoC 1 vs. CoC 4. Synthetic APW was then used to better represent CoC 4 condition. The effectiveness of different antiscaling chemicals were tested using synthetic APW.

7.2.2 Materials and Methods

7.2.2.1 Ash Pond Water Characterization and Preparation for Laboratory Testing

APW from the Reliant Energy coal-based thermoelectric power plant, located at Cheswick, PA, was used for testing in laboratory experiments, as well as for equilibrium chemical modeling. Water samples were collected on October 2, 2007, and analyzed for a range of water quality constituents. The water samples were collected with a 1-L polyethylene sampler and then transferred to appropriate polyethylene or glass sample containers provided by the commercial laboratory, TestAmerica (Pittsburgh, PA). Appropriate preservatives were added to the sample bottles prior to sampling. Analyses performed are summarized in Table 7.1.1.

Parallel to the sampling for chemical analysis, a larger amount of the APW was collected for laboratory experiments. The water was concentrated in the laboratory by heat evaporation at 35-40°C to reach 4 cycles of concentration (CoC 4) as determined by 75% water volume reduction. This concentration level is representative of the CoC used in recirculating cooling tower systems operated with impaired waters.

7.2.2.2 Equilibrium Modeling of APW Scaling Potentials

The chemistry of the APW cooling water at different CoC was modeled using MINEQL+ version 4.5 (Schecher and McAvoy, 1992; 1999) to gain insight into the effects of CoC on scaling. The primary objective for this effort was to estimate the amount and composition of mineral solids that would precipitate and the water chemical composition that would occur under typical cooling tower operation conditions as a function of CoC. The major constituents and their chemical speciation were assessed and the dominant scale-producing reactions were identified.

The following four operational conditions were simulated for the APW water:

1) The aqueous system was open to the atmosphere ($PCO_2 = 10^{-3.5}$ atm) to allow the alkalinity to be in equilibrium with $CO_2(g)$ and solids were allowed to precipitate.

2) The aqueous system was open to the atmosphere ($PCO_2 = 10^{-3.5}$ atm) to allow the alkalinity to be in equilibrium with $CO_2(g)$ and solids were not allowed to precipitate (i.e., water can be super-saturated).

3) The aqueous system was closed to the atmosphere with total alkalinity fixed and solids were allowed to precipitate.

4) The aqueous system was closed to the atmosphere with total alkalinity fixed and solids were not allowed to precipitate.

The four conditions represent the extreme effects of atmospheric CO_2 and solution supersaturation. It is reasonable to expect that the actual conditions for field testing would fall within these boundary conditions.

7.2.2.3 Bench-scale Tests with REAPW

The objective of the bench-scale studies with APW was to test the effectiveness of different scaling inhibition chemicals and their combinations. A total of four commonly used antiscalants were selected based on literature review and consultations with experts. They included polyacrylic acid (PAA), polymaleic acid (PMA), 2-phosphonobutane-1,2,4-tricarboxylic acid (PBTC), and tetrapotassium pyrophosphate $K_4P_2O_7$ (TKPP). PAA and PMA are short-chain polymers, while PBTC and TKPP are phosphorous-based (i.e., phosphates/phosphonates). For each experiment, two antiscalants were added in combination to recirculating water, with PAA and PMA as one combination, and PBTC and TKPP as the other. In addition, the effect of cycles of concentration (CoC) is demonstrated with actual ash pond water.

7.2.3 Results and Discussion

7.2.3.1 Precipitation Modeling with Equilibrium Calculations

MINEQL+ (version 4.5) was used in detailed evaluation of the cooling water chemistries, as noted in Section 4.2. Scaling potentials at different cycles of concentration, as measured by the two most commonly referenced practical saturation indexes and direct predictors of precipitation formation, were analyzed. The pH values with respect to cycles of concentration were also calculated.

Detailed modeling results consist of the following:

- The Langelier Saturation Index (LSI) and Ryznar Stability Index (RSI) under open/closed conditions as a function of CoC (Figure 7.2.1);
- Amount and form of solid precipitates under open/closed conditions as a function of CoC (Figure 7.2.2);
- Changes of aqueous pH with increasing CoC (Figure 7.2.3).

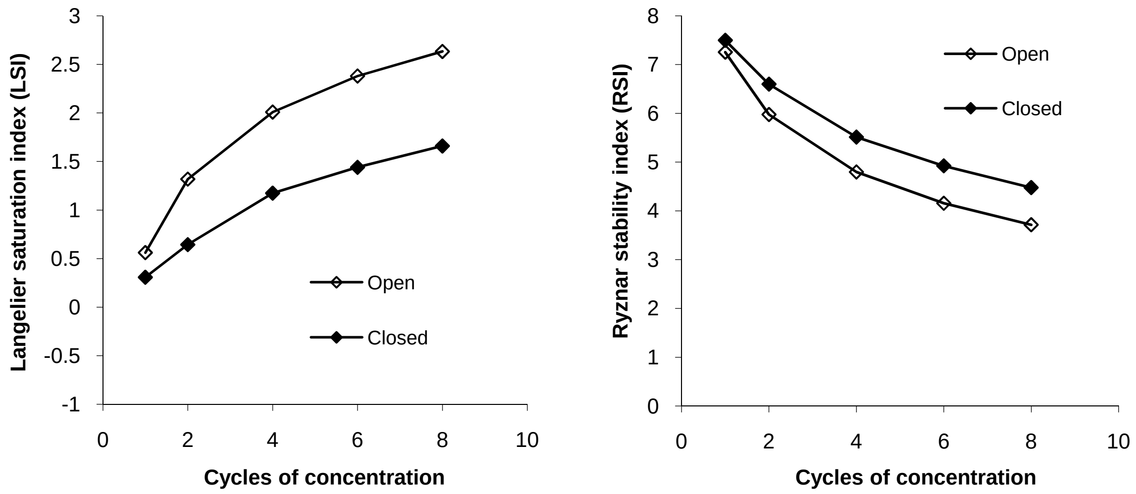

Figure 7.2.1. Modeling results of LSI (left) and RSI (right) for both open and close to air cases.

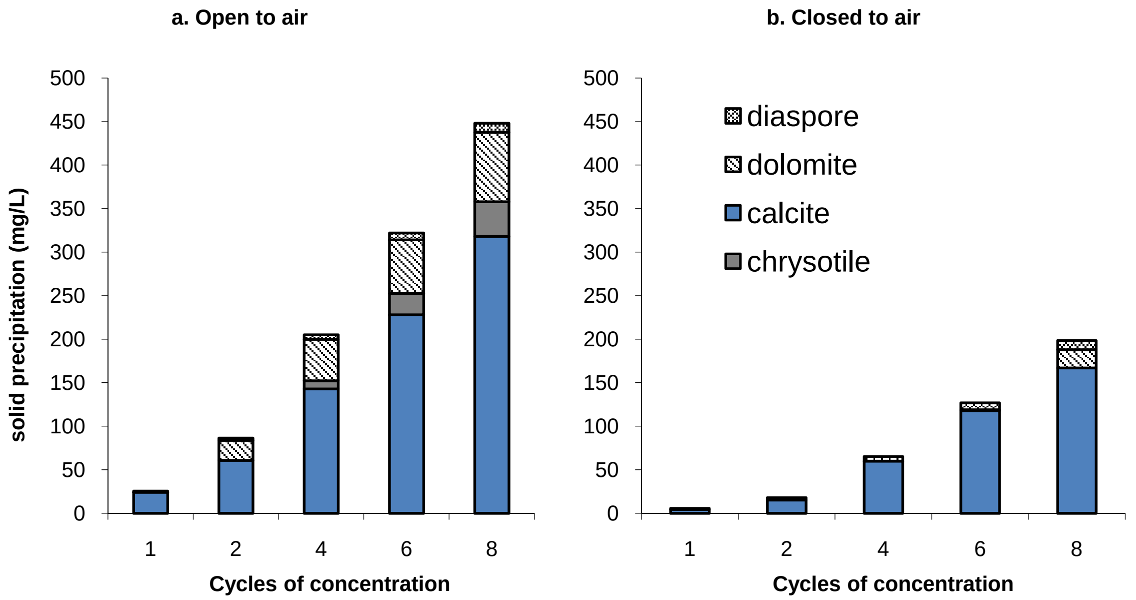

Figure 7.2.2. Predicted solid precipitation from the Reliant Energy ash pond water, calculated by MINEQL+.

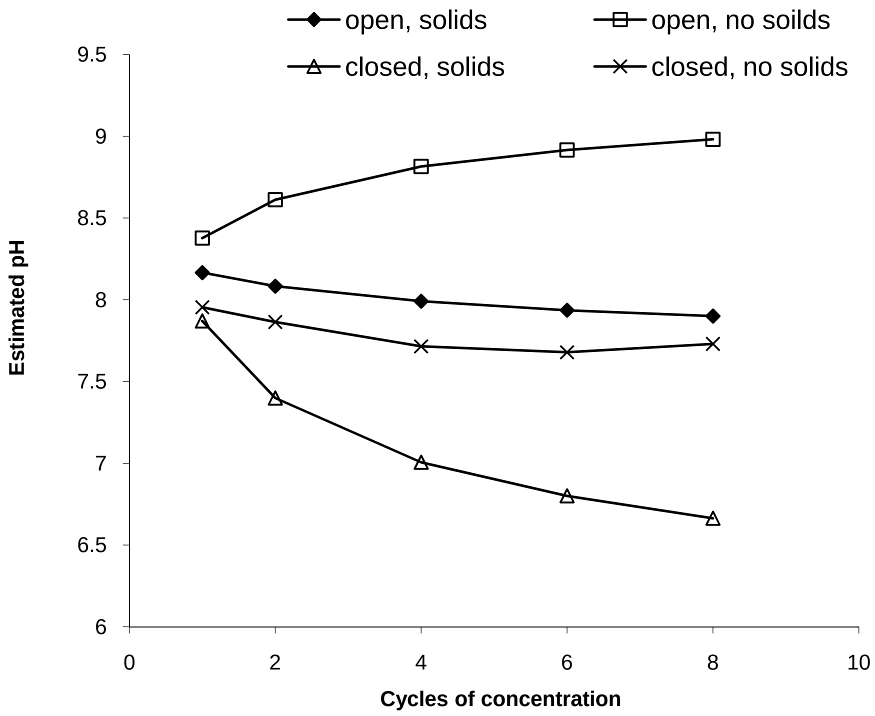

Figure 7.2.3. Predicted solution pH at different CoC under four different operation scenarios (open or closed to air; solid precipitation is allowed or not).

The Langelier Saturation Index (LSI) increased with cycles of concentration, as did the scaling potential. For the Ryznar Stability Index (RSI), it is calculated by a different formula and usual demonstrates an opposite trend compared to the LSI. The RSI values in Figure 7.2.1 decreased with the cycles of concentration (as did the corrosion potential). Under all conditions, RSI values were below 8, indicating mild corrosion potentials.

Calcite and dolomite are the major solid precipitates predicted by MINEQL+ to form in the Reliant Energy ash pond water under typical recirculating cooling tower conditions. From Figure 7.2.2, greater amount of solids precipitated out of solution when operated at an open-to-air condition, because under this condition CO_2 was allowed to be dissolved from the air into solution to provide carbonate species for the formation of calcite and dolomite. Nevertheless, solids formation from the APW water was very minimal compared to other impaired waters studied in this project.

When the water was open to the atmosphere to allow equilibrium with CO_2(g), the pH values were between 8 and 9. When the water was closed to the atmosphere, the water became acidic. Under open condition, the pH tended to increase with increasing CoC when no solids were allowed to form. This was because of the accumulation of alkalinity with CoC. On the other hand, the pH tended to decrease with increasing CoC when solids formation took place because the alkalinity was consumed by the formation of calcite and dolomite.

7.2.3.2 Bench-scale Recirculating System Experiments

Tests with actual APW

Differences in scaling were observed when comparing the amount of mass deposited from the actual ash pond water at CoC 1 vs. CoC 4 (Figure 7.2.4). After the water was recirculated in a bench-scale water recirculating system for 96 h (4 d), more deposits were collected from the CoC 1 water. Such behavior is contrary to expectations because the water at CoC 1 (i.e., raw water) contains initially only one quarter the concentration of mineral solutes. Results depicted in Figure 7.2.5, which compares predicted and measured TDS in a solution that is being concentrated by evaporation, offer an explanation for this discrepancy. During the concentration process involving water evaporation to reach CoC 4, significant amount of solids was precipitated out of solution. As a result, the TDS contained in the CoC-4 water (as determined by a 75% volume reduction) is less than four times of the TDS contained in the raw water. Results from the modeling prediction by MINEQL+ revealed similar behavior in Figure 7.2.5.

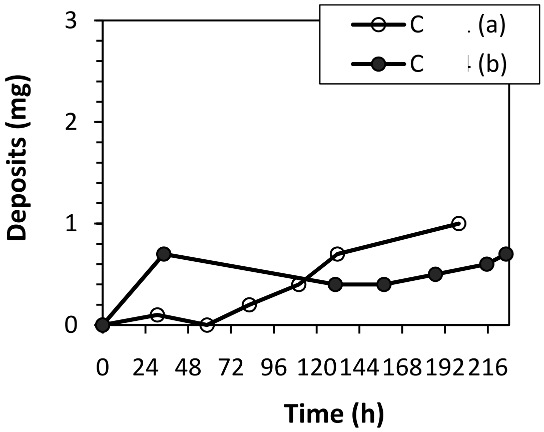

Figure 7.2.4. Scaling behavior of the actual Reliant Energy ash pond effluent in bench-scale tests: effect of cycles of concentration.

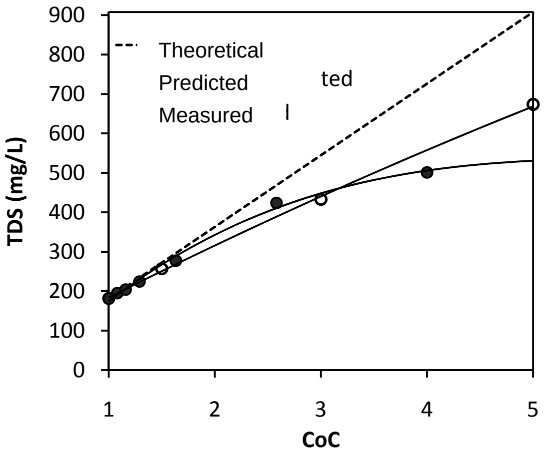

Figure 7.2.5. Changes in solution TDS as a function of CoC for Reliant Energy ash pond water. Theoretically, TDS should increase linearly with increasing CoC (dashed line). However, both MINEQL+ predictions (open circles) and experimental observations (filled circles) deviate from the theoretical curve as CoC increases. TDS measurements were performed with actual water concentrated by water evaporation.

The loss of solids during evaporation did not, however, fully explain the reversal in the scaling of the actual APW at CoC 1 vs. CoC 4. To further explore the causes of this interesting behavior, the chemical composition of the scale collected from the CoC-1 water was analyzed by energy dispersive X-tray spectrometry (EDS). The analysis revealed a significant amount of iron in the scale. Because the actual APW contains very little iron (< 1 mg/L), it is inferred that the iron deposits probably originated from the corrosion of mild steel coupons that were inserted for simultaneous corrosion studies. This is corroborated by the fact that the corrosion rate of the mild steel was measured to be 105 MPY, more than 10 times greater than the corrosion rate observed in the concentrated APW (CoC 4). (Three other corrosion-study coupons made of aluminum, copper, and copper-nickel were also present but their corrosion rates were negligible compared to mild steel. To remove the complications of mild steel corrosion, the rest of experiments were performed with corrosion coupons removed from the water recirculating systems, unless stated otherwise (corrosion studies were performed in a separate recirculating system).

The significance of corrosion complication to scaling depends on the relative amount of iron oxidized and dissolved from the mild steel coupons to water. In the bench-scale recirculating systems, the amount of iron corroded and added to the solution can be significant given the relatively small volume of water used (i.e., 2-3 L of total water for each experiment). On the other hand, corrosion would not affect scaling as much in the field testing where both corrosion and scaling coupons have to be used simultaneously, because the water volume used in the pilot scale cooling towers was much greater (i.e., 75 L). Nevertheless, these findings are meaningful in that the scaling characterization for industrial cooling tower systems should be carefully designed to take into account the contribution of corrosion products to scale formation.

Tests with synthetic APW

Based on the observation with the actual APW at CoC 1 vs. CoC 4, it was decided to use synthetic APW water that simulates the chemical composition of the CoC 4 APW to study the scaling behavior of APW and its control by different antiscalants at CoC 4. The chemical composition of the synthetic APW is listed in Table 7.2.1. The effectiveness of scaling control by PAA, PMA, and PBTC was examined first with individual tests of each agent (Figure 7.2.6). PMA was more effective than PAA, and PBTC was equally effective as PMA. To further test the synergistic effect of polymer and phosphonate at a 2:1 dosage ratio, which is a widely adopted mix ratio by industrial practice for scaling control in cooling systems (Christophersen, 2007), PMA and PBTC dosed at 10 ppm and 5 ppm respectively were added to the synthetic ash pond water (CoC 4). It was observed that the addition of 5 ppm of PBTC to 10 ppm of PMA further improved the antiscaling effectiveness but not to a significant degree (the difference in the scale mass was less than 10%).

Table 7.2.1. Chemical composition of synthetic ash pond water effluent (representing 4 cycles of concentration).

Cation	Concentration		Anion	Concentration	
	mM	mg/L		mM	mg/L
Ca^{2+}	4.41	177	SO_4^{2-}	4.08	392
Mg^{2+}	1.63	39.6	HCO_3^-	5.12	312
Na^+	9.45	217	Cl^-	8.81	312
Fe^{3+}	0.28	15.6			

Note: The Fe concentration used in the synthetic water represents an average iron concentration level among different ash pond waters (e.g., Reliant Energy: 0.34mg/L; TVA plants: 0.03-5.29mg/L). Initial TDS = 449 (cations) + 1016 (anions) = 1465mg/L. Ionic strength = 32.5mM.

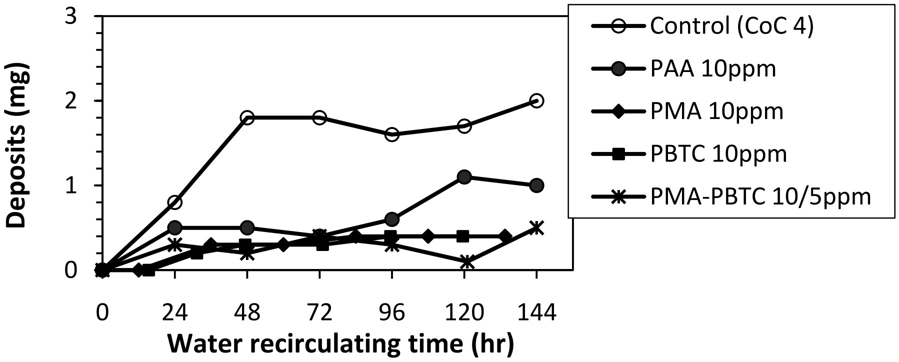

Figure 7.2.6. Scaling behavior of synthetic ash pond effluent in bench-scale tests: effectiveness of different antiscalants at CoC 4.

Changes in the aqueous concentrations of calcium and magnesium were monitored for each experiment with the synthetic ash pond water. The calcium concentration depleted faster and more significantly in the CoC 4 synthetic APW in the absence of any antiscalants than in the presence of PAA (Figure 7.2.7). In both cases, no substantial magnesium reduction was observed. Since Ca and Mg were the major cationic constituents of the APW synthetic water, it was concluded that calcium depletion in solution was the major contributor to the high level of scaling as depicted in Figure 7.2.6 (“control” curve). The connection between scale formation and calcium depletion was demonstrated in an experiment with the addition of PAA: the trend in calcium depletion is virtually mirrored in the observed increase in scale deposits in Figure 7.2.6 (“PAA 10ppm” curve). Ca depletion began to accelerate after 3-4 days of the experimental run, corresponding to the acceleration in scale formation after the same time period. Thereby, both curves pointed to a possible reduction in the effect of scaling inhibition by PAA after 3-4 days.

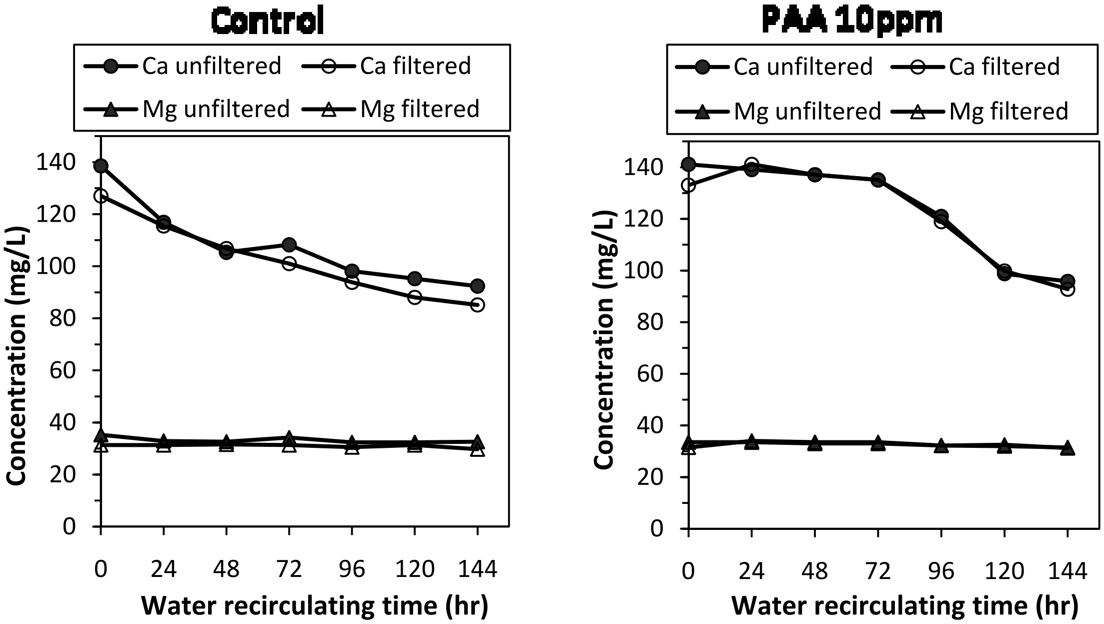

Figure 7.2.7. Changes in the aqueous concentrations of calcium and magnesium in the synthetic ash pond water in bench-scale tests. Left: Calcium depletion in the absence of scaling control chemicals. Right: Calcium depletion with PAA treatment. Solid data points represent unfiltered samples while hollow points represent filtered.

Conversely, PMA and PBTC demonstrated a more sustained scaling inhibition capacity over the entire experimental run that lasted 6 days. Solution Ca remained essentially constant during both experiments (Figure 7.2.8). Figure 7.2.8 also suggests that PBTC was slightly better in retaining Ca in solution than PMA, although such distinction was not confirmed by the mass gain measurement shown in Figure 7.2.6.

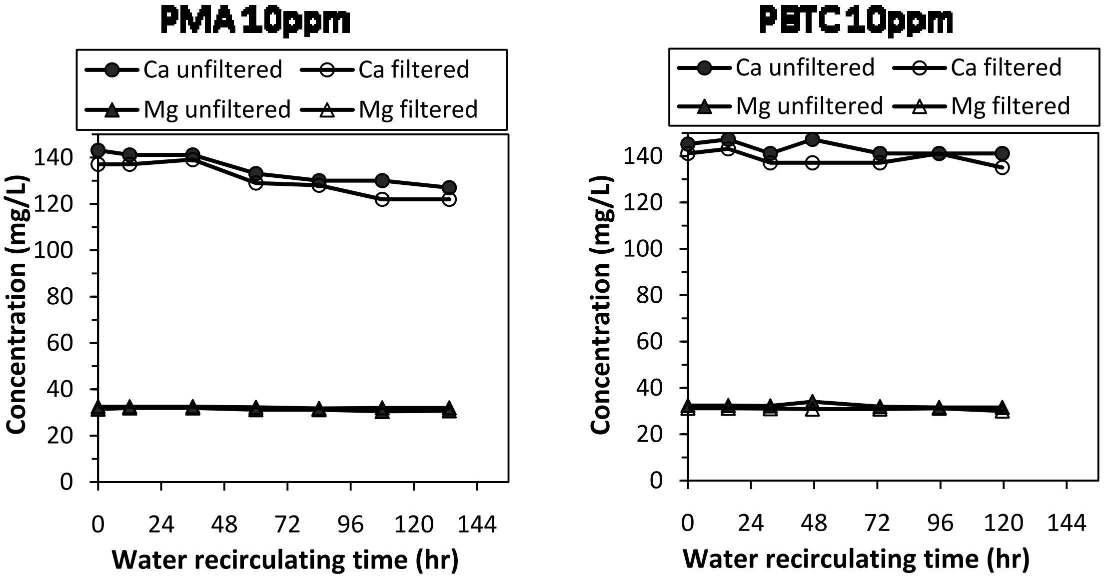

Figure 7.2.8. Aqueous concentrations of calcium and magnesium in the synthetic ash pond water with antiscaling control by PMA (left) or PBTC (right).

The scaling inhibition by the combination of antiscalants PMA and PBTC produced the most effective results. Ca was completely stabilized in solution over the entire experimental run of 6.5 d (Figure 7.2.9). Correspondingly, only limited amount of deposits was detected under these conditions (Figure 7.2.6). Changes in PMA concentration over time was shown in the right pane of Figure 7.2.9. Most of the polymer antiscalant remained in water over the duration of the experiment.

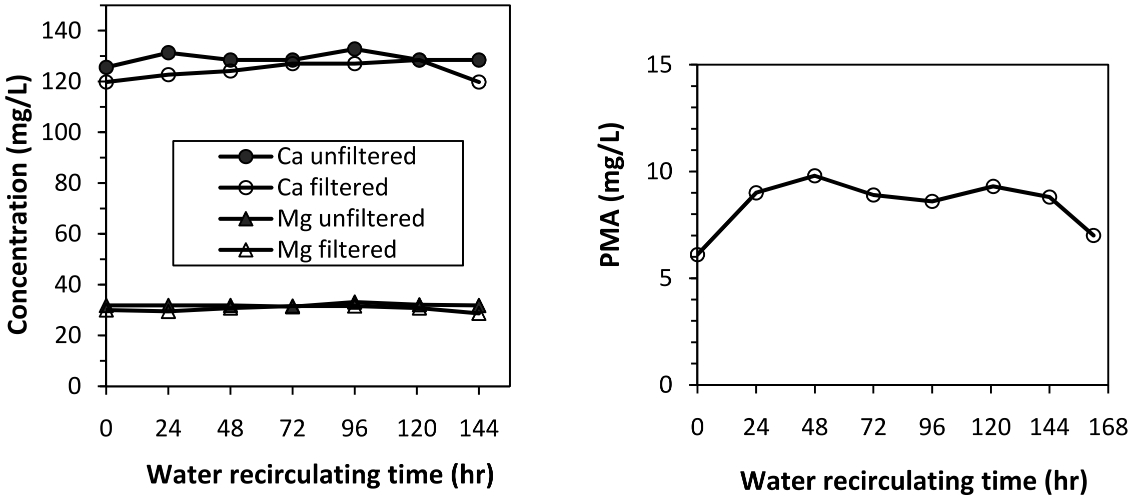

Figure 7.2.9. The stabilization of aqueous concentrations of calcium and magnesium in the synthetic ash pond water under anti-scaling control by PMA-PBTC (left) is in agreement with the relatively constant PMA concentration in the water (right).

7.2.4 Summary and Conclusion for Scaling Control in Reused Ash Pond Water

Use of synthetic ash pond water with well-controlled solution chemistry allowed testing of the effectiveness of scaling control by different antiscalants. The CoC 4 condition was achieved by preparing the solution chemistry according to the chemical composition listed in Table 7.2.1.

Both the MINEQL+ model calculations and the experimental results with the ash pond water showed that scaling in this impaired water is less of a problem than with the other two impaired waters previously studied in this project. The major constituents of the scaling solids were calcium minerals. Addition of 10 ppm of PMA or 10 ppm of PBTC proved to be very effective in further suppressing scaling to minimal levels. They both prevented calcium from forming deposits and their effectiveness lasted longer than that of PAA.

7.3 Biofouling Control for Ash Transport Water Used for Cooling

Abstract

The scarcity of freshwater is becoming more pronounced in many parts of the US and has become a pertinent issue for policy and decision makers. Reuse of ash transport water in coal-fired power plants has been discussed along with the rapid expansion of electricity generation industry since the 1980s. In this study, batch and bench-scale experiments were conducted to investigate disinfectant demand and dosage needed to control biological growth in cooling towers using ash transport water as cooling water makeup. Ash transport waters at one and four cycles of concentration were investigated in both batch tests and bench-scale recirculating system. Because of low amount of organic compounds, chlorine demand in clarified ash transport water was comparatively low compared to secondary treated municipal wastewater. Chlorination by free chlorine may be a feasible option for biocontrol in the cooling systems using ash transport water as makeup. Maintaining free chlorine between 0.2 - 0.5 ppm as Cl_2 can decrease planktonic HPC below the target criterion of 10^4 CFU/mL. Corrosion and scaling inhibitors can form a protective layer and precipitate divalent ions, which further assisted in controlling biofouling in the bench scale recirculating system.

7.3.1 Introduction

Ash transport water is commonly produced in coal fired power plants and is used to convey solids (fly ash and bottom ash) to their final disposal sites. Fly ash is produced by coal combustion and usually contains high amount of Si, mostly in the form as SiO_2 (Openshaw et al., 1992). Bottom ash consists of oxides of silica, alumina, iron oxide, and small amount of magnesium oxides, sulfates and other compounds (Moulton, 1973; TFHRC, 2009). Both fly ash and bottom ash are usually transported to a settling pond together with scrubber waste. Therefore, these inorganic compounds primarily affect the characteristics of the ash transport water.

In order to control biomass growth in cooling systems, disinfectants are either continuously or intermittently added to cooling water. Among all disinfection strategies, chlorination is commonly used to inhibit biomass growth in cooling systems (Frayne, 1999). Free chlorine is defined as chlorine residual concentration of dissolved Cl_2, HOCl and OCl^- in the water. At pH > 8, the predominant form of chlorine is OCl^-. Another form of chlorine in water is combined chlorine, which is defined as combination of chlorine and ammonia or organic amines. Total chlorine residual is the sum of free chlorine and combined chlorine in water (SDWC, 1980)

Once the chlorine demand due to organic matter and ammonia is satisfied, free chlorine residual can efficiently suppress biogrowth in cooling systems. Because the ash transport water typically does not contain significant concentration of organic compounds, adding free residual chlorine is a reasonable approach for biofouling control in cooling systems using ash transport water as cooling system makeup. Because ammonia and organic matter in ash pond water are present at relatively low levels, the chlorine demand of ash transport water should also be low. However, a large amount of chlorine may be required to maintain free residual chlorine in the cooling system because the high air flow and high water temperature will strip chlorine from the water.

7.3.2 Materials and Methods

7.3.2.1 Impaired Water Acquisition and Characterization

Clarified ash transport water was obtained from the Reliant Energy coal-based thermoelectric power plant near Cheswick, PA. Initial samples from this site were collected on October 2, 2007 and stored in 5-gallon carboys at temperatures below 5°C for up to one month. The water samples were analyzed by Test America, PA for the constituents listed in Table 7.1.1. Samples were collected again on March 14, 2008 for additional characterization and to obtain larger water volumes for bench scale testing. The most notable characteristics are low ammonia and phosphate concentrations and negligible BOD.

Raw Reliant Energy ash pond water (REAPW) was considered to be at 1 cycle of concentration (CoC 1). This water was concentrated to CoC 4 by heating at 40°C until the volume of water was reduced to one-fourth of the initial volume.

7.3.2.2 Batch Experiments

The chlorine demand of Reliant Energy ash pond water (REAPW) was determined following Method 2350 B: Chlorine demand/requirement (APHA, 1998)**.** Two hundred milliliters of REAPW was poured into a glass stoppered bottle. Sodium hypochlorite was sequentially applied at dosages of 4 ppm, 3 ppm and 2 ppm as Cl_2 and the total available chlorine and free available chlorine were measured by the DPD colorimetric method (APHA, 1998).

7.3.2.3 Experiments with Bench-Scale Recirculation System

A bench-scale circulating system was developed to simulate the temperature, flow velocity and water quality similar to those in a real recirculating cooling tower system. Figure 7.1.1 shows a schematic diagram of the bench-scale recirculating system. The system includes a centrifugal pump, a water bath on a hotplate to control the water temperature, and a pipe rack made of ¾ inch PVC to hold coupons for biofilm monitoring. Temperature was controlled at about 40°C and flow rate was maintained at 3 gpm. Circular stainless steel coupons were used for biofilm monitoring.

In a typical experiment, REAPW at CoC 4 was recirculated in the system for 3 days and sodium hypochlorite solution was applied at predetermined time intervals. In the first test, a mixture of corrosion and scaling inhibitors [TKPP at 20 ppm (as PO_4) and TTA at 2 ppm] was also added at the beginning of the experiment. In the second test, no corrosion/scaling inhibitors were applied. In both tests, sodium hypochlorite solution was applied at predetermined time intervals with the aim of maintaining free chlorine level close to 0.5 ppm as Cl_2. Planktonic heterotrophic plate counts, total chlorine, and free chlorine were measured throughout each test.

7.3.3 Results and Discussion

7.3.3.1 Chlorine Demand of Ash Pond Water

Figure 7.3.1 show free chlorine and total chlorine residual in REAPW water at CoC 1 for three different initial concentrations. It can be seen from these results that to maintain free chlorine close to 0.5 ppm as Cl_2, the typical target value in cooling systems using fresh water (Frayne, 1999), a chlorine dose of more than 1 ppm as Cl_2 per day will be required to compensate for the loss of free chlorine in the system.

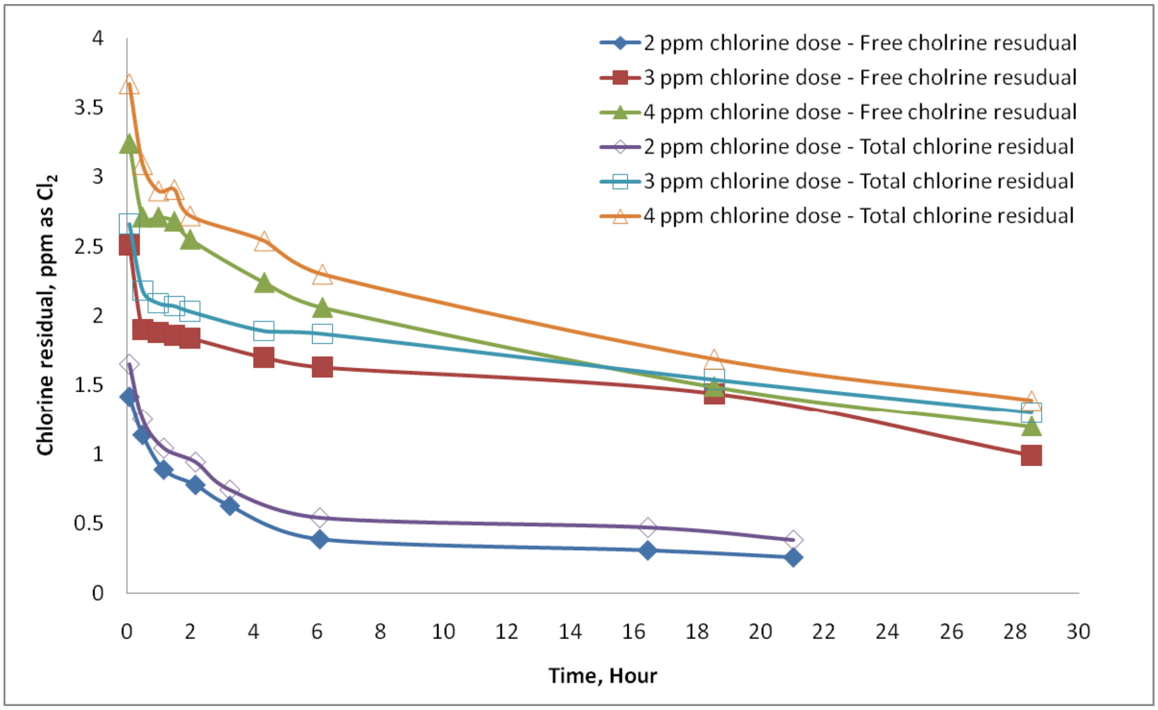

Figure 7.3.1. Free chlorine residual and total chlorine residual in ash pond water

7.3.3.2 Chlorine Demand of Ash Pond Water in a Bench-Scale Recirculating System

Tables 7.3.1 and 7.3.2 show the microbiological results in REAPW at CoC 4 without and with corrosion/scaling inhibitors when free chlorine in the bench scale recirculating system was maintained at 0.5 ppm as Cl_2. It can be seen that HPC did not decrease significantly until free chlorine was available in the system even if the total chlorine level was close to 0.5 ppm as Cl_2. Since there was no detectable ammonia in the ash pond water, this total chlorine level may represent high portion of organic chloramine which has lower disinfection efficiency. However, planktonic bacteria decreased sharply to nondetectable levels when free chlorine exceeded 0.2 ppm as Cl_2. Additional corrosion inhibitor (TTA) was added to the bench scale recirculating system in second test after four hours. Results in Table 7.3.2 revealed that free chlorine concentration did not change significantly after inhibitor addition. Furthermore, the comparison of Tables 7.3.1 and 7.3.2 suggests that the presence of corrosion/scaling inhibitors does not have any significant impact on the disinfection efficiency of free chlorine in the recirculating system.

Table 7.3.1. Microbiological results for bench-scale experiments with free chlorine at 0.2-0.5 ppm without corrosion/scaling inhibitors in REAPW at CoC 4.

Chlorine addition	Time (h)	Free Chlorine (ppm as Cl_2)	Total Chlorine (ppm as Cl_2)	HPC (CFU/mL)
	0	-	-	1.5E+05
add 1 ppm Cl_2	0.08	ND	0.31	8.4E+03
add 0.5 ppm Cl_2	0.20	ND	0.46	1.2E+03
add 0.5 ppm Cl_2	0.27	ND	0.51	-
add 0.5 ppm Cl_2	0.37	0.23	0.55	ND
add 0.5 ppm Cl_2	0.50	0.42	0.56	ND
add 0.5 ppm Cl_2	1.00	0.25 (B) / 0.45 (A)	0.41 (B) / 0.59 (A)	ND (B) / ND (A)
add 0.5 ppm Cl_2	1.50	0.50 (A)	0.58 (A)	-
add 0.5 ppm Cl_2	2.00	0.51 (A)	0.64 (A)	-
add 0.5 ppm Cl_2	2.50	0.31 (B) / 0.53 (A)	0.41 (B) / 0.61 (A)	-
add 0.5 ppm Cl_2	3.00	0.23 (B) / 0.53 (A)	0.39 (B) / 0.61 (A)	ND (B) / ND (A)

Note: "HPC" = Heterotrophic Plate Count; "ND" = non-detectable (detection limit for chlorine is 0.01 ppm as Cl_2 and for HPC is 300 CFU /mL; "B" = Before the Cl_2 addition; "A" = After the Cl_2 addition; "-" = Not measured

Table 7.3.2. Microbiological results for bench-scale experiments with free chlorine between 0.2 - 0.5 ppm with corrosion/scaling inhibitors in REAPW at CoC 4.

Chlorine addition	Time (h)	Free Chlorine (ppm as Cl_2)	Total Chlorine (ppm as Cl_2)	HPC (CFU/mL)
	0.00	-	-	2.9E+04
add 0.33 ppm Cl_2	0.08	ND	0.26	2.5E+04
add 0.66 ppm Cl_2	0.33	0.26	0.35	ND
add 0.5 ppm Cl_2	1.00	ND (B)/ 0.11 (A)	0.34 (B) / 1.47 (A)	ND (A)
add 1 ppm Cl_2	3.00	ND (B)/0.34 (A)	0.71 (B)/ 1.19 (A)	1.1E+03 (B)/ND (A)
	3.50	0.26	0.46	-
add 1 ppm Cl_2	3.67	0.74	1.05	-
add 1 ppm Cl_2	4.17	0.68		-
add 2 ppm TTA	4.25	0.62	0.88	-
	4.92	0.28	0.85	ND

Note: "HPC" = Heterotrophic Plate Count; "ND" = non-detectable (detection limit for chlorine is 0.01 ppm as Cl_2 and for HPC is 300 CFU /mL; "B" = Before the Cl_2 addition; "A" = After the Cl_2 addition; "-" = Not measured

7.3.3.3 Biofouling Potential of Ash Pond Water in Bench-Scale Recirculating System

The sessile bacteria count was measured in the bench-scale recirculating system using REAPW without and with corrosion and scaling inhibitors. Figure 7.3.2 and 7.3.3 show that the number of sessile bacterial colonies remained below the biofouling control criteria of 10^4 CFU/cm^2 after 7 days operation without corrosion, scaling inhibitors and biocide. However, the number of sessile bacteria colonies was restrained to lower than 10^3 CFU/cm^2 with corrosion and scaling inhibitors. Studies have revealed that formation of biofilm requires substratum and divalent ions to facilitate the attachment onto the metal surface (Bradshaw et al., 1997 and Lapping-Scott et al., 2003). Addition of corrosion and scaling inhibitors can form a protective layer on metal surface and precipitate divalent ions, such as calcium, magnesium, which have adverse impact on the ability of microorganisms to form a biofilm. Therefore, it can be concluded that the presences of corrosion and scaling inhibitors did benefit the biofouling control even if there was no biocide addition.

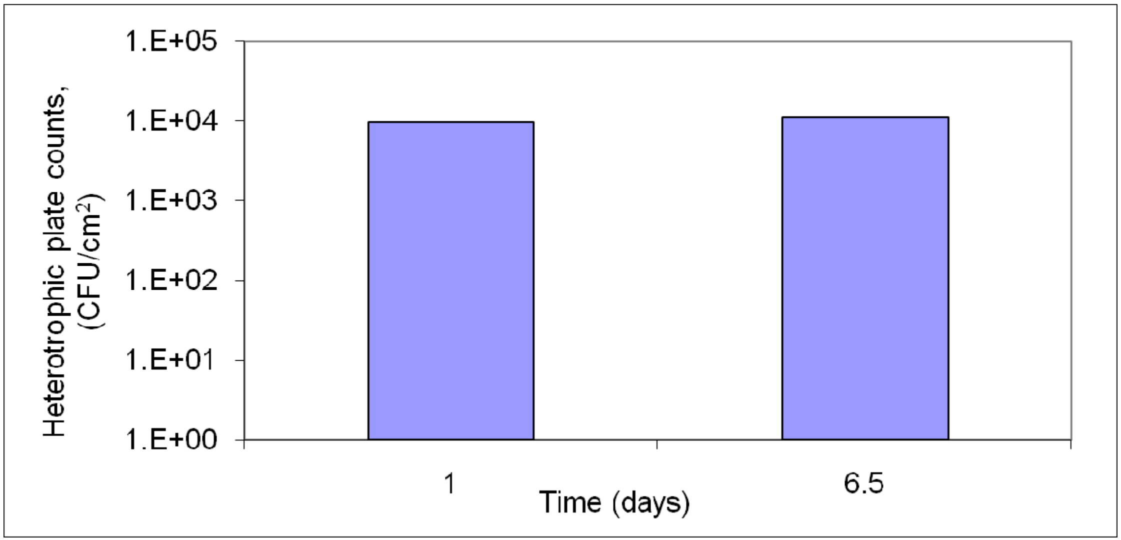

Figure 7.3.2. HPC of sessile bacteria from stainless steel coupons in bench scale recirculating system without corrosion and scaling inhibitors.

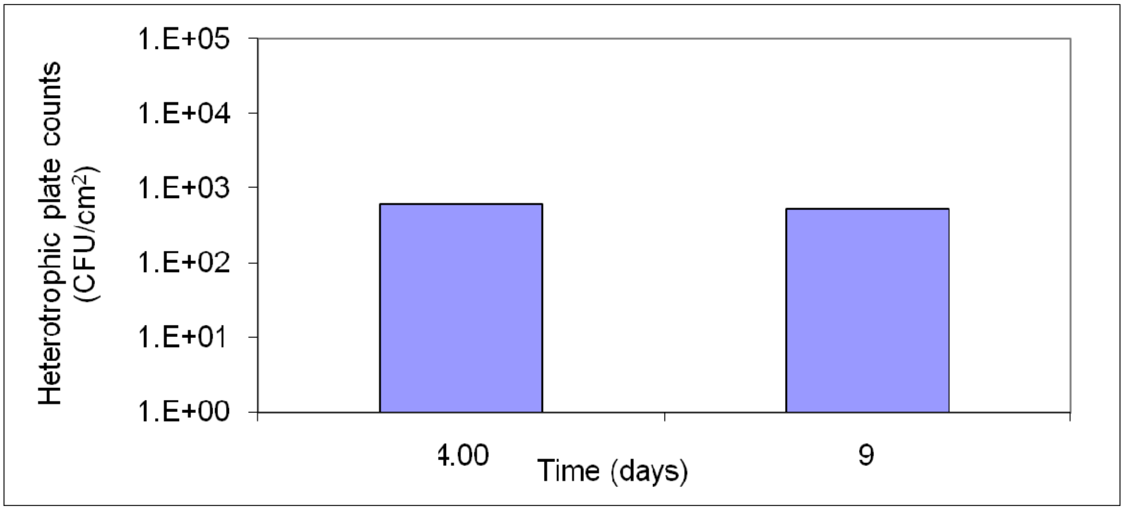

Figure 7.3.3. HPC of sessile bacteria from stainless steel coupons in bench scale recirculating system with corrosion and scaling inhibitors.

7.3.4 Summary and Conclusions for Biofouling Control in Reused Ash Pond Water

Batch and bench-scale recirculating system results showed that chlorine can be an effective oxidizing biocide to control biological activity in clarified ash transport water. Maintaining free chlorine residual close to 0.5 ppm as Cl_2 brought HPC to nondetectable levels in REAPW at both CoC 1 and CoC 4. Such effectiveness is partly due to the fact that this water has low organic content. Addition of TKPP and TTA as corrosion and scaling inhibitors did not affect free chlorine disinfection efficiency in any measurable way. In fact, the presence of corrosion and scaling inhibitors restrained the bioactivity in ash pond water.

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8.0 Blowdown Management for Use of Impaired Waters in Cooling Systems

Cooling tower operation includes periodic discharge of concentrated recirculating water in order to maintain desired cycles of concentration and control the buildup of solids in the system resulting from continuous influx of solids with makeup water and evaporative losses in the system (Figure 8.1.1). This periodic discharge of recirculating water is called blowdown and it contains elevated levels of solids as well as chemicals that are typically added to the system to control corrosion, scaling and biofouling. Due to fairly low water quality, blowdown is typically subjected to some level of treatment in order to meet discharge requirements that are governed by the final disposal options. The primary objective of blowdown management is to treat blowdown to attain quality that is equal to or better than the makeup water so that it can be reused as makeup water. Alternatively, blowdown may be subjected to different treatment processes to meet discharge requirements or to minimize its volume for easier disposal.

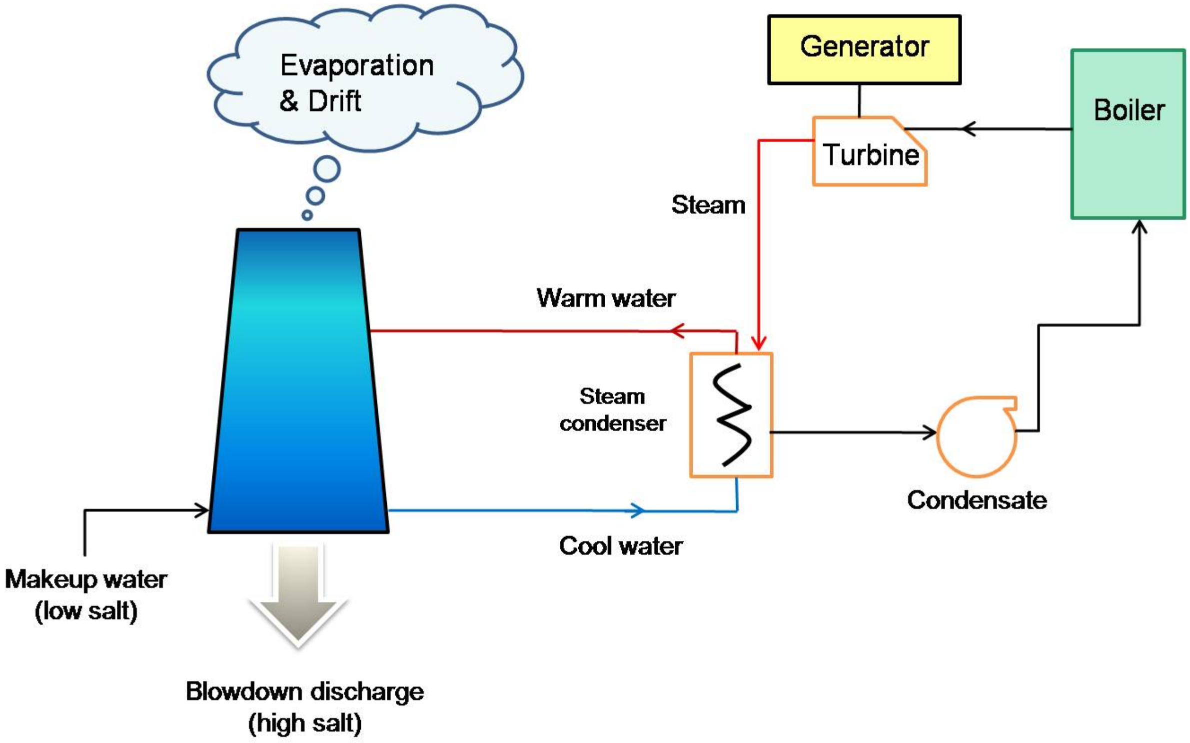


Figure 8.1.1. Schematic of a recirculating cooling water system in a coal-fired power plant.

8.1 Blowdown Management Options

Management options available for cooling tower blowdown typically depend on its water quality, local discharge regulations and capabilities of treatment processes under consideration. Typical options for power plant blowdown management include:

- Discharge to surface waters. This is the main option for once-through cooling systems that is not feasible for recirculating cooling systems because of the blowdown quality.
- Discharge to wastewater treatment plants (WWTPs): This is probably the most cost effective management alternative but may not be feasible for many plants since the WWTP may not accept the blowdown without any pre-treatment due to extremely high solids and presence of other chemicals in the blowdown that were added to control corrosion, scaling and biofouling.
- Zero liquid discharge (ZLD): This alternative involves extensive treatment of blowdown to facilitate its reuse combined with some form of volume reduction to minimize or eliminate the need for liquid discharge. As seen in Table 8.1.1, most power plants using wastewater for cooling would choose this option where the concentrated solids are the only waste leaving the plant.

Table 8.1.1. Treatment technologies and types of discharge of blowdown form power plants using reclaimed waters.

Plant Name	State	Type of discharge	Treatment technologies
Magnolia	CA	ZLD	Lime-soda softening, media filtration, RO, evaporator, evaporation pond
Emery	IA	WWTP	
Panda Brandywine	MD	WWTP	
Jones Station	TX	ZLD, irrigation	Evaporation pond
San Juan	NM	ZLD	Evaporator, evaporation pond, RO
Linden	NJ	WWTP	
Nixon	CO	ZLD	RO, evaporator
MVPP	CA	WWTP, recycle	RO
Palo Verde	AZ	ZLD	Evaporation pond
Walnut Creek Energy Park	CA	WWTP	

Notes: ZLD: zero liquid discharge.
WWTP: discharge to wastewater treatment plants or sanitary sewer system.

8.1.1 Direct Discharge to Surface Waters

Federal, state and local regulations govern the discharge requirements for cooling system blowdown. If allowed, direct discharge of blowdown to surface water or ground water would be a simple and economical choice. However, the assimilative capacity of receiving water to handle the blowdown is limited and the quality of blowdown has to meet criteria that address the regulatory requirements for public health and environmental protection. Considering the cooling tower blowdown quality, discharge to surface water is only feasible for once-through cooling systems.

At federal level, Clean Water Act (CWA) Section 402 established the National Pollutant Discharge Elimination System (NPDES), which requires that all point-source discharges of pollutant to surface waters must be authorized by an NPDES permit. General NPDES permits can be water quality based or technology based. The water quality limitations, which are mainly concerned with the concentrations of toxic chemicals, depend on the quality of the receiving stream and its assimilative capacity. For each point source with NPDES permit, its water quality is calculated, monitored, and regulated based on the surface water quality limitation. Based on different technologies implemented in cooling tower design and operation, the concentrations of available chlorine, chromium, and zinc are likely to be the confining factors. Otherwise, the effluent guidelines title 40, part 423 of Code of Federal Regulations (40 CFR 423) specifying a

30-30 rule for both TSS and BOD (30 mg/L each) with a maximum concentration of 100 mg/L for TSS and are applicable to cooling tower blowdown as a categorical waste. However, site specific evaluation is usually needed for a given point discharge.

The state regulations or guidelines often include restrictions that limit the level of bacteria in blowdown (i.e., fecal or total coliforms). Furthermore, certain chemical constituents may also be a concern when present in excessive quantities. For example, in April 2009, Pennsylvania DEP released a “Permitting Strategy for High Total Dissolved Solids (TDS) Wastewater Discharges” which specifies 500 mg/L (max 750 mg/L) for TDS and 250 milligrams per liter for chlorides and sulfates, if the discharge is located in the Monongahela River watershed.

In summary, each cooling tower is subjected to different local regulations based on the blowdown characteristics and intended discharge alternative and there is no unifying standard for cooling tower blowdown discharge, especially when impaired waters are used as makeup water.

8.1.2 Discharge to Wastewater Treatment Plants

Blowdown discharge to a local wastewater treatment plant (WWTP) may be an attractive and economical option if accepted by the WWTP. The acceptance may be contingent on chemicals present in the blowdown, especially for the power plants that do not include tertiary treatment, because of the potential to compromise its own NPDES permit. Blowdown discharge to a WWTP reduces the burden on power plants but increases the demand on local WWTPs. The size and treatment options are the two key factors that determine whether a WWTP can accept the cooling tower blowdown from a thermoelectric power plant.

Table 8.1.2 provides chemical composition of blowdown samples that were collected from pilot-scale cooling towers operated with two different impaired waters: treated acid mine drainage (AMD) and secondary municipal wastewater (MWW). The data in Table 8.1.2 indicate that high TDS in blowdown from towers operated with AMD and those operated with MWW as well as high sulfate concentration in the towers operated with AMD are the main characteristics of concern.

Usual secondary treatment in WWTPs (Figure 8.1.2) includes biological treatment step in the aeration tank, which is the key step in treating organic compounds in municipal wastewaters. If the TDS in the feed water is too high, it will adversely impact microbial activity in the aeration tank and reduce the overall treatment efficiency of the WWTP. Therefore, every

WWTP has pre-treatment requirements for each industrial contributor and will only accept the blowdown from a thermoelectric power plant if it will not compromise its treatment efficiency.

Table 8.1.2. Chemical composition of the blowdown waters from pilot-scale cooling towers (all units are in mg/L unless specified otherwise).

Constituent	AMD	MWW
Ca	800	140
Mg	238	50
Na	446	700
K	29	60
Al	ND	0.2
Cu	ND	0.2
Fe	ND	0.5
Mn	0.2	0.4
Zn	ND	0.2
Cl	216	1030
SO_4	2930	300
SiO_2	59	25
NO_3-N	1.1	16
NH_3-N	0.6	2.2
PO_4	0.6	15
Total Alk. (as $CaCO_3$)	407	301
HCO_3 Alk. (as $CaCO_3$)	276	189
BOD	ND	72
TOC	13.8	120
TDS	5160	2580
TSS	11.7	95.7
Turbidity (NTU)	12	55
Conductance (mS/cm)	6.3	4.8
pH	8.9	8.5

Notes: ND: not detected.
Both blowdown waters were collected from pilot-scale cooling towers, whose water treatment recipe for corrosion, scaling, and biofouling control is available in previous sections of this reports.

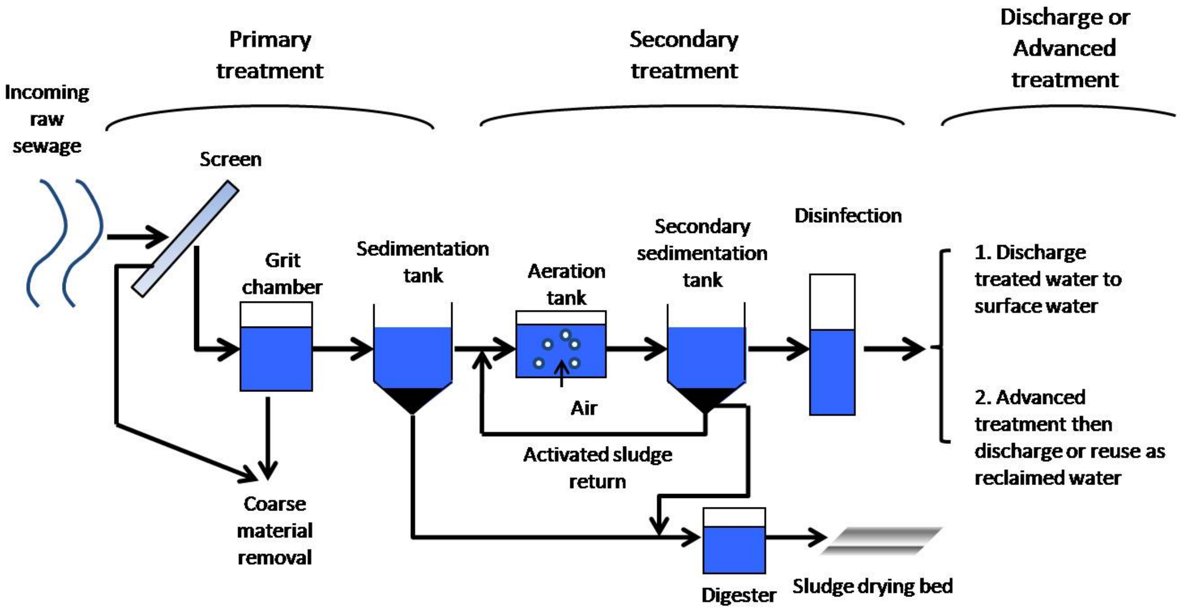


Figure 8.1.2. Typical wastewater treatment processes in WWTPs.

Panda Brandywine power plant (PBPP), which is operated by Panda Global Services, is an example of a power plant that uses municipal wastewater as makeup water and discharges its blowdown back to the wastewater treatment plant. PBPP is located in Brandywine, Prince George's County, Maryland, about 15 miles southeast of Washington, DC. PBPP began its operating in October 1996 with a capacity of 230 MW (Veil, 2007). It is a natural gas-fired combined-cycle plant with two 84 MW combustion turbines, two heat recovery steam generators and one 80 MW Steam turbine. The plant uses about 1.5 MGD of tertiary-treated water from the Washington Suburban Sanitary Commission (WSSC) Mattawoman Wastewater Treatment Plant which has a design capacity of 15 MGD. The Reclaimed municipal wastewater, which travels through an 18-mile pipeline to the PBPP (in Figure 8.1.3), has been used at the Panda plant since 1997 and comprises more than 95% of the total cooling water. Additional makeup water comes from a local groundwater source.

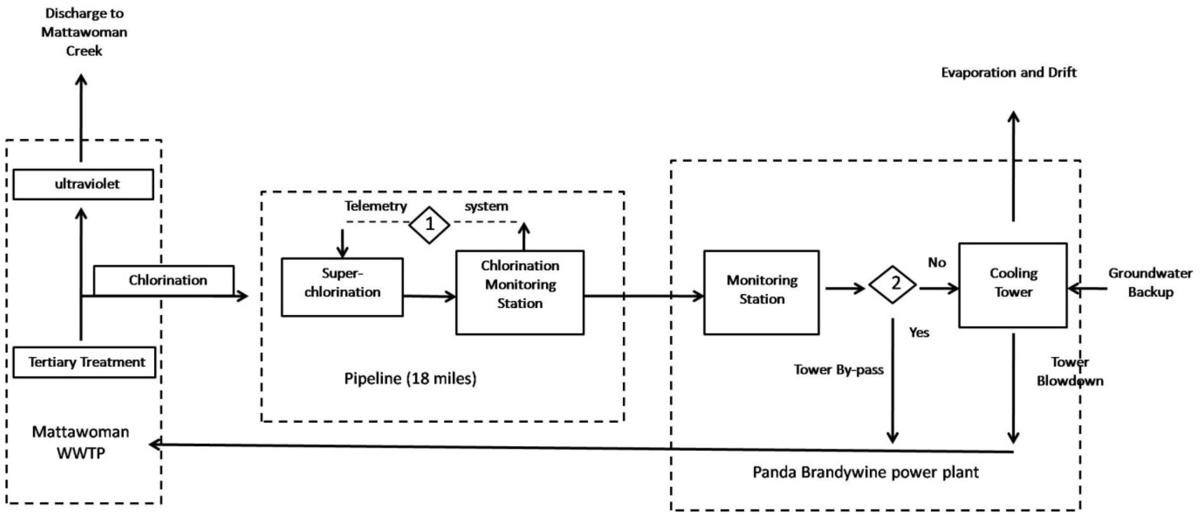


Figure 8.1.3. Panda Brandywine power plant systems.

Until recently, Mattawoman WWTP chlorinated the wastewater for disinfection, then dechlorinated prior to discharge through its NPDES outfall. However, Mattawoman switched to ultraviolet as its main method of disinfection. The plant still chlorinates the side stream of water that enters the reclaimed water pipeline. Prior to the switch to UV disinfection, the water sent to PBPP was withdrawn prior to dechlorination, so that chlorine residual could be maintained in the pipeline. When the reclaimed water reaches PBPP, it is chlorinated again using liquid sodium hypochlorite before it is used in the cooling systems. Panda Brandywine also adds other chemicals (e.g., corrosion inhibitors) for process control that would be added regardless of the source of cooling water.

Recirculating cooling water is removed as blowdown after 7 cycles of concentration and piped back to the Mattowoman treatment plant along with other sewage originating at the plant. The average blowdown flowrate is 10% on a continuous basis.

8.1.3 Zero Liquid Discharge

Given the option, most power plants using reclaimed water for their recirculating cooling systems would choose zero liquid discharge (ZLD) as the main blowdown management option. The main reasons are high solids concentration and presence of specific chemicals added to control corrosion, scaling and biofouling, which are usually not allowed to be discharged directly. Zero liquid discharge means that blowdown is treated and used internally in power plant. Internal use alternatives include cooling tower makeup or other systems, such as flue gas desulfurization or ash sluice, which need lower quality water. Compared to other discharge options, ZLD is preferred as it helps to decrease environmental impacts of power generation. ZLD typically includes one or more of the following advanced treatment technologies: (1) Lime-soda ash softening; (2) Reverse osmosis (RO); (3) Electrodialysis (ED); and (4) Evaporation. Lime-soda ash softening will be discussed in the subsequent sections and the other three technologies included in typical ZLD treatment are described below.

8.1.3.1 Reverse Osmosis

Osmosis is defined as the spontaneous passage of a liquid through a semi-permeable membrane from a dilute to a more concentrated solution (Leonard & Richard, 1986). By applying pressure to the concentrated stream, the direction of flow can be reversed. In the reverse osmosis (RO) membrane treatment process, water is forced through a semi-permeable membrane that allows the passage of water molecules but prevents the passage of most dissolved solids. As a result, the permeate stream contains purified water while the concentrated waste brine is retained on the feed side.

In RO process, pressures of 350~600 psi are commonly used to achieve the desired separation. Among many inorganic and synthetic organic materials that possess the can retain dissolved solids, cellulose acetate and polyamide are the most common membrane materials employed (Zeien and York, 1980). There are two types of commercial RO membrane configurations: hollow fiber and spiral wound. Hollow fiber membranes are not normally used in wastewater applications due to greater susceptibility to fouling. Spiral wound configuration is generally used for both industrial and utility wastewater applications. Large-scale industrial reverse osmosis systems usually consist of a large number of membrane modules, each of which contains several spiral wound elements. A typical RO module is illustrated in Figure 8.1.4, while Figure 8.1.5 depicts a typical reverse osmosis system consisting of several modules. In each spiral wound element, two membrane separated by a support are sealed together and attached to a perforated tube, which receives the permeate. A feed-side spacer is placed between the membranes and the two are rolled together around the tube. Brine flows across the membrane surface, while the permeate flows between the sealed membranes toward the perforated tube. As shown in Figure 8.1.4, a series of coupled elements are installed in an outer pressure vessel, with provision made for feed entry and for the removal of permeate and concentrate steams (Holiday, 1982).

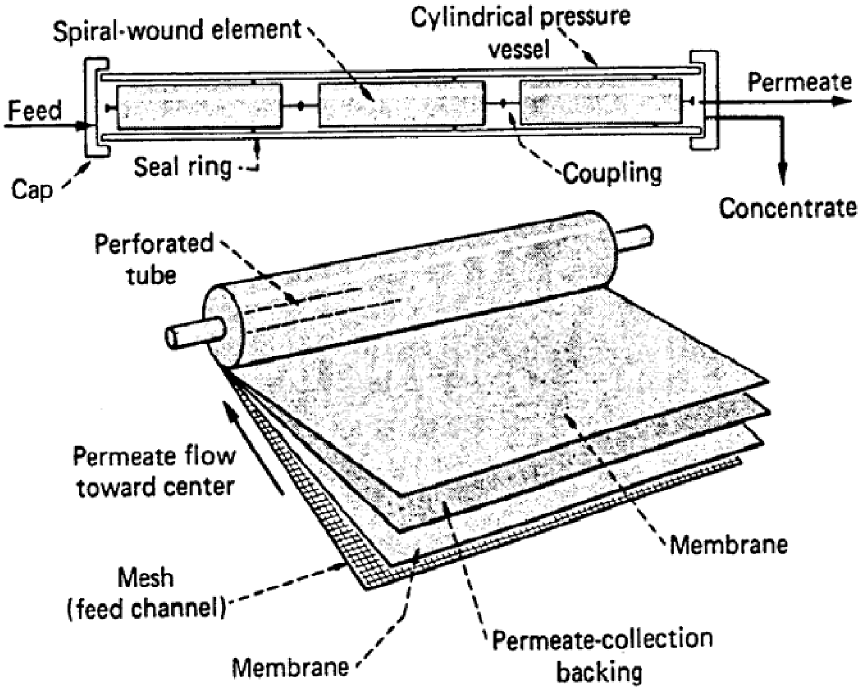


Figure 8.1.4. Typical reverse osmosis module containing three spiral-wound elements. (Holiday, 1982)

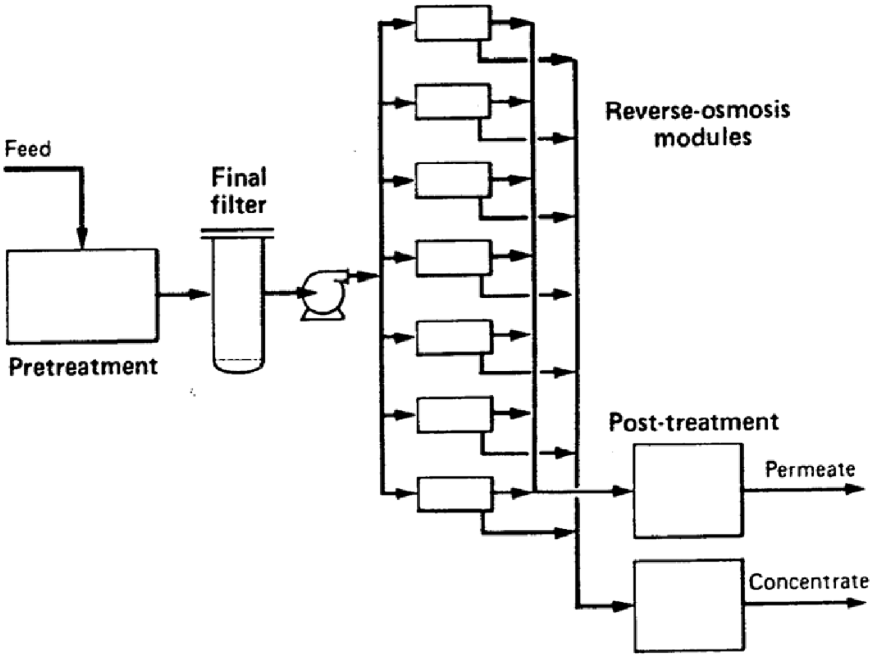


Figure 8.1.5. Typical reverse osmosis system containing several modules. (Holiday, 1982)

In order to reduce the hardness, metals and suspended solids in the feed water to prevent scaling and fouling of the membranes, extensive wastewater pretreatment is usually required ahead of RO membranes, especially when the water feed quality is not very good. The pretreatment systems usually include processes like chemical softening, media filtration and ion exchange. While the principal use of RO is to separate inorganic salts and minerals from water, the membrane can also be effective in removing organic pollutants.

During the past few decades, reverse osmosis systems have gained widespread applications in a variety of industrial utilities, such as desalination of salt and brackish water, treatment of municipal wastewater effluent and certain types of industrial wastewater treatment. Table 8.1.1 lists three power plants which employ RO unit to treat cooling tower blowdown and achieve zero liquid discharge. The use of RO system in San Juan Generating Station will be described in detail at the end of this section.

8.1.3.2 Electrodialysis

Similar to reverse osmosis systems, eletrodialysis (ED) also uses semi-permeable membranes to separate a liquid solution into purified product and concentrated waste streams. However, in the case of ED, a direct current is used to drive ionic species through the membranes in contrast to the hydraulic pressure that is used in reverse osmosis systems. The ED process usually utilizes separate anion and cation ion-exchange membranes; these membranes are very similar in composition to ion-exchange resins used in softening and demineralization. A schematic illustration of a typical ED system is shown in Figure 8.1.6, where the anion and cation membranes are labeled “A” and “C”. The anion and cation membranes are placed in an alternating stacked array and the electrodes are located at the two ends of the stack (Holiday, 1982).

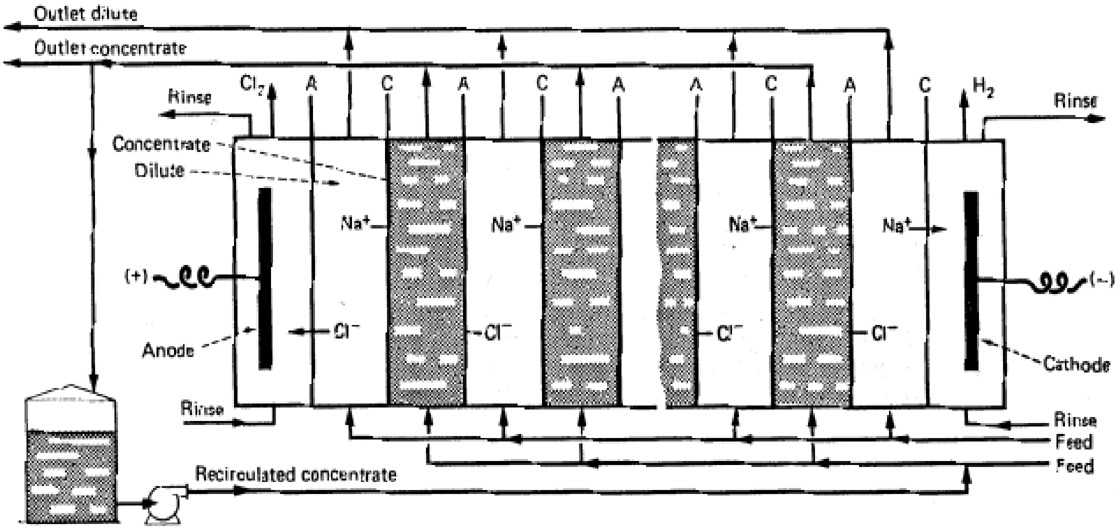


Figure 8.1.6. Schematic illustration of a typical electrodialysis system. (Holiday, 1982)

The influence of the imposed electrical potential causes the cations and anions to move in the opposite directions. The cations easily move through the cation membrane into the concentration chamber, but are not able to pass through the anion exchange membrane and are retained in a concentrate stream. The anions are driven toward the anode and are also trapped in the concentration chamber. The feed stream enters the bottom of the unit and is directed via a manifold to multiple compartments. As the stream passes through each compartment, a portion of the salt is transferred through the membranes by the applied electrical potential gradient and the alternative chambers, into which the salt is transported, contain more concentrated stream. The inlet and output manifolds keep the diluted and concentrated streams separated (Zeien, 1980).

Electrodialysis systems are limited to removing ionic species from wastewaters and are unable to remove organic contaminants or other scalable compounds, such as silica. In addition, membrane scaling and fouling have long hampered ED for water treatment as they require extensive pretreatment to protect the membranes. In some cases, as shown in Figure 8.1.6, the diluted and concentrated steams are recirculated to keep flow velocity high enough to reduce scale formations. In fact, a modified eletrodialysis system called “electrodialysis reversal (EDR)” has been developed to mitigate the scaling and fouling problems. In EDR process, a membrane cleaning action is influenced by periodic reversal of the DC polarity applied to the cell, which is made possible by the symmetric configuration of the cell. This cleaning action is comparable to the backflushing of filters. The polarity reversal makes the system more tolerant to scaling and fouling contaminants and reduces pretreatment requirements compared to traditional ED systems (Strauss, 1985).

Electrodialysis technology has been widely used in many municipal and industrial applications, including desalination of salt and brackish water, recovery of salt by concentration of sea water or recovery of metals from plating wastes, as well as roughing demineralizers for boiler feedwater upstream of ion exchange demineralizers (Strauss, 1985).

Electrodialysis system has been tested for the treatment of cooling tower blowdown (Ostanowski, 1984). Two pilot-scale tests were conducted in the U.S and South Africa separately. At Etiwanda Station in Etiwanda, CA, a nine-month pilot study was conducted to test a conventional eletrodialysis system to treat the cooling tower blowdown which had been pretreated by softening, clarification and filtration. Another pilot test in South Africa was conducted at Grootvile Power Station with an EDR system, which also required a pretreatment process consisting of softening, recarbonation, filtration, chlorination and activated carbon. Based on the results of these two pilot studies, the first full-scale eletrodialysis system was commissioned for a 3,600 MW power station in the following year.

8.1.3.3 Evaporation

Evaporators or evaporation ponds are used as another technology to achieve ZLD. Evaporation is a natural process of transforming water in liquid form to water vapor in the air, which depends on local humidity, temperature, and wind conditions. Drier climates generally favor evaporation as a waste management technique. The simplest approach to evaporation involves placing produced wastewater in a pond, pit, or lagoon with a large surface area (Figure 8.1.7). Water can be left to passively evaporate from the surface as long as evaporation rate exceeds inflow rate. Evaporation is used to remove water from the cooling tower blowdown in many power plants, such as Magnolia in CA, Jones Station in TX or San Juan in NM.

Figure 8.1.7. Evaporation ponds. (*Source: BC Technologies Ltd.*)

Evaporation rates depend on the size and depth of the pond and influent characteristics. For example, in semiarid regions, hot, dry air moving from a land surface will result in higher evaporation rates for smaller ponds. The evaporation rate of a solution will decrease with an increase in ionic strength. Blowdown can be managed at small onsite evaporation ponds or can be sent offsite to commercial facilities that employ large evaporation basins. One potential problem with evaporation ponds stems from their attractiveness to migratory waterfowl. If evaporation ponds contain oil or other hydrocarbons on the surface, birds landing in the ponds could become coated with oil. Covering the ponds with netting helps to avoid this problem.

Somewhat different from evaporation ponds, evaporators use different technologies to increase rate of the liquid vaporization and overcomes the limits of natural conditions. Vapor recompression evaporators sometimes referred as “brine concentrators” represent a proven technology whose performance and reliability have been demonstrated at several power plants (Leonard & Richard, 1986). However, the capital and operating costs of evaporators are relatively high.

A vapor recompression evaporator is typically a long, tubular, vertical, falling film system that uses a vapor compression cycle. A schematic illustration of a typical vapor recompression evaporation system is shown in Figure 8.1.8. The pH of the wastewater is adjusted to between

5.5 and 6.5 by the addition of sulfuric acid. This acidified stream is pumped through a heat exchanger to recover the sensible heat from the distillable fraction before being fed into a deaerator to strip noncondensible gases, including carbon dioxide, oxygen and nitrogen from the water and vent them to the atmosphere. After the deaerator, water enters the primary feed heater, where its temperature is raised close to boiling by recovering sensible heat contained in the hot product water. The waste feed then enters the evaporator sump, where it is mixed with a concentrated slurry and recirculated to the top of the evaporator. It then falls in a thin film along the inside walls of the evaporator tubes. As the waste falls, it is partially converted to steam, which is then compressed and used as a heating medium on the shell side of the evaporator. When the steam is compressed, its saturation temperature is increased, thus making its sensible heat available at a higher temperature level. The major energy requirement is the electrical power used to compress the steam. The steam exiting from the shell side is condensed. The condensate is pumped through the feed heater and recovered as product water.

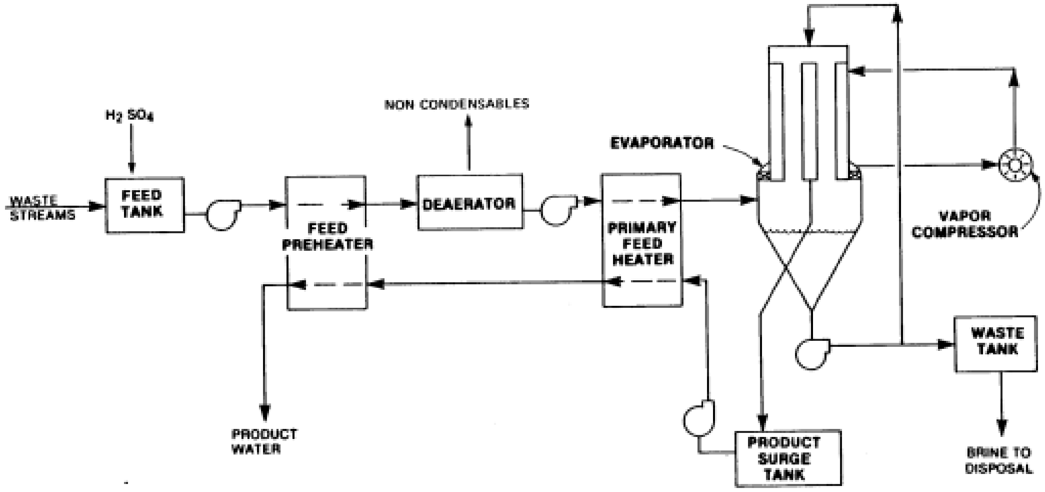


Figure 8.1.8. Schematic illustration of a typical vapor compression evaporation process.(Zeien, 1980)

Demisters are used to prevent entrainment and carryover from contaminating the purified water, which is usually of high enough quality to be used as boiler feedwater. Excess product water not needed for the boiler can be used as cooling tower makeup, which permits the cycles of concentration to be increased because of the purity of the makeup (Zeien, 1980; Pasricha, 1980).

Scale formation on the evaporator tubes can be problematic. To avoid this problem, calcium sulfate crystals can be added into the feed solution to induce preferential precipitation of scale-forming compounds on the crystals. The use of the seed slurry process permits a high concentration ratio while preventing scaling of the evaporator tubes (Leonard & Richard, 1986). Normally, 95-98% of the feed can be recovered as high quality distillate. The small volume that remains as concentrated brine and slurry can be disposed of in evaporation ponds or spray drier, depending on the net evaporation rate and other site-specific factors, such as land availability and cost.

An alternative to vapor recompression evaporators is offered by the "vertical tube foaming evaporators (VTFE)". The principal differences between the VTFE system and vapor recompression evaporators include: (1) the VTFE one uses turbine exhaust steam as the source of heat for evaporation to reduce energy cost; (2) a surfactant is added to create a foamy flow on the tubes (Leonard & Richard, 1986). In principle, the use of the surfactants is expected to reduce the rate of scaling formation, lower hydrostatic losses and enhance the heat transfer efficiency in the evaporator (Paul, 1986). However, a potential problem of the VTFE system involves the direct coupling of the power generating cycle and the evaporator due to the use of the turbine exhaust steam because of the possible impact of evaporator problems on the availability of the power cycle.

Case study of a power plant using ZLD:

San Juan Generating Station (SJGS)

The San Juan Generating Station (SJGS) is located in the northwest plateau of New Mexico, about 20 miles west of Farmington (Leonard & Richard, 1986). It is a semi-arid region with an average annual precipitation of approximately eight inches and minimal ground water supply. Water for the station is supplied entirely from the San Juan River, which is located about 10 miles south of the plant as one of the tributaries of the Colorado River.

In addition to the river water, the station also uses reclaimed water as cooling tower makeup water and receives it by pipeline. The reclaimed water originates as mine drainage from another part of their facility about one mile from the plant. Although the reclaimed water comprises less than 1% percent of the total 15000 gpm makeup flow, it is important to include it in consideration since San Juan Generating Station is a zero liquid discharge facility.

SJGS consists of four coal-fired units with a total generating capacity of 1800 MW. The water flow diagram for the entire site is shown in Figure 8.1.9. As one of the early pioneers in the use of sophisticated water recycling systems at power plants, the San Juan Generating

Station went through continuous development during the 1980's and improved its processes in wastewater treatment to comply with ZLD requirements. The principal water recycling and conservation system employs five evaporators and four reverse osmosis units. The evaporators are the vertical tube foaming evaporators (VTFEs) and a calcium sulfate as the surfactant is used to control scale formation. The main improvements involved the addition of lime-soda ash softening equipment, neutralization tanks and clarifiers upstream of the RO units and an additional brine concentrator with a capacity of 350 gpm. In fact, each one of four RO systems has a capacity of 500 gpm of wastewater and recovers 400 gpm of the high quality permeate. Each RO unit consist of spiral-wound acetate module configured in a two-pass array with 15 pressure vessels in the first pass and 9 pressure vessels in the second one.

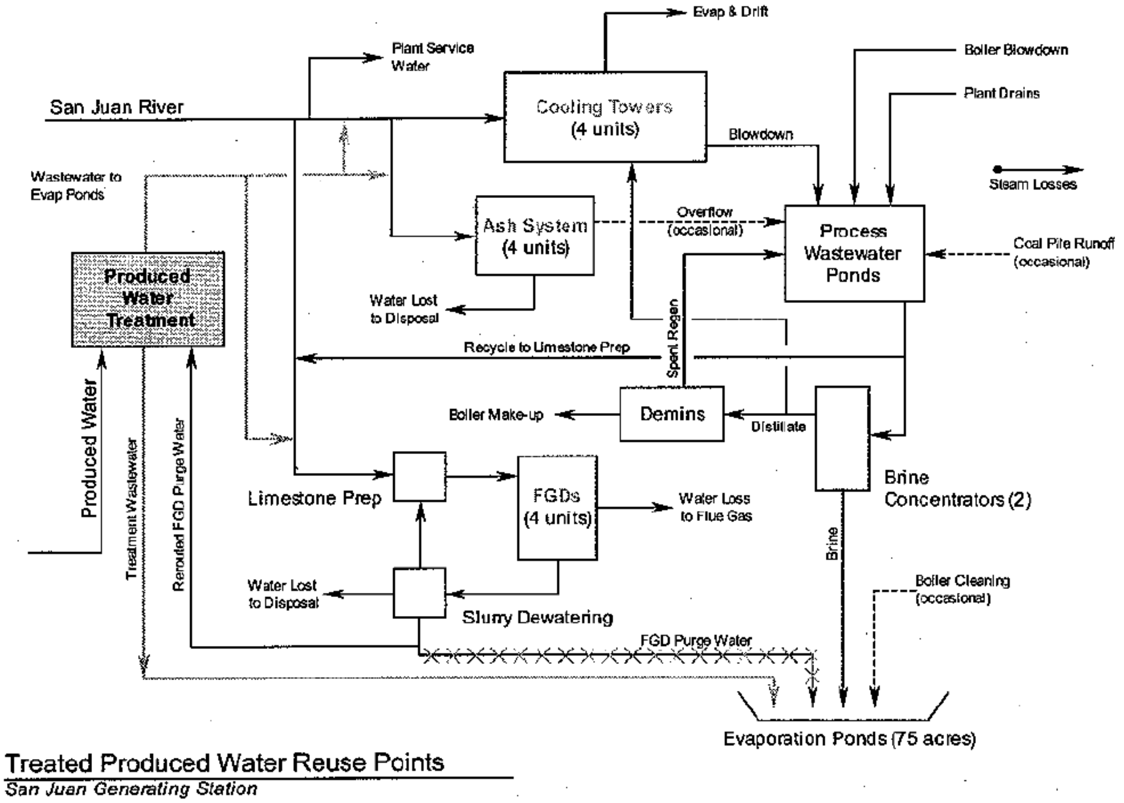


Figure 8.1.9. San Juan Generating Station. *(Source: PNM Company. "San Juan Generating Station.")*

At the SJGS, conventional recirculating wet cooling towers are employed. Since they are using high quality feed water as makeup, the towers in SJGS is being operated at 12 cycles of concentration and use standard cooling water treatment methods. A phosphonate-type inhibitor is continuously added to permit operation at concentrations above the solubility of calcium sulfate. Sulfuric acid is added to maintain the pH of the recirculating water between 7.9 and 8.3

to prevent calcium carbonate scaling. The towers are shock-treated for 1 hour twice a day with chlorine to prevent biofouling. The cooling towers are also equipped with drift eliminators to prevent water loss from the cooling towers and maintain the total particulate emissions limit for the entire plant.

The operation of the feed water pretreatment system and the RO/evaporator system produces both liquid and solid wastes. The average blowdown flowrate in the SJGS cooling system is around 800 GPM. The concentrated waste brine from the vapor recompression evaporators is pumped to evaporation ponds with a total surface area of 75 acres while the recovered water is sent back to the plant to be used as boiler makeup water. Solids from the clarifiers and evaporators are dewatered in centrifuges and disposed of in a polyethylene-lined sludge pit (Paul, 1984).

8.2 Blowdown Treatment Alternatives

When the cooling tower blowdown cannot be discharged back to a WWTP or discharged directly to receiving waters, the blowdown needs to be treated. The treatment objective is to recover portion of the blowdown that will have the quality equal to or better than the makeup water so that it can be returned to the cooling loop to achieve ZLD operation. Specific treatment approaches depend largely on the characteristics of the blowdown water, which in turn depend on makeup water sources and cooling tower operating conditions (e.g., cycles of concentration).

The treatment needs for the blowdown from the pilot-scale cooling towers operated with secondary treated municipal wastewater ("MWW blowdown") and acid mine drainage ("AMD blowdown") were independently assessed. The two types of blowdowns were collected from the cooling towers and analyzed for their chemical characteristics. Major constituents of concerns for discharge limits or reusability in terms of scaling and corrosion issues when returned to the cooling loop were identified. Two treatment approaches were then considered: softening and membrane filtration. Softening treatment targeted to reduce scale forming constituents and was evaluated by estimating the dosing requirements of lime and/or soda ash for each blowdown. This was followed by modeling simulations with MINEQL+ to predict finished water quality (hardness removal and TDS reduction). Treatability studies with various types of membranes were carried out for the MWW and AMD blowdown water employing a bench-scale membrane filtration unit. A variety of operating parameters, including membrane types, trans-membrane pressure (TMP), and feed water pH, were tested for optimal treatment performance in terms of filtration flux and water quality improvement.

8.2.1 Lime-soda Ash Softening

Equilibrium calculations were performed to examine the feasibility of softening and precipitation treatment processes with traditional lime and/or soda ash addition to the blowdown waters discharged from pilot-scale cooling towers. Both blowdown waters, i.e., AMD and MWW, were examined for their respective water quality characteristics (Table 8.1.2). The blowdown water quality used for the calculations was based on the chemical analysis of water samples taken from the pilot-scale cooling towers that received a complete chemical treatment for control of scaling, corrosion, and biofouling during normal tower operation.

Figure 8.2.1 shows the bar diagrams for the two blowdowns, which represent key cations and anions in each water. These ions govern the chemical dosage requirements for softening. Both types of the blowdown water contain relatively high amounts of noncarbonate hardness, which requires the addition of both lime and soda ash for hardness removal (AWWA, 1999). It is estimated that for the AMD blowdown water, approximately 1400 mg/L lime as $CaCO_3$ and 2600 mg/L soda ash as $CaCO_3$ would be required for hardness removal; for the MWW blowdown water, approximately 560 mg/L lime as $CaCO_3$ and 250 mg/L soda ash as $CaCO_3$ would be required. Based on these estimates, appropriate ranges of lime and soda ash were selected for in-depth modeling calculations by MINEQL+, which is a chemical equilibrium model used previously in this study.

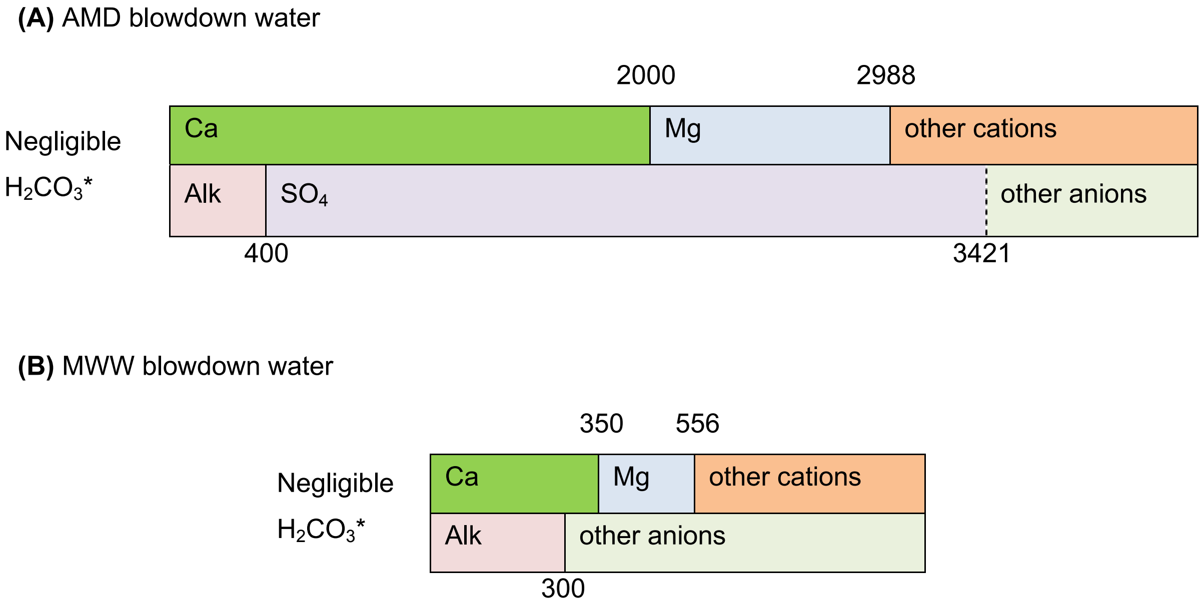


Figure 8.2.1. Bar diagrams of the chemical composition of the two blowdown waters, indicating the proportions of the chemical species relevant to softening treatment. Values are in mg/L as $CaCO_3$.

Figure 8.2.2 shows details of changes in total soluble Ca and Mg concentration of the AMD blowdown water when only lime was added for softening. Due to insufficient carbonate alkalinity, calcium was not removed. Similar results were observed with the MWW blowdown water as well. These results suggest the need for additional soda ash to provide alkalinity levels needed for effective Ca removal.

When both lime and soda ash were added to the AMD blowdown water (in appropriate proportion as estimated based on the bar diagram in Figure 8.2.2), both Ca and Mg were precipitated (Figure 8.2.3). The data shown also indicates that Ca removal requires higher doses of lime-soda ash.

Figure 8.2.4 demonstrates that excess lime-soda ash cannot remove sulfate species. At low dosage, soluble sulfate mainly exists as aqueous $MgSO_4$ and $CaSO_4$; at high dosage, sulfate exists as anions because most Ca and Mg have been precipitated out of solution. As such, the sulfate level in the AMD blowdown water is not reduced by the addition of excess lime-soda ash. Chemical equilibrium calculations suggest that sulfate is not removed through co-precipitation with calcium to form gypsum that would be precipitated from the AMD water.

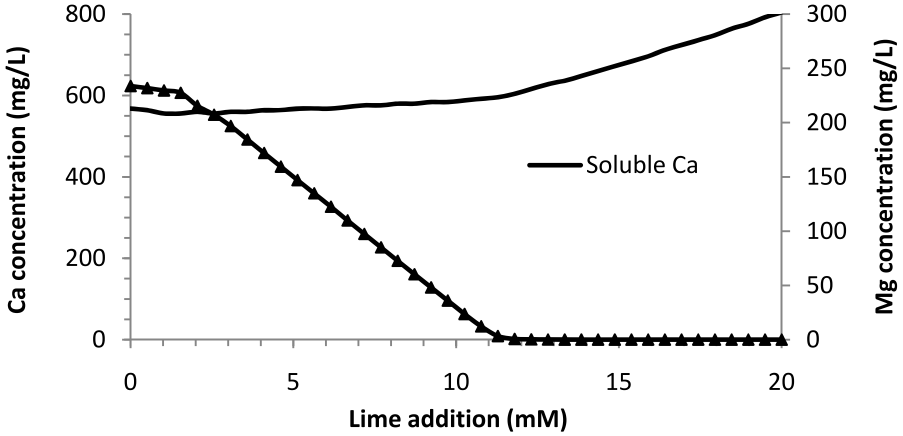


Figure 8.2.2. Lime only treatment of the AMD blowdown water.

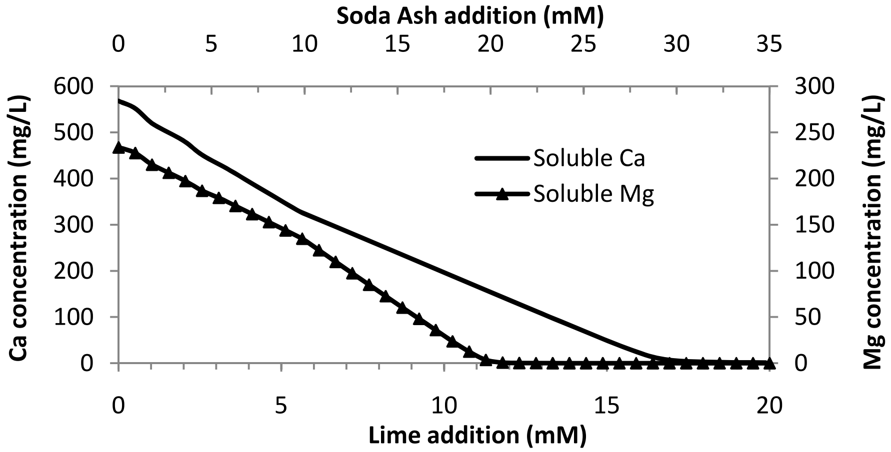


Figure 8.2.3. Precipitation of Ca/Mg during excess lime-soda ash treatment of the AMD blowdown water.

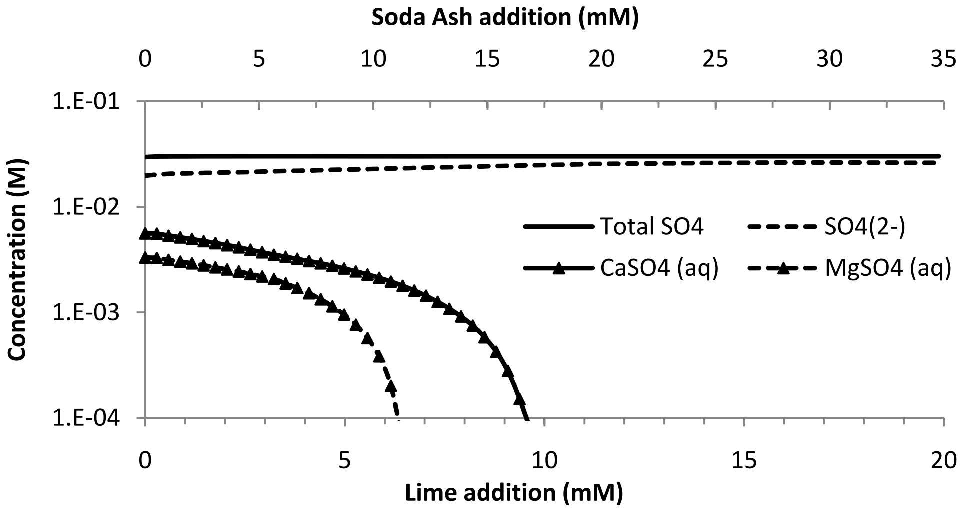


Figure 8.2.4. No removal of sulfate from the AMD water with excess lime-soda ash treatment.

Table 8.2.1 summarizes the modeling results in terms of chemical requirements and finished water quality. For the AMD water, special attention was given to sulfate removal in the modeling effort because sulfate levels are a major concern for AMD blowdown discharge (Milcic, 2008).

It was observed that despite satisfactory removal of calcium and magnesium achieved by excess lime-soda ash treatment for both types of blowdown water, the TDS levels in the finished water remained virtually unchanged (Table 8.2.1). Hardness removal by excess lime-soda ash can be at the expense of sodium addition form of soda ash. As a result, the total dissolved solids are not reduced by the softening process for either of the blowdown waters. Through softening, the chemical composition was shifted from Ca/Mg dominant to Na dominant. In addition to the inability of the softening treatment to reduce TDS, solution pH values were raised to very high levels, which is also undesirable.

Since neither TDS nor sulfate are effectively reduced by the softening/precipitation process, other treatment approaches were investigated. The feasibility of membrane filtration in reducing both TDS and sulfate were experimentally tested for the two blowdown waters. Results from the membrane experiments are presented in Section 8.2.2.

Table 8.2.1. MINEQL+ modeling of chemical precipitation treatment of the cooling tower blowdown waters (target removal of hardness: 90%). Both waters received chemical treatment for control of scaling, corrosion, and biofouling in the cooling tower (Units: mg/L).

		AMD Blowdown		**MWW Blowdown**	**Target Limit**
Treatment Chemicals	Lime (dose)	1110	-	300	
	Soda Ash (dose)	2760	2760	210	
Precipitated solids	Calcite	3360	1100	595	
	Brucite	500	0	20	
	Chrysotile[1]	127	88	55	
	Dolomite	0	1635	174	
	Hydroxyapatite [2]	0	0	34	
Finished water quality	Soluble Ca	55 (800) [a]	5	11 (140)	
	Soluble Mg	0 (238)	0	5 (50)	
	Soluble SO_4	2900 (2390)	2900	ND (300)	250
	Alk. (as $CaCO_3$)	7	502	15	
	TDS	4840 (5160)	4790	2270 (2580)	500
	pH	11.8	8.9	10.5	

Notes: [1] $Mg_3(Si_2O_5)(OH)_4$. [2] $Ca_5(PO_4)_3(OH)$.
[a] Numbers in parenthesis are the initial TDS values before softening treatment.

8.2.2 Membrane Filtration

Membrane filtration experiments were conducted to evaluate the feasibility of using microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) or Reverse Osmosis (RO) in cooling tower blowdown water treatment.

Membranes are defined as barriers, which can separate two phases and restrict transport of various chemicals in a selective manner (Figure 8.2.5). As a result of increasingly stringent discharge standards, the use of membrane technology in wastewater treatment is growing rapidly. The wastewater, referred to as the feed, is driven through a membrane by an applied driving force. The fraction of the feed fluid that passes through the membrane is called the “permeate” and the fraction that is retained by the membrane is called the “retentate”. The driving force for separation can be pressure, concentration, electrical potential or a thermal force. The most common driving force and the one used in this study is pressure.

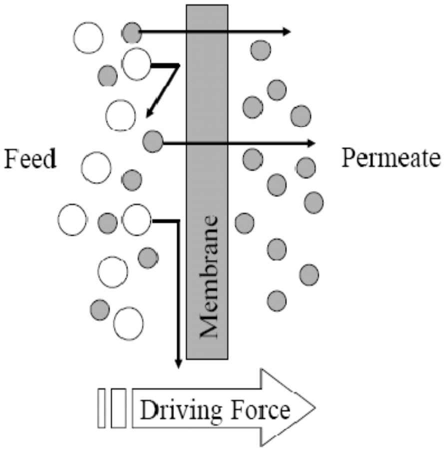


Figure 8.2.5. Membrane separation. (Bendick, 2003.)

The various membrane processes are categorized by the size of the particles that are able to pass through the membrane. Membrane processes are classified as microfiltration, ultrafiltration, nanofiltration and reverse osmosis. Table 8.2.2 shows differences in size exclusion, typical operating pressures, and types of particles that are rejected for each membrane classification. The selection of NF membranes for blowdown treatment may be the most appropriate due to their ability to reject salts at lower operating pressures.

Table 8.2.2. Membrane classifications (Bendick, 2003)

Membrane classifications	Size range	Operation pressure (bar)	Rejected particles
Microfiltration	0.01 – 1 µm	0.5-2	Bacteria, Silts, Cysts, Spores
Ultrafiltration	1 nm – 100 nm	1-5	Proteins, Viruses, Endotoxins, Pyrogens
Nanofiltration	200 – 1000 MWCO(1)	3-15	Sugars, Pesticides, Salts
Reverse Osmosis	< 200 MWCO(1)	10-60	Salts

(1)MWCO-Molecular Weight Cut Off.

Four mechanisms for particle rejection are shown in Figure 8.2.6. Surface sieving rejects particles by the size of the membrane pores. Surface collection rejects particles by the affinity of the particles to attach to the membrane due to surface charge or other non-specific attractive forces. Surface cake collection influences particles rejection by the formation of a cake that accumulates on the membrane surface and effectively reduces the pore opening of the membrane. Internal pore adsorption occurs when particles adhere to the inside of the membrane pores and are excluded from the permeate. The particles that accumulate on the membrane surface and within the membrane are known as the fouling layer.

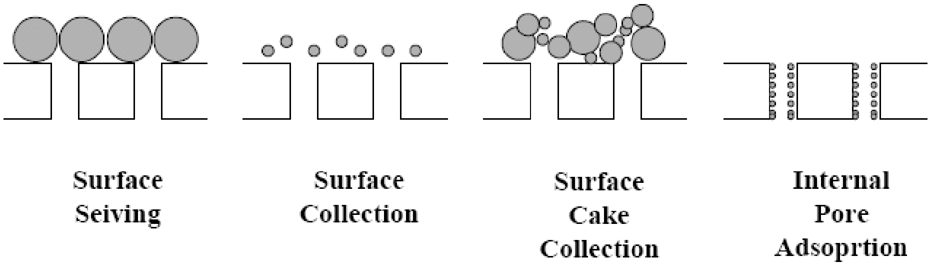


Figure 8.2.6. Filtration mechanisms. *(Sources: John A. Bendick, 2003, Feasibility of Cross-flow Microfiltration for Combined Sewer Overflows.)*

8.2.2.1 Materials and Methods

Membrane processes can be further classified by the membrane material and the system configuration. Four basic types of membrane configurations are dead-end, spiral wound, cross-flow, and hollow fiber. The different configurations have been developed to facilitate higher permeate flux rates, process flexibility, and ease of maintenance and operation for specific applications. A dead-end configuration was used in these experiments.

The objective of these tests were to characterize permeate water quality and flux rate that can be achieved for both MWW and AMD blowdown collected from pilot-scale cooling tower test using different types of membranes. Figure 8.2.7 shows the schematic diagram of the bench scale dead-end membrane unit employed in these tests. The unit consists of a stainless steel cylindrical cell that is connected to a feed reservoir. The cell has a holding capacity of 350 mL and an effective filtration area of 36.3 cm^2. It also incorporates a magnetic stirrer to provide shear force needed to reduce cake buildup on the membrane surface. A sinter metal plate at the cell bottom provides mechanical support for membrane during filtration. Pressurized nitrogen gas from a gas tank can be introduced into the feed reservoir to maintain necessary trans-membrane pressure (TMP). Such pressure drives the feed solution through the membrane.

During a batch experiment, permeate is collected in a glass beaker sitting on a top-loading electronic balance. The amount of permeate collected was recorded (accuracy ±0.01 g) at predetermined time intervals for calculating the flux rates.

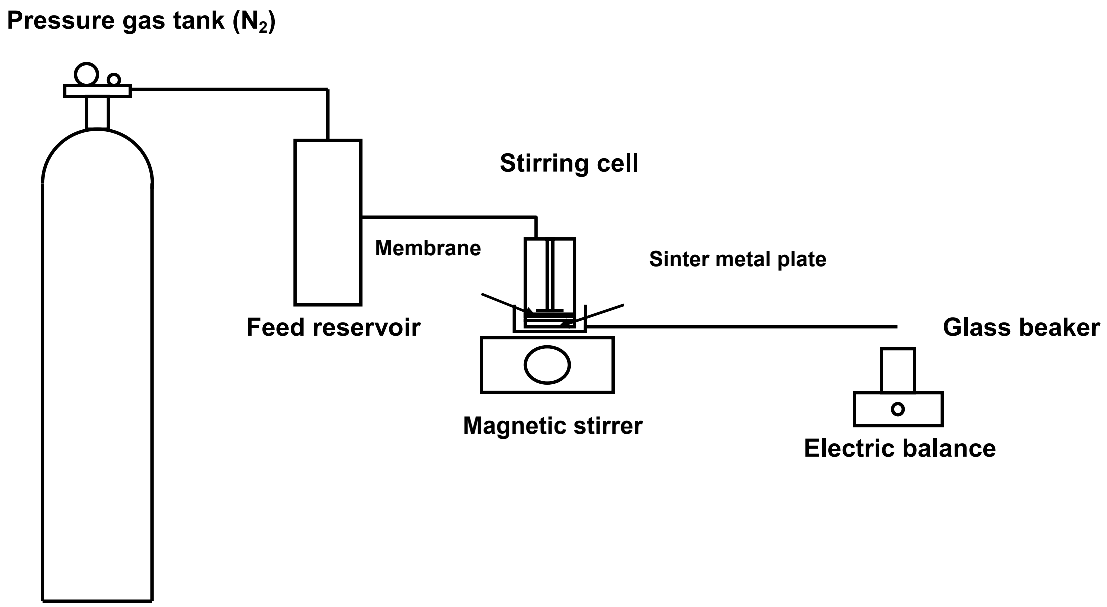


Figure 8.2.7. Schematic diagram of the membrane filtration system used for blowdown treatability studies

For each of the two types of blowdowns tested in this study (AMD and MWW), both synthetic and actual blowdowns were used as feed to obtain additional insight into the performance of different membranes. The synthetic water was designed to simulate the actual blowdown from pilot-scale cooling towers that were operated at four cycles of concentration (CoC 4) with secondary treated municipal wastewater (MWW) and acid mine drainage (AMD). Tables 8.5 and 8.6 provide the chemical compositions of the synthetic MWW and AMD blowdown water, respectively. To be more representative, the chemical recipe developed for synthetic MWW (CoC 4) was based on average values from different MWW reported in the literature, which are not necessarily the same as the chemical composition specific to the Franklin Township MWW used in pilot-scale testing. Nevertheless, membrane filtration performance based on the synthetic water and actual blowdown water collected from pilot-scale cooling towers will be compared in this section. The actually blowdown water was stored in air-tight tanks at 4°C before use.

Table 8.2.3. Chemical composition of the MWW blowdown water representing 4 cycles of concentration synthesized for membrane filtration tests

Cation	Concentration		Anion	Concentration	
	mM	mg/L		mM	mg/L
Ca^{2+}	7.61	305	SO_4^{2-}	2.84	273
Mg^{2+}	7.16	174	HCO_3^-	13.44	820
Na^+	13.44	309	Cl^-	31.16	1105
K^+	0.70	27	PO_4^{3-}	0.21	20
NH_4^+ (as N)	7.14	100			

Table 8.2.4. Chemical composition of the AMD blowdown water representing 4 cycles of concentration synthesized for membrane filtration tests

Cation	Concentration		Anion	Concentration	
	mM	mg/L		mM	mg/L
Ca^{2+}	20.58	825	SO_4^{2-}	31.04	2981
Mg^{2+}	10.45	254	HCO_3^-	4.52	276
Na^+	12.51	288	Cl^-	8.74	310
K^+	0.75	29	SiO_3^{2-}	0.78	59

A variety of thin-film composite flat-sheet polymeric membranes were tested in this study. Membrane characteristics in terms of pore size, water affinity, and porosity are shown in Table 8.2.5 (data provided by membrane manufacturers).

Table 8.2.5. Characteristics of the membranes used in the study

Membrane		**Manufacturer**	**Material**	**Water affinity**	**Pore size (µm)**	**Clean water flux (gal/m^2·min·psi)**
MF	AC+0.2	PALL	Acrylic copolymer	Hydrophilic	0.2	7.00
UF	MX500	Filtration Solutions	Modified polyacrylonitrile Polymer	Hydrophilic	0.05	----
NF	NF270	FILMTEC	Polyamide Thin-Film Composite	NF270 > NF90 > BW30	NF270 > NF90 > BW30	0.039
	NF90	FILMTEC	Polyamide Thin-Film Composite			0.020
	BW30	FILMTEC	Polyamide Thin-Film Composite			0.00087
RO	SW30	FILMTEC	Polyamide Thin-Film Composite	BW30 > SW30	BW30 > SW30	0.00016

Based on a review of the federal and state regulations, such as National Pollutant Elimination Discharge System (NPDES), and the water quality of the two blowdowns, it was determined that the following parameters are the critical for the permeate quality: pH, TSS, TDS, sulfate, TOC (only for MWW), nitrate (only for MWW), and phosphate (only for MWW).

The synthetic wastewater was stirred for 24 hours to allow sufficient time for precipitation prior to testing. The actual blowdown water, preserved in a refrigerator (4°C), was well mixed before use. All experiments were conducted at room temperature (22 ± 1°C) and the entire test system, including water samples, was allowed to equilibrate at room temperature prior to each test.

All membranes were subjected to similar preparation procedure. They were cut into 68-mm diameter discs to fit in the dead-end filtration cell and wetted with deionized water prior to use.

Permeate was collected over a period of 6 hours during which time a fixed TMP of 15 psi (for MF), 60 psi (for UF), 135 psi (for NF) or 380 psi (for RO) was maintained. For MWW blowdown, permeate flux with an NF membrane (model # BW30, DOW) was measured at various pH values (6.0, 7.4, 9.0). The effect of TMP pressure (135, 150 and 200 psi) on the flux rate and permeate quality was also evaluated using NF membrane. In addition to testing single

NF membrane, a combined use of two different NF membranes was compared to the results with RO membrane treatment of actual AMD blowdown.

Surface morphology and fouling characteristics of the membrane subjected to different flux conditions was examined after the filtration test. The membrane was carefully removed from the cell and air-dried before scanning electron microscope (SEM) analysis. The SEM used in this study was a field-emission gun (FEG)-equipped Philips XL30. Images were obtained in the secondary electron (SE) imaging mode. The accelerating voltage and working distance, magnification, scale, etc., were recorded on the images. Samples were coated with Pd metal using a Denton vacuum evaporator to reduce charging during microscopy.

8.2.2.2 Results and Discussion

Filtration of MWW Blowdown

Real MWW blowdown from field studies and synthetic MWW blowdown were filtered with five different membranes: MF (AC+0.2), UF (MX500), and three NF membranes (NF90, NF270 and BW30) to determine the feasibility of removing TDS, including specific cations and anions. Sulfate was specifically of interest because it is often high and difficult to treat in impaired waters. The quality of the permeate resulting from the treatment of synthetic MWW blowdown by each membrane is listed in Table 8.2.6. The data summarized in Table 8.2.6 clearly indicate that MF and UF were unable to remove TDS or the anions of concern. Of the three NF membranes tested, NF90 and BW30 were able to remove some dissolved species from the synthetic MWW. These two membranes were tested with actual MWW blowdown and the permeate quality from these test is summarized in Table 8.2.7. These data indicate that the BW30 membrane can be used to treat MWW blowdown to satisfactory levels, yielding permeate quality that meets discharge limits for TDS and sulfate.

Table 8.2.6. Permeate quality for synthetic MWW blowdown (Units: mg/L)

		pH	TSS	TDS	SO_4^{2-}	PO_4^{3-}
Raw water		8.4	17.1	2906	282	12.5
	Membrane Treatment:					
	MF(AC +0.2)	8.5		2880	280	7.2
	UF (MX500)	8.5		2861	282	7.0
	NF270	8.3		2794	274	5.5
Filtered water	**NF90**	8.0		1980	228	5.6
	BW30	8.4		1492	130	5

Table 8.2.7. Permeate quality for actual MWW blowdown filtered with NF membranes (Units: mg/L)

		pH	TSS	TDS	TOC	SO_4^{2-}	PO_4^{3-}	NO_3^-
Raw water		7.8	45	3060	149	282	22	68
	Membrane Treatment:							
Filtered water	**NF90**	7.6		2176	68	326	10	66
	BW30	7.1		376	11	31	2	23

In addition to permeate quality, another important aspect of membrane treatment is the permeate flux (volume of permeate produced per unit surface area of the membrane per unit time). Permeate flux needs to be sufficiently high to make this process economically attractive.

A comparison of water flux data from the three NF membranes tested with both synthetic and actual MWW blowdown is shown as Figure 8.2.8. For both waters, NF 270 provided the highest water flux. However, the permeate quality using this membrane was not acceptable and it was not evaluated any further. The fluxes from both NF90 and BW30 were very similar when using synthetic MWW blowdown. However, BW30 yielded higher permeate flux and quality with actual MWW blowdown when compared to NF90. In addition, permeate flux with BW30 membrane and actual MWW blowdown leveled off at about 5 L/m^2·h after 6 h of filtration, which indicates fairly robust performance in terms of membrane fouling.

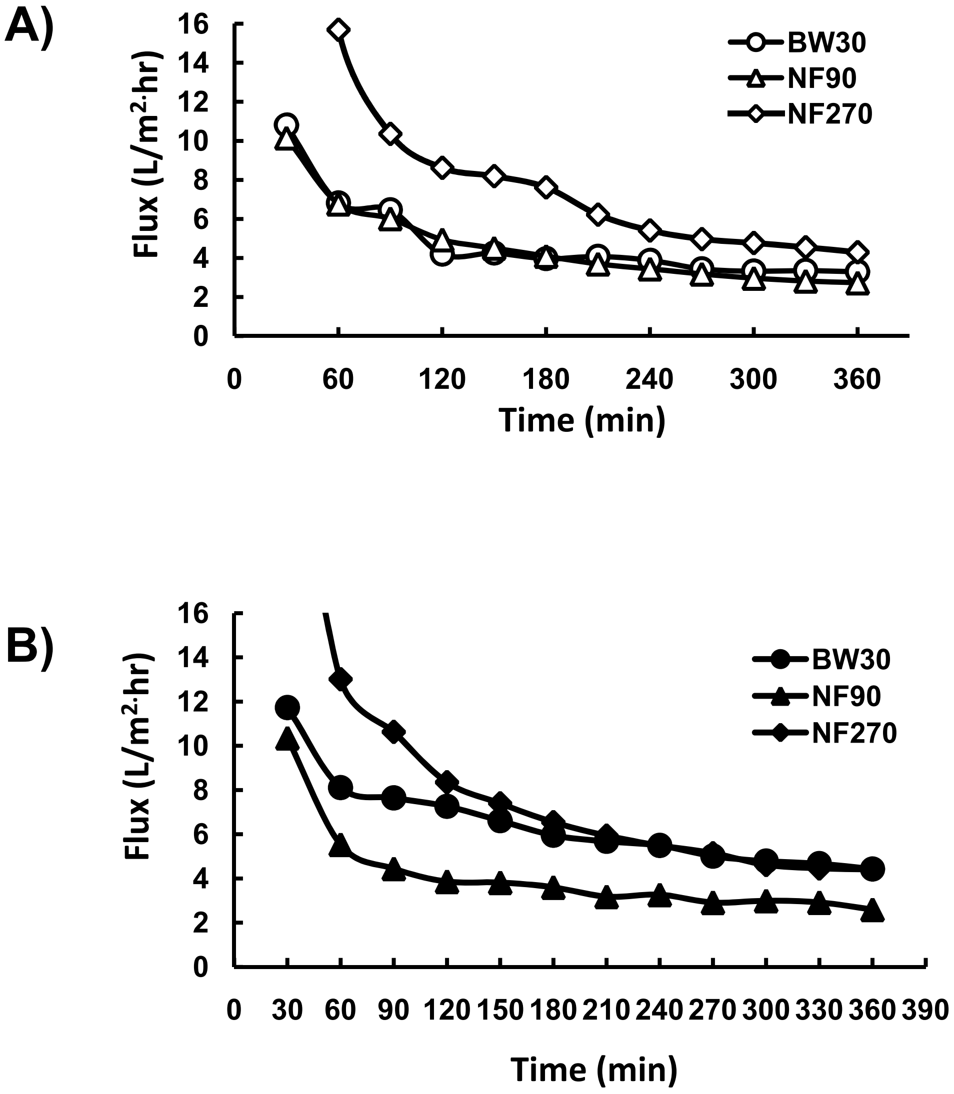


Figure 8.2.8. Permeate flux with NF membranes tested on A) synthetic MWW blowdown and B) actual MWW blowdown at TMP = 135 psi

It is interesting to note that the BW30 membrane yielded higher permeate flux when filtering the actual MWW blowdown than synthetic MWW blowdown (Figure 8.2.9). It is postulated that such behavior may be due to the difference in filtering mechanism with two blowdown samples. To test this hypothesis, the membrane surface morphology after the filtration test is compared in Figure 8.2.10. A distinctly different "cake" layering was observed for the filtrate on the same membrane from two different water samples. It is believed that the more crystalline nature of the cake formed on the BW30 membrane surface operated with the actual wastewater (Figure 8.2.10b) is more permeable than that observed for the membrane that treated synthetic MWW blowdown. Formation of this layer is attributed to the retention of suspended solids (i.e., organic matter and colloidal particles) originally present in the actual wastewater whereas the synthetic wastewater had lower TSS. This cake layer may have served as a preliminary filter to help mitigate membrane fouling.

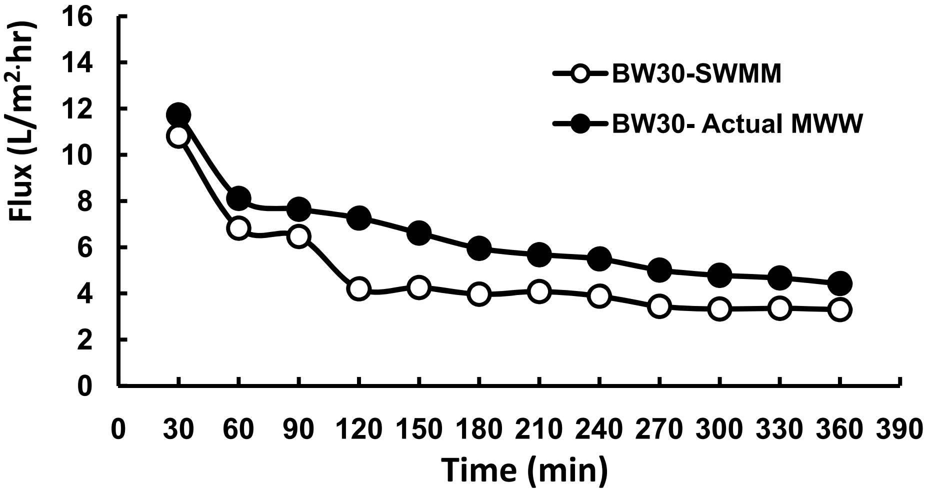


Figure 8.2.9. Water flux of the BW30 membrane for synthetic and actual MWW blowdown waters.

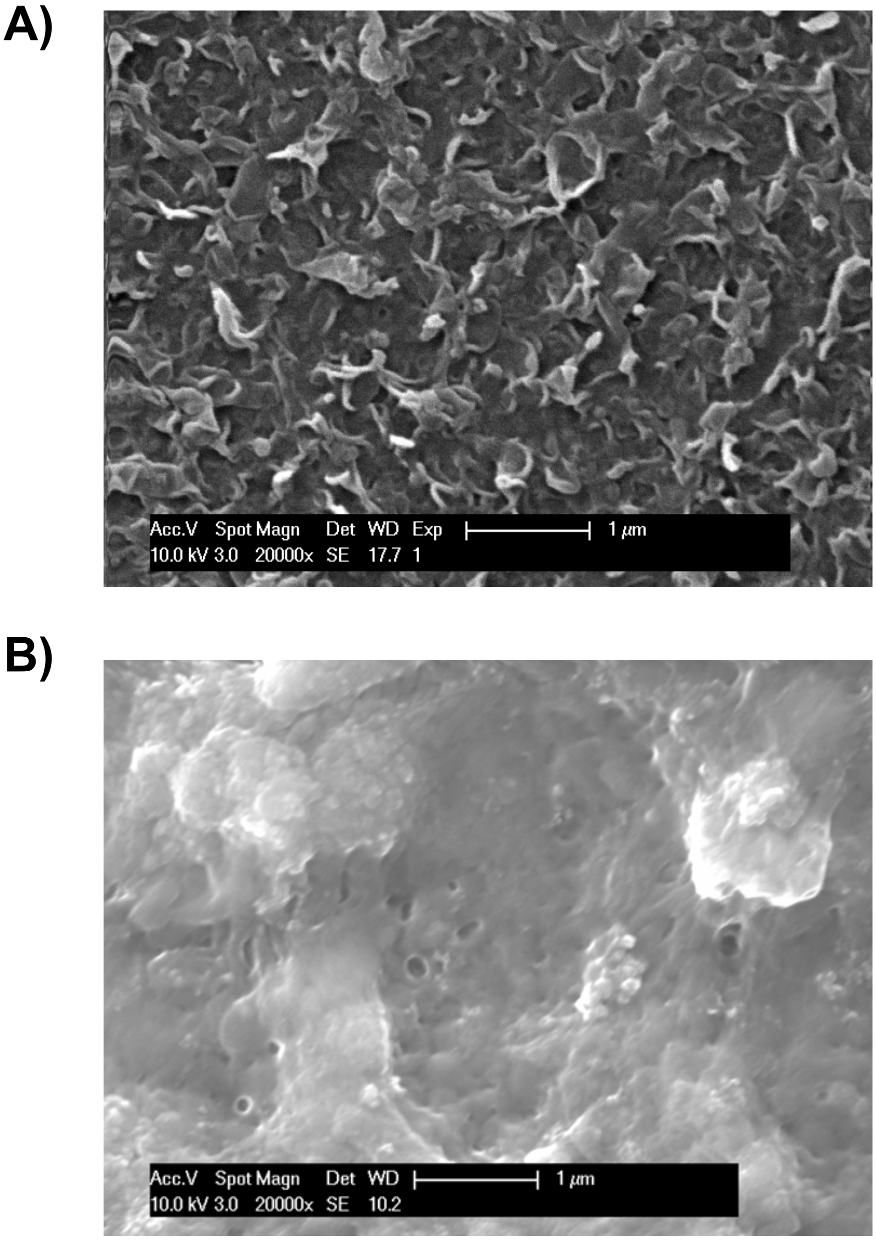


Figure 8.2.10. SEM images of the BW30 membrane after filtering (a) synthetic and (b) actual MWW blowdown for 6 h at TMP = 135 psi.

Several TMP values were tested to evaluate its impact on water flux in order to determine optimal operating conditions for BW30 NF membrane in treating actual MWW blowdown. Despite the initial differences in fluxes, there was little difference in steady state flux when TMP values were increased from 135 to 200 psi (Figure 8.2.11). This phenomenon may arise from a potential adverse impact of TMP on membrane fouling. For example, an increase in

TMP may compress the coating layer (Figure 8.2.10b), thereby rendering it less permeable. In addition, higher initial permeate flux at higher TMP may even push some of the layer materials into the membrane pores, thereby increasing the overall filtration resistance of the membrane. Both processes may lead to more severe fouling that would diminish the expected increase in water flux due to an increase in TMP (Figure 8.2.12). Therefore, considering the cost of operating membrane filtration at higher TMP, it can be concluded that filtration at TMP above 135 psi cannot be justified.

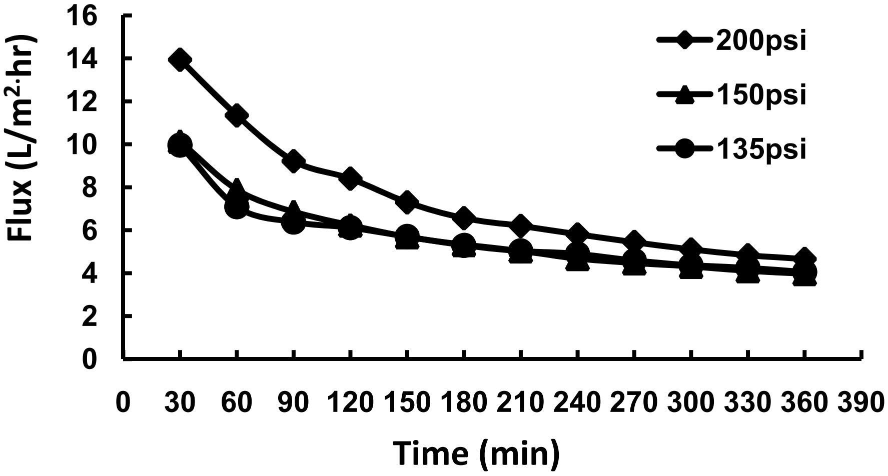


Figure 8.2.11. Impact of TMP on water flux of BW30 operated with actual MWW blowdown.

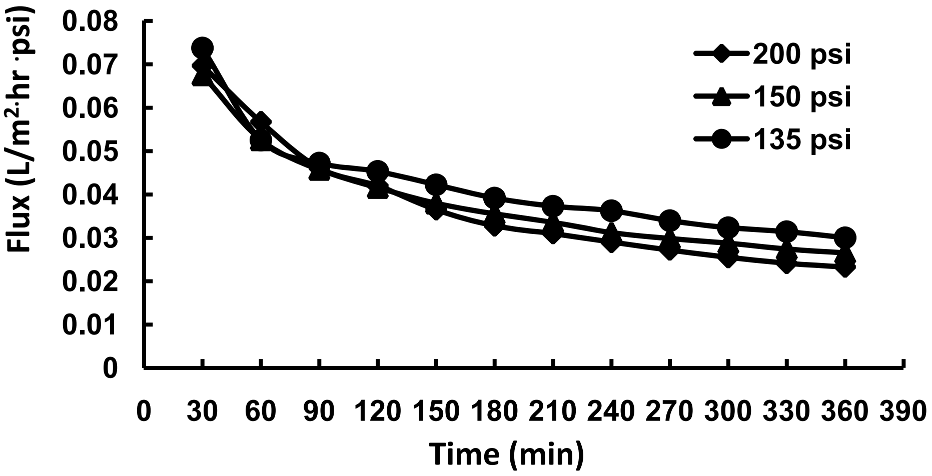


Figure 8.2.12. Impact of unit TMP on water flux of BW30 operated with actual MWW blowdown at different pressure.

The impact of pH adjustment on water flux was examined using BW30 operated at 135 psi with actual MWW blowdown (Figure 8.2.13). It was observed that lowering pH resulted in higher permeate flux. Elevated pH led to rapid attainment of steady state fluxes at a lower level. It is most likely that higher pH lead to excessive precipitation and severe scaling on the membrane surface (e.g., by $CaCO_3$ precipitation), which contributed to more pronounced membrane fouling and lower flux. Lower pH waters did not reach steady state within the timeframe of the experiment. So lowering the pH would be beneficial for maintaining higher permeate flux.

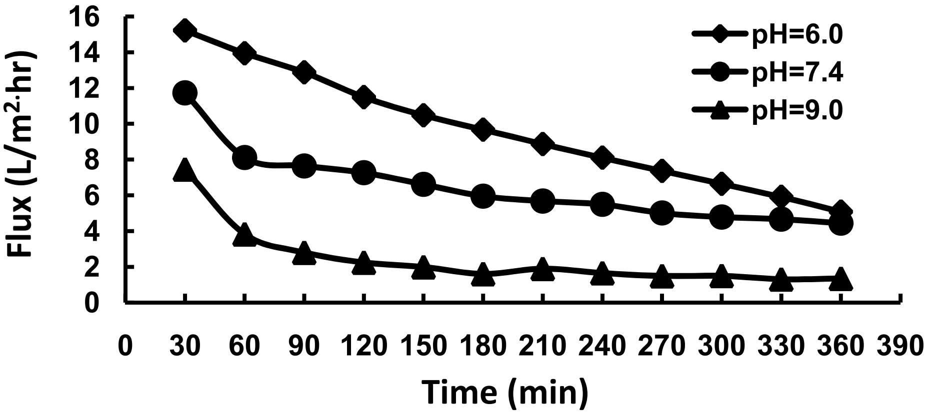


Figure 8.2.13. Impact of pH adjustment on permeate flux with BW30 operated with actual MWW blowdown at TMP = 135 psi.

The fouling mechanism was qualitatively investigated by comparing SEM images of membranes used in these tests. The membrane fouling layer resulting from treating blowdown at pH 6 was observed to be more porous and with looser structure than that observed at pH 9 (Figure 8.2.14a). The layer at pH 9 was more compact and had a gel-like appearance (Figure 8.2.14b). An alternative mechanism that may have contributed to the higher water flux at pH 6 is that the acidic water may partially decompose the fouling layer formed on the membrane surface, thereby having somewhat of a self-cleaning mechanism.

Although lowering the pH of the feed water could bring benefit of higher flux, the cost associated with construction and operation of an acid-base dosing unit should be carefully evaluated before a pH adjustment strategy can be implemented.

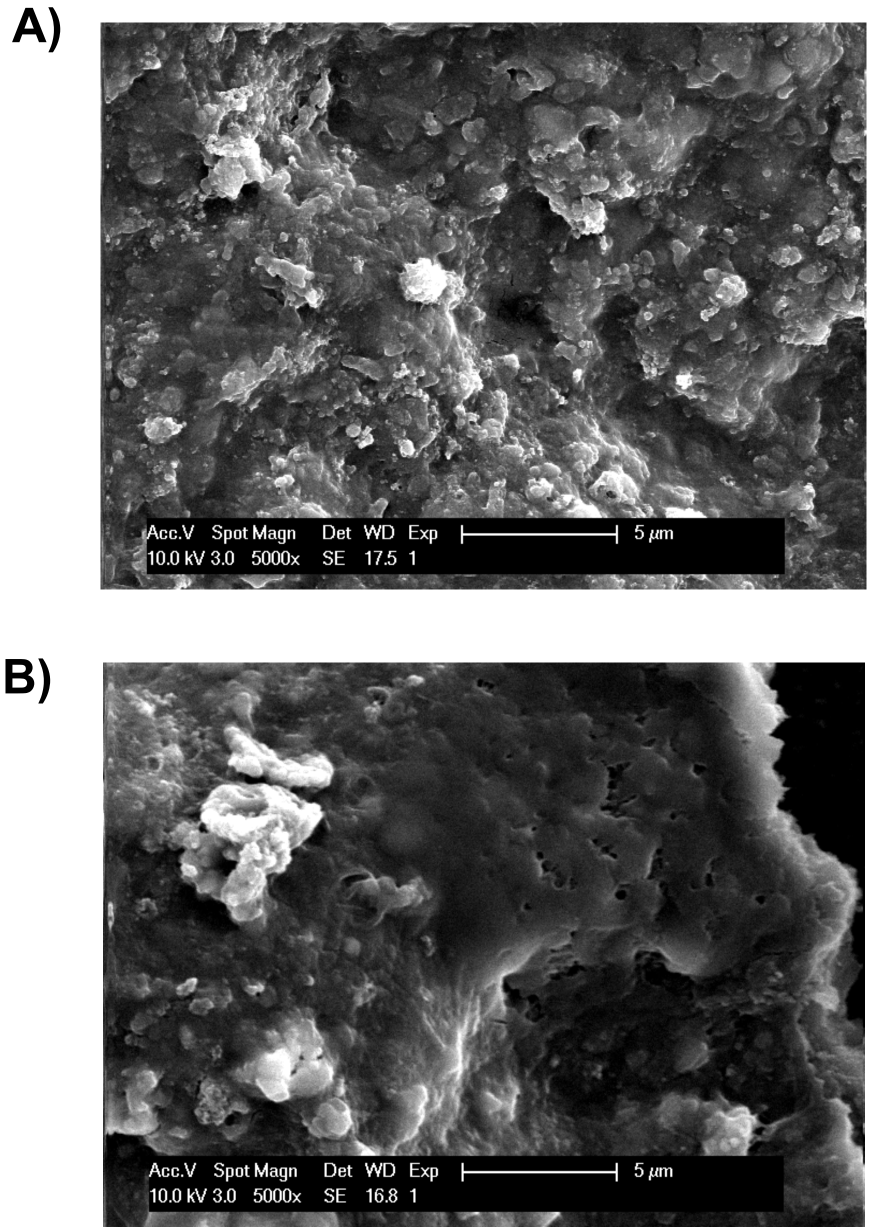


Figure 8.2.14. SEM images of the BW30 membrane after filtering the actual MWW blowdown at (a) pH 6 and (b) pH 9.

Filtration of AMD Blowdown

Membrane filtration was evaluated as a treatment option for AMD blowdown that would allow its reuse as cooling tower makeup. The performance of membranes tested for TSS and TDS removal from MWW blowdown was considered when selecting the membranes to be tested for AMD blowdown treatment. The three NF membranes, namely NF90, NF270 and BW30, were chosen for this phase of the study that was conducted using the same experimental protocols as those employed for MWW blowdown treatment. The permeate quality that was achieved by these membranes is summarized in Table 8.2.8. The data in Table 8.2.10 suggest that NF90 and BW30 membranes may be able to control TDS and sulfate levels in the permeate at levels that could allow its reuse as cooling tower makeup water.

Table 8.2.8. Permeate quality for synthetic AMD blowdown with different NF membranes (Units: mg/L)

		pH	TSS	TDS	SO_4^{2-}
Raw water		8.0	22	4815	2495
	Membrane Treatment:				
Filtered water	**NF270**	7.9		4129	1889
	NF90	7.6		1405	690
	BW30	7.4		1478	647

Further testing of these two NF membranes was conducted using the actual AMD blowdown and the permeate quality achieved in these test is summarized in Table 8.2.9. Results with actual AMD mirrored the synthetic AMD: NF90 and BW30 were observed to improve the quality of blowdown but neither membrane produced permeate that meets the regulatory limits for surface discharge.

Further processing of the AMD blowdown is necessary in order to meet the discharge limits for TDS and sulfate. Two options were tested to further reduce TDS and sulfate in the permeate of AMD blowdown: the sequential use of NF90 and BW30 filters (use BW30 to filter the permeate of NF90), as well as a RO-membrane SW30. The reverse osmosis membrane SW30 was operated at 380 psi and had no additional pretreatment. The results of the sequential NF90-BW30 treatment and SW30 reverse osmosis filtration are shown in Table 8.2.10. Both approaches decreased TDS and sulfate to the levels that meet typical NPDES discharge requirements. While both treatment options meet regulatory limits, there are tradeoffs. The RO membrane can produce the required permeate quality but operates at much higher pressure and lower recovery than a combination of two NF membranes. The sequential NF90-BW30 treatment offers better permeate quality but it needs two membrane modules. The choice between the two approaches requires detail process and cost-benefit analysis.

Table 8.2.9. Permeate quality for actual AMD blowdown (Units: mg/L)

		pH	TSS	TDS	SO_4^{2-}
Raw water		8.3	5.6	5810	3079
	Membrane Treatment:				
Filtered water	**NF90**	7.1		761	285
	BW30	7.5		999	420

Table 8.2.10. Permeate quality for actual AMD blowdown filtered through two NF membranes in series or single RO membrane (Units: mg/L)

		pH	TSS	TDS	SO_4^{2-}
Raw water		8.3	5.6	5810	3079
	Membrane Treatment:				
Filtered water	**NF90-BW30**	7.0		192	107
	SW30	7.2		255	138

Variations in the chemical composition of the feed stream can sharply affect the treatment efficiency of nanofiltration membranes operated under identical conditions. The high TDS measured in AMD and MWW blowdown waters as well as high sulfate concentration in AMD water are the main concern for blowdown treatment. The TDS and sulfate removal efficiencies for MWW and AMD blowdown using NF90 and BW30 membranes are shown in Tables 8.2.11 and 8.2.12, respectively. These bench-scale experiments suggest that nanofiltration with BW30 membrane is an effective treatment method to reduce concentration of dissolved species, including sulfate and TDS in MWW blowdown, whereas the NF90 membrane has a small advantage in treating AMD blowdown water. Therefore it is important to pair the membranes filtration technology to the water characteristics in order to achieve the produced water quality goals.

Table 8.2.11. Comparison of treatment efficiency of BW30 and NF90 with synthetic MWW and AMD blowdown.

	TDS		SO_4^{2-}	
	NF90	BW30	NF90	BW30
Synthetic MWW	32%	49%	19%	54%
Synthetic AMD	71%	69%	72%	74%

Table 8.2.12. Comparison of treatment efficiency of BW30 and NF90 with actual MWW and AMD blowdown

	TDS		SO_4^{2-}	
	NF90	BW30	NF90	BW30
Actual MWW	29%	88%	0%	89%
Actual AMD	87%	83%	91%	86%

In addition to permeate quality, the permeate flux is an additional consideration for determining the feasibility of membrane treatment for AMD blowdown. The water flux across the three membranes tested with synthetic AMD is shown in Figure 8.2.15a and actual AMD blowdown wastewater in Figure 8.2.15b. For synthetic AMD blowdown, there were negligible differences in permeate flux between these membranes. However, NF90 had a higher flux than BW30 when tested with the actual AMD blowdown. Permeate flux for NF90 membrane for actual AMD blowdown reached a steady rate of about 8 L/m^2·h over the 6 h period of testing, indicating a more robust anti-fouling performance than the other two NF membranes. Of the three membranes tested, NF90 had the highest permeate flux as well as the highest single pass water quality.

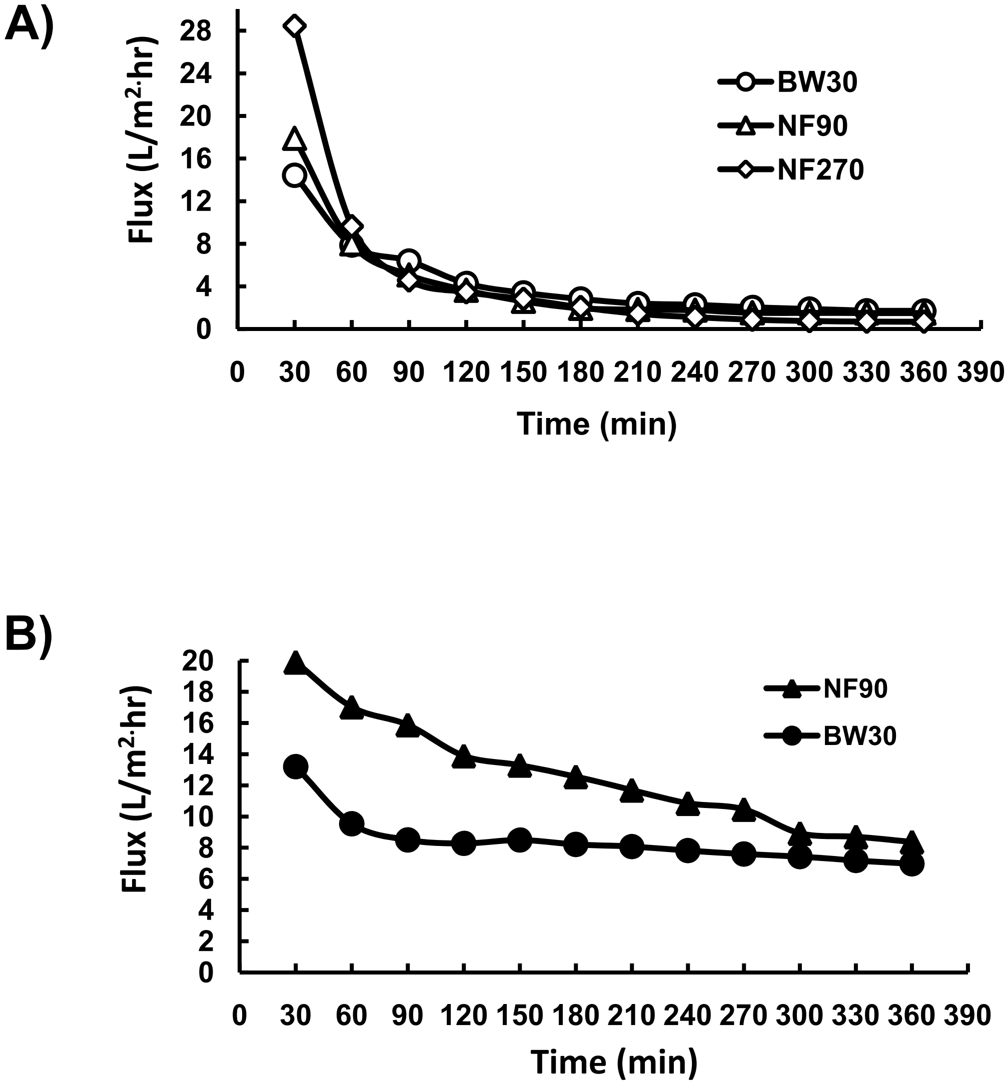


Figure 8.2.15. Water flux of NF membranes tested on a) synthetic AMD water and b) actual AMD blowdown (TMP = 135 psi).

Figure 8.2.16 shows the permeate flux for SW30 and serial NF90-BW30 membrane filtration for actual AMD blowdown. As can be seen from this figure, the sequential filtration with NF membranes (NF90 followed by BW30) has the higher flux in comparison to filtration with RO membrane (SW30). In addition, the NF90-BW30 combination produced permeated with higher quality. Both configuration tested have shown high permeate flux compared to results with single NF membranes (Figure 8.2.15b). Given these results, it was determined that the sequential nanofiltration membrane combination NF90-BW30 is the most effective method to treat AMD blowdown.

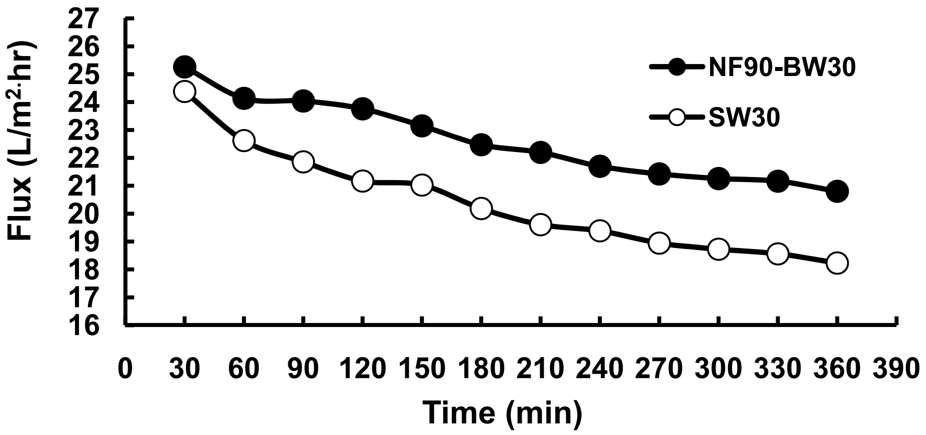


Figure 8.2.16. Water flux of actual AMD blowdown for RO and sequential NF filtration.

8.2.3 OPUS Technology

N.A. Water Systems developed an Optimized Pretreatment and Unique Separation (OPUS) process for desalination of feed water with high concentrations of silica, organics, hardness, boron and particulates that can be used to treat MWW and AMD blowdown. It consists of multiple treatment steps ending with reverse osmosis filtration at a pH near 10.7. A process diagram for OPUS technology is shown on Figure 8.2.17. The pretreatment processes ahead of the RO are designed to reduce the hardness, metals and suspended solids in the feed water. This technology generates high quality water with a low waste volume.

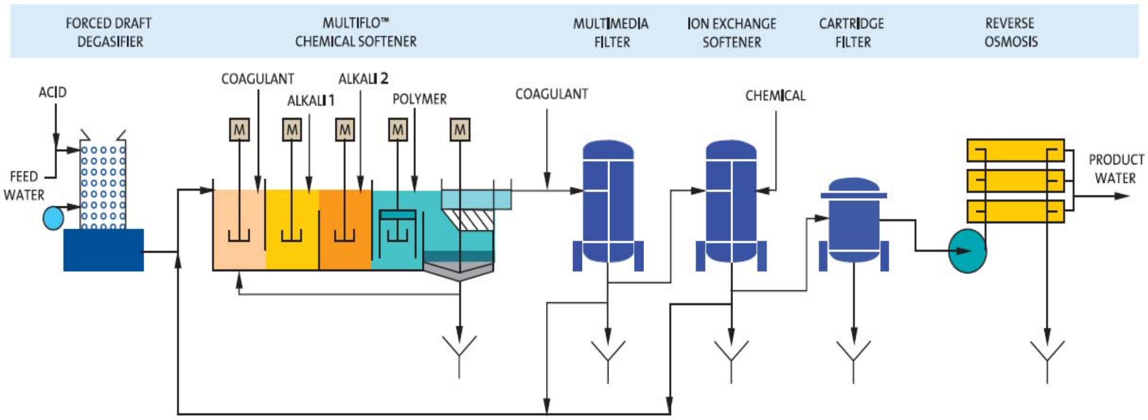
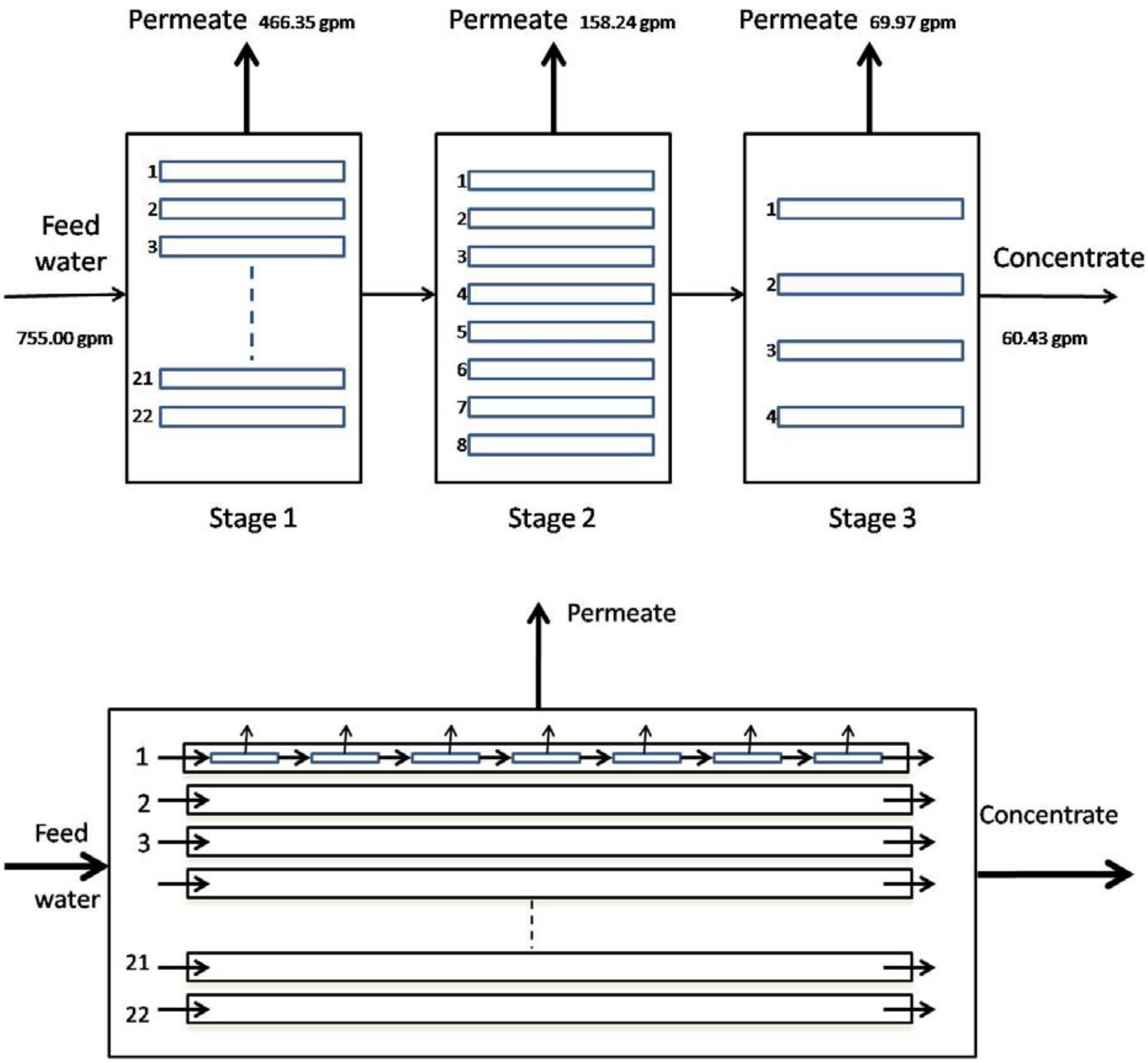


Figure 8.2.17. Processes diagram of OPUS technology developed by N.A.Water Systems, a Veolia Water Solutions & Technologies company.

In the OPUS technology, the RO unit for blowdown treatment consists of three stages and each stage separately has 22, 8 and 4 pressure vessels which all include 7 elements each, as shown in Figure 8.2.18. Tables 8.2.13 and 8.2.14 display the specifications of the systems designed for MWW and AMD blowdown treatment, respectively. Modeling studies regarding the use of OPUS technology to treat MWW and AMD blowdown conducted by NA Water Systems indicate that OPUS technology would be able to meet performance specifications for removing chloride, sulfate, TDS, and other ions as necessary to meet NPDES or relevant discharge regulations. Compared to the nanofiltration membranes tested in laboratory studies, the most important benefit of OPUS technology is the high water recovery rate of 92%. Additionally the elevated pH 10.7 that is used in the finishing RO process effectively controls biological, organic and particulate fouling, eliminates scaling due to silica, and increases the rejection of silica and boron.



Stage 1 : 22 pressure vessels with 7 element

Figure 8.2.18. Schematic of RO process in OPUS technology.

Table 8.2.13. OPUS system details for MWW blowdown

Stage	Element	#PV	#Ele	Feed Flow (gpm)	Feed Press (psi)	Conc. Flow (gpm)	Conc. Press (psi)	Perm. Flow (gpm)	Perm. Press (psi)	Avg. Flux (gfd)	Perm. TDS (mg/L)
1	EXPSW370/34i	22	7	754.96	49.05	91.58	39.82	63.38	0.00	1.71	29.19
2	EXPSW370/34i	8	7	291.54	14.82	31.42	04.16	60.16	0.00	1.13	71.30
3	EXPSW370/34i	4	7	131.42	49.16	0.36	40.25	1.07	0.00	0.88	173.92

Pass Streams (mg/L as Ion)

Name	Feed	Adjusted Feed	Concentrate			Permeate			
			Stage 1	Stage 2	Stage 3	Stage 1	Stage 2	Stage 3	Total
NH_4	2.40	2.40	5.50	10.97	21.28	0.45	1.01	2.22	0.76
K	60.00	60.00	151.58	329.27	700.48	2.37	5.78	13.99	4.34
Na	953.89	1072.34	2763.85	6107.76	13240.55	7.94	19.89	49.61	14.96
Mg	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ca	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sr	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ba	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CO_3	15.43	321.36	875.92	1975.36	4310.63	0.71	2.82	10.15	1.84
HCO_3	356.20	46.79	71.18	115.2	216.9	2.67	5.49	10.30	4.42
NO_3	70.90	70.90	175.62	375.17	784.04	5.01	11.87	27.90	8.93
Cl	1043.75	1043.75	2689.16	5940.76	12873.74	8.36	20.94	52.32	15.76
F	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
SO_4	300.00	300.00	776.06	1720.48	3742.98	0.44	1.08	2.70	0.82
SiO_2	25.00	25.00	64.21	141.45	305.58	0.33	0.82	2.04	0.62
Boron	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CO_2	1.19	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
TDS	2827.57	2951.06	7580.94	16721.86	36198.77	29.19	71.30	173.92	53.80
pH	8.50	10.70	10.66	10.51	10.18	9.73	9.97	10.20	9.09

Permeate Flux reported by ROSA is calculated based on ACTIVE membrane area.

Table 8.2.14. OPUS system details for AMD blowdown

Stage	Element	#PV	#Ele	Feed Flow (gpm)	Feed Press (psi)	Conc Flow (gpm)	Conc Press (psi)	Perm Flow (gpm)	Perm press (psi)	Avg Flux (gfd)	Perm TDS (mg/L)
1	EXPSW370/34i	22	7	755.00	383.30	288.65	374.17	466.35	0.00	11.79	22.09
2	EXPSW370/34i	8	7	288.65	484.17	130.41	473.75	158.24	0.00	11.00	55.42
3	EXPSW370/34i	4	7	130.41	718.75	60.43	709.99	69.97	0.00	9.73	136.65

Pass Streams (mg/L as Ion)									
Name	Feed	Adjusted Feed	Concentrate			Permeate			
			Stage 1	Stage 2	Stage 3	Stage 1	Stage 2	Stage 3	Total
NH_4	0.50	0.50	1.15	2.29	4.39	0.10	0.22	0.47	0.16
K	29.00	29.00	75.26	165.45	354.32	0.37	0.94	2.32	0.69
Na	1853.53	2021.80	5276.57	11656.87	25099.54	7.26	18.65	46.73	13.83
Mg	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ca	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sr	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ba	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CO_3	81.53	492.53	1334.26	2977.67	6406.35	1.21	4.83	16.91	3.15
HCO_3	461.30	44.11	60.82	95.07	189.23	3.60	7.31	13.22	5.89
NO_3	4.90	4.90	12.01	25.16	51.19	0.50	1.18	2.67	0.87
Cl	370.60	37060	964.61	2125.91	4565.24	2.94	7.60	19.11	5.63
F	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
SO_4	2930.00	2930.00	7657.11	16935.83	36513.89	4.16	10.63	26.67	7.90
SiO_2	59.00	59.00	153.06	336.37	720.06	0.78	2.00	4.99	1.48
Boron	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CO_2	0.52	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00
TDS	5790.36	5960.96	15541.67	34324.60	73908.52	22.09	55.42	136.65	41.36
pH	8.90	10.70	10.60	10.37	10.40	9.84	10.09	10.32	10.01

Permeate Flux reported by ROSA is calculated based on ACTIVE membrane area.

Potential disadvantage of the OPUS technology is the total cost (i.e., capital and operating costs) of this system. Preliminary calculations indicate that the cost for engineering and procurement of the OPUS equipment necessary for a system that is capable of treating 1MGD of MWW or AMD blowdown is between six and seven million dollars. It is likely that the extensive pretreatment required for the application of RO membranes on MWW and AMD blowdown would make this approach significantly more expensive in comparison to BW30 nanofiltration system for MWW blowdown or a combined NF90-BW30 nanofiltration system for AMD wastewater. It is therefore possible that nanofiltration could represent sufficient treatment to restore water quality of MWW and AMD blowdown to at least the source water levels and allow its reuse in the cooling system as makeup water.

8.3 Summary and Conclusion

Management of cooling tower blowdown is one of the key components of cooling tower operation and requires significant attention due to important economic and environmental implications. Due to fairly low water quality, blowdown is typically subjected to some treatment in order to meet local, state or federal discharge requirements that are governed by the final disposal options. Management or disposal options available for cooling tower blowdown depend mainly on its quality, local discharge regulations and capabilities of treatment processes under consideration. Typical options for power plant blowdown management include:

- Discharge to surface waters. This is the main option for once-through cooling systems that is not feasible for recirculating cooling systems because of the low blowdown quality.
- Discharge to wastewater treatment plants (WWTPs): This is probably the most cost effective management alternative but may not be feasible for many plants since the WWTP may not accept the blowdown without any pre-treatment due to extremely high solids and presence of other chemicals in the blowdown that were added to control corrosion, scaling and biofouling.
- Zero liquid discharge (ZLD): Zero liquid discharge means that blowdown is treated and used internally in power plant. This alternative involves extensive treatment of blowdown to facilitate its reuse combined with some form of volume reduction to minimize or eliminate the need for liquid discharge. Most power plants using reclaimed water for their recirculating cooling systems would choose ZLD as the main blowdown management option.

Compared to other discharge options, ZLD is preferred as it helps to decrease environmental impacts of power generation. ZLD typically includes one or more of the following advanced treatment technologies: (1) Lime-soda ash softening; (2) Reverse osmosis (RO); (3) Electrodialysis (ED); and (4) Evaporation.

The high TDS observed in both AMD and MWW blowdown and high sulfate concentration in AMD blowdown are the main concern in blowdown disposal. The treatment objectives of cooling tower blowdown is to recover portion of the blowdown that will have the quality equal to or better than the makeup water so that it can be returned to the cooling loop. The treatment needs for the blowdown from the pilot-scale cooling towers operated with secondary treated municipal wastewater ("MWW blowdown") and acid mine drainage ("AMD blowdown") were independently assessed in this study. The two types of blowdowns were collected from the cooling towers and analyzed for their chemical characteristics and two treatment alternatives, i.e., softening and membrane filtration, were analyzed through modeling and treatability studies.

Softening treatment targeted to reduce scale forming constituents and was evaluated by estimating the dosing requirements of lime and/or soda ash for each blowdown quality. This was followed by modeling simulations with MINEQL+ to predict finished water quality (hardness removal and TDS reduction). Equilibrium modeling calculations predict that softening treatment by excess lime-soda ash can remove Ca and Mg effectively. However, neither TDS nor sulfate can be substantially removed by this treatment approach.

Treatability studies with various types of membranes including MF, UF, NF and RO, were carried out for the MWW and AMD blowdown in a bench-scale membrane filtration unit. A variety of operating parameters, including membrane types, trans-membrane pressure (TMP), and feed water pH, were tested for optimal treatment performance in terms of permeate flux and water quality.

Bench-scale experiments provide evidence that nanofiltration with BW30 membrane is an effective treatment method to reduce concentration of dissolved species, including sulfate and TDS in MWW blowdown: TDS and sulfate decreased from 3,060 and 326 mg/L to 379 and 31 mg/L, respectively. Preliminary studies indicate that maintaining a trans-membrane pressure of 135 psi is capable of providing acceptable permeate flux; increasing TMP to 200 psi did not show significant increases in flux due to potentially adverse impact of increased pressure on membrane fouling. Furthermore, lowering pH of the feed water from 7.4 to 6.0 resulted in a higher permeate flux, while increasing it to 9.0 resulted in lower permeate flux. However, a detail cost benefit analysis of the pH adjustment is required before such approach can be recommended.

Treatment of actual AMD blowdown required sequential filtrations by NF90 and BW30 membranes (NF90-BW30) to decrease the TDS and sulfate from 5,810 and 3,079 mg/L to 192 and 107 mg/L, respectively.

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9.0 Summary and Conclusions

As the availability of freshwater for use in cooling in thermoelectric power production becomes increasingly limited, alternative sources of water for power plant cooling are of interest for both existing power plants and those in planning and development. This study evaluated the feasibility of using three waters of impaired quality – secondary treated municipal wastewater, passively treated abandoned mine drainage, and effluent from ash sedimentation ponds at power plants – for use as makeup water in recirculating cooling water systems at thermoelectric power plants. The evaluation included assessment of (1) availability based on proximity (geographical accessibility), (2) relevant regulations, and (3) the feasibility of managing cooling water quality with traditional chemical management schemes. Options for chemical treatment to prevent corrosion, scaling, and biofouling were identified through review of current practices, and were tested at bench and pilot-scale. Key conclusions reached with respect to the major components of the study are summarized below.

9.1 Availability of Three Impaired Waters for Use in Power Plant Cooling

Of the three impaired waters considered, secondary treated municipal wastewater is the most widely available and it is available in large quantities. Passively treated mine drainage is only available in the coal and metal mining regions of the U.S. In those areas it is available in large quantity but often not close to power production facilities. Ash transport water is available at many thermoelectric power production facilities and could be internally reused in cooling without much additional treatment. While ash transport water does not represent a new source of water to a power plant, its reuse in cooling systems would reduce the total amount of freshwater withdrawal at a plant.

An analysis was conducted of the availability of secondary treated wastewater relative to the locations of existing and proposed power plants. Using a database obtained from the US EPA with the locations and discharge flowrates of existing publicly owned treatment works (POTWs), and databases from the Energy Information Administration with the locations of 407 existing and 110 proposed power plants, the availability of secondary treated municipal wastewater to meet the cooling needs of the existing and proposed plants was evaluated. POTWs within radii of 10 and 25 miles of the existing and proposed plants were identified, and the total available flowrate was calculated and compared to the estimated cooling water demand. Considering POTWs within 25 miles, 97 percent of the proposed power plants could obtain sufficient secondary treated wastewater from 1-2 large POTWs in their vicinity to meet their cooling needs. The availability analysis of existing power plants indicated that secondary treated wastewater can satisfy more than 75% of the cooling water demand from POTWs within 25 miles. While particular POTWs may not be in a position to direct all of their effluent to thermoelectric power plants for cooling, the fact that a small number of POTWs can meet the cooling water needs of existing and proposed power plants suggests that secondary treated municipal wastewater has potential as a reliable source of cooling water for power plants in regions where other sources are not available.

Regulations Pertaining to Use of Impaired Waters in Power Plant Cooling

Review of state and federal regulations relevant to impaired water use in power plant cooling systems shows that the federal government has not established regulations specifically related to this type of water reuse, but a number of states have done so. Among those states, California, Florida, Hawaii, New Jersey, North Carolina, Oregon, Texas, Utah, and Washington were investigated for their development of specific regulations and/or guidelines related to water reuse in recirculating, evaporative cooling water systems at power plants. Regulations pertaining to interbasin transfer of water were also examined, as some potential sources of impaired water for power plants will be in different drainage basins, and perhaps different states, than the power plant.

The relevant, existing state regulations focus on water aerosol “drift” emitted from cooling towers, which has the potential to contain elevated concentrations of chemicals and microorganisms and thus poses a possible health risk to the public. Drift has the same water quality as the recirculating cooling water. The possible presence of microorganisms in drift is of primary concern. With regard to regulation of drift from cooling towers, the various state regulations and guidelines include the following provisions:

1) require reclaimed water used in cooling to be secondary treated and disinfected or tertiary treated (CA, FL, HI, NJ, NC, OR, TX, UT, WA),
2) and/or require the chlorine residual to be above a certain amount after a period of contact time (FL, HI, NJ, WA),
3) and/or require the cooling tower to be equipped with a drift eliminator (CA, FL, HI), demonstration of public health assurance (OR), or other special requirements (TX, UT, WA),
4) and/or require the fecal/total coliform concentration to be under a certain concentration (CA, FL, HI, NJ, NC, OR, TX, UT, WA).

Thus, the focus of existing regulations pertaining to reuse of impaired water in evaporative cooling systems is the potential exposure of workers and public to drift in air emissions from the cooling tower, and especially to the potential for exposure to microorganisms in the drift.

9.2 Modeling of Water Quality in Recirculating Cooling Systems

A chemical mass balance model was developed for a recirculating cooling system, including consideration of chemical mass loss by scaling and mass input by corrosion. The objectives of the mass balance modeling were to evaluate the effects of increasing cycles of concentration on cooling system water quality and required blowdown flowrate, the effects of corrosion and scaling on cooling water constituent loads, and the optimal cycles of concentration for the bench- and pilot-scale testing.

The chemical mass balance modeling provided a number of useful insights into chemical behavior in a recirculating cooling water system, and also enabled predictions of water chemistry evolution. The model demonstrated the well known relationship between blowdown flowrate and cycles of concentration, i.e., that required blowdown rate decreases with increase of cycles of concentration. The model simulations also indicated, however, that chemical mass generation by corrosion and loss by scaling can significantly affect cooling water constituent loads and thus the required blowdown. It usually will not be beneficial to operate above 10 cycles of concentration as additional reductions in blowdown volume are small at higher cycles of concentration.

Chemical equilibrium modeling was also performed to assess the scaling potentials of the three impaired waters evaluated. Based on the predicted amount of solid precipitates, the solution ionic strength, and the ratio of total precipitated solids to total suspended solids, bench- and pilot-scale experiments were conducted at CoC levels below 5, to avoid the excessive amounts of precipitates that were predicted to form when the waters were operated beyond CoC 5. From the chemical equilibrium modeling performed for CoC < 5, the impaired water with the lowest potential for precipitate formation was the ash sedimentation pond effluent while the mine drainage water exhibited the greatest potential for precipitate formation. The solid precipitate most commonly predicted to form upon concentration of the impaired waters was calcite, $CaCO_3(s)$, implying that it is important to control the amount of calcium and carbonate species in cooling systems employing impaired water.

9.3 Use of Secondary Treated Municipal Wastewater as Cooling System Makeup Water

It was determined that corrosion, scaling, and biofouling can be controlled adequately in cooling systems using secondary treated municipal wastewater at 4-6 cycles of concentration. The unique challenges of using secondary treated wastewater relate to the presence of ammonia, phosphate, organic matter, and suspended solids in the water at concentrations substantially higher than in freshwater systems. Ammonia, a corrosive species, was found to volatilize in the cooling tower, reducing in concentration significantly and thus not complicating corrosion control. Phosphate can act as a corrosion inhibitor, but was found to precipitate in the bench- and pilot-scale testing, thus exacerbating the scale control challenge. The organic matter was found to reduce the corrosivity of the water, but to make biofouling control more difficult. The suspended solids were primarily organic in composition and thus contributed to the enhanced biofouling control challenge. More information about these findings and trade-offs in cooling water quality management is provided below.

The corrosion rates of mild steel, aluminum, copper, and cupronickel in contact with secondary treated municipal wastewater were examined at bench- and pilot-scale. It was found that the corrosion of metal alloys (except aluminum, which had a pitting corrosion problem) tested was not a concern even without any addition of corrosion inhibitors when reusing secondary treated municipal wastewater. This was demonstrated in bench-scale experiments and also in pilot-scale cooling towers operated at 4 cycles of concentration and 40°C with the addition of monochloramine to control biomass growth. The low corrosivity of the secondary treated municipal wastewater was due to the high scaling potential that resulted in a protective layer of scales on the surface of the metal alloys tested.

Scaling control of secondary treated municipal wastewater concentrated to CoC 4 in recirculating cooling systems can be achieved by water chemistry management. Commonly used polymer-based scaling inhibitors were effective in controlling potentially severe scaling when using this impaired water as cooling water makeup. Polymaleic acid (PMA) was very effective at scaling inhibition when applied at 10-20 ppm level. However, the scaling inhibition by PMA can be compromised by free chlorine, often used as a biocide in cooling systems, because PMA was destroyed by this oxidizing agent. Ammonia present in the wastewater suppressed the aggressiveness of the free chlorine on PMA in bench tests. However, ammonia was significantly removed from the cooling tower systems in pilot tests due to volatilization. Monochloramine, an alternative biocide to free chlorine, was applied in the pilot tests and was found to be less aggressive on PMA than free chlorine, while still being an effective biocide.

Orthophosphate, which is abundant in secondary treated wastewater, contributed to scale formation and to phosphorous removal via precipitation with Ca and Mg. Phosphorous based corrosion inhibitors are not appropriate due to their reversion to orthophosphate and subsequent precipitation. Although scaling is undesirable in cooling systems, it was determined that scale layers formed on metal surfaces could provide a certain degree of corrosion protection for the metal alloys tested.

Chloramination can effectively restrain biofouling when using secondary treated municipal wastewater which carries some residual organic matter. Continuous aeration through filling materials in the pilot-scale cooling tower tests contributed to a high pH and low ammonia concentration, which helped maintain the stability of chloramination in the cooling system. It was determined that maintaining a monochloramine residual concentration above 1 ppm as Cl_2 in the cooling system could sufficiently limit the growth of planktonic heterotrophic bacteria in the recirculating water. By raising the dosage to maintain monochloramine residual concentration between 1-3 ppm as Cl_2, the growth of biofilm, which is mostly sessile bacteria, could be controlled under 10^4 CFU/cm^2. Pre-formed monochloramine yielded better biocidal control than that formed in situ due to unstable ammonia concentrations in the cooling system.

9.4 Use of Passively Treated Mine Drainage as Cooling System Makeup Water

It was determined that corrosion and biofouling can be controlled adequately in cooling systems using passively treated abandoned mine drainage (AMD) at 4-6 cycles of concentration. The unique challenges of using treated AMD relate to the high concentration of dissolved solids and appreciable amount of particulate matter, which makes scaling control challenging. More information about these findings and trade-offs in cooling water quality management is provided below.

When reusing passively treated mine drainage in cooling towers operated at CoC 4 and 40°C with the addition of monochloramine to control biomass growth, cupronickel exhibited acceptable corrosion rate without corrosion inhibitor. With the addition of the inhibitor mixture consisting of orthophosphate 5 ppm as PO_4, TTA 2 ppm, and polymaleic acid 15-25 ppm, the corrosion rates of mild steel and copper were reduced to acceptable levels. Aluminum had pitting corrosion and thus was found not suitable to use. Overall, it was determined that corrosion can be controlled with inhibitors when using passively treated mine drainage in cooling systems.

Scaling control of AMD concentrated to CoC 4-6 in recirculating cooling systems was not adequate with the addition of commonly used polymer-based scaling inhibitors alone. The high concentration of dissolved solids rendered difficulties in scaling inhibition and requires more comprehensive pretreatment and scaling controls. Nevertheless, the added PMA at concentrations of 15-25 ppm lent some stability to suspended mineral solids (high water turbidities) and there was less deposition in the pipe flow sections of the cooling towers tested. Deposits from the AMD exhibited varied affinities to different surfaces. More deposits were collected on the PVC surfaces of the tower packing material. Hydrodynamics also played a role in deposition. Low flow velocities encountered in the plastic packing and bottom sump sections of cooling tower resulted in greater sedimentation. Significant amount of deposits were observed at the bottom of the tower sump, especially in the tower receiving no PMA treatment. The finding suggests that scaling took place in a non-uniform manner throughout the pilot-scale cooling tower system. Therefore, scaling measurements should be performed at tower sections where deposition is of concern.

Microbial activity in the raw mine drainage selected for this study was rather limited in both bench- and pilot-scale tests. It was determined that chlorination or chloramination can control biofouling with a minimal 0.5 ppm dosage as Cl_2 when using AMD. The effectiveness of monochloramine as a biocide was also investigated and it was found that chloramination exhibited higher disinfection efficiency and lower decay rate than chlorination. Maintaining a total monochloramine residual concentration of 1-2 ppm was sufficient to suppress biomass growth in the pilot-scale cooling tower tests.

9.5 Use of Ash Transport Water as Cooling System Makeup Water

It was determined that corrosion, scaling, and biofouling can be controlled adequately in cooling systems using ash sedimentation pond effluent at 4-6 cycles of concentration. Ash transport water was the simplest of the three impaired waters studied in terms of composition. The unique challenges of using ash transport water relate to its low alkalinity and hardness, which makes the water more corrosive. More information about these findings and trade-offs in cooling water quality management is provided below.

When using ash transport water as cooling water at CoC 4 and 40°C with the addition of monochloramine to control biomass growth, cupronickel was found to be the most corrosion resistant material, even in the absence of corrosion inhibitor. Protection of copper required corrosion inhibitor, such as tolyltriazole (TTA) at 2 ppm. The occurrence of pitting corrosion of aluminum even in the presence of corrosion inhibitor limits its usefulness as a cooling system material. Protection of mild steel required phosphorous-based corrosion inhibitor, such as TKPP at 20 ppm as PO_4. Overall, metal alloy corrosion could be controlled by applying corrosion inhibitors TTA and TKPP when using ash transport water as cooling system makeup.

Scaling in the ash transport water concentrated to CoC 4 was less of a problem than with the other two impaired waters previously studied in this project. Both the chemical equilibrium modeling calculations and the experimental results showed that the major constituents of scaling solids were calcium minerals. Addition of 10 ppm of PMA or 10 ppm of PBTC proved to be very effective in suppressing scaling to minimal levels. Both of these scale inhibitors prevented calcium from forming deposits and their effectiveness lasted longer than that of PAA.

Bench-scale batch and recirculating system results revealed that chlorination can be an effective biocidal control option for clarified ash transport water. Maintaining a low free chlorine residual close to 0.5 ppm as Cl_2 provided effective biocidal control since this water has a low organic load. It was also determined that a mixture of scaling and corrosion inhibitors with free chlorine residual does not affect biofouling control.

9.6 Blowdown Treatment and Discharge

The management of blowdown from recirculating cooling systems using impaired water is complicated relative to systems using freshwater because of the additional types and amounts of constituents in the TDS. The primary objective of blowdown management is to treat blowdown to attain quality that is equal to or better than the makeup water so that it can be reused as makeup water. The high TDS in the blowdown waters from pilot-scale testing units with both passively treated mine drainage and secondary treated municipal wastewater and the high sulfate concentration in the mine drainage blowdown water were identified as the main challenges for treatment.

Equilibrium modeling calculations predicted that lime-soda ash softening treatment could remove Ca and Mg effectively from secondary treated municipal wastewater or passively treated mine drainage. However, the calculations showed that neither TDS nor sulfate could be substantially removed by softening.

The effectiveness of membrane treatment for reducing TDS, sulfate, and other constituents in the blowdown water generated from the pilot-scale testing with secondary treated municipal wastewater and with passively treated mine drainage was evaluated. In the pilot-scale testing, each of the waters was concentrated 4-6 times. Tests were conducted with several different types of membranes using a dead-end membrane test cell. Nanofiltration with a BW30 membrane was determined to be an effective treatment method to reduce concentrations of dissolved species, including sulfate and TDS in the blowdown water from the pilot-scale testing with secondary treated municipal wastewater. The blowdown from the pilot-scale testing with passively treated mine drainage needed the sequential treatment with nanofiltration using membrane NF90 followed by membrane BW30. For nanofiltration of these waters, maintaining a trans-membrane pressure of 135 psi provided acceptable water flux. Further increasing the trans-membrane pressure did not show significant improvement in flux. Overall, the testing with the blowdown waters demonstrated that membrane treatment can be employed to reduce TDS and sulfate concentrations to acceptable levels for reuse of the blowdown in the cooling systems as makeup water. This can be accomplished by membrane filtration treatment with commercially available membranes at conventional operating conditions.

Reuse of Treated Internal or External Wastewaters in the Cooling Systems of Coal-Based Thermoelectric Power Plants

September 2009

Final Technical Report
APPENDICES

July 1, 2006 - June 30, 2009

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Cooperative Agreement Number: DE-FC26-06NT42722

Pilot-scale cooling towers installed at FTMSA, PA

Submitted to:

U.S. Department of Energy
National Energy Technology Laboratory
626 Cochrans Mill Road
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Department of
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Pittsburgh, PA 15261-2294

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APPENDIX A: GIS Manual

Geographic information system (GIS) was developed to help power industry estimate the available wastewater flowrate from publicly owned treatment works (POTWs) at any given location for existing or future power plants.

Introduction

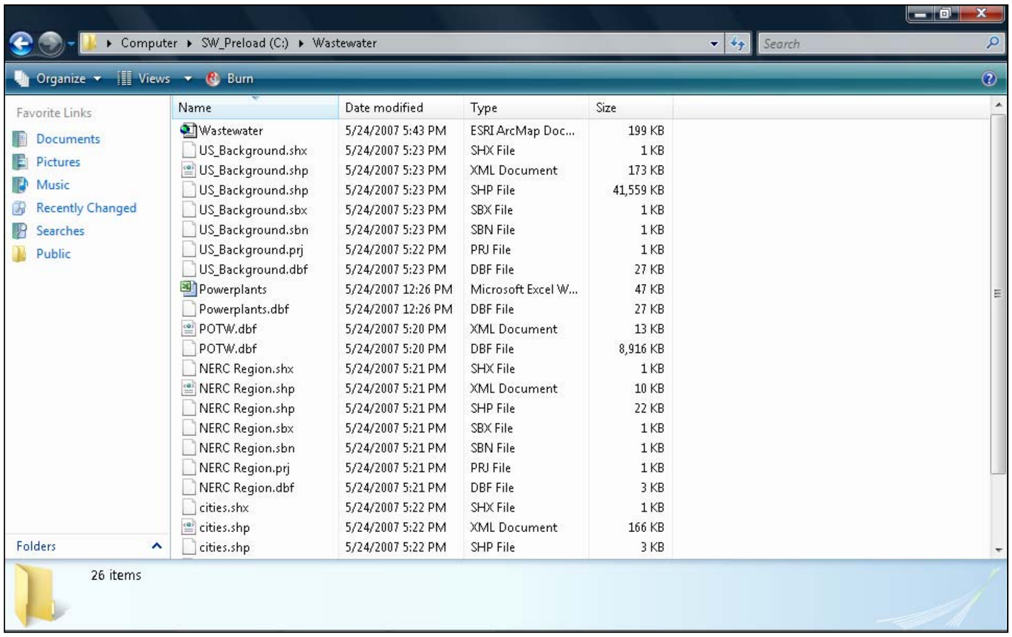
The U.S. environmental protection agency (USEPA) provides an online geographic information system (GIS), Enviromapper for Water (USEPA, 2007), that contains information on wastewater discharge from any source in the continental U.S. The database for Enviromapper for Water was based on Clean Watersheds Needs Survey (CWNS) and has information on publicly-owned wastewater collection and treatment facilities, facilities for control of sanitary sewer overflows, combined sewer overflows, stormwater control activities, nonpoint sources, and programs designed to protect the nation's estuaries.

Another useful tool provided by USEPA is Ask WATERs, which can help to compile information on wastewater discharges in a specific EPA region, state or county. Although the Enviromapper for Water and Ask WATERs provide enough information on wastewater discharges and can help to locate any treatment facility, this information is not detailed enough to assist in decision making. A more accurate wastewater flowrate analysis for a particular location is needed for power industry to make appropriate decision. Therefore, the information about the name of facilities, its total wastewater flowrate, and its geographic location (latitude and longitude) was extracted from Enviromapper of Water database and transferred into a basic GIS that was built on ArcGIS, version 9.2, ESRI. Wastewater facilities included in the database are wastewater treatment plants, sewage treatment plants, water recycle plants, water pollution control plant and lagoons. Information about the proposed thermoelectric power plants that were also included in the GIS are derived from Energy Information Administration, Form EIA-860, "Annual Electric Generator Report.", USEIA, 2007.

The steps described on the following pages explain how to use the GIS developed in this study to determine the total available wastewater flowrate at any given location in continental US.

Instructions

1. Preparation
    a. Download file Wastewater.zip (30.7MB) and extract into C:\Wastewater\ folder.
    b. Make sure all 26 files are saved in the same folder.



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US_Background.shp	5/24/2007 5:23 PM	SHP File	41,559 KB
US_Background.sbx	5/24/2007 5:23 PM	SBX File	1 KB
US_Background.sbn	5/24/2007 5:23 PM	SBN File	1 KB
US_Background.prj	5/24/2007 5:22 PM	PRJ File	1 KB
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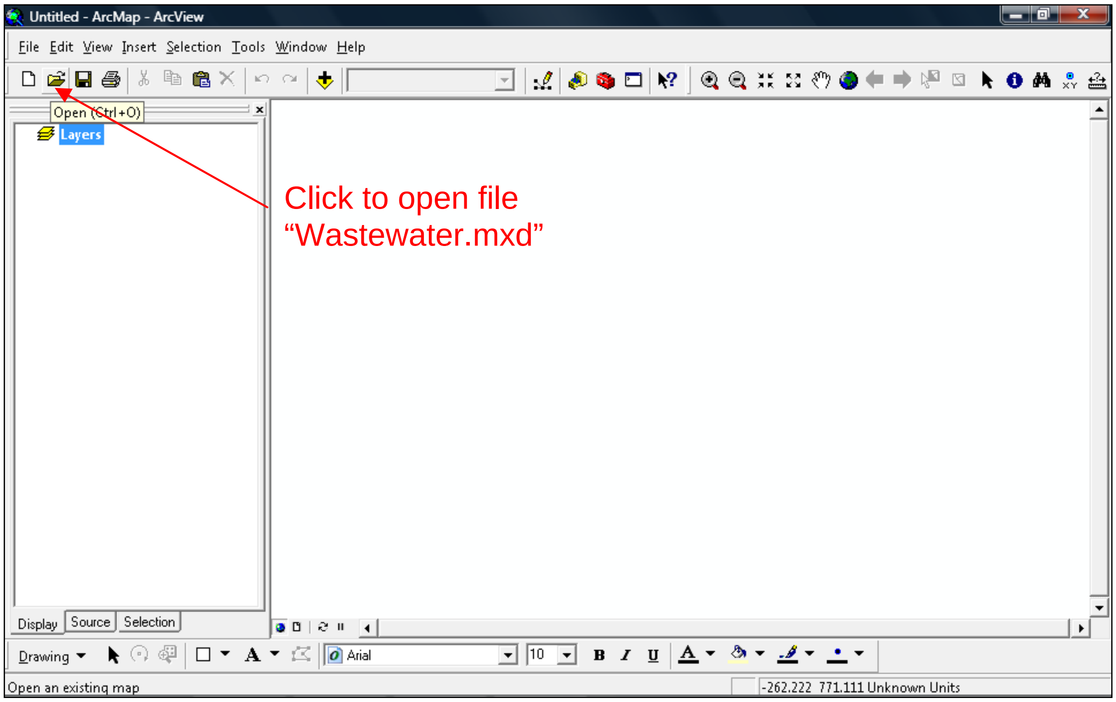
POTW.dbf	5/24/2007 5:20 PM	DBF File	8,916 KB
NERC Region.shx	5/24/2007 5:21 PM	SHX File	1 KB
NERC Region.shp	5/24/2007 5:21 PM	XML Document	10 KB
NERC Region.shp	5/24/2007 5:21 PM	SHP File	22 KB
NERC Region.sbx	5/24/2007 5:21 PM	SBX File	1 KB
NERC Region.sbn	5/24/2007 5:21 PM	SBN File	1 KB
NERC Region.prj	5/24/2007 5:21 PM	PRJ File	1 KB
NERC Region.dbf	5/24/2007 5:21 PM	DBF File	3 KB
cities.shx	5/24/2007 5:22 PM	SHX File	1 KB
cities.shp	5/24/2007 5:22 PM	XML Document	166 KB
cities.shp	5/24/2007 5:22 PM	SHP File	3 KB

26 items

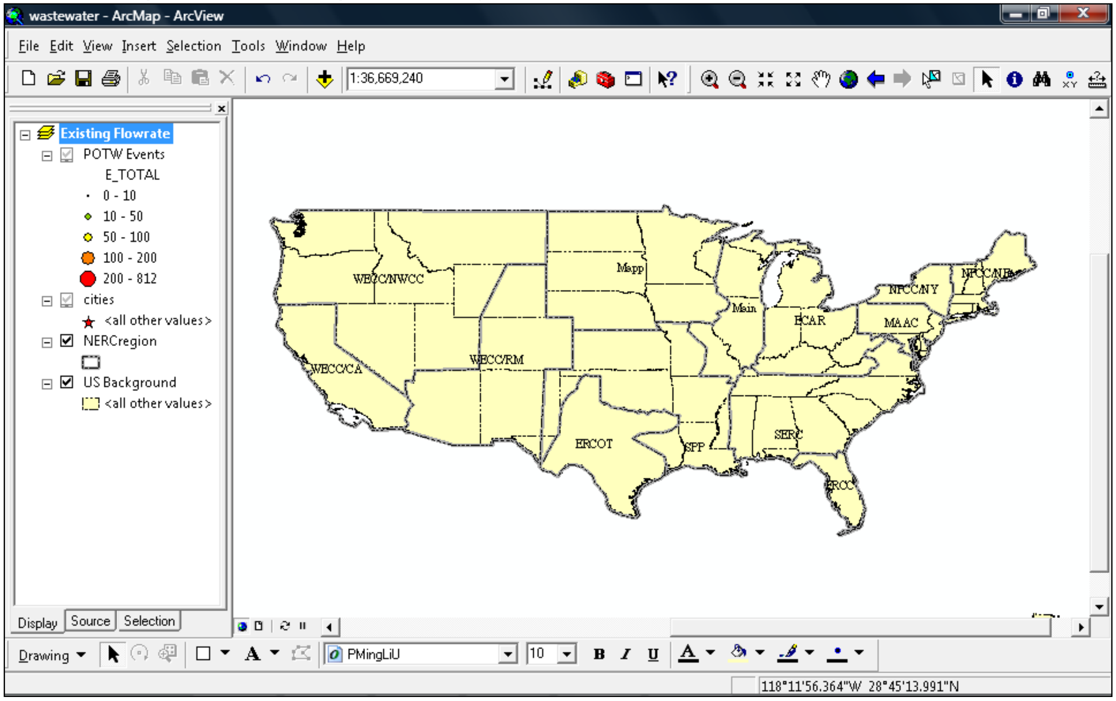
2. Open target files
    a. This can be done by double clicking on the file or opening Wastewater.mxd in ArcView, which is shown below.



Click to open file “Wastewater.mxd”

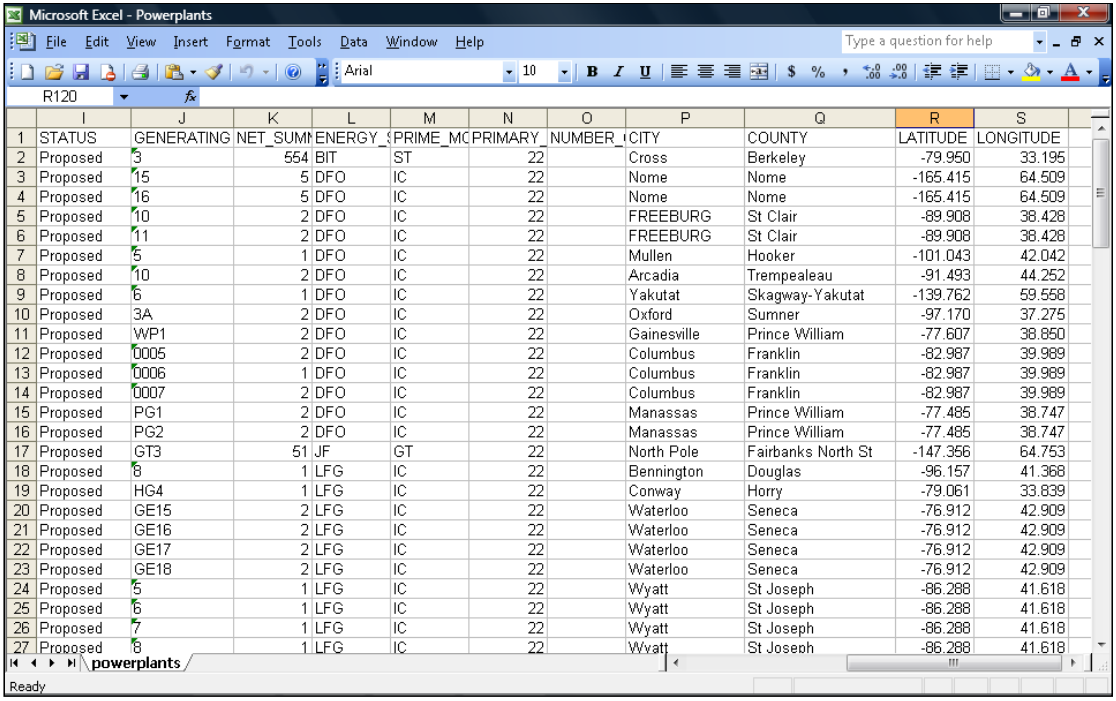
    b. The U.S. base Map will appear on the screen. In addition to state boundaries, North

American Electric Reliability Corporation (NERC) region boundaries are also provided to help with analysis.



3. Add data about desired location for analysis

The information for about the future plant site should be saves it into *.txt, *.xls, or *.dbf formats. Latitude and longitude of the site is needed for analysis. The file Powerplants.xls lists proposed U. S. electric generating units and a new plant can be added to the list.



	I	J	K	L	M	N	O	P	Q	R	S
1	STATUS	GENERATING	NET_SUMI	ENERGY_	PRIME_MO	PRIMARY_	NUMBER_	CITY	COUNTY	LATITUDE	LONGITUDE
2	Proposed	3	554	BIT	ST	22		Cross	Berkeley	-79.950	33.195
3	Proposed	15	5	DFO	IC	22		Nome	Nome	-165.415	64.509
4	Proposed	16	5	DFO	IC	22		Nome	Nome	-165.415	64.509
5	Proposed	10	2	DFO	IC	22		FREEBURG	St Clair	-89.908	38.428
6	Proposed	11	2	DFO	IC	22		FREEBURG	St Clair	-89.908	38.428
7	Proposed	5	1	DFO	IC	22		Mullen	Hooker	-101.043	42.042
8	Proposed	10	2	DFO	IC	22		Arcadia	Trempealeau	-91.493	44.252
9	Proposed	6	1	DFO	IC	22		Yakutat	Skagway-Yakutat	-139.762	59.558
10	Proposed	3A	2	DFO	IC	22		Oxford	Sumner	-97.170	37.275
11	Proposed	WP1	2	DFO	IC	22		Gainesville	Prince William	-77.607	38.850
12	Proposed	0005	2	DFO	IC	22		Columbus	Franklin	-82.987	39.989
13	Proposed	0006	1	DFO	IC	22		Columbus	Franklin	-82.987	39.989
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15	Proposed	PG1	2	DFO	IC	22		Manassas	Prince William	-77.485	38.747
16	Proposed	PG2	2	DFO	IC	22		Manassas	Prince William	-77.485	38.747
17	Proposed	GT3	51	JF	GT	22		North Pole	Fairbanks North St	-147.356	64.753
18	Proposed	8	1	LFG	IC	22		Bennington	Douglas	-96.157	41.368
19	Proposed	HG4	1	LFG	IC	22		Conway	Horry	-79.061	33.839
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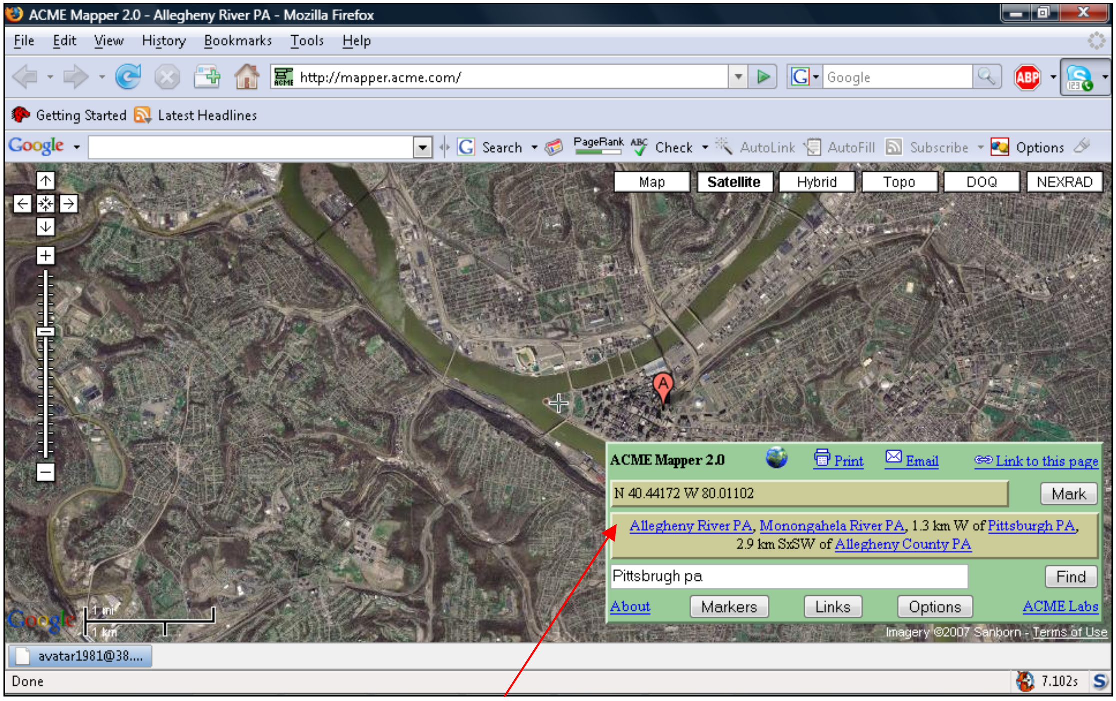
22	Proposed	GE17	2	LFG	IC	22		Waterloo	Seneca	-76.912	42.909
23	Proposed	GE18	2	LFG	IC	22		Waterloo	Seneca	-76.912	42.909
24	Proposed	5	1	LFG	IC	22		Wyatt	St Joseph	-86.288	41.618
25	Proposed	6	1	LFG	IC	22		Wyatt	St Joseph	-86.288	41.618
26	Proposed	7	1	LFG	IC	22		Wyatt	St Joseph	-86.288	41.618
27	Proposed	8	1	LFG	IC	22		Wyatt	St Joseph	-86.288	41.618

a. For example, new 50MW natural gas plant is to be built in Pittsburgh, Pennsylvania. Online GIS locator can be used to find latitude and longitude for a selected location. (ACME Mapper, from http://mapper.acme.com/)



ACME Mapper 2.0

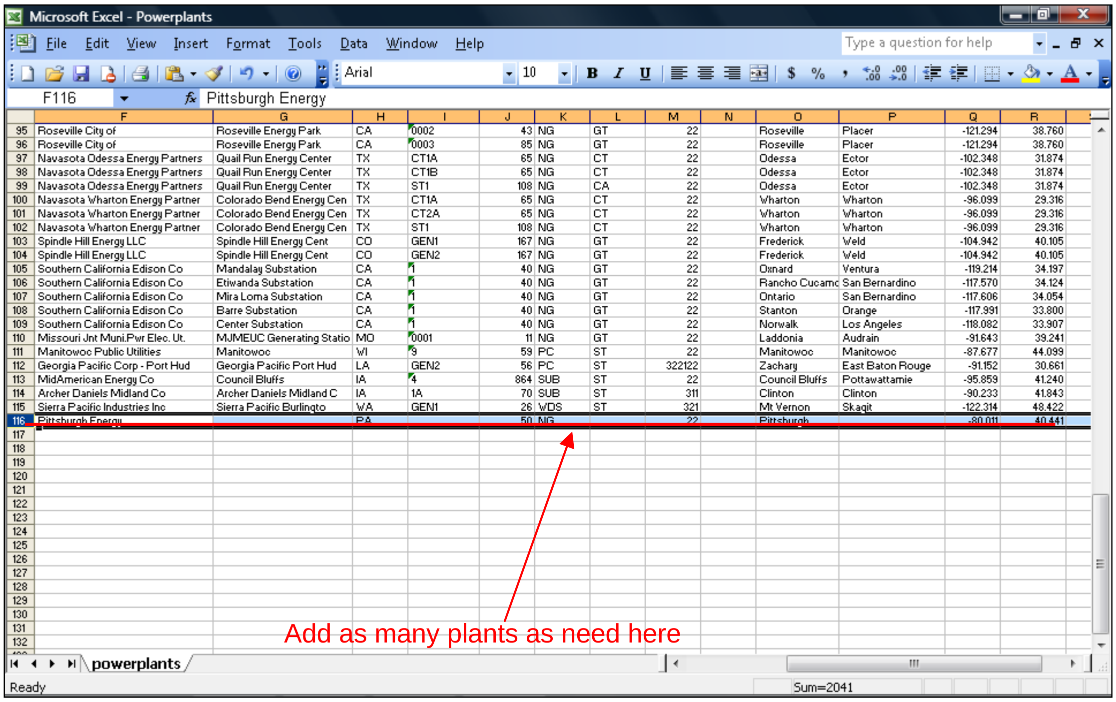
N 40.44172 W 80.01102

Allegheny River PA, Monongahela River PA, 1.3 km W of Pittsburgh PA, 2.9 km SxSW of Allegheny County PA

Pittsbrugh pa

Latitude and longitude data

b. Latitude and longitude for a selected location and other information about the proposed 50MW power plant should be added into Powerplants.xls lists and the file should be saved.



F116 Pittsburgh Energy

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96	Roseville City of	Roseville Energy Park	CA	0003	85	NG	GT	22		Roseville	Placer	-121.294	38.760
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98	Navasota Odessa Energy Partners	Quail Run Energy Center	TX	CT1B	65	NG	CT	22		Odessa	Ector	-102.348	31.874
99	Navasota Odessa Energy Partners	Quail Run Energy Center	TX	ST1	108	NG	CA	22		Odessa	Ector	-102.348	31.874
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102	Navasota Wharton Energy Partner	Colorado Bend Energy Cen	TX	ST1	108	NG	CT	22		Wharton	Wharton	-96.099	29.316
103	Spindle Hill Energy LLC	Spindle Hill Energy Cent	CO	GEN1	167	NG	GT	22		Frederick	Weld	-104.942	40.105
104	Spindle Hill Energy LLC	Spindle Hill Energy Cent	CO	GEN2	167	NG	GT	22		Frederick	Weld	-104.942	40.105
105	Southern California Edison Co	Mandalay Substation	CA	1	40	NG	GT	22		Oxnard	Ventura	-119.214	34.197
106	Southern California Edison Co	Etiwanda Substation	CA	1	40	NG	GT	22		Rancho Cucamo	San Bernardino	-117.570	34.124
107	Southern California Edison Co	Mira Loma Substation	CA	1	40	NG	GT	22		Ontario	San Bernardino	-117.606	34.054
108	Southern California Edison Co	Barre Substation	CA	1	40	NG	GT	22		Stanton	Orange	-117.991	33.800
109	Southern California Edison Co	Center Substation	CA	1	40	NG	GT	22		Norwalk	Los Angeles	-118.082	33.907
110	Missouri Jnt Muni.Pwr Elec. Ut.	MJMEUC Generating Statio	MO	0001	11	NG	GT	22		Laddonia	Audrain	-91.643	39.241
111	Manitowoc Public Utilities	Manitowoc	WI	9	59	PC	ST	22		Manitowoc	Manitowoc	-87.677	44.099
112	Georgia Pacific Corp - Port Hud	Georgia Pacific Port Hud	LA	GEN2	56	PC	ST	322122		Zachary	East Baton Rouge	-91.152	30.661
113	MidAmerican Energy Co	Council Bluffs	IA	4	864	SUB	ST	22		Council Bluffs	Pottawattamie	-95.859	41.240
114	Archer Daniels Midland Co	Archer Daniels Midland C	IA	1A	70	SUB	ST	311		Clinton	Clinton	-90.233	41.843
115	Sierra Pacific Industries Inc	Sierra Pacific Burlingto	WA	GEN1	26	WDS	ST	321		Mt Vernon	Skagit	-122.314	48.422
116	Pittsburgh Energy		PA		50	NG		22		Pittsburgh		-80.011	40.441
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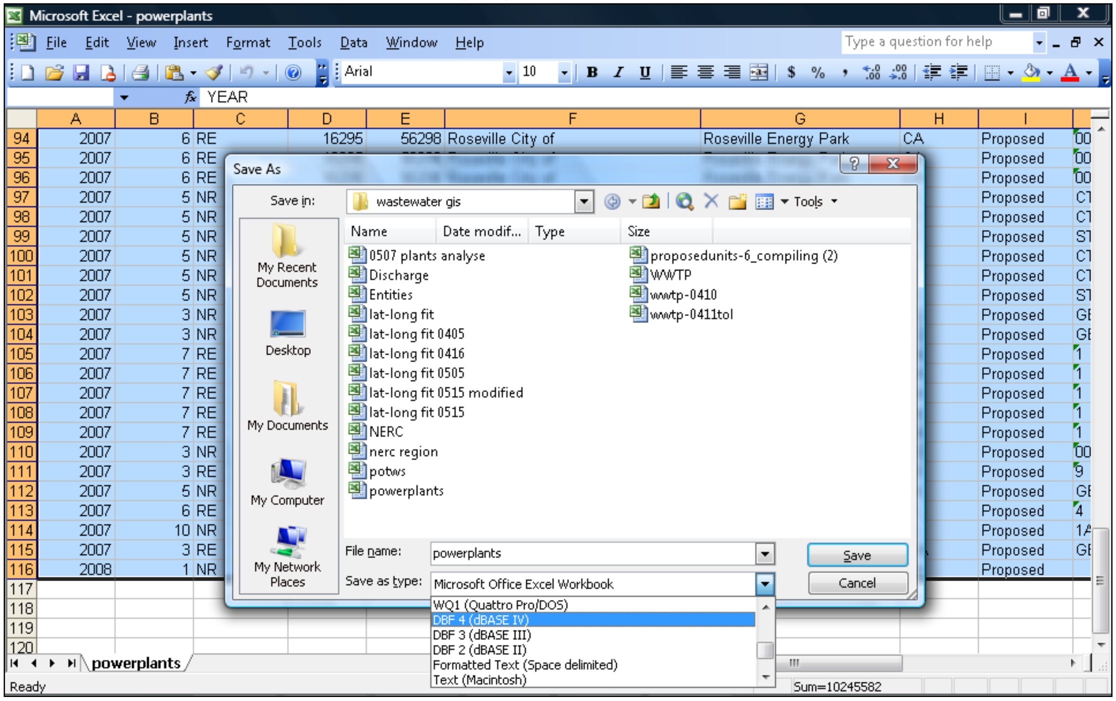
Add as many plants as need here

c. The Excel file should be saved as “Powerplants.dbf” because only database file with .dbf extension can work properly in ArcGIS.



File name: powerplants

Save as type: Microsoft Office Excel Workbook

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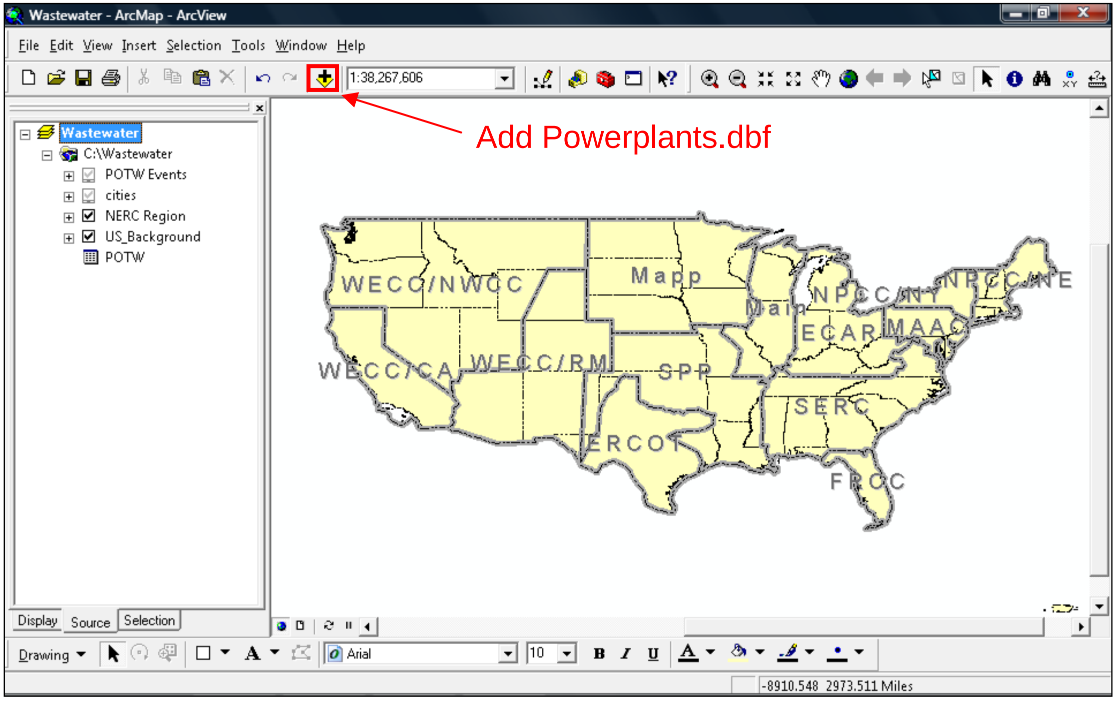
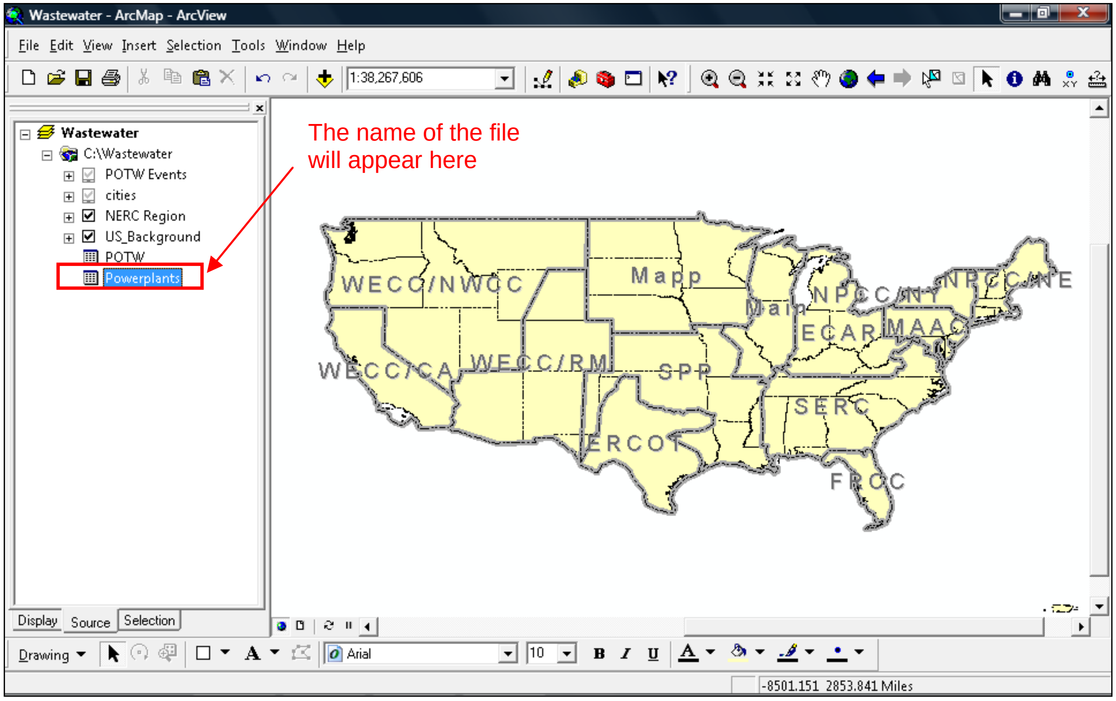
95	2007	6	RE						Proposed
96	2007	6	RE						Proposed
97	2007	5	NR						Proposed
98	2007	5	NR						Proposed
99	2007	5	NR						Proposed
100	2007	5	NR						Proposed
101	2007	5	NR						Proposed
102	2007	5	NR						Proposed
103	2007	3	NR						Proposed
104	2007	3	NR						Proposed
105	2007	7	RE						Proposed
106	2007	7	RE						Proposed
107	2007	7	RE						Proposed
108	2007	7	RE						Proposed
109	2007	7	RE						Proposed
110	2007	3	NR						Proposed
111	2007	3	RE						Proposed
112	2007	5	NR						Proposed
113	2007	6	RE						Proposed
114	2007	10	NR						Proposed
115	2007	3	RE						Proposed
116	2008	1	NR						Proposed

4. The new input file should be linked with ArcGIS so that the location of proposed power plant can be displayed in GIS.
   a. Go back to the ArcGIS program, click on “Add Data” and add the target file (e.g. Powerplants.dbf)

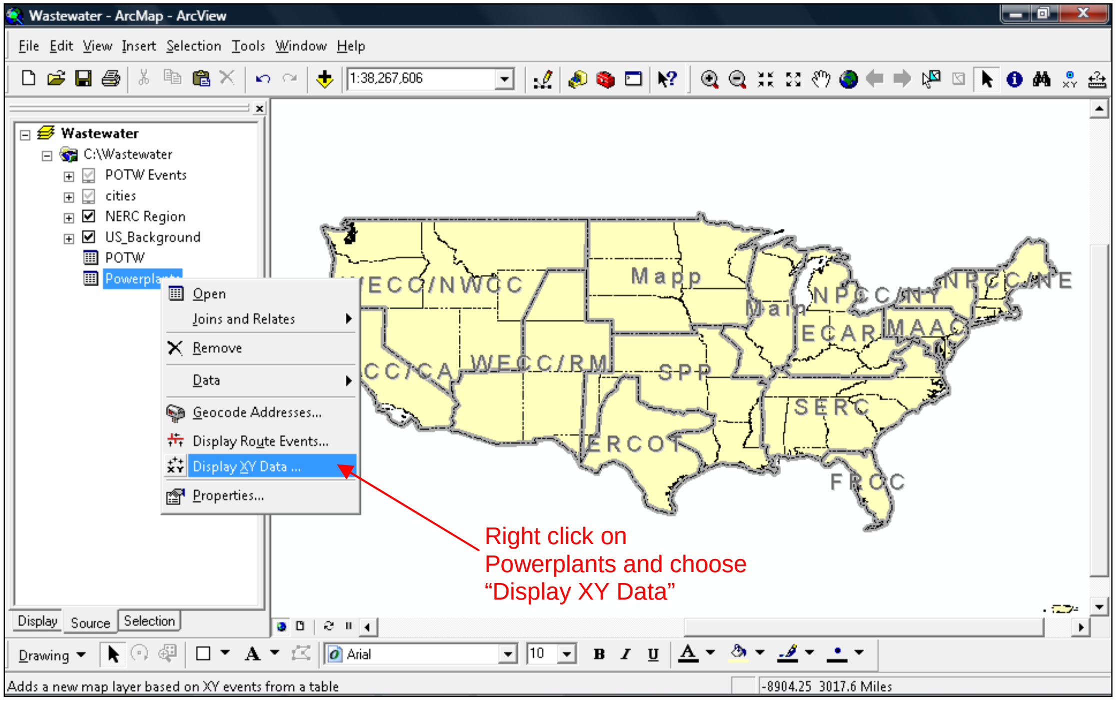


b. The file will be added in the menu on left side. Right clicking on the Powerplants table and selecting “Open Attribution table” can be used to verify that the information was added correctly.



The name of the file will appear here

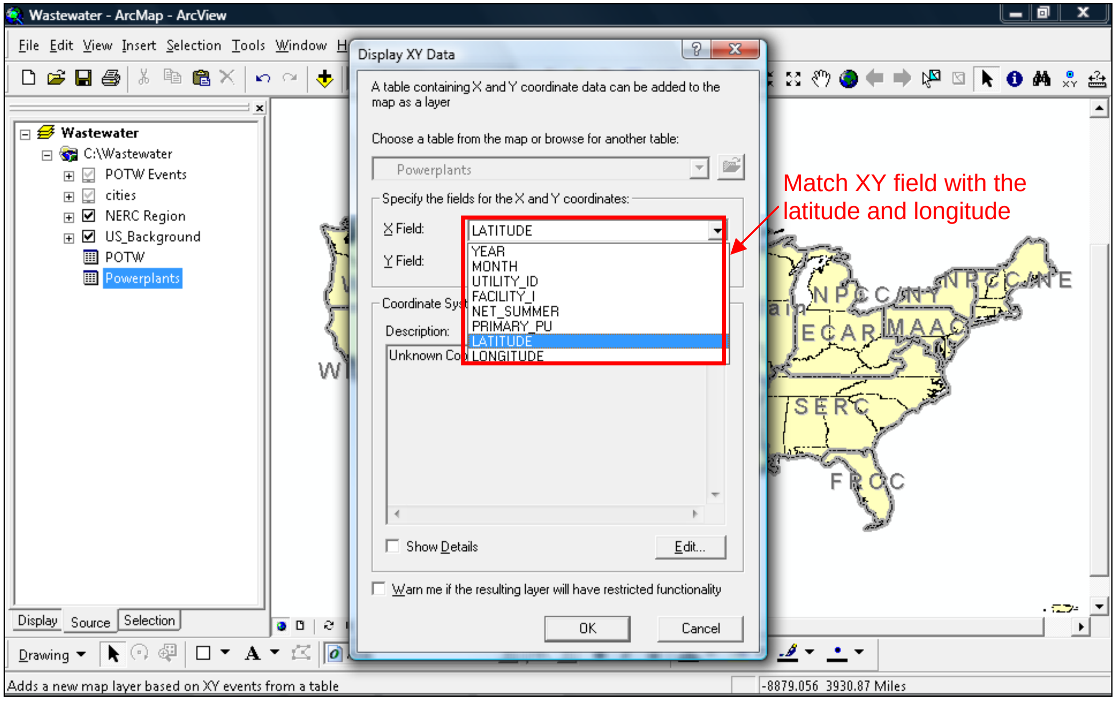
c. In order to display all power plants included in the table, it is required to import their locations (i.e., latitude and longitude) as X-Y data pairs.



Adds a new map layer based on XY events from a table

Right click on Powerplants and choose “Display XY Data”

d. Match X axis field with latitude and Y axis field with longitude.


Display XY Data

A table containing X and Y coordinate data can be added to the map as a layer

Choose a table from the map or browse for another table:

Powerplants

Specify the fields for the X and Y coordinates:

X Field: LATITUDE

Y Field:

YEAR
MONTH
UTILITY_ID
FACILITY_I
NET_SUMMER
PRIMARY_PU
LATITUDE
LONGITUDE

Coordinate Sys

Description:

Unknown Co

☐ Show Details

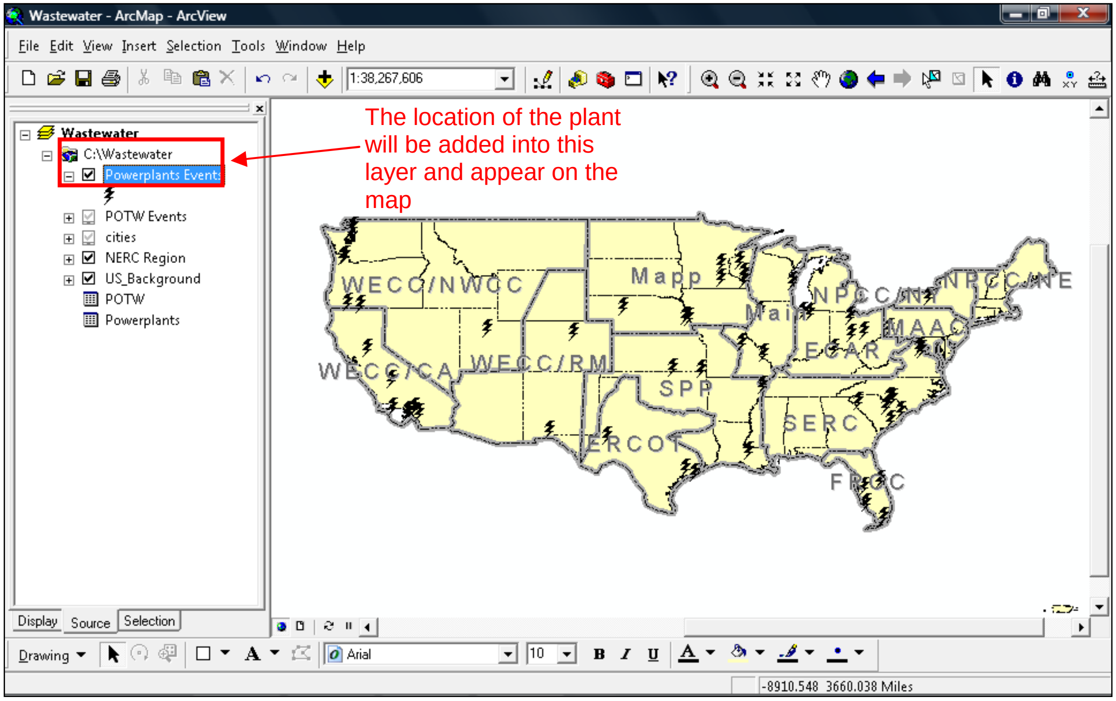
☐ Warn me if the resulting layer will have restricted functionality

Match XY field with the latitude and longitude

Adds a new map layer based on XY events from a table

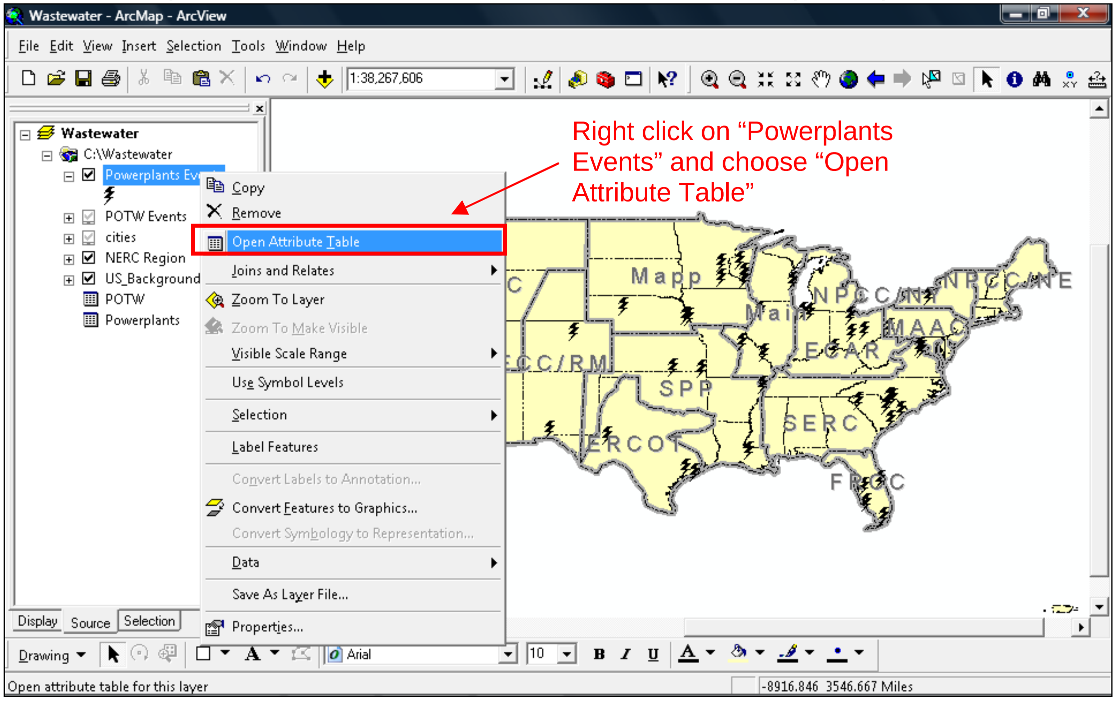
-8879.056 3930.87 Miles

e. Each plant listed in the table will be shown as a symbol (symbols may vary each time) on the map.


The location of the plant will be added into this layer and appear on the map

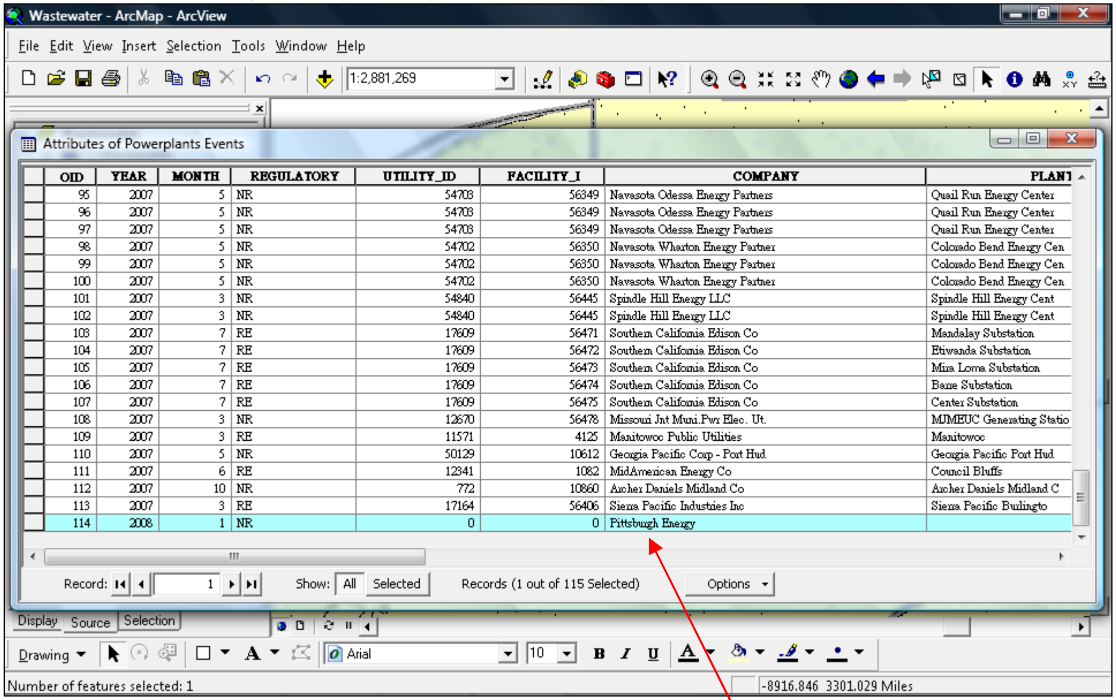
-8910.548 3660.038 Miles

5. Determine the location of existing POTWs in the vicinity of selected power plant.
   a. Open the table that contains information about all power plants.



Right click on “Powerplants Events” and choose “Open Attribute Table”

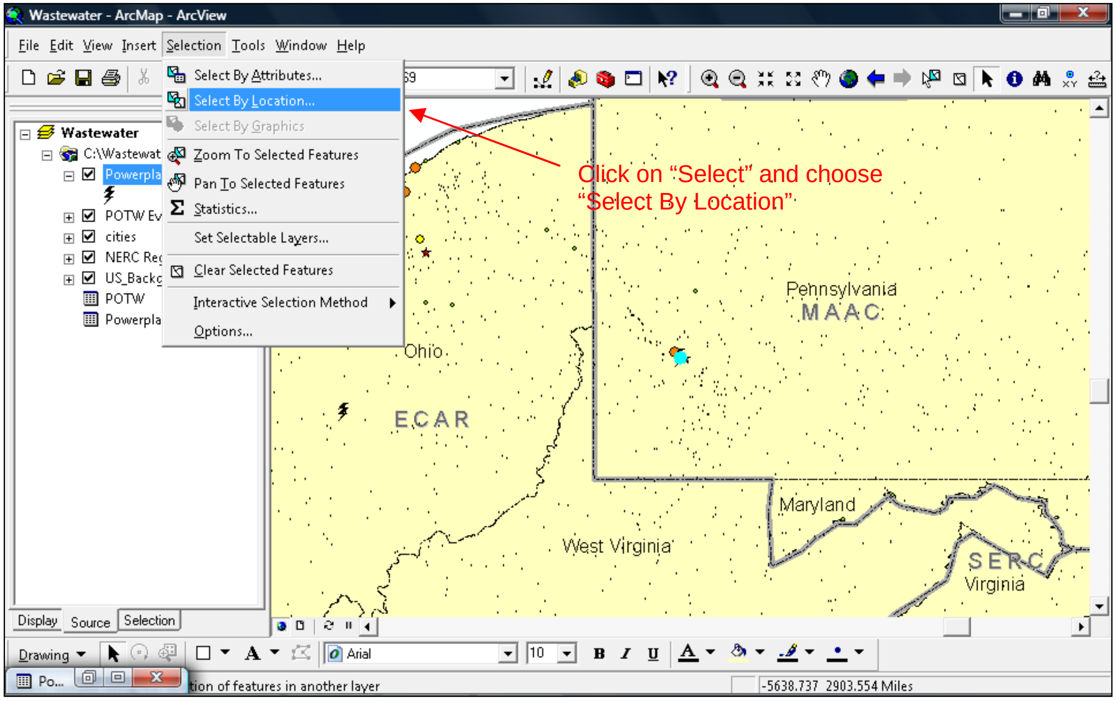
   b. Select specific power plant for analysis.



OID	YEAR	MONTH	REGULATORY	UTILITY_ID	FACILITY_I	COMPANY	PLANT
95	2007	5	NR	54703	56349	Navasota Odessa Energy Partners	Quail Run Energy Center
96	2007	5	NR	54703	56349	Navasota Odessa Energy Partners	Quail Run Energy Center
97	2007	5	NR	54703	56349	Navasota Odessa Energy Partners	Quail Run Energy Center
98	2007	5	NR	54702	56350	Navasota Wharton Energy Partner	Colorado Bend Energy Cen
99	2007	5	NR	54702	56350	Navasota Wharton Energy Partner	Colorado Bend Energy Cen
100	2007	5	NR	54702	56350	Navasota Wharton Energy Partner	Colorado Bend Energy Cen
101	2007	3	NR	54840	56445	Spindle Hill Energy LLC	Spindle Hill Energy Cent
102	2007	3	NR	54840	56445	Spindle Hill Energy LLC	Spindle Hill Energy Cent
103	2007	7	RE	17609	56471	Southern California Edison Co	Mandalay Substation
104	2007	7	RE	17609	56472	Southern California Edison Co	Etiwanda Substation
105	2007	7	RE	17609	56473	Southern California Edison Co	Mira Loma Substation
106	2007	7	RE	17609	56474	Southern California Edison Co	Barre Substation
107	2007	7	RE	17609	56475	Southern California Edison Co	Center Substation
108	2007	3	NR	12670	56478	Missouri Jnt Muni.Pwr Elec. Ut.	MJMEUC Generating Statio
109	2007	3	RE	11571	4125	Manitowoc Public Utilities	Manitowoc
110	2007	5	NR	50129	10612	Georgia Pacific Corp - Port Hud	Georgia Pacific Port Hud
111	2007	6	RE	12341	1082	MidAmerican Energy Co	Council Bluffs
112	2007	10	NR	772	10860	Archer Daniels Midland Co	Archer Daniels Midland C
113	2007	3	RE	17164	56406	Sierra Pacific Industries Inc	Sierra Pacific Burlingto
114	2008	1	NR	0	0	Pittsburgh Energy	

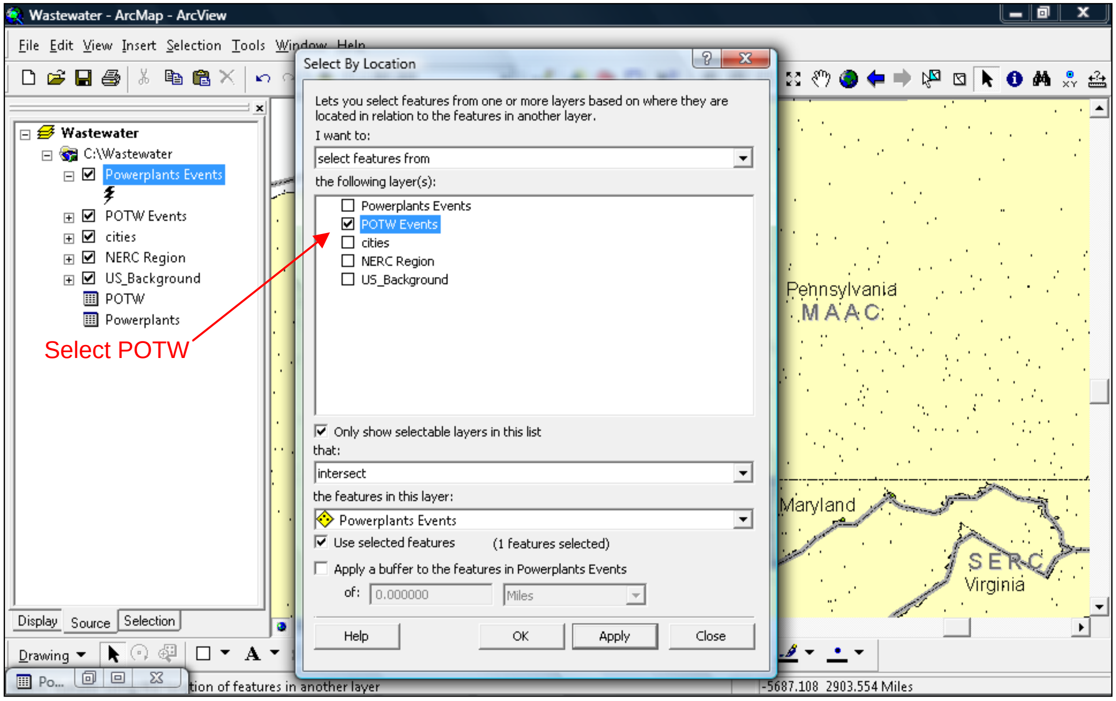
Scroll down the table and double click to select a particular power plant and then minimize the window

c. Extract the location of POTWs near the selected power plant.



Click on “Select” and choose “Select By Location”

d. Select the POTWs as the only object to be included in the analysis.



Select By Location

Lets you select features from one or more layers based on where they are located in relation to the features in another layer.

I want to: select features from

the following layer(s):

☐ Powerplants Events
☑ POTW Events
☐ cities
☐ NERC Region
☐ US_Background

☑ Only show selectable layers in this list

that: intersect

the features in this layer: Powerplants Events

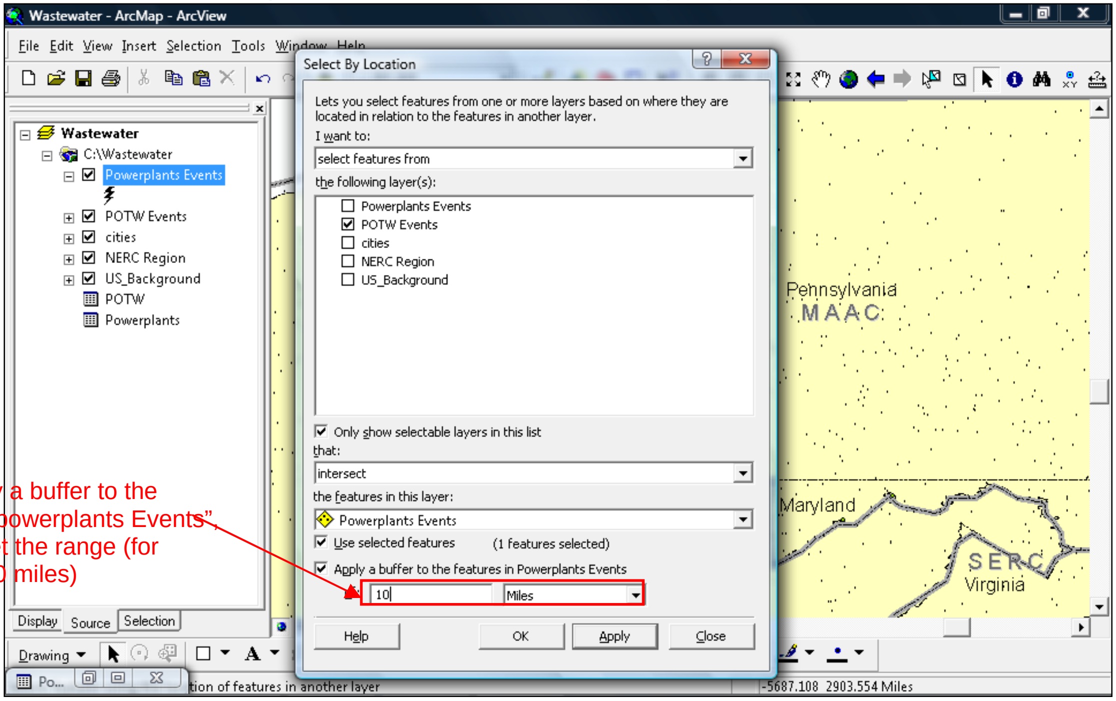
☑ Use selected features (1 features selected)

☐ Apply a buffer to the features in Powerplants Events

of: 0.000000 Miles

Select POTW

e. Set the distance from the power plant of interest for this analysis (i.e., select POTWs within a specified distance from a powerplant).


Wastewater - ArcMap - ArcView

Select By Location

Lets you select features from one or more layers based on where they are located in relation to the features in another layer.

I want to: select features from

the following layer(s):

☐ Powerplants Events
☑ POTW Events
☐ cities
☐ NERC Region
☐ US_Background

☑ Only show selectable layers in this list

that: intersect

the features in this layer: Powerplants Events

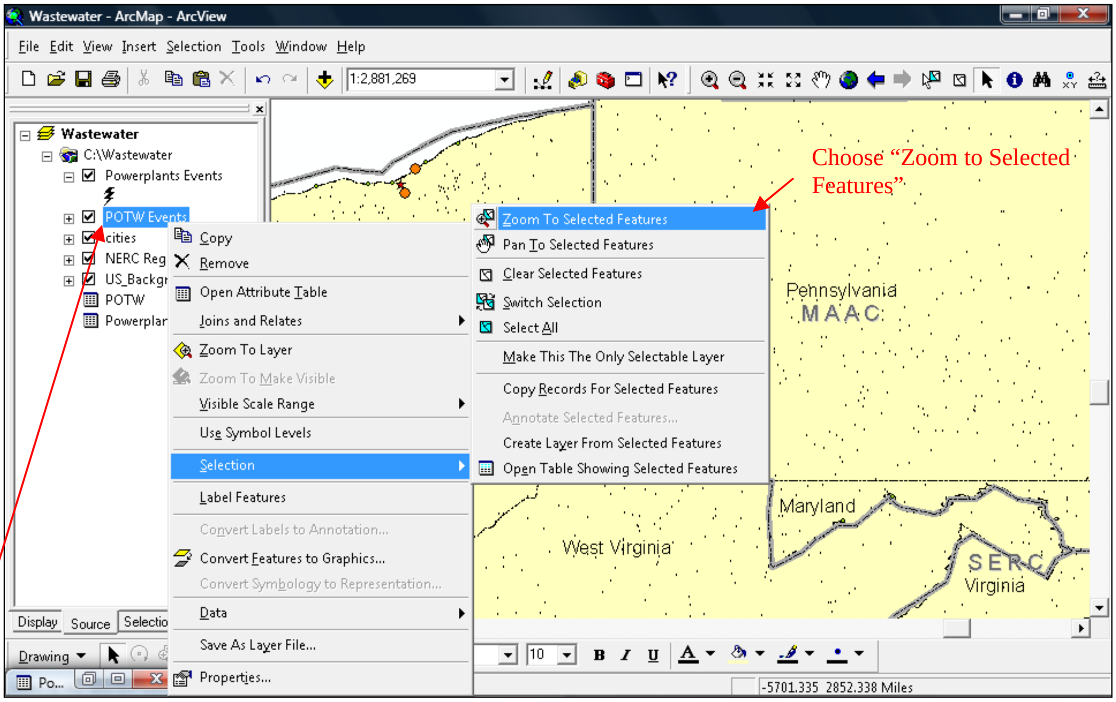
☑ Use selected features (1 features selected)

☑ Apply a buffer to the features in Powerplants Events

10 Miles

Click “Apply a buffer to the features in powerplants Events”, and then set the range (for example, 10 miles)

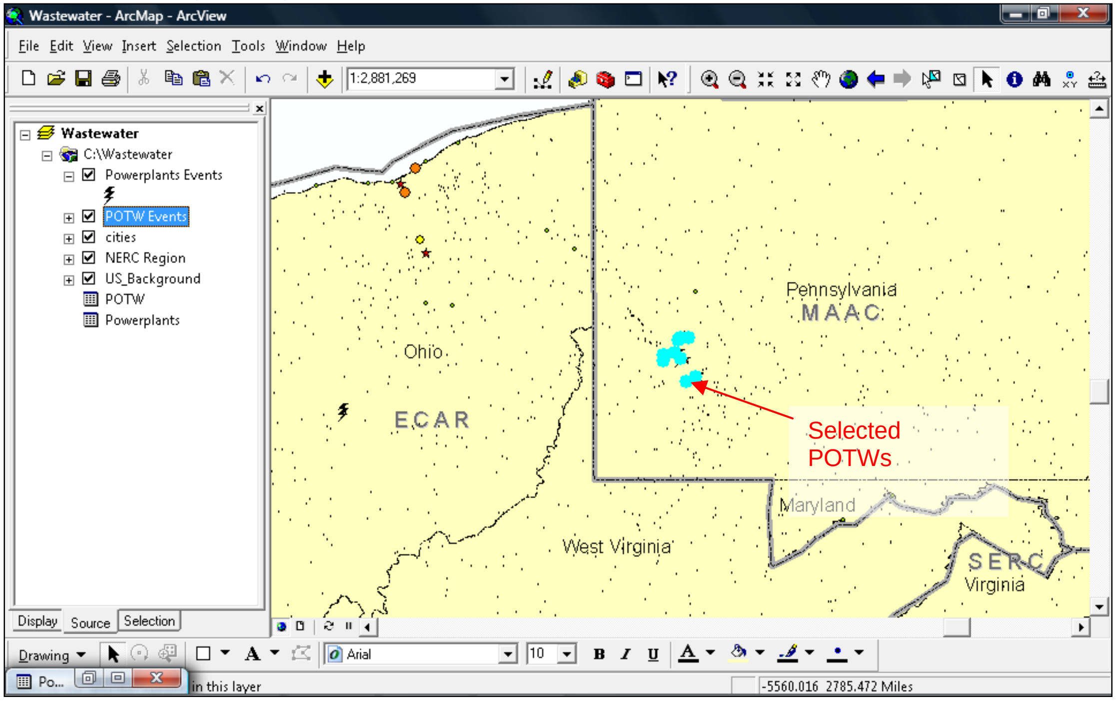
f. In order to display those selected POTWs on the map, right click on the “POTW Events” and choose “Zoom to Selected Features” under “Selection”.



Choose “Zoom to Selected Features”.

Right click on “POTWs”, choose “Selection”, and submenu will pop out.

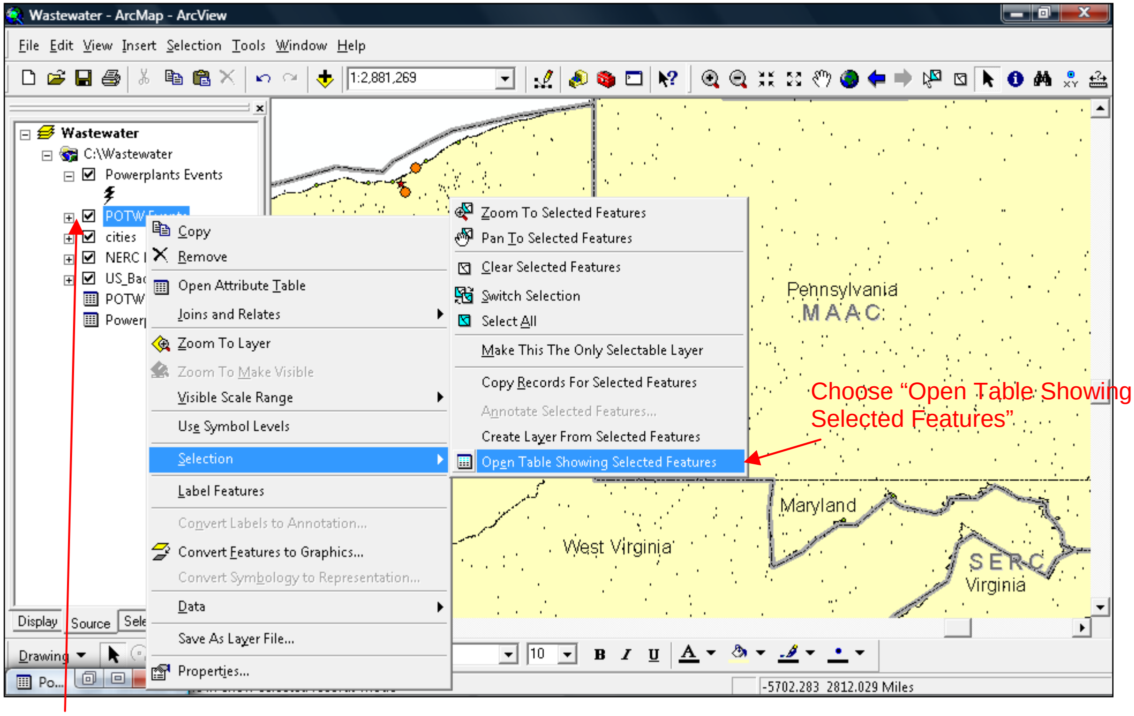
g. The GIS will zoom to the region and display all POTWs with a selected distance from the power plant.



Selected POTWs

6. Extract information about selected POTWs for further analysis.

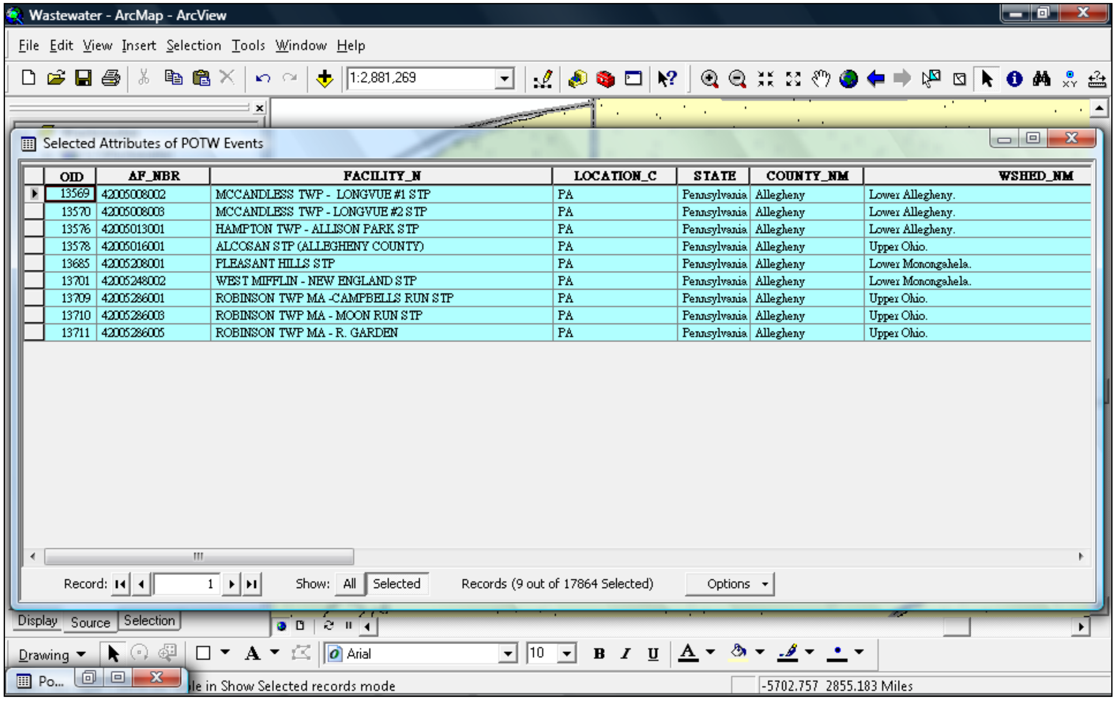
a. Display the available data for POTWs in a given region around the powerplant.



Choose “Open Table Showing Selected Features”.

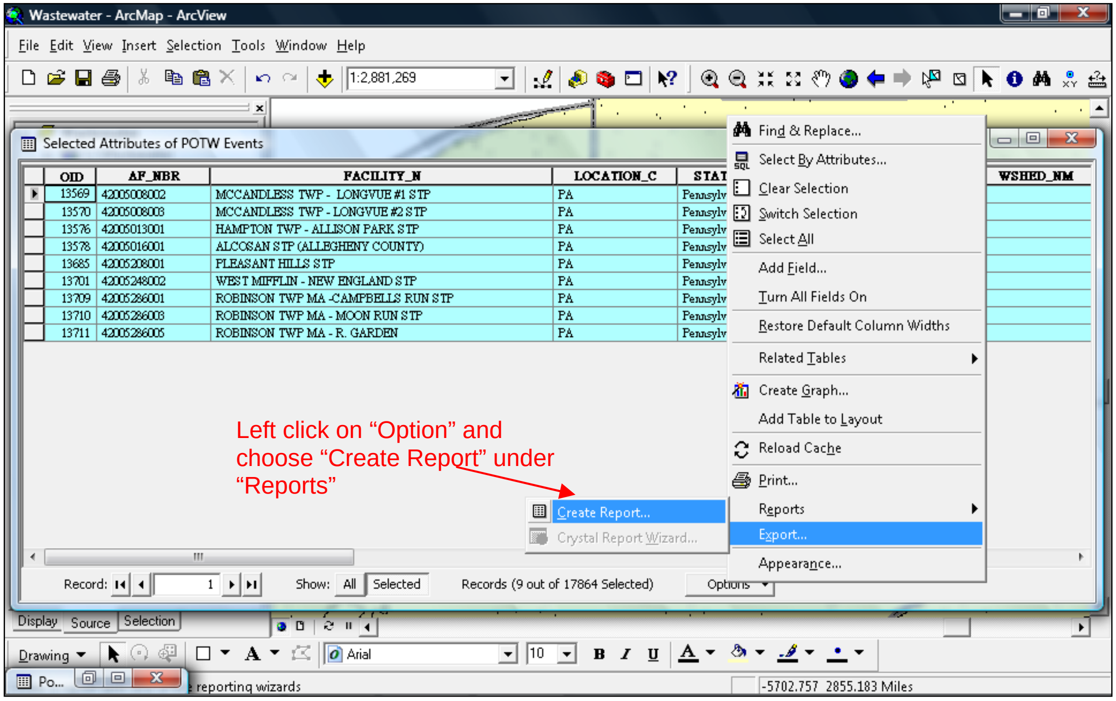
Right click on “POTWs”, choose “Selection”, and submenu will appear

b. List of POTWs and their properties will appear in a separate screen.



OID	AF_NBR	FACILITY_N	LOCATION_C	STATE	COUNTY_NM	WSHED_NM
13569	42005008002	MCCANDLESS TWP - LONGVUE #1 STP	PA	Pennsylvania	Allegheny	Lower Allegheny.
13570	42005008003	MCCANDLESS TWP - LONGVUE #2 STP	PA	Pennsylvania	Allegheny	Lower Allegheny.
13576	42005013001	HAMPTON TWP - ALLISON PARK STP	PA	Pennsylvania	Allegheny	Lower Allegheny.
13578	42005016001	ALCOSAN STP (ALLEGHENY COUNTY)	PA	Pennsylvania	Allegheny	Upper Ohio.
13685	42005208001	PLEASANT HILLS STP	PA	Pennsylvania	Allegheny	Lower Monongahela.
13701	42005248002	WEST MIFFLIN - NEW ENGLAND STP	PA	Pennsylvania	Allegheny	Lower Monongahela.
13709	42005286001	ROBINSON TWP MA -CAMPBELLS RUN STP	PA	Pennsylvania	Allegheny	Upper Ohio.
13710	42005286003	ROBINSON TWP MA - MOON RUN STP	PA	Pennsylvania	Allegheny	Upper Ohio.
13711	42005286005	ROBINSON TWP MA - R. GARDEN	PA	Pennsylvania	Allegheny	Upper Ohio.

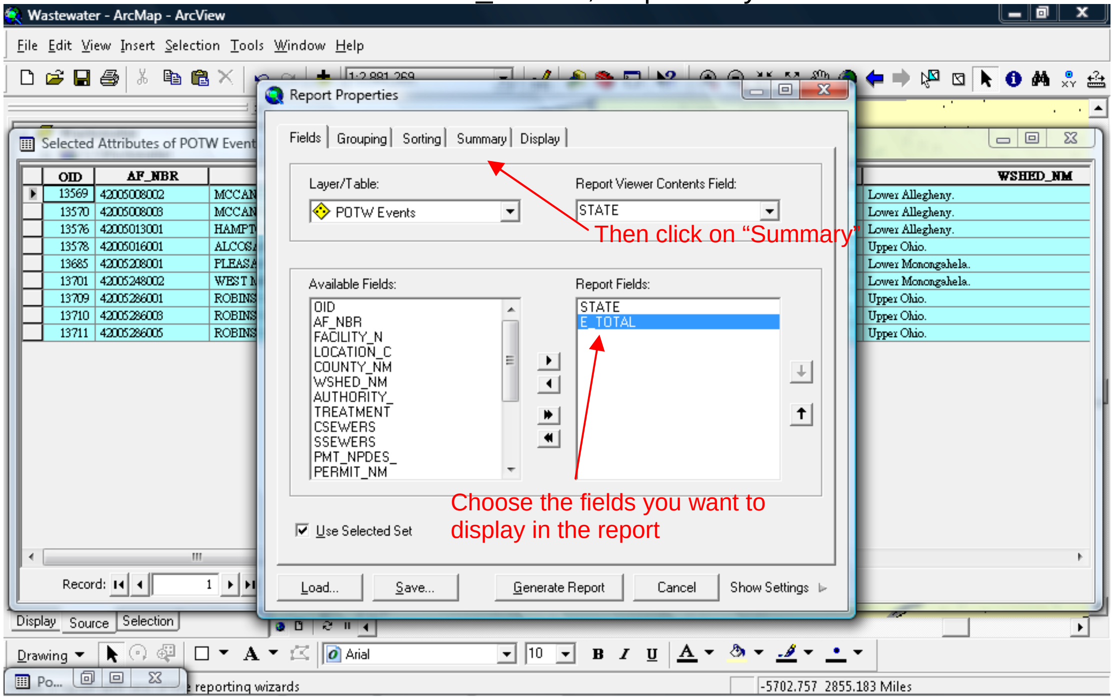
c. Use the build-in tool to create report including total wastewater flow rate.



OID	AF_NBR	FACILITY_N	LOCATION_C	STAT	WSHED_NM
13569	42005008002	MCCANDLESS TWP - LONGVUE #1 STP	PA	Pennsylv	
13570	42005008003	MCCANDLESS TWP - LONGVUE #2 STP	PA	Pennsylv	
13576	42005013001	HAMPTON TWP - ALLISON PARK STP	PA	Pennsylv	
13578	42005016001	ALCOSAN STP (ALLEGHENY COUNTY)	PA	Pennsylv	
13685	42005208001	PLEASANT HILLS STP	PA	Pennsylv	
13701	42005248002	WEST MIFFLIN - NEW ENGLAND STP	PA	Pennsylv	
13709	42005286001	ROBINSON TWP MA -CAMPBELLS RUN STP	PA	Pennsylv	
13710	42005286003	ROBINSON TWP MA - MOON RUN STP	PA	Pennsylv	
13711	42005286005	ROBINSON TWP MA - R. GARDEN	PA	Pennsylv	

Left click on “Option” and choose “Create Report” under “Reports”

d. Select the type of information that should be included in the report. For example, state where POTWs is located and the total existing wastewater flowrate, which are denoted as STATE and E_TOTAL, respectively.



Layer/Table: POTW Events

Report Viewer Contents Field: STATE

Available Fields: OID, AF_NBR, FACILITY_N, LOCATION_C, COUNTY_NM, WSHED_NM, AUTHORITY_, TREATMENT, CSEWERS, SSEWERS, PMT_NPDES_, PERMIT_NM

Report Fields: STATE, E_TOTAL

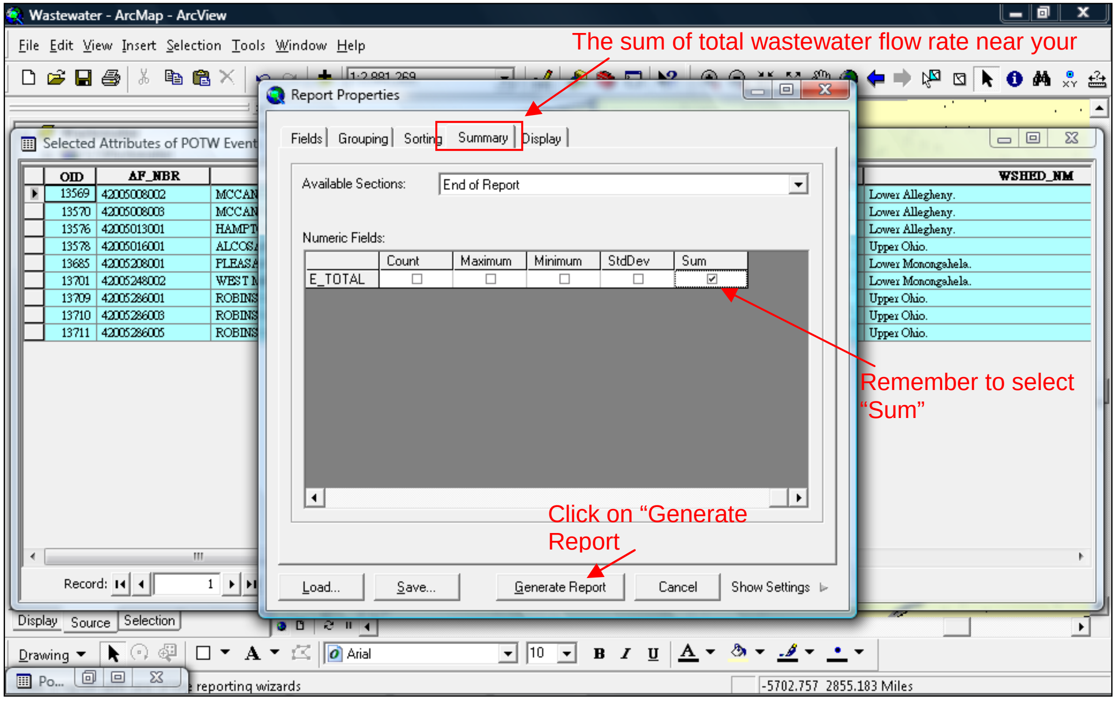
☑ Use Selected Set

OID	AF_NBR	WSHED_NM
13569	42005008002	Lower Allegheny.
13570	42005008003	Lower Allegheny.
13576	42005013001	Lower Allegheny.
13578	42005016001	Upper Ohio.
13685	42005208001	Lower Monongahela.
13701	42005248002	Lower Monongahela.
13709	42005286001	Upper Ohio.
13710	42005286003	Upper Ohio.
13711	42005286005	Upper Ohio.

Then click on “Summary”

Choose the fields you want to display in the report

e. Use summary tool to calculate the total number of POTWs in a selected region, maximum and minimum wastewater flow rate, standard deviation, and total flowrate for all selected POTWs. After selecting desired features to be reported, click on “Generate Report”.



Available Sections: End of Report

Numeric Fields:

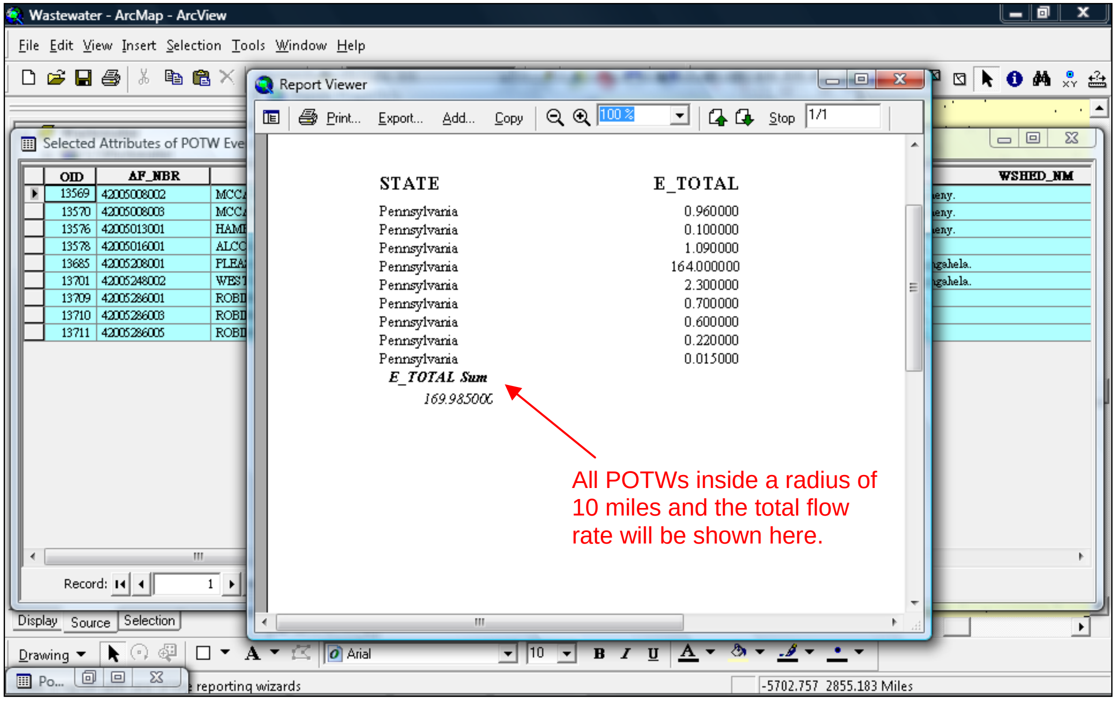
	Count	Maximum	Minimum	StdDev	Sum
E_TOTAL	☐	☐	☐	☐	☑

The sum of total wastewater flow rate near your

Remember to select “Sum”

Click on “Generate Report

f. A report is displayed on the screen.



	OID	AF_NBR	
▶	13569	42005008002	MCC
	13570	42005008003	MCC
	13576	42005013001	HAM
	13578	42005016001	ALC
	13685	42005208001	PLEA
	13701	42005248002	WES
	13709	42005286001	ROB
	13710	42005286003	ROB
	13711	42005286005	ROB

STATE	E_TOTAL
Pennsylvania	0.960000
Pennsylvania	0.100000
Pennsylvania	1.090000
Pennsylvania	164.000000
Pennsylvania	2.300000
Pennsylvania	0.700000
Pennsylvania	0.600000
Pennsylvania	0.220000
Pennsylvania	0.015000

E_TOTAL Sum

169.98500

All POTWs inside a radius of 10 miles and the total flow rate will be shown here.

APPENDIX B: Details of Regulations/Guidelines Cited in This Report

ARIZONA

Regulation/Guidelines/Policy	
Water Reuse	**** AAC, R18-9-704*** *G. Prohibited activities.* *c. Direct reuse for evaporative cooling or misting.* **** AAC, R18-9-701*** *1."Direct reuse" means the beneficial use of reclaimed water for a purpose allowed by this Article. The following is not a direct reuse of reclaimed water:* *c. The use of industrial wastewater or reclaimed water, or both, in a workplace subject to a federal program that protects workers from workplace exposures.* **** AAC, R18-9-602*** ***F. The following requirements for minimum separation distance apply. A person shall:*** *1. Locate a pipeline conveyance no closer than 50 feet from a drinking water well unless the pipeline conveyance is constructed as specified under subsection (F)(3);* *2. Locate a pipeline conveyance no closer than two feet vertically nor six feet horizontally from a potable water pipeline unless the pipeline conveyance is constructed as specified under subsection (F)(3);* *3. Construct a pipeline conveyance that does not meet the minimum separation distances specified in subsections (F)(1) and (F)(2) by encasing the pipeline conveyance in at least six inches of concrete or using mechanical joint ductile iron pipe or other materials of equivalent or greater tensile and compressive strength at least 10 feet beyond any point on the pipeline conveyance within the specified minimum separation distance; and* *4. If a reclaimed water system is supplemented with water from a potable water system, separate the potable water system from the pipeline conveyance by an air gap.*
Water Discharge	**** AAC, R18-9-701*** *1."Direct reuse" means the beneficial use of reclaimed water for a purpose allowed by this Article. The following is not a direct reuse of reclaimed water:* *a. The use of water subsequent to its discharge under the conditions of a National Pollutant Discharge Elimination System permit;* **** AAC, R18-9-702*** *G. Exclusions. The following discharges do not require an AZPDES permit:* *2. The introduction of sewage, industrial wastes, or other pollutants into POTWs by indirect dischargers. Plans or agreements to switch to this method of disposal in the future do not relieve dischargers of the obligation to have and comply with a permit until all discharges of pollutants to navigable water are eliminated. This exclusion does not apply to the introduction of pollutants to privately owned treatment works or to other discharges through a pipe, sewer, or other conveyance owned by the state, a municipality, or other party not leading to treatment works;* *6. Discharges into a privately owned treatment works, except as the Director requires under 40 CFR 122.44(m), which is incorporated by reference in R18-9-A905(A)(3)(d)*

CALIFORNIA

Regulation/Guidelines/Policy	
Water Reuse	*** State Water Resources Control Board, Resolution No. 75-58** (Water Quality Control Policy on the Use and Disposal of Inland Waters Used for Powerplant Cooling) *It is the Board's position that from a water quantity and quality standpoint the source of powerplant cooling water should come from the following sources in this order of priority depending on site specifics such as environmental, technical and economic feasibility consideration: (1) wastewater being discharged to the ocean, (2) ocean, (3) brackish water from natural sources or irrigation return flow, (4) inland wastewaters of low TDS, and (5) other inland waters.* *** Warren-Alquist Act, Section 25602** (Public Resources Code, Section 25602) *The commission shall carry out technical assessment studies on all forms of energy and energy-related problems …* *(d) Expanded use of wastewater as cooling water and other advances in powerplant cooling.* *** Water Code, Section 462** (Action by the Department of Water Resources) *The department shall conduct studies and investigations on the availability and quality of wastewater and the uses of reclaimed water for beneficial purposes, including, but not limited to, groundwater recharge, municipal and industrial use, irrigation use, and cooling for thermal electric powerplants.* *** 22CCR60306** (California Code of Regulations, Title 22, Division 4, Chapter 1, Article 3, Section 306: Use of recycled water for cooling) *(a) Recycled water used for industrial or commercial cooling or air conditioning that involves the use of a cooling tower, evaporative condenser, spraying or any mechanism that creates a mist shall be a disinfected tertiary recycled water.* *(b) Use of recycled water for industrial or commercial cooling or air conditioning that does not involve the use of a cooling tower, evaporative condenser, spraying, or any mechanism that creates a mist shall be at least disinfected secondary-23 recycled water.* *Note:* *Disinfected tertiary recycled water: defined in 22CCR60301.225* *Disinfected secondary-23 recycled water: defined in 22CCR60301.230*
Water Discharge	*** State Water Resources Control Board, Resolution No. 75-58** (Water Quality Control Policy on the Use and Disposal of Inland Waters Used for Powerplant Cooling) • *The discharge to land disposal sites of blowdown waters from inland powerplant cooling facilities shall be prohibited except to salt sinks or to lined facilities approved by the Regional and State Boards for the reception of such wastes.* • *The discharge of wastewaters from once-through inland powerplant cooling facilities shall be prohibited unless the discharger can show that such a practice will maintain the existing water quality and aquatic environment of the State's water resources.*

	• *The Regional Boards may grant exceptions to these discharge prohibitions on a case-by-case basis in accordance with exception procedures included in the “Water Quality Control Plan for Control of Temperature In the Coastal and Interstate Waters and Enclosed Bays and Estuaries of California.”*
Air Emission	***22CCR60306** (Use of recycled water for cooling) *(c)Whenever a cooling system, using recycled water in conjunction with an air conditioning facility, utilizes a cooling tower or otherwise creates a mist that could come into contact with employees or members of the public, the cooling system shall comply with the following:* *(1) A drift eliminator shall be used whenever the cooling system is in operation.* *(2) A chlorine, or other, biocide shall be used to treat the cooling system recirculating water to minimize the growth of Legionella and other microorganisms.* • **17CCR93103** (Regulation for chromate treated cooling towers) *… not add any hexavalent chromium-containing compounds to the cooling tower circulating water, and keep the hexavalent chromium concentration in the cooling tower circulating water less than 0.15 milligrams hexavalent chromium per liter of circulating water, …*

FLORIDA

Regulation/Guidelines/Policy	
Water Reuse	*** FAC 62-610-668** (Florida Administrative Code, Chapter 62, Section 610-668: Cooling Water Applications) *(1) Once-through cooling.* *(a) Reclaimed water may be used for once-through cooling.* *(b) Setback distances shall be as established in Rule 62-610.662, F.A.C.* *(c) Reclaimed water, upon flowing out of the once-through, non-contact, cooling system, that is returned to the domestic wastewater facilities for additional treatment or disposal or reuse, shall be defined to be a “domestic wastewater.” This definition is made solely for the purposes of classifying wastewater treatment, reuse, and effluent disposal facilities associated with the domestic wastewater facilities. This definition shall apply only if the sole change to the quality of the reclaimed water during the once-through, non-contact, cooling process is a temperature increase, and conditioning chemicals, other than chlorine and other chemicals accepted by the Department, have not been added to the reclaimed water.* *(d) Reclaimed water which has not been disinfected may be used for once-through cooling purposes at industrial facilities if the following conditions are met:* *1. The reclaimed water has received at least secondary treatment as defined in subparagraph 62-600.420(1)(b)2., F.A.C.* *2. The reclaimed water is conveyed and used in closed systems which are not open to the atmosphere.* *3. The reclaimed water is returned to the domestic wastewater treatment facility.* *(e) Water used for once-through cooling under the provisions of paragraph 62-610.668(1)(d), F.A.C., shall be considered “reclaimed water” and the use of this water shall be considered “reuse.”* *(2) Open cooling towers.* *(a) Reclaimed water may be used in open cooling towers, if the requirements in paragraphs 62-610.668(2)(b), (c), or (d), F.A.C., are met.* *(b) All requirements of Part III of Chapter 62-610, F.A.C., including minimum system size requirements, shall be met.* *(c) As an alternative to the requirements in paragraph 62-610.668(2)(b), F.A.C., all of the following requirements shall apply:* *1. Preapplication waste treatment shall result in reclaimed water that meets secondary treatment and basic disinfection.* *2. A 300-foot setback distance shall be provided from the cooling tower that receives reclaimed water to the site property line.* *3. The cooling tower shall be designed and operated to minimize aerosol drift to areas beyond the site property line that are accessible to the public.* *4. The cooling tower shall be designed, operated, and maintained utilizing best engineering practices to control biological growth.* *(d) As an alternative to the requirements in paragraph 62-610.668(2)(b), F.A.C., all of the following requirements shall be met in the facility’s industrial wastewater permit:* *1. The high-level disinfection requirements of subsection 62-600.440(5), F.A.C.* *2. The filtration requirements of subsection 62-610.460(3), F.A.C.*

	3. The continuous monitoring requirements of subsection 62-610.463(2), F.A.C. *4. In lieu of the operation, staffing, and reliability provisions in Rule 62-610.462, F.A.C., operation, maintenance, staffing and reliability requirements shall be addressed in the facility's industrial wastewater permit in accordance with applicable industrial wastewater rules.* *5. The cooling tower shall be designed, operated, and maintained utilizing best engineering practices to control biological growth.*
Water Discharge	**FAC 62-302-520** (Thermal Surface Water Criteria) **FAC 62-660.400** (Effluent limitations)
Air Emission	*** FAC 62-610-668(2)(c)3** *The cooling tower shall be designed and operated to minimize aerosol drift to areas beyond the site property line that are accessible to the public.*

HAWAII

Regulation/Guidelines/Policy	
Water Reuse	*** Guidelines for the Treatment and Use of Recycled Water, III, B** (Uses For R-2 Water) *2. R-2 Water is suitable for, from a public health standpoint, the purposes cited under R-3 Water in these guidelines and shall be restricted to the following purposes:* *d. Use in an industrial process that does not generate mist, does not involve facial contact with recycled water, and does not involve incorporation into food or drink for humans or contact with anything that will contact food or drink for humans;* *** Guidelines for the Treatment and Use of Recycled Water, III, C** (Uses For R-1 Water) *2. R-1 Water is suitable for, from a public health standpoint, the purposes cited under R-2 Water, and R-3 Water in these guidelines and shall be restricted to the following purposes:* *j. Industrial cooling in a system that does not have a cooling tower, evaporative condenser, or other feature that emits vapor or droplets to the open atmosphere or to air to be passed into a building or other enclosure occupied by person;* *k. Supply for addition to a cooling system or air conditioning system with a cooling tower, evaporative condenser, or other feature that emits vapor or droplets to the open atmosphere or to air to be passed into a building or other enclosure occupied by a person, when all of the following shall occur:* *(1) A high efficiency drift reducer is used and the system is maintained to avoid greater rate of generation of drift than that with which a high efficiency drift reducer is associated;* *(2) A continuous biocide residual, sufficient to prevent bacterial population from exceeding 10,000 per milliliter, is maintained in circulating water; and* *(3) The system is inspected by an operator, capable of determining compliance with this subdivision, at least once per day;* *l. In the absence of one or more of the three conditions in paragraph "k" above, it is suitable for addition to such a cooling or air conditioning system when the purveyor of R-2 Water uses has demonstrated to the satisfaction of DOH that the probability of intestinal infection with virus will not exceed 1 in 10,000 under the specific conditions of use and that growth of Legionella will be controlled to avoid a concentration that could pose a significant hazard to health;* *Note:* *R-1 Water: Significant reduction in viral and bacterial pathogens* *R-2 Water: Disinfected secondary-23 recycled water, which means secondary treatment with disinfection to achieve a median fecal coliform limit of 23 per 100 ml based on the last seven days for which analyses have been completed* *R-3 Water: Undisinfected secondary recycled water*
Air Emission	*** Guidelines for the Treatment and Use of Recycled Water, III, C** (Uses For R-1 Water) *2, k, (1), (2), and (3)*

MARYLAND

Regulation/Guidelines/Policy	
Water Discharge	*COMAR 26.08.03.06* *A. Biocide Residual Levels. Biocide residual levels shall be controlled in the effluents discharged to all surface waters of this State.* *C. All Other Water Use Designations. A person may not discharge any chlorine or chlorine products into Use I, I-P, II, IV, or IV-P waters of this State in excess of the limits set forth below:* *(1) For steam electric power stations using once-through cooling water from plants with total rated generating capacity of 25 or more megawatts, the limit shall be 0.2 milligram/liter daily maximum of total residual chlorine as determined using the amperometric titration method;* *(2) For steam electric power stations using once-through cooling water from plants with total rated generating capacity of less than 25 megawatts, the limit shall be 0.2 milligram/liter monthly average and 0.5 milligram/liter daily maximum of free available chlorine as determined using the amperometric titration method;* *(3) The limit for cooling tower blowdown from steam electric generating plants shall be 0.2 milligram/liter monthly average and 0.5 milligram/liter daily maximum of free available chlorine as determined using the amperometric titration method;* *(4) For any other discharge category for which the EPA has published effluent limitation guidelines, the limit shall be the limits specified in the published guidelines;*

NEW JERSEY

Regulation/Guidelines/Policy	
Water Reuse	*** Reclaimed Water for Beneficial Reuse, V, A** (Minimum Effluent Treatment Requirements for RWBR) *4. Type IV RWBR – Industrial Systems, Maintenance Operations and Construction Industrial RWBR involves the use of reclaimed water in industrial applications such as cooling water and/or washing operations. The uniqueness of each industrial reuse application makes it impossible to establish specific treatment standards for this general category of reuse. Prior to implementation, all industrial reuse systems require a case-by-case review by the Department. Some applications, such as the reuse of effluent for non-contact cooling water, may require very little, if any changes to the level of treatment the wastewater is already receiving at the wastewater treatment plant.* *** Reclaimed Water for Beneficial Reuse, Appendix A** (Effluent Reuse Treatment Guideline Table) • *Types of Reuse:* *RWBR Industrial Systems* *Includes closed loop system. For example, sewer jetting, non-contact cooling water, boiler makeup water.* • *Treatment & RWBR Quality:* *Permit levels must be met.* • *RWBR Monitoring:* *Submission of Standard Operations Procedure that ensures proper material handling.* *User/Supplier Agreement* *Annual usage report* • *Comments:* *Worker contact with RWBR shall be limited to individuals who have received specialized training to deal with the RWBR systems.* *Additional requirements dependant on application.* *Note:* *Type I RWBR: Public Access Systems* *Type II RWBR: Restricted Access and Non Edible Crop Systems* *Type III RWBR: Agricultural Edible Crop Systems* *Type IV RWBR: Industrial Systems, Maintenance Operations and Construction*

NORTH CAROLINA

	Regulation/Guidelines/Policy
Water Reuse	*** 15A NCAC 02T.0906** (North Carolina Administrative Code, Chapter 15A, Subchapter 02T, Section 0906: Reclaimed Water Effluent Standards) *(a) The reclaimed water treatment process shall be documented to produce a tertiary quality effluent (filtered or equivalent) prior to storage, distribution, or irrigation that meets the parameter limits listed below:* *(1) monthly average BOD_5 of less than or equal to 10 mg/l and a daily maximum BOD_5 of less than or equal to 15 mg/l;* *(2) monthly average TSS of less than or equal to 5 mg/l and a daily maximum TSS of less than or equal to 10 mg/l;* *(3) monthly average NH_3 of less than or equal to 4 mg/l and a daily maximum NH_3 of less than or equal to 6 mg/l;* *(4) monthly geometric mean fecal coliform level of less than or equal to 14/100 ml and a daily maximum fecal coliform of less than or equal to 25/100 ml; and* *(5) Maximum turbidity of 10 NTUs.* *(b) Reclaimed water produced by industrial facilities shall not be required to meet the above criteria if the reclaimed water is used in the industry's process and the area of use has no public access.* *** 15A NCAC 02T.0910** (Reclaimed Water Utilization) *(b) Reclaimed water used for purposes such as industrial process water or cooling water, aesthetic purposes such as decorative ponds or fountains, fire fighting or extinguishing, dust control, soil compaction for construction purposes, street sweeping (not street washing), and individual vehicle washing for personal purposes shall meet the criteria below:* *(1) Notification shall be provided by the permittee or its representative to inform the public or employees of the use of reclaimed water (Non Potable Water) and that the reclaimed water is not intended for drinking.* *(4) The generator of the reclaimed water shall develop and maintain a program of education and approval for all reclaimed water users.* *(5) The generator of the reclaimed water shall develop and maintain a program of record keeping for distribution of reclaimed water.* *(6) The generator of the reclaimed water shall develop and maintain a program of routine review and inspection of reclaimed water users.*
Water Discharge	**15A NCAC 02B.0208** (Standards For Toxic Substances and Temperature) **15 A NCAC 02B.0211** (Fresh Surface Water Quality Standards For Class C Waters) **Thermal (Temperature) Variances to North Carolina Water Quality Standards** (Effective April 23, 2006. Information detailing variances from water quality standards for dischargers to North Carolina surface waters)

OREGON

Regulation/Guidelines/Policy	
Water Reuse	**** OAR 340-055*** *(Oregon Administrative Rules, Title 34, Division 55 Section 0012: Regulations Pertaining to the Use of Reclaimed Water (Treated Effluent) from Sewage Treatment Plants)* *"(E) Industrial, commercial, or construction uses limited to: industrial cooling, rock crushing, aggregate washing, mixing concrete, dust control, nonstructural fire fighting using aircraft, street sweeping, or sanitary sewer flushing;"* *(G) Any beneficial purpose authorized in writing by the department pursuant to OAR 340-055-0016(6).* *(b) Treatment. Class C recycled water must be an oxidized and disinfected wastewater that meets the numeric criteria in subsection (c) of this section.* *(c) Criteria. Class C recycled water must not exceed a median of 23 total coliform organisms per 100 milliliters, based on results of the last seven days that analyses have been completed, and 240 total coliform organisms per 100 milliliters in any two consecutive samples.* *(d) Monitoring. Monitoring for total coliform organisms must occur once per week at a minimum.*
Air Emission	**** OAR 340-055-0012*** *(C) If aerosols are generated when using recycled water for an industrial, commercial, or construction purpose, the aerosols must not create a public health hazard.*

TEXAS

<table>
<tr><th></th><th>Regulation/Guidelines/Policy</th></tr>
<tr><td>Water Reuse</td><td>
* TAC 30-210.32
(Texas Administrative Code, Title 30, Chapter 210, Rule 210.32: Specific Uses of Reclaimed Water)
<i>(1) Type I Reclaimed Water Use. This type of use includes irrigation or other uses in areas where the public may be present during the time when irrigation takes place or other uses where the public may come in contact with the reclaimed water.</i>
<i>(2) Type II Reclaimed Water Use. This type of use includes irrigation or other uses in areas where the public is not present during the time when irrigation activities occur or other uses where the public would not come in contact with the reclaimed water. The following are examples of uses that would be considered Type II uses.</i>
<i>(F) Cooling tower makeup water. Use for cooling towers which produce significant aerosols adjacent to public access areas may have special requirements.</i>
<i>(3) Any Type I reclaimed water may also be utilized for any of the Type II uses identified in subsection (2) of this section.</i>

* TAC 30-210.33
(Quality Standards for Using Reclaimed Water)
<i>Reclaimed water quality on a 30-day average</i>
<table>
<tr><th></th><th></th><th colspan="2"><i>Type II</i></th></tr>
<tr><th></th><th><i>Type I</i></th><th><i>For a system other than pond system</i></th><th><i>For a pond system</i></th></tr>
<tr><td><i>BOD5 (or CBOD5) (mg/l)</i></td><td><i>5 (or 5)</i></td><td><i>20 (or 5)</i></td><td><i>30 (or N/S)</i></td></tr>
<tr><td><i>Turbidity (NTU)</i></td><td><i>3</i></td><td><i>N/S</i></td><td><i>N/S</i></td></tr>
<tr><td><i>Fecal Coliform (CFU/100 ml)</i></td><td><i>20*</i></td><td><i>200*</i></td><td><i>200*</i></td></tr>
<tr><td><i>Fecal Coliform (max) (CFU/100 ml)</i></td><td><i>75**</i></td><td><i>800**</i></td><td><i>800**</i></td></tr>
</table>
<i>Definition:</i>
<i>N/S: Not specified</i>
<i>* : Geometric mean</i>
<i>** : Single grab sample</i>
</td></tr>
<tr><td>Water Discharge</td><td>TAC 30-307.8
(Texas Surface Water Quality Standards/Application Standards)
<i>(d) Once-through cooling water discharges. When a discharge of once-through cooling water does not measurably alter intake concentrations of a pollutant, then water-quality based effluent limits for that pollutant are not required. For facilities which intake and discharge cooling-water into different water bodies, this provision only applies if water quality and applicable water quality standards in the receiving water are maintained and protected.</i></td></tr>
</table>

Air Emission	*** TAC 30-210.32** ***(1)(2)(F)*** *Use for cooling towers which produce significant aerosols adjacent to public access areas may have special requirements.* **TAC 30-113.220** (NESHAPS/Industrial Process Cooling Towers) *The Industrial Process Cooling Towers Maximum Achievable Control Technology standard as specified in 40 Code of Federal Regulations Part 63, Subpart Q, is incorporated by reference as amended through June 23, 2003 (68 FR 37348).*

UTAH

	Regulation/Guidelines/Policy
Water Reuse	*** Water Reuse in Utah (Apr. 2005)** *** Utah's Water Resources Planning for the Future, Chapter 5 (May, 2001)** *** UAC R317-3-11** (Utilization and Isolation of Domestic Wastewater Treatment Works Effluent) *11.5 Use of Treated Domestic Wastewater Effluent Where Human Exposure is Unlikely (Type II)A. Used allowed* *5. Cooling water. Use for cooling towers which produce aerosols in populated areas may have special restrictions imposed.* *B. Required Treatment Process* *C. Water Quality Limits*
Air Emission	*** UAC R317-3-11** *11.5 A. 5. Use (reclaimed water) for cooling towers, which produce aerosols in populated areas, may have special restrictions imposed.*

WASHINGTON

Regulation/Guidelines/Policy	
Water Reuse	*** RCW 90.46** (Reclaimed Water Use) *** Water Reclamation and Reuse Standards, SECTION 1, Article 4, Section 15** (Industrial Cooling) *(a) Reclaimed water used for industrial cooling purposes where aerosols or other mist are not created shall be at all times Class C reclaimed water or better.* *(b) Reclaimed water used for industrial cooling purposes where aerosols or other mist are created shall be at all times Class A reclaimed water or better.* *Note:* *Class A water: oxidized, coagulated, filtered, and disinfected; total coliform 2.2/100 ml (7-day mean), 23/100 ml (single sample)* *Class C water: oxidized and disinfected; total coliform 23/100 ml (7-day mean), 240/100 ml (single sample)* *** Water Reclamation and Reuse Standards, SECTION 1, Table 2** (General Requirements) *BOD and TSS: 30 mg/l (monthly mean)* *Turbidity: 2 NTU (monthly), 5 NTU (not to exceed at any time)* *Minimum chlorine residual: mg/l after a contact time of 30 minutes*
Air Emission	*** Water Reclamation and Reuse Standards, SECTION 1, Article 4, Section 15**

WYOMING

Regulation/Guidelines/Policy	
Water Reuse	***STANDARDS FOR THE REUSE OF TREATED WASTEWATER*** ***CHAPTER 21,WQD,*** ***Authority and Purpose****.* *"It is the intent of these regulations to encourage and facilitate the productive and safe reuse of treated wastewater as a viable option in the management of the state's scarce water resources. The use of treated wastewater for non-potable purposes through "source substitution" or replacing potable water used for non-potable purposes is encouraged. This part contains the minimum standards for the reuse of treated wastewater as defined in these regulations."* *"These regulations establish standards that address the primary health concerns associated with the reuse of treated wastewater. The regulations establish criteria to address the risk of pathogen exposure and infectious disease risks associated with various specified uses of treated wastewater."*
Water Discharge	***STANDARDS FOR THE REUSE OF TREATED WASTEWATER*** ***CHAPTER 2, WAQS&R,*** *APPENDIX D* *Additional Requirements Applicable to* *Manufacturing, Commercial, Mining and Silvicultural Facilities* *Discharging Only Non-process Waste Water*

Related Websites for Regulations

Code of Federal Regulations (CFR)	http://www.access.gpo.gov/
Arizona State Legislature (ASL)	http://www.azleg.state.az.us/
The Arizona Administrative Code (AAC)	http://www.azsos.gov/public_services/Table_of_Contents.htm
California Code of Regulations (CCR)	http://ccr.oal.ca.gov/linkedslice/default.asp?SP=CCR-1000&Action=Welcome
The Florida Administrative Code(FAC)	http://fac.dos.state.fl.us/
Code of Maryland (COMAR)	http://www.dsd.state.md.us/comar/search_all.htm
New Jersey department of environmental protection (NJDEP)	http://www.state.nj.us/dep/dwq/techman.htm
North Carolina Administrative Code(NCAC)	http://reports.oah.state.nc.us/ncac.asp
Texas Administrative Code (TAC)	http://info.sos.state.tx.us/pls/pub/readtac$ext.viewtac
Utah Administrative Code(UAC)	http://www.rules.utah.gov/main/index.php?module=Pagesetter&func=viewpub&tid=1&pid=9
Washington State Legislature (WSL)	http://apps.leg.wa.gov/RCW/default.aspx?cite=90.46
Warren-Alquist Energy Resources Conservation and Development Act	http://www.energy.ca.gov/2005publications/CEC-140-2005-001/CEC-140-2005-001-ED2.PDF
Clean Water Act (CWA)	http://www.epa.gov/region5/water/cwa.htm
New Jersey Administrative Code (NJAC)	http://michie.lexisnexis.com/newjersey/lpext.dll?f=templates&fn=main-h.htm&cp=uanjadmin
California Water Code	http://www.leginfo.ca.gov/calaw.html
Code of Maryland Regulation (COMAR)	http://www.dsd.state.md.us/comar/

Table C.1 Inventory of U.S. Power Plants Using Reclaimed Water in Cooling Water System

	State	City	Name	Ownership	Energy Source (1)	Reclaimed water usage (MGD)	Cap. (MW)	Reuse Water Source (2)	Additional (off-plant/in-plant) treatment prior to use / ZLD	Water reuse since	Reference
1	AZ	Arlington	Redhawk Power Station	Arizona Public Service Co.	G	2.7	1060	**W-** Wastewater Treatment and Tolleson Wastewater Treatment Plants	tertiary wastewater ;ZLD	2002	2,3
2	AZ	Wintersburg	Palo Verde	Arizona Public Service Co. (29.1%)	N	55	4000	**W-** Phoenix Municipal Waste Treatment	tertiary treated municipal wastewater; ZLD	1992	4,5,6,7,8
3	CA	Burbank	City of Burbank Power Plant	Burbank Public Service Dept.		5	152.5	**W-**	tertiary treated municipal wastewater	1967	7,9,10
4	CA	Burbank	Magnolia	Southern California Public Power Authority	G	2	310	**W-** Burbank waste-water treatment plant	microfiltration,chemical treatment,hyperfiltration,ion exchange; ZLD	2005	11,12
5	CA	City of Industry	Walnut Creek Energy Park	Edison Mission Energy(EME)	G	0.75	500	**W-** San Jose Creek Wastewater Reclamation Plant	high-purity, tertiary-treated	applied (2005)	13,14
6	CA	Glendale	Glendale Steam Electric Generating Plant	Glendale Public Service Dept.	G	0.26	272.5	**W-** Los Angeles Glendale Water Reclamation Plant	tertiary treated municipal wastewater	1990	7,10,15,16,17
7	CA	Los Angeles	Puent Hills Powerplant		LG	0.32	50				15,18
8	CA	Los Angeles	Spadra Gas-to-Energy Plant		LG	0.05	8				15,18
9	CA	Los Angeles	DWP Scattergood Generating Station	Los Angeles Dept. of Water and Power	G	0.25	803	**W-** WBWRP(West Basin Water Reclamation Plant)	nitrified tertiary treatment	1994	10,19,20
10	CA	Oroville	Pacific Oroville Power, Inc.	Pacific Oroville Power Co.		0.06	22				15,21
11	CA	Redlands	Mountainview Power Plant	Southern California Edison	G		1054	**W** - City of Redlands WWTP		2005	**A3**
12	CO	Colorado Springs	Martin Drake	Colorado Springs Utilities	C	3.4~5.6		**W-** local wastewater treatment facility		2004	22,23
13	FL	Auburndale	Auburndale Power Plant	Calpine Energy	G		150	**W-** City of Auburndale reuse system		1994	24,25
14	FL	Gainesville	Progress Energy	University of Florida Co-Generation Facility	G		42				**A2**
15	FL	Lakeland	McIntosh Power Plant (Unit 3)	Lakeland and the Orlando Unitities Commission	G/C	5.4	334	**W-** Lakeland domestic wastewater treatment facility	tertiary treated municipal wastewater; intermediate level disinfection; ZLD	1982	7,26,27
16	FL	Lakeland	McIntosh Power Plant (Unit 4)	Lakeland Utilities Commission	C		137	**W-** Northside and W. Carl Dicks WWTP	secondary treated sewage effluent	2002	27,28,29
17	FL	Orlando	Curtis Stanton Energy Facility	Orlando Utilities Commission	C	8	450	**W-** Orange County wastewater facility	high-level disinfected reclaimed water; ZLD	1987	9,26,30,31
18	FL	Spring Hill	Pasco County Resource Recovery Facility	Pasco County	SW		31.2	**W-** Shady Hills Subregional WWTP; stormwater runoff	disinfected; secondary sewer treatment effluent	1991	32,33,34
19	FL	St. Petersburg	Pinellas County Resource Recovery Facility	Pinellas County	SW	1	75	**W-** City of Largo reuse and St. Petersburg reuse systems		1983	25,35,36
20	FL	Tallahassee	Sam O. Purdom Generating Station	City of Tallahassee	G		320	**I, W-** St. Marks Powder, Inc.;City of St. Marks wastewater treatment plant	ZLD	2002	37,38,39
21	FL	Tampa	City of Tampa McKay Bay Refuse to Energy Facility	City of Tampa	SW	4.9	22	**W-** City of Tampa reuse system; Hookers Point Treatment Plant; the Howard F. Curren WWTF	high-level disinfection reclaimed water	1985	25,26,36, 40
22	FL	Tempa	Hillsborough County Resource Recovery Facility	Hillsborough County Solid Waste Management	SW		29	**W-** Hillsborough County South/Central reuse system	secondary sewer treatment effluent	1987	32
23	FL	Vero Beach	Vero Beach Municipal Power Plant	Vero Beach Municipal Utilities	O	0.1		**W-** Vero Beach wastewater treatment facility	high-level disinfected reclaimed wate	1976	26,41
24	IA	Clear Lake	Emery Generating Station	Interstate Power & Light Co.	O/G	5.7	565	**W-** Clear Lake Sanitary District 40%(CLSD); (Groundwater:60%)	tertiary treatment processes for further filtering and disinfection	2004	42,43
25	MA	Charlton	Millennium Power	Millennium Power Plant	G	2.75	400	**W-** Southbridge's municipal wastewater treatment plant; Quinebaug River		2005	44
26	MA	North Andover	North Andover	Wheelabrator	SW		40	**W-**	tertiary treated municipal wastewater	1985	45
27	MD	Brandywine	Panda-Brandywine generating facility	Panda Energy Corporation	G	1.3	230	**W-** Mattawoman WWTP	tertiary treated	1996	7,46
28	MN	Minneapolis	Riverside Power Plant	Xcel Energy	G		439			2009	**A4**

Table C.1 Inventory of U.S. Power Plants Using Reclaimed Water in Cooling Water System

29	State	City	Name	Ownership	Energy Source (1)	Reclaimed water usage (MGD)	Cap. (MW)	Reuse Water Source (2)	Additional (off-plant/in-plant) treatment prior to use / ZLD	Water reuse since	Reference
30	NJ	Linden	Linden Generating Station	Public Service Enterprise Group (PSEG)	G	6.1	1544	**W-** Linden-Roselle Sewerage Authority wastewater treatment plant	USFilter filtration; treated further to prevent scaling and foaming	2002	47,48,49
31	NJ	Ridgefield	Bergen Generating Station	Public Service Enterprise Group (PSEG)	G	0.6	1242	**W-** Bergen County Utilities Authority	USFilter is supplying reverse osmosis (RO)	2002	47,50,51
32	NM	Farmington	San Juan Generating Station	PNM	C		1800	**I-** produced water	water is reused 10 times before leaving the plant; ZLD	1973	52
33	NV	Las Vegas	Sunrise	Nevada Power Company	G	3		**W-** Clark County Water Reclamation District	secondary sewage effluent ;in-plant treatment	1958	53,54,55, 56
34	NV	Las Vegas	Clark	Nevada Power Company	G			**W-** Clark County Water Reclamation District	secondary sewage effluent	1958	54,56
35	NV	Valmy	Valmy Power Plant	Sierra Pacific Power Company and Idaho Power Company	C	7.2	500	**M-** mine dewatering at Lone Tree		1996	57
36	OK	Oklahoma	Redbud Power Plant	InterGen North America	G	11.3	1100	**W-** North Canadian Wastewater Treatment		2003	58,59
37	OR	Klamath Falls	Klamath Cogeneration Project	City of Klamath Falls	G		475	**W-** sewer system in Klamath Falls		2001	60,61
38	PA	Frackville	Gilberton Power Company	Gilberton Power Company	WC	1.37	80	**M-** Unnamed mine pool	Aeration tower, pH adj., polymer addition, solids contact tank filtration,	before 1985	62
39	PA	Frackville	Wheelabrator Frackville Energy Co.	Wheelabrator Frackville Energy Co.	WC	0.58~1.01	42	**M-** Morea mine	pH adj., chlorination, polymer addition and flocculation, lamellar plate separation	1988	62
40	PA	Limerick	Limerick Generating Station	Excelon Nuclear	N	14.4	2400	**M-** Wadesville Mine Pool and Still Creek Reservoir at Tamaqua		2003	63,64,65
41	PA	McAdoo	Northeastern Power Company	Northeastern Power Company	WC	0.14	50	**M-** Drainage tunnel for Silverbrook mine	oxygen, polymer addition, settling basin	1989	62,66
42	PA	Nesquehoning	Panther Creek Generating Station (main cooling: dry; auxiliary: wet)	Constellation Energy Group, Inc. (50%)	WC	1.1	83	**M-** Lausanne mine tunnel	pH adj., polymer addition, coagulation and flocculation, clarification, filtration	1992	62
43	PA	Shenandoah	Schuylkill Energy Resources, Inc.	Schuylkill Energy Resources, Inc.	WC	1.58	80	**M-** Maple Hill mine drainage	aeration, chlorination, pH control, polyer addition, coagulation, clarification, filtration	1989	62,67
44	PA	Tremont	WPS - Westwook Generating Plant	WPS - Power Development	WC	1.15	31	**M-** Lyken mine	coagulation, tube settlers, filtration	1988	62
45	RI	Johnston	Rhode Island State Energy Partners	FPL Energy (Florida Power and	G	5	550	**W-** Crayston WWTF		2002	68
46	TX	Amarillo	Nichols Station	Southwestern Public Service	G	N+H=15	457	**W-** treated sewage effluent	in-plant treatment; ZLD	1971	69,70,72
47	TX	Amarillo	Harrington Station	Southwestern Public Service	C	N+H=15	1066	**W-** treated sewage effluent	in-plant treatment; ZLD	1971	69,70,55, 71
48	TX	Austin	Austin Energy	Sand Hill Energy Center	G	2.88	180	**W** - South Austin Regional WWTP		2006	A1
49	TX	Cleburne	Cleburne Cogeneration Facility	Ponderosa Pine Energy Partners and Delta Power	G	2	263	**W-** Cleburne city water and treated waste water from the Cleburne Sewage Treatment Plant	Type 1 effluent	1997	72,73
50	TX	Denton	Spencer Power Plant	Garland Power & Light (sold by Denton Municipal Electric in 2001)	G	0.5~3	166	**W,I-** Pecan Greek Wastewater Plant; City of Denton Industrial reuse water		2004	74,75,76
51	TX	El Paso	(El Paso Electric Company)	El Paso Electric Company		2.4		**W-** EPWU			77
52	TX	Lubbock	Jones Station	Southwestern Public Service	G	3~5	486	**W-** treated sewage effluent from Lubbock	in-plant treatment; ZLD	1971	55,78
53	VA	Williamsburg	James City Energy Park		G	5	580	**W-** Hampton Roads Sanitation District's Williamsburg wastewater treatment plant		project appr. 2006	79,80

Notes: (1) C: coal G: natural gas LG: landfill gas N: Nuclear O: oil SW: solid waste WC: waste coal

(2) I: industrial processed water M: (treated) mine pool water W: treated municipal wastewater

APPENDIX D: Pilot-Scale System Design, Construction, and Testing

D.1 Pilot-Scale System Design and Construction

A system of four counter-flow cooling towers was constructed of ½” thick Plexiglas acrylic and equipped with all necessary control and measurement equipment to facilitate accurate operation and monitoring of each cooling tower. The counter-flow fill for the cooling tower system will be provided by Brentwood Industries (OF21-MA). To be able to conduct scaling, corrosion, and biofouling monitoring, the cooling tower system is comprised of the following components:

- Air handling system to ensure proper air velocity through each cooling tower. Air velocity and relative humidity must be measured for both the intake air and the exhaust air using portable probes positioned in front of the cooling towers and in a exhaust duct for each cooling towers. Exhaust air should send through a drift eliminator to ensure that at least 95% of saturated air is captured prior to discharge into the environment.
- Water handling system to ensure proper water flow rate and temperature for each cooling tower as well as proper addition of makeup water and blow down protocol. Blow down schedule should be adjusted to achieve 4 cycles of concentration as measured by water conductivity (total suspended solids should be measured in parallel to ensure higher reliability of tower operation and control).
- Continuous feeding of the biocide must be precisely controlled to ensure proper dosage of disinfectant in each tower. Biocide should be added to the bottom basin (sump) to ensure proper mixing of the disinfectant throughout the system.

In addition to these protocols, common operational criteria used by industrial cooling towers were also employed for the pilot scale cooling tower design. The fundamental design criteria (Table D.1) for the pilot scale cooling towers include 3 GPM water flowrate in the recirculating system and 10 degrees Fahrenheit cooling capacity. Theoretical airflow rate and temperature at different locations are calculated to achieve design criteria.

An airflow rate of 150 cubic feet per minute inside the column is required to provide 10 degrees Fahrenheit cooling capacity. The temperature in the heat exchanger is calculated to be at least 150 degrees Fahrenheit to make up the heat loss by evaporative cooling and to maintain the temperature of water in the basin at 95 F and the temperature of water at the nozzle at 105 F.

Based on these basic protocols, prototype cooling tower was built for trial. A schematic of the design is depicted in Figure D.1. Four major components of the pilot scale cooling towers are 1) Cooling Session – this portion simulates the cooling tower used by power plants, 2) Heating session – this portion simulates the hot stream leaving heat exchanger, 3) Sampling Session – this portion contains main stream and a coupon stream. Coupons for scaling, corrosion, and biofouling experiments can be inserted into 19 separate tees, 4) Water Control Session – this portion will include automatically makeup and blowdown control devices. The CoC is indirectly controlled by the water management mechanism.

Table D.1 Operational and empirical parameters of cooling tower

Parameter	Value	Unit
Water flowrate	3	GPM
Temperature difference	10	ºF
Airflow rate	150	CFM
Temperature of water in the heater	150	ºF
Temperature of water in the basin	95	ºF
Temperature of water at the nozzle	105	ºF

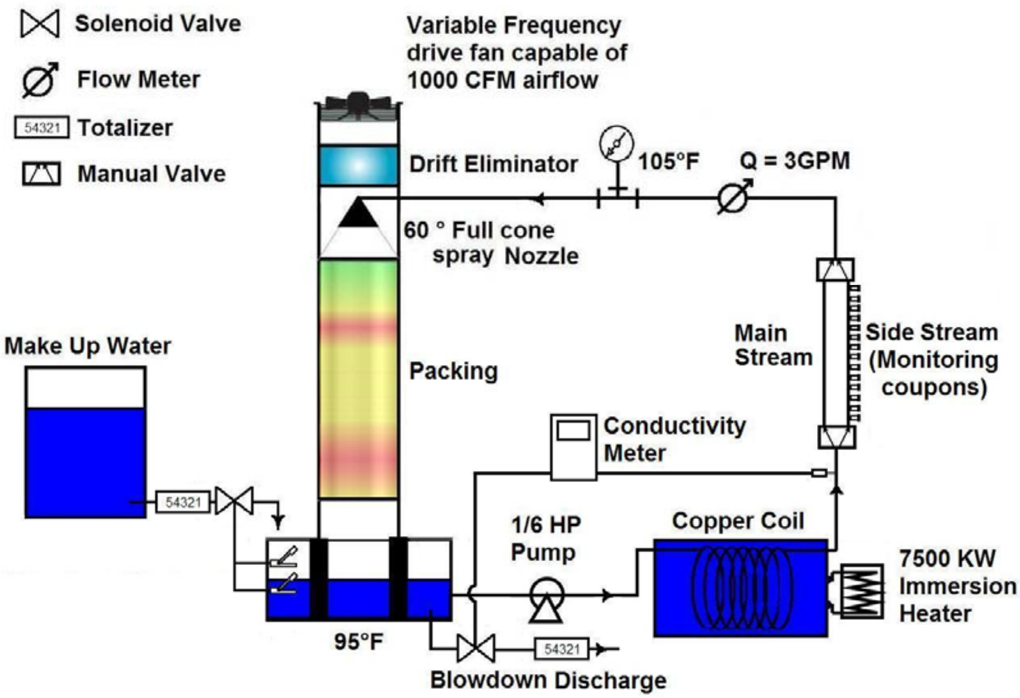


Figure D.1. Schematic of pilot-scale cooling tower design. The tower was broken down into individual segments which were developed as discrete components and described below in detail.

The portion of the cooling session is depicted in Figure D.2. The Plexiglas was selected for tower construction to facilitate viewing inside the tower. Packing material (OF21-MA) is designed for 3 GPM, Maximum temperature 140 °F by Brentwood Industrials. The surface area of the packing is 45 ft^2/ft^3.This cooling section stands on four 2 ft. long stainless steel legs (1 x 1 in.) inside the water collecting basin.

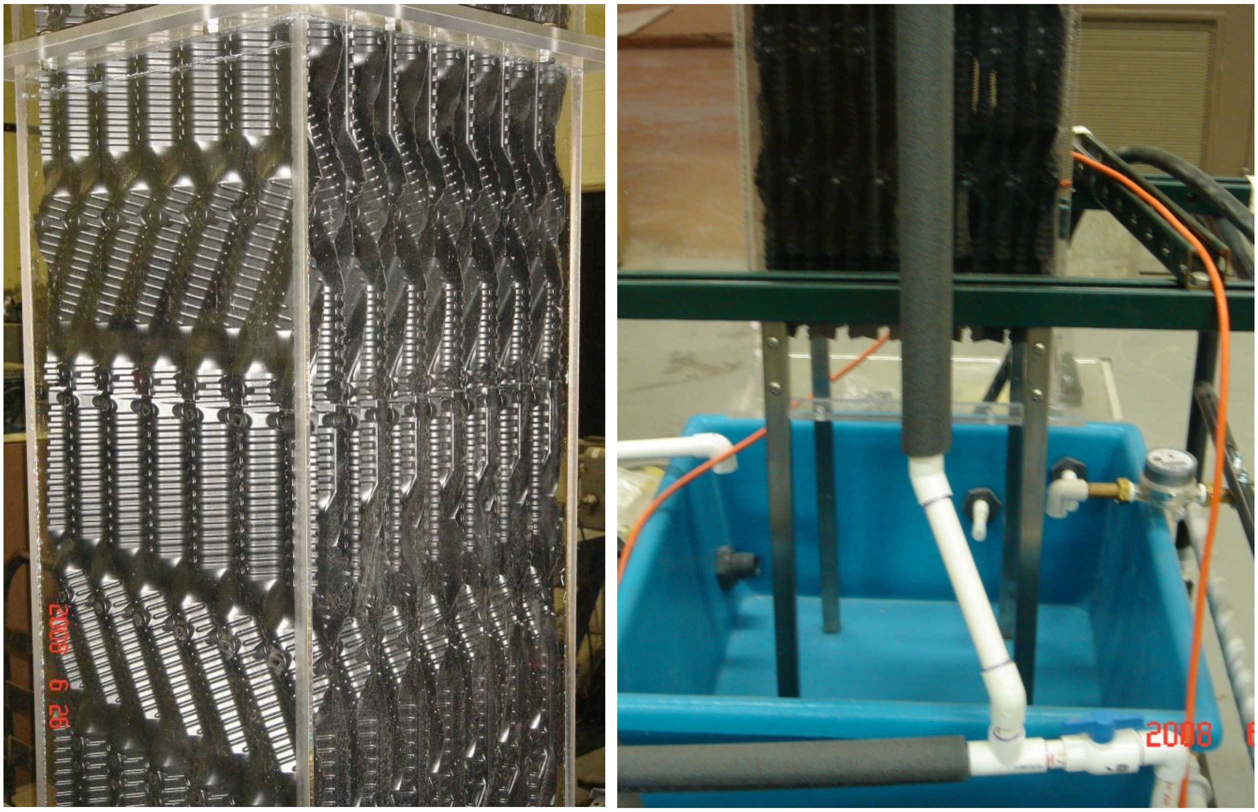


Figure D.2. Plastic packing of the tower. This section of the tower was designed such that flanges on the top and bottom were used to mount other sections (above would be the nozzle section, below the water collection system) and to attach it to the structural frame.

As indicated in Figure D.1, the water leaves the basin at 95 °F using a centrifugal circulating pump. The water will be heated from 95 °F to 105 °F through a coil that is immersed in a hot water bath which is heated by immersion heaters that are controlled through temperature sensors (Figure D.3).

Loss of heat was observed during first trial thus causing significant decrease of water temperature at influent stream, which was below designed temperature, 105 °F. The reason of this phenomenon was that the original hot water bath was exposed to the air and the metal platform. In order to decrease the heat loss from direct heat conduction, the stainless steel bath was installed inside a plastic storage box with heat insulation. The entire heating element is then protected to resist outdoor environment. The heat insulation is the Owens Corning PINK R-19 Fiber Glass Insulation. The heating path in the copper coil is 13 meters and the copper coil is replaceable. Both end of copper coil have a ½” to ¾” reducer welded and connect to CPVC unions. CPVC unions can stand for high temperature up to 220ºF without any distortion.

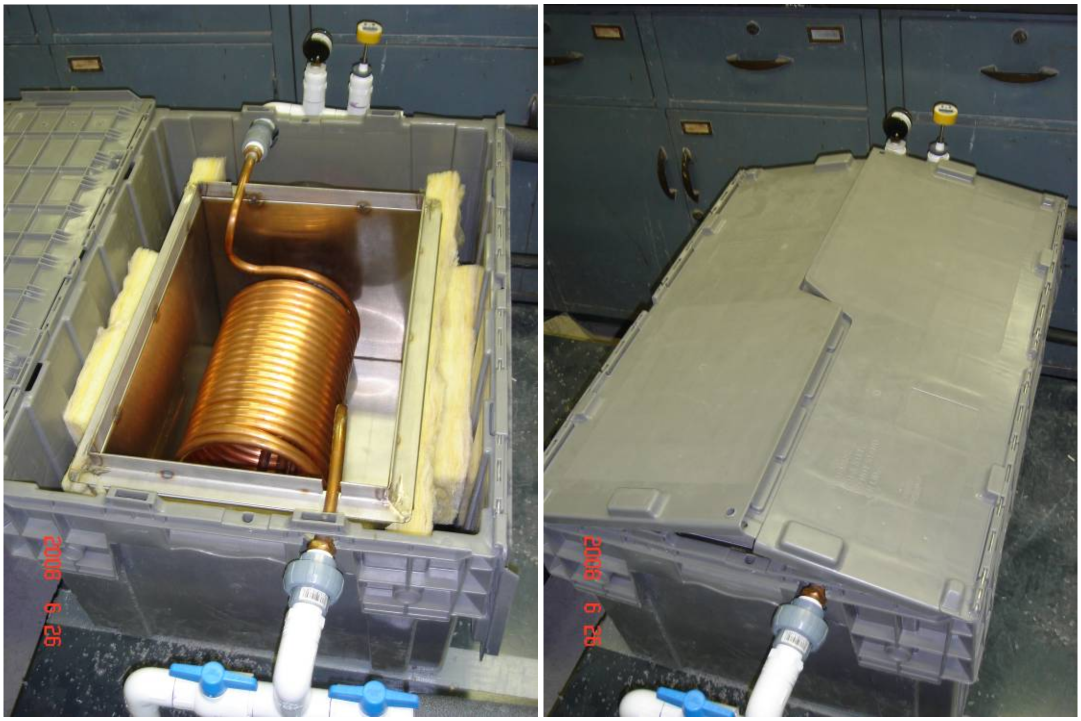
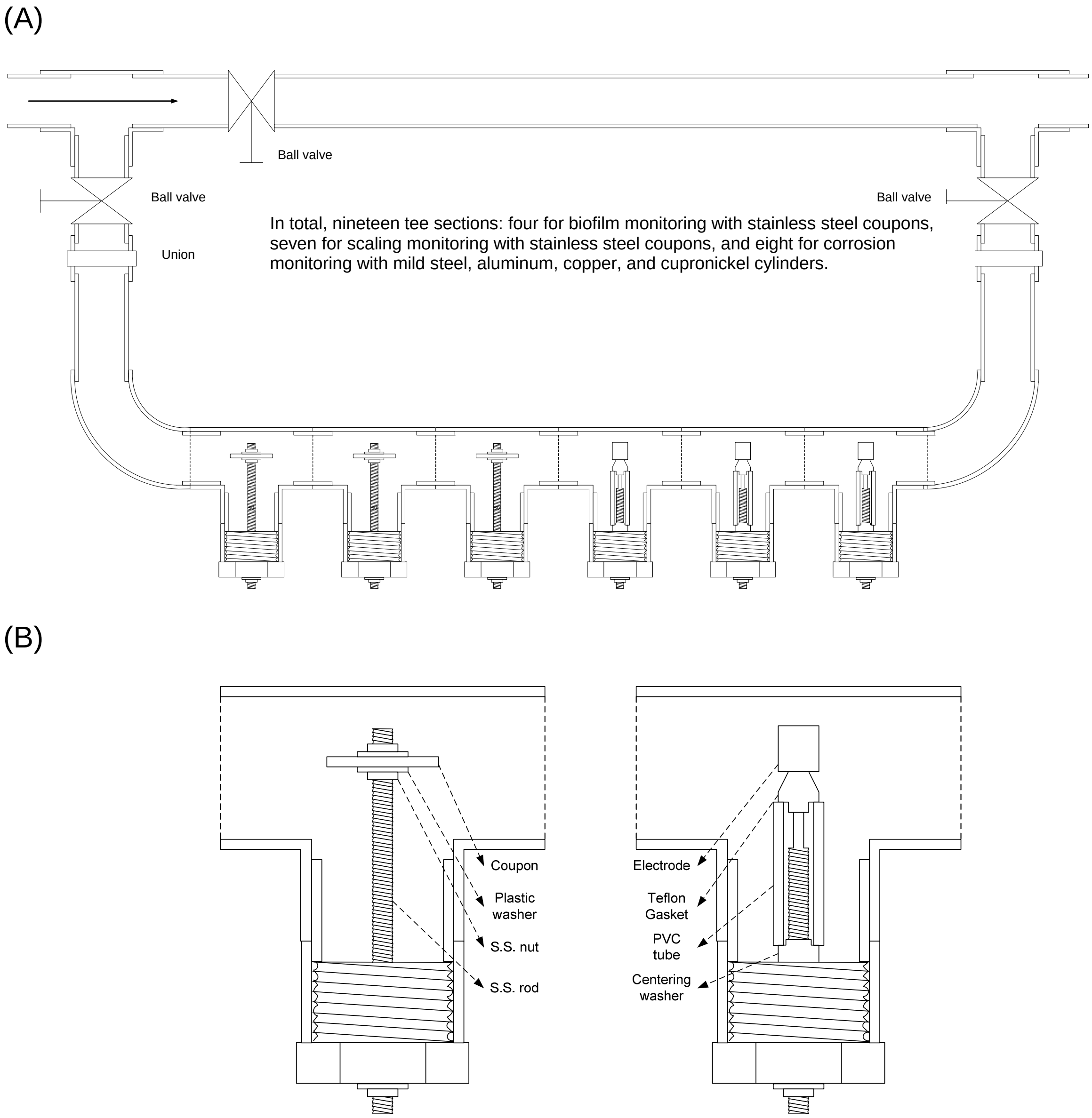


Figure D.3. Replaceable copper coil and the weather proof box for the heating system. The heating bath was filled with deionized water to ensure low oxidation of the copper coil and high heat conduction.

In case the pump speed cannot be controlled accurately, we have designed a flow system controlled by a needle valve that allows precisely the desired water flow (3 GPM) to enter the recirculation line, while diverting the rest of the water back into the holding basin. This will also protect the pump from water surges that may arise.

Water will exit the heating system and enter the recirculation line that consists of ¾ in. PVC pipe, which is divided into two streams: a side stream which contains the corrosion and bio-film measurement system and the main stream. Both streams are joined together prior to the distribution nozzle and each stream (side and main) is isolated at the top and the bottom using ball valves. Detailed design of the corrosion and bio-film measurement system of the two streams is depicted in Figure D.4. The side stream for the corrosion and bio-film measurement system will rejoin the main flow at the top of the tower, and enter the nozzle, completing the circulation pathway.



In total, nineteen tee sections: four for biofilm monitoring with stainless steel coupons, seven for scaling monitoring with stainless steel coupons, and eight for corrosion monitoring with mild steel, aluminum, copper, and cupronickel cylinders.

Figure D.4. (A) Detailed design of the corrosion and bio-film measurement system, and (B) detailed design of tee-sections in the side stream system.

The corrosion, scaling, and bio-film measurement system is shown in schematic as Figure D.4. (A), showing tee-sections to be implemented and their connections to the main recirculation stream. Heated water enters from the pump and heat exchanger at the top left where a side stream is diverted into the corrosion and bio-film measurement system, with the flow controlled by valves. The corrosion, scaling, and bio-film study loop consists of PVC tee-sections that have screw mounts where the study coupon will be put into place. Figure D.4. (B) shows the details of two types of tee-sections: 1) mounted with washer-like coupons and 2) mounted with cylinder electrodes. The washer-like coupons can be used for bio-film, scaling deposits, and corrosion rate (mass loss method) analysis, while the cylinder electrodes is to be used for corrosion rate analysis by electrochemical study (linear polarization resistance method). Corrosion test materials consist of solid test cylinders of the metals and metal alloys of interest whereas the bio-film substrate is made of washer-like deposit surfaces. The side stream rejoins the main stream on the right, enters the nozzle, and is injected into the tower for cooling.

Water is collected from the packing portion of the tower and is recirculated. The water loss is reduced by the packing and mist eliminator. The mist eliminator (Brentwood Industries) and fan (EBM Pabst, Germany) are mounted to the tower using the flange portion of the cooling section and uni-strut main frame (Figure D.2). The main frame is mounted to a cart that has brake-locked wheels, allowing easy transportation.

The entire system is instrumented with temperature sensors, pressure gauges at the exhaust, and flow sensors at critical points that include water collection point, immediately before nozzle, and water bath.

Since precise and reliable measurement is required to ensure sufficient water supply for the cooling system, several electronic devices are used to achieve automatically control. Figure D.5 shows the design of makeup water measurement and monitoring system. The system includes a water meter, a solenoid valve, and two float switches. Float switch A will send signal to stop solenoid valve thus stopping injecting makeup water into the water collecting basin. On contrary, switch B sends signal to open the valve thus starting to inject water. During the water injection, the water meter can record how much makeup water is used for a certain period of time. A sensitive water meter (4155K41, McMaster-Carr) with lowest recordable flow of 0.13 GPM is used to ensure accurate mass transfer rate of makeup and blowdown water. The dual-point control system is applied and will help precisely measuring the amount of water loss/required makeup water of the cooling tower.

The control and measure system for makeup water and blowdown is modified to fit the truck. The makeup water measure and control system is now fixed on the handler and the makeup water is connected from the tank through a flexible pipe (Figure D.6).

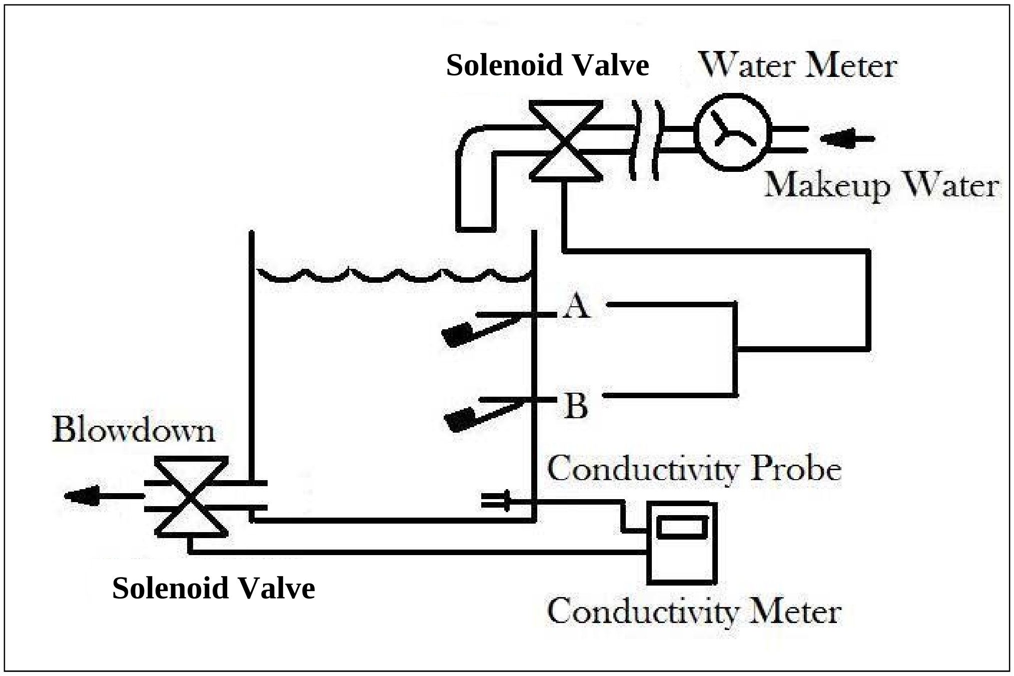


Figure D.5. Sketch of duel-point makeup water control system based on water surface level and automatic blowdown discharge control system based on conductivity measurement.

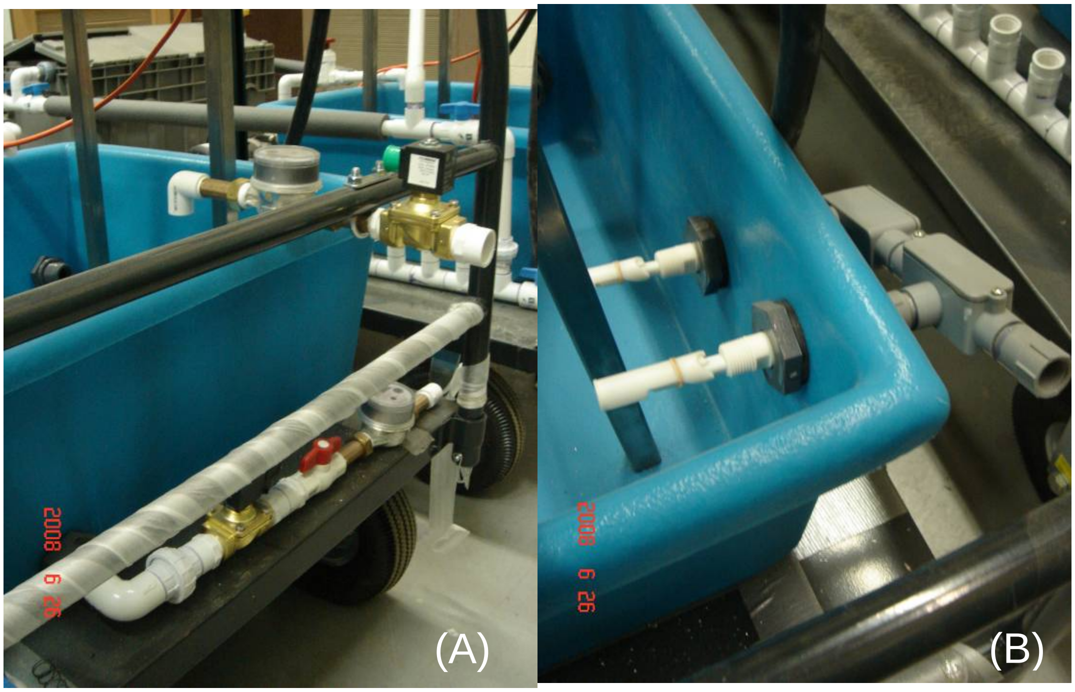


Figure D.6. Measure and control system for makeup water and blowdown discharge, included totalizers, solenoid valves, ball valve, float switches. (A) Upper PVC union connected to makeup water tank with a flexible pipe (B) Float switches controled the water level in the water basin. Once the water level was lower than the float switch B, the makeup water value automatically opened and filled with makeup water.

Previous studies showed the measurement of conductivity was a reliable method to decide the cycles of concentration of recirculating cooling towers. Therefore, a conductivity measurement system is built with an automatic blowdown discharge system. The whole system includes a conductivity meter, a conductivity probe, and a solenoid valve. The conductivity probe can be applied either in the basin or the subs-stream to measure present conductivity in the recirculating system. The cycles of concentration is derived by dividing the conductivity of the recirculating system with the conductivity of makeup water. The conductivity meter will send a signal to solenoid valve to start discharging once the conductivity of recirculating water reaches the predetermined level.

The main cooling tower column is secured by unistrut structure. Three beams and one pillar are combined to prevent the column from tilting and also provide the support for the electrical J-box. Electrical J-box is in the size of 6”x12”x12” and includes three power switches, six cord grips, five terminal blocks, one breaker, potentiometer for fan control, and integrated power system (Figure D.7). Three switches control the power of solenoid valves, float switches, and conductivity meter (red), pump (black), and fan (fan). The heater has an individual power control and the temperature is controlled by a thermostat. The central power control is on the power panel and protected by fuse and plastic sheet. A breaker is also installed to control the temperature change by thermostat. The potentiometer has a 15 level dial and can provide various fan speed.

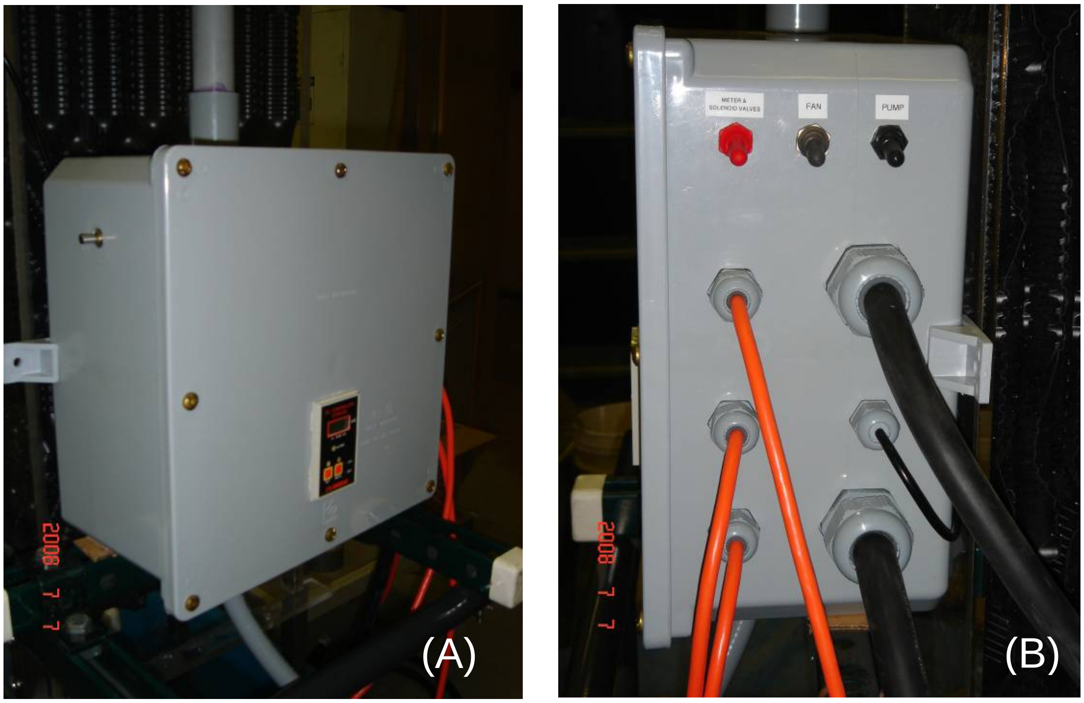


Figure D.7. Electrical J-box, including power switches, terminal blocks, conductivity meter, power inlet/outlet, current divider, and potentiometer for controlling fan speed. (A) Potentiometer and 15 level dial with conductivity meter in the front panel, (B) Power switches for pump, fan, and conductivity meter.

Entire construction of four pilot scale cooling tower was completed on June 28th and tested before sent to field (Figure D.8).

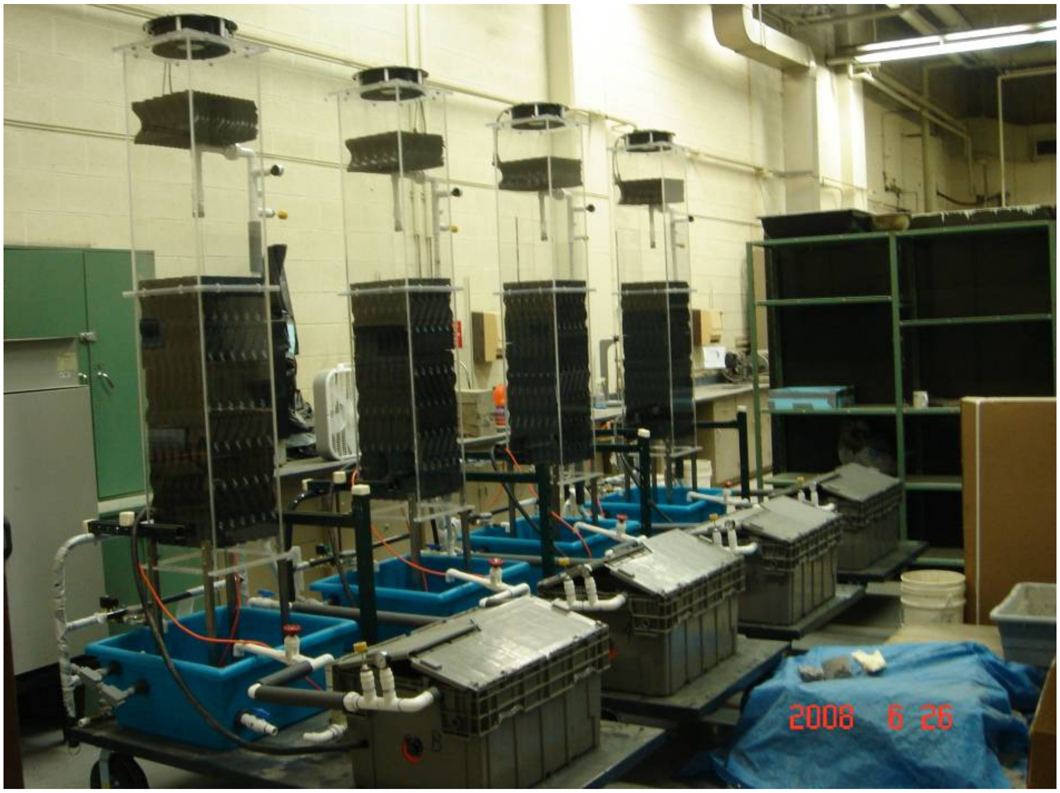


Figure D.8 Pilot-scale cooling towers, which were modified to withstand the outdoor environment

D.2 Pilot-Scale System Testing

During the construction phase, a prototype cooling tower was tested for basic operational parameters, including 1) General characteristics of pilot scale cooling tower; 2) Air flow inside the cooling column; 3) Water distribution pattern throughout the packing.

D.2.1 General characteristics of pilot scale cooling tower

The heater was set to maintain 150 ºF in the heating bath and the water flowrate in the cooling system was set at 3 gallons per minute. The water temperature was measured as it enters the heating bath, leaves the bath, enters the cooling tower, and at the basin (water collector). Measurements were performed every three hours or every six hours for four days. The daily evaporation volume and blowdown volume were average over a two-day period.

The characteristics of the cooling tower are averaged over a period of four days. Table D.2 shows the operational information for the cooling tower. The cycles of concentration (CoC) is controlled by water conductance and four CoC is chosen for this study.

Total water volume in the recirculating system is 36 gallons. The daily evaporation rate is 43.2 gallons while the daily blowdown ranged from 4.8 to 8.8 gallons. The amount of blowdown is varying because of the non-continuous makeup water recharging. In order to record the water consumed by the cooling system, each makeup water recharge is controlled as 3.6 gallon per recharge and each recharge occurs approximately every two hours.

Table D.2. Characteristics of cooling tower

Parameter	Value	Unit
Copper coil length (heating length)	13	Meter
Volume of water in the cooling system	36	Gallon
Volume of each makeup discharge	3.6 ± 0.08	Gallon
Daily evaporation	43.2	Gallon
Daily blowdown	4.8~8.8	Gallon
Evaporation rate	1.8	Gallon per hour
Cooling performance at 3 GPM	11.6	ºF
Air flow rate	25~230	CFM
Time required to reach CoC 4 (based on conductivity)	<48	Hour
Time required to reach CoC 4 (based on evaporation rate)	60	Hour

Table D.3 summarizes several characteristics of cooling tower at different airflow rates. Results show that the increase in airflow rate shifts the temperature gap to a lower value. A difference of 10 °F can be kept under all circumstances. In addition, evaporation rate does not vary with the increase in airflow rate.

Daily evaporation of the cooling tower is about 43.2 gallons regardless of the airflow rates. However, daily discharge (blowdown) is neither regular nor in accordance with the increasing airflow rate. The range of blowdown volume is from 4.8 to 8.78 gallons.

Table D.3. Cooling tower performance at different fan speed

Fan setting / Parameter		5	6	7	8	9	10
Fan performance	CFM	55~95	75~120	95~140	125~165	155~190	170~230
Daily evaporation	Gallon/Day	43.2	42.7	42.7	43.6	44.4	42.12
Blowdown	Gallon/Day	7.25[1]	8.78[2]	7.85[3]	6.60[3]	6.40[3]	4.80[3]
Evaporation rate	Gallon/Hour	1.80	1.78	1.78	1.82	1.85	1.71
Temperature drop across the tower	ºF	11.5	12.0	11.8	11.3	11.4	11.4
Temperature of water entering tower	ºF	104.4	102.0	99.2	95.0	91.1	91.4
Temperature of water at basin	ºF	92.9	90.0	87.3	83.7	79.7	80.0

1. The conductance of CoC 4 was set at 2.00 µS.
2. The conductance of CoC 4 was set at 2.80 µS, and the number was estimated from 5 hours results.
3. The conductance of CoC 4 was set at 2.80 µS.

D.2.2 Air flow inside the cooling column

The fan is manufactured in Germany and distributed by EBMpapst (ID: W3G250). This axial fan has a diameter of 250 mm and rotates counter-clockwise. In addition, it can provide an air flow of 2120 m^3/h, which is 1810 CFM with 10 volts of continuous current (VDC). In order to adjust the air flow rate, a voltage divider was installed to decrease the voltage to 3.1 VDC thus providing suitable air flow rate for the cooling tower. With a potentiometer having scale from 0 to 10, the fan speed could be increased in proportion to the scale.

The measurement of air velocity at different locations in the cooling tower was done by using an anemometer (Hot wire thermo-anemometer, Model 407123, Extech, MA). The locations of three measuring points are shown in Figure D.9. Location A is right above the fan and has variable air velocities from the edge to the center of the fan. Location B and C were accessed by inserting the probe into the column (2 inches from the wall) and record the minimum and maximum air velocity during 20 seconds. Airflow of each point was measured five times.

The air velocity of location C was also measured in the middle of the column (point X), along the edge of column (point Z), and at the middle between these two locations (point Y) (Figure D.10).

The results show the airflow was only unstable at the middle of column. The ranges of airflow rate of different level settings at point X, Y, and, Z were shown in Figure D.11, D.12, and D.13 respectively. The fan performance was calculated by merging the air velocity data at point X, Y, and Z. Figure D.14 shows that the fan has an air output ranging from 25 to 230 CFM under different settings. For all graphs, the X-axis is the scale reading on the potentiometer and the Y-axis is the air velocity times the sectional area (1x1 feet^2).

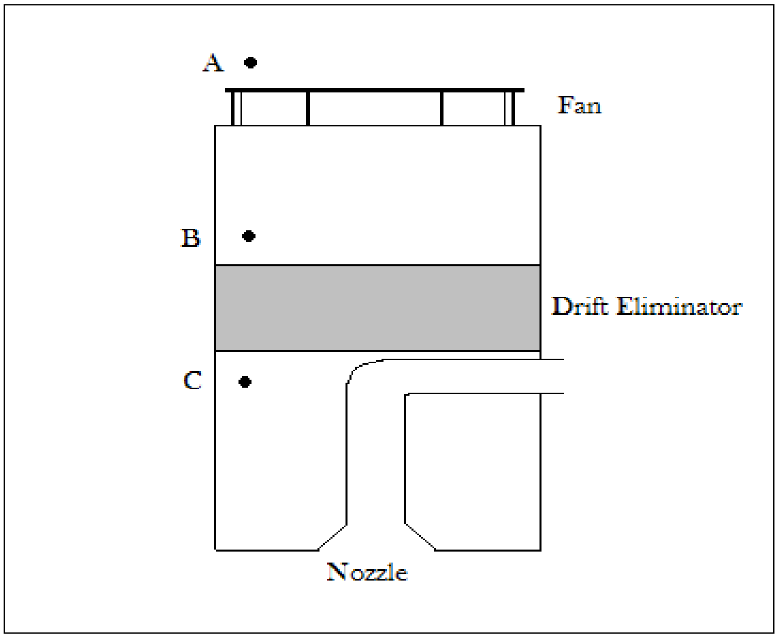


Figure D.9. Air velocity measuring location. Location A was 2 inches above the fan and locations B and C were 2 inches away from the wall.

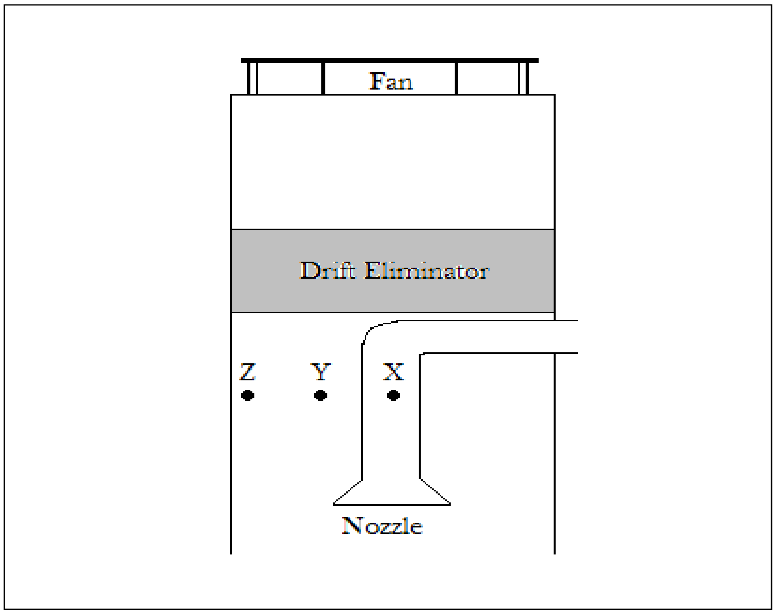


Figure D.10. Air velocity measuring points of Locaiton C. Point X was near the center of column close to the nozzle, Y was close to the wall, and point B was at the middle between point X and Z.

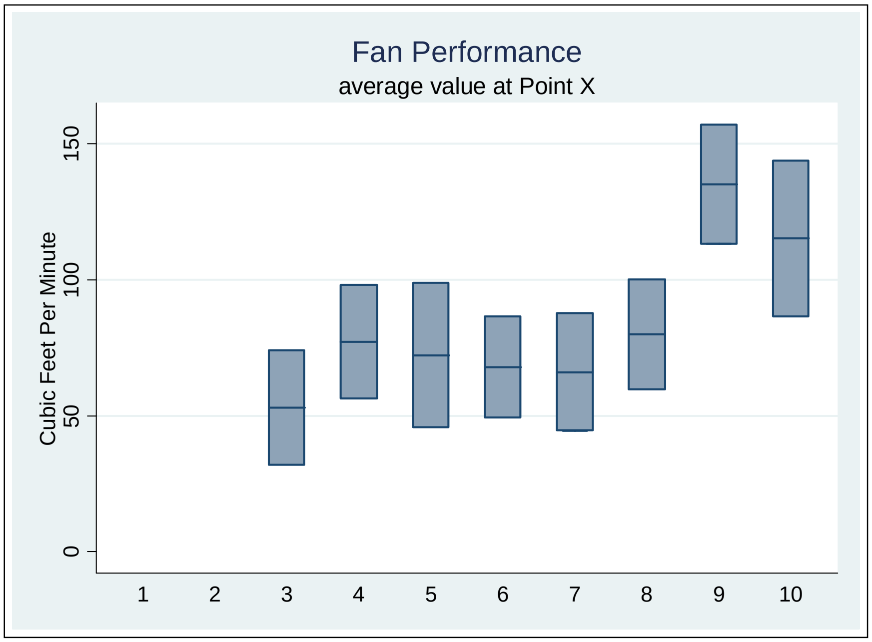


Figure D.11. Minimum, mean, and maximum air flow rate at point X for different potentiometer setting

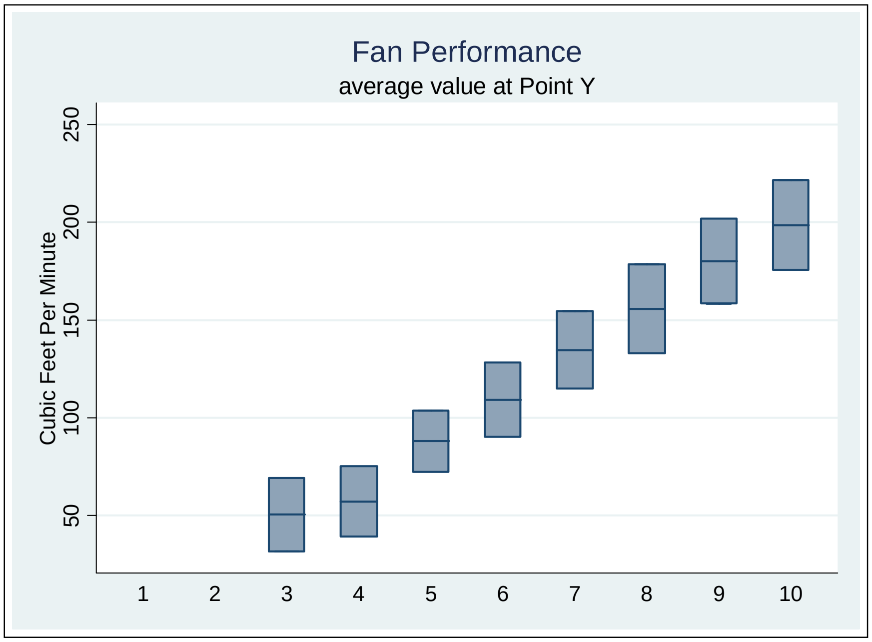


Figure D.12. Minimum, mean, and maximum air flow rate at point Y for different potentiometer setting

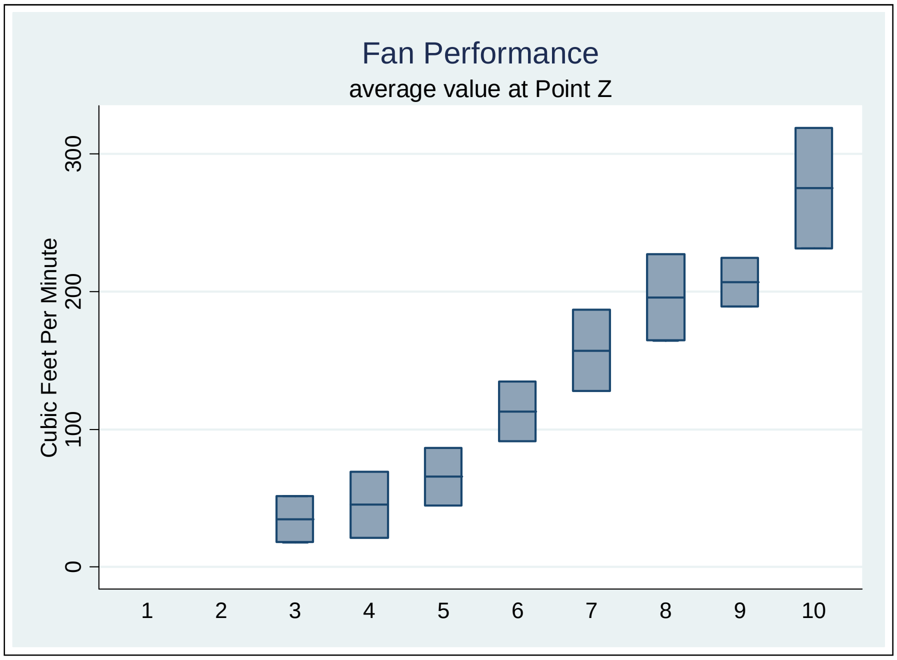


Figure D.13. Minimum, mean, and maximum air flow rate at point Z for different potentiometer setting.

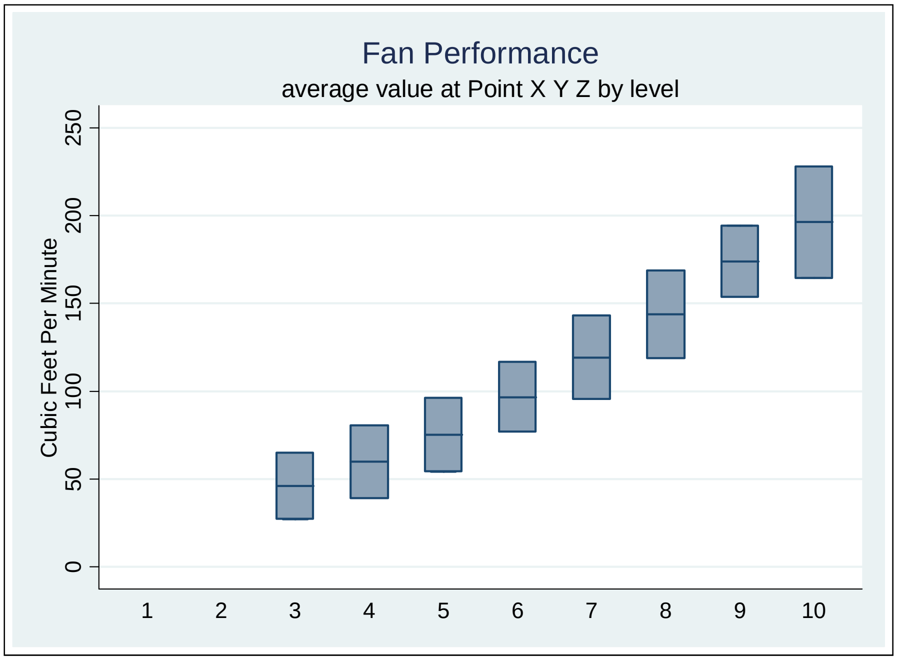


Figure D.14. The relationship between potentiometer scale and air flow rate.

D.2.3 Water distribution pattern though packing

Water distribution in the cooling tower was measured at the temperature of water entering the nozzle of 103.3 ºF and at the airflow rate of 40~75 cubic feet per minute. A 250-ml beaker was used to collect water dripping from the packing (Figure D.15). The time required to fill the beaker to 200 ml was recorded together with water temperature. During the experiment, the beaker was placed at the bottom of the cooling column at different locations.

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Figure D.15. Instrument used to measure the water flowrate through the packing in the cooling tower.

Figure D.16 shows the locations of measuring points and the results are summarized in Table D.4. The flow rate of water in the middle of the cooling tower (point A) was only 41~58 % of the theoretical water flowrate because of the nozzle design. The water can be cooled by 3.7~17.2 ºF depending on the pathway. Comparison of the water passing through the middle of the packing, and that which drips along the wall reveals about 10 ºF temperature difference.

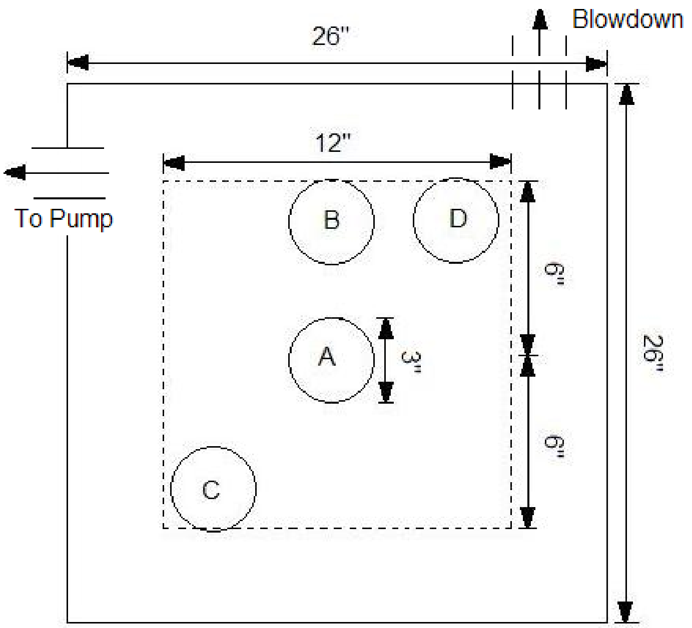


Figure D.16. Measurement locations of water distribution in cooling tower.

Table D.4. Comparison of Temperature and Water Flowrate at different locations

Location	Flowrate, GPM	Temperature, ºF
A_1	0.086 ± 0.008	88.8 ± 1.2
A_2	0.061 ± 0.004	86.1 ± 0.6
B	0.240 ± 0.023	96.7 ± 1.4
C	0.125 ± 0.008	99.6 ± 0.6
D	0.130 ± 0.028	96.9 ± 0.8
Theoretical value	0.147	-

D.3 Cooling Tower Cleaning Procedure

At the end of the experiment with secondary treated wastewater, we observed that the water flowrate decreased from 3 GPM to 2.2 GPM for towers B and C, and to 2 GPM for tower A. It was assumed that either 1) the pump is not function correctly, or 2) scaling/biofouling increase the total water head thus decreasing the water flowrate. Therefore, we assume the cleaning procedure will be mostly removing scaling/biofouling in the system.

Severe scaling/biofouling problem has been discovered earlier during the experiment from the in-line flowmeter. Figure D.17 shows the flowmeter from tower B after 2 days and 10 days operation. Visually we can observe a thick layer of scaling/fouling formed on the inner surface; furthermore, there was a mass of sludge deposited on the float in the flowmeter. The sludge was collected and analyzed. Results of analysis will be covered in later session.

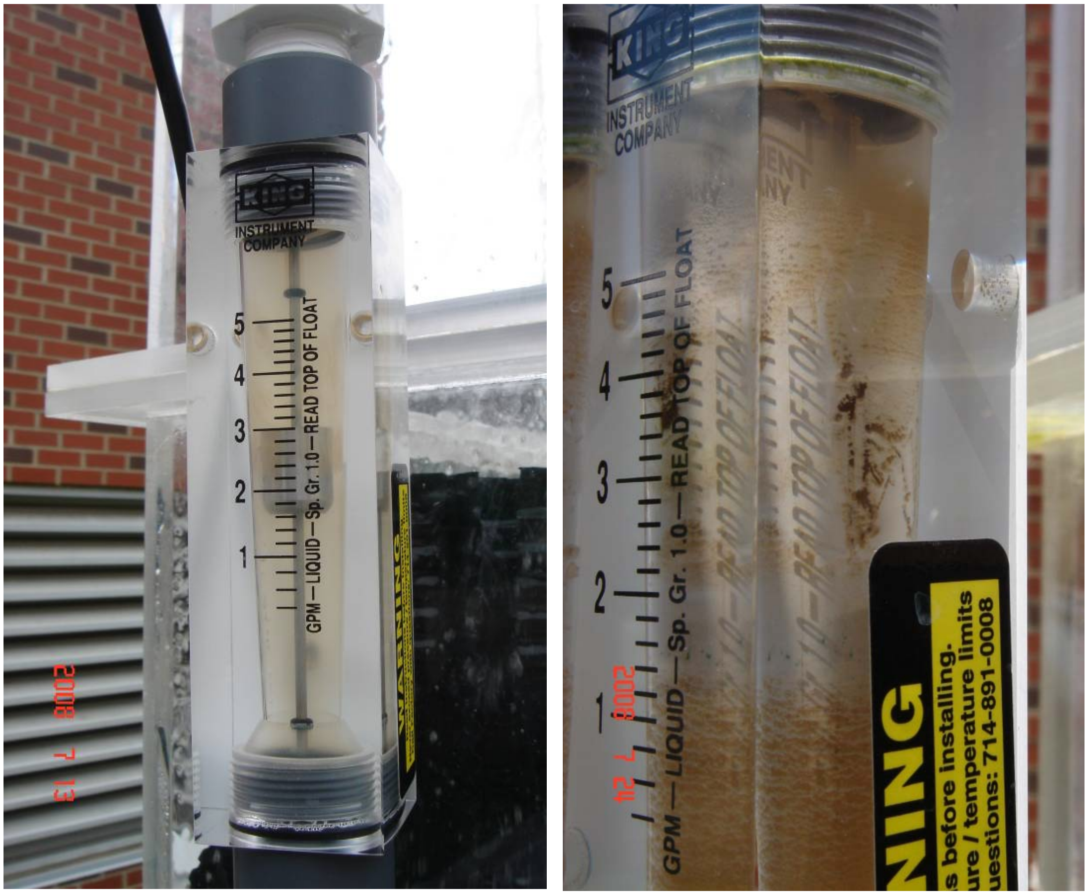


Figure D.17. Flowmeter from Tower B (a fouling layer covered the inside surface and caused clogging).

After 3 weeks of operation, scaling/ biofouling can also be visually observed on the inside wall of column and packing. Figure D.18 shows the condition of biofouling and scaling during last week. From left to right, figures show the condition of scaling/ biofouling on the packing and wall of column on July 31st, August 2nd, and August 4th. The white layer is identified as phosphate precipitation and brown/dark green flocs might be a mixture of calcium precipitation and algae/bacteria.

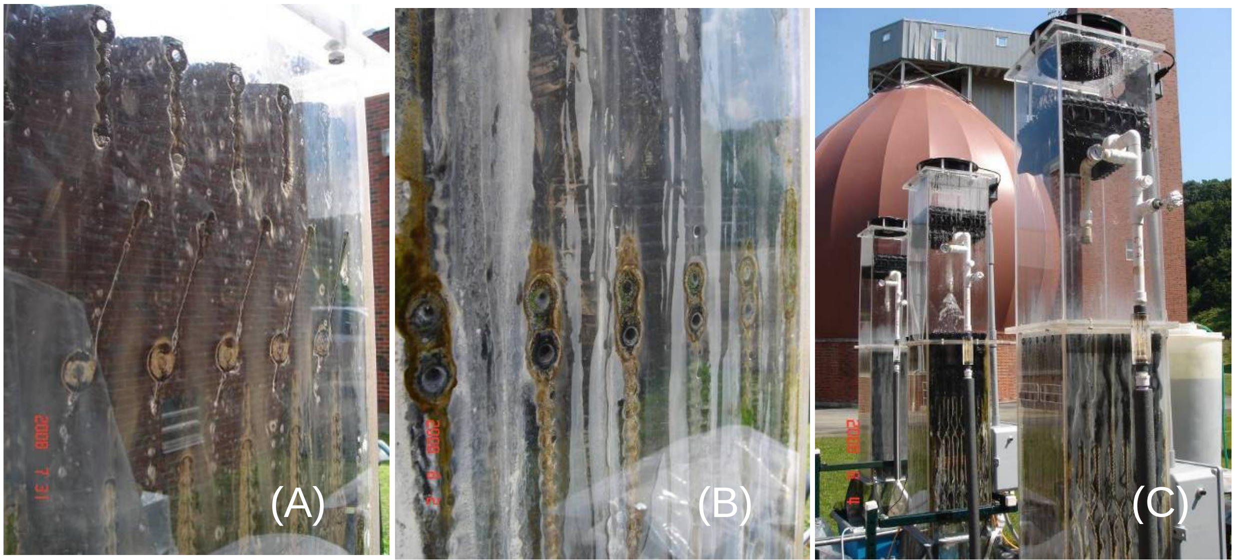


Figure D.18. From left to right, figures show the condition of biofouling/scaling on the packing and wall of column on July 31st, August 2nd, and August 4th. On August 4th, tower A and tower B were shut down already because of the failure of solenoid valve and pump.

In addition, algae growth also caused serve problem in the recirculating system. We observed algae growth in the makeup water tank, in the pump conduit and makeup water conduit. These microorganisms eventually clogged the solenoid valve and caused the makeup water overflow from the basin. As Figure D.18 shows, towers A and B suffered the algae problem and failed on August 4th. Figure D.19 demonstrates the algae problem in the cooling tower system. In order to prevent the algae problem happening, periodically rinsing and brushing the inner wall of makeup water tank is recommended.

Figure D.19 Algae growth was observed in the cooling tower system – A) Makeup water tank B) Makeup water conduit C) Pump conduit. For future studies, it is recommended to wash the makeup water tank regularly to decrease the amount of algae released into the recirculating system.

D.3.1 Cleaning the Cooling Tower Column

During the cleaning procedure, the three towers were first deconstructed on August 5th 2008. After removing the packing from the column, the lower part of cooling column was rinsed with tap water and air dried for an hour. After an hour, most large particles scaled off the wall and then we brushed the wall with tap water to remove the white layer on the inside wall. Commercial 4% vinegar was used to help remove the scaling layer. After gently applying diluted acid solution onto the inside wall, we used brush to clean the scaling layer and rinse with tap water after. Applying acid solution to wash the column is very efficient and 99% of scaling can be removed except unreachable corners. The procedure of cleaning column is shown on Figure D.20.

Figure D.20. From left to right, figures are showing the cleaning procedure on August 5th , including: 1. Air dried for one hour after operation stopped; 2. Cleaned by using brush and tap water; 3. Cleaned by using brush, tap water, and 4% vinegar.

D.3.2 Cleaning Copper Coil in Heat Exchanger

Next step is to clean the copper coil in the heat exchanger. At the beginning, we did not know what reduces the water flowrate in the copper coil, so we propose two methods to clean 1) running low pH acid solution to remove scaling inside the copper coil, 2) running 500 ppm free chlorine to remove biofouling inside the copper coil. Results show only acid solution will recover the water flowrate rate to about 3 GPM.

Figure D.21 shows how the acid wash is performed. We used flexible pipe to build a side recirculating system running through pump, heat exchanger, and acid tank. Acid solution was prepared by diluting one gallon 4% vinegar to 10 gallon with tap water. The side recirculating system was operated for 30 to 60 minutes until we derived roughly 3.5~4 GPM in the side recirculating system (4 GPM is the maximum water flowrate which is derived by running water through new pump, new heat exchanger, and acid tank). The used acid solution was collected and analyzed back into the laboratory. Analysis shows the precipitation inside the copper coil is mainly phosphate deposit.

Figure D.21. Ten gallon side recirculating system was used to clean the copper coil. One gallon of vinegar was diluted to roughly 10 gallons with tap water. After 30 to 60 minutes of recirculating time. The acid wash procedure could remove the scaling. The water turned to dark brown after the procedure.

D.3.3 Cleaning Basin, Pipe System, In-line Instruments, and makeup water tank

The recirculating water was drained back to the secondary effluent channel in FTMSA after we shut down the cooling tower system. The enclosing screen around the basin was removed and cleaned. The basin was filled with thin layer of sludge. After taking samples of the sludge, we refilled the basin with tap water and used siphon pipe to remove the bottom sludge. The float switches, through wall fitting, and stainless steel legs were washed with brush and diluted acid solution. After several times siphonal cleaning, we disinfected the basin with low dose hypochlorite and vinegar by turns. Cleaning procedure and result are shown in Figure D.22.

Figure D.22. Basin was simply cleaned by using brush and tap water and waste water was drained by siphon tube; small amount vinegar was used to remove solid precipitation on stainless steel legs.

The pipe system and in-line instruments were decomposed and soaked in diluted vinegar for one day and then cleaned with small brush. Metal components including the inner parts of flowmeter and nozzles were soaked in pH 2 solutions for days to have better cleanness; plastic components including thermometer, and shells of flowmeter were soaked in pH 3 solution. PVC pipes, solenoid valves, totalizers, and pressure gauges were soaked into diluted vinegar. All components were rinsed with tap water after and air dried until the beginning of second experiment (Figure D.23).

All of makeup water tanks were filled with algae after 25 days operation although regularly cleaning was performed during the experiment (Figure D.24). Especially at the bottom of the tank and near the through wall fitting, the algae populated and formed thick layer around the bottom. The makeup water tanks have height of 44” and can only be washed with long shaft brush. We used tap water and long shaft brush to remove most visible algae and then fill the tanks up with small amounts of vinegar and sodium hypochlorite by turns. We rotated the makeup water tanks to let vinegar and sodium hypochlorite fully in contact with the inner surface. About 1 gallon of diluted hypochlorite was left in the tank as residual disinfectant until the beginning of another experiment.

In summary, standard methods for maintaining and cleaning pilot scale cooling towers have been built and results indicate these towers can be reutilized after proper cleaning procedure. Stable performance data from secondary run with secondary treated wastewater illustrates that the cooling towers are durable and reliable after suffering serve scaling/biofouling problem.

Figure D.23. Pipe system and in-line instruments are cleaned with acid solution, the left figure shows inner parts of flowrate meter is being acid washed with pH 2 solutions. Middle figure shows the cleaning of thermometer and shell of flowrate meter with pH 3 solution. Right figure shows that the pipe system, parts of solenoid valves, nozzles, and parts of totalizers were immersed into diluted vinegar solution.

Figure D.24. Algae populated the bottom of the makeup water tank and near the through wall fitting. Since the tank was 44” height, we could only use long shaft brush to clean the bottom. After removing most visible algae, we disinfected the tanks with vinegar and low dosage of sodium hypochlorite in turns.

APPENDIX E: Pilot-Scale Cooling Tower Performance with Secondary Treated Municipal Wastewater and Passively Treated Acid Mine Drainage

Field testing of cooling tower performance with three impaired waters involved the use of three small, pilot-scale cooling towers. The three towers were operated together at Franklin Township Municipal Sanity Authority (FTMSA) for about 3-4 weeks with each impaired water. During this period, the rate of corrosion of metals in contact with the cooling water, the scaling potential, and biomass growth were investigated for the various waters and operational conditions examined. After that, the three towers were cleaned and disinfected for next testing.

E.1 Pilot-Scale Cooling Tower Performance When Using Secondary Treated Wastewater as Makeup

In July 2008, the three cooling towers were operated with secondary and tertiary effluent in FTMSA for two consecutive 25 day periods. During these trials, detailed information on tower operation was recorded, including temperature of water at specific locations, airflow rate inside the cooling column, conductivity of recirculating water, makeup water volume, blowdown volume, water flowrate, and ambient conditions (weather, temperature, relative humidity). Between first and second trial, three towers were cleaned with acid solution and disinfected by free chlorine.

The first run started on July 11th 2008 and finished on August 3rd 2008; the second run started on August 11th 2008 and finished on September 4th 2008. During the first run, all towers were using secondary effluent as makeup water. For the second run, two towers (CTA and CTB) were using secondary effluent and CTC was using tertiary effluent as makeup water source. It was found that the raw wastewater had conductivity ranging from 0.76 to 1.32 mS/cm. Therefore, 1.2 mS/cm was chosen as a base to calculate the 4 cycles of concentration (CoC); in other words, the target 4~5 CoC refers to the recirculating water having conductivity as 4.5 ~ 5 mS/cm. For the second run, the target of CoC in the range was set at 4.5 ~ 5 mS/cm.

E.1.1 Water flowrate in the recirculating system

The designed flowrate in the recirculating system was 3 GPM. An inline flowmeter with range of 1~5 GPM (Acrylic Flowmeter, 7511212B-08, King Instrument Company, CA) was used to monitor the variance of flowrate. Results are shown on Figure E.1 and Figure E.2.

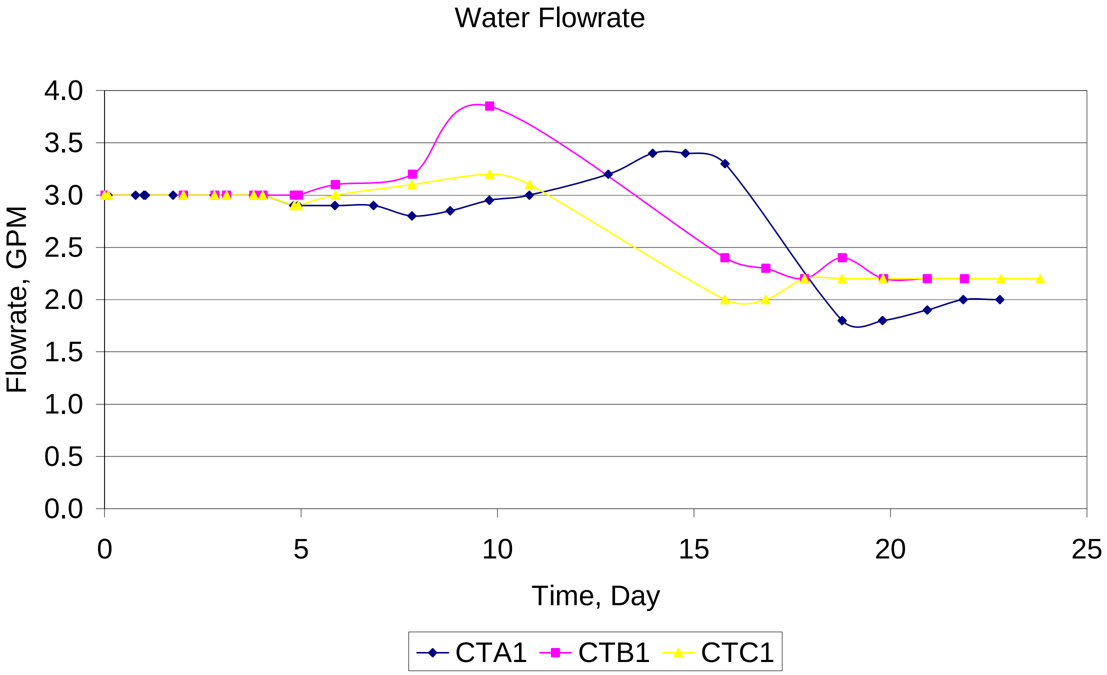


Figure E.1. Water flowrate measured in the system during the first run in FTMSA (target flowrate was 3 GPM).

In the first run with secondary effluent as makeup water source, the water flowrate started to vary after 5 days of operations. It was found that scaling formed in the in-line flowmeter and caused the faulty reading. All flowmeters were replaced on Day 15 and the water flowrate in all towers decreased to below 2.5 GPM. After 21 days, the recirculating system was evaluated and cleaned with acid. It is found that scaling formed inside the heat exchanger and caused the drop in the flowrate.

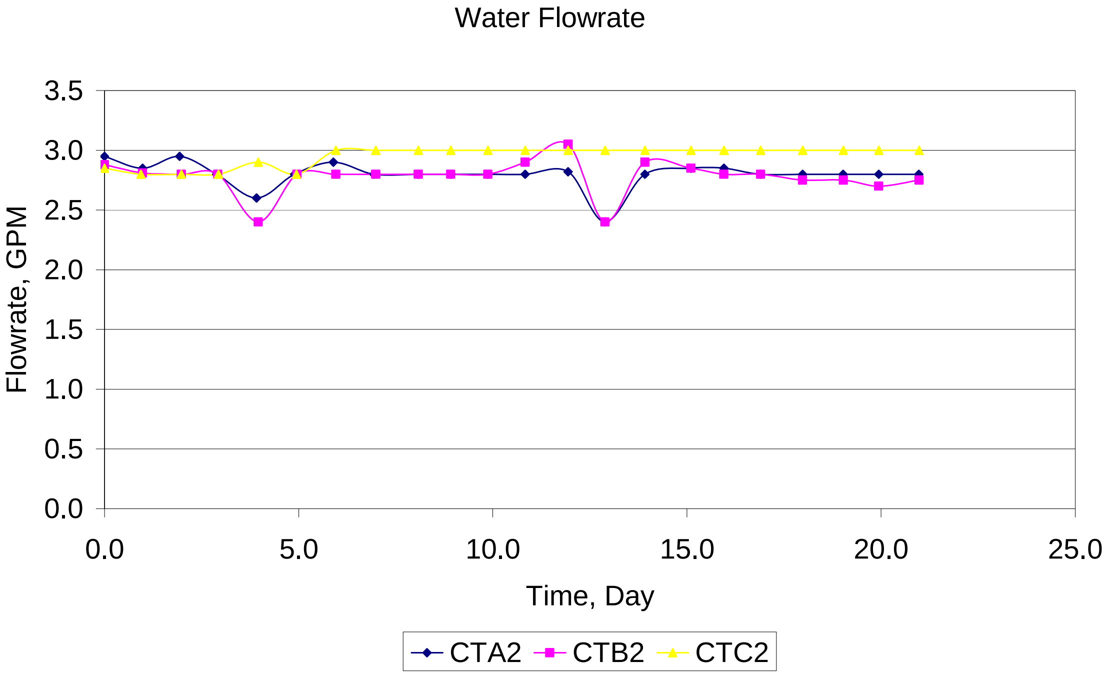


Figure E.2. Water flowrate measured in the system during the second run in FTMSA (target flowrate was 3 GPM). CTA2, and CTB2 were using secondary effluetn as makeup water source, while CTC2 was using tertiary effluent as makeup water.

In the second run, towers CTA2 and CTB2 were using secondary effluent as makeup water source and tower CTC2 was using tertiary effluent as makeup water source. Since scaling problem was found from first run, changing flowmeter and acid wash were included in the experimental protocol to prevent faulty reading and the loss of flowrate. Tower CTA2 and CTB2 were washed with acid on Day 4 and Day 13. It was observed that tower CTC2 did not require acid wash since no significant scaling formed.

In summary, the water flowrate in the recirculating system was better controlled and monitored in second run and could provide more stable water velocity. However, minor loss of water flowrate was still found in tower CTA2 and CTB2 due to possible scaling in the heat exchanger. Further discuss will be covered in scaling study.

E1.2 Temperature and Air Flowrate through the Cooling Tower

The ambient temperature used in the design of the cooling system was average wet bulb temperature in Pittsburgh, which is 79ºF (26.1ºC) in summer. Figure E.3 shows the daily ambient temperature and relative humidity in FTMSA, Murrysville, PA during the first and second runs. Average ambient temperatures for first and second runs were 28 ºC with a relative humidity of 64.7 % and 24.8 ºC with a relative humidity of 68%, respectively.

The measured ambient temperatures are within the designed temperature at 79.1 ºC ± 5 ºF (2 ºC). Results on Figures E.3 and E.4 indicate that ambient temperature varied daily with the local weather condition, which may cause some differences in cooling tower performance. The temperature difference (cooling capacity) is mainly affected by the airflow rate through the cooling column and the temperature in heat exchanger. Therefore, fine adjustment of input airflow rate and heating output were performed continuously to ensure desired temperature values at different points in the system.

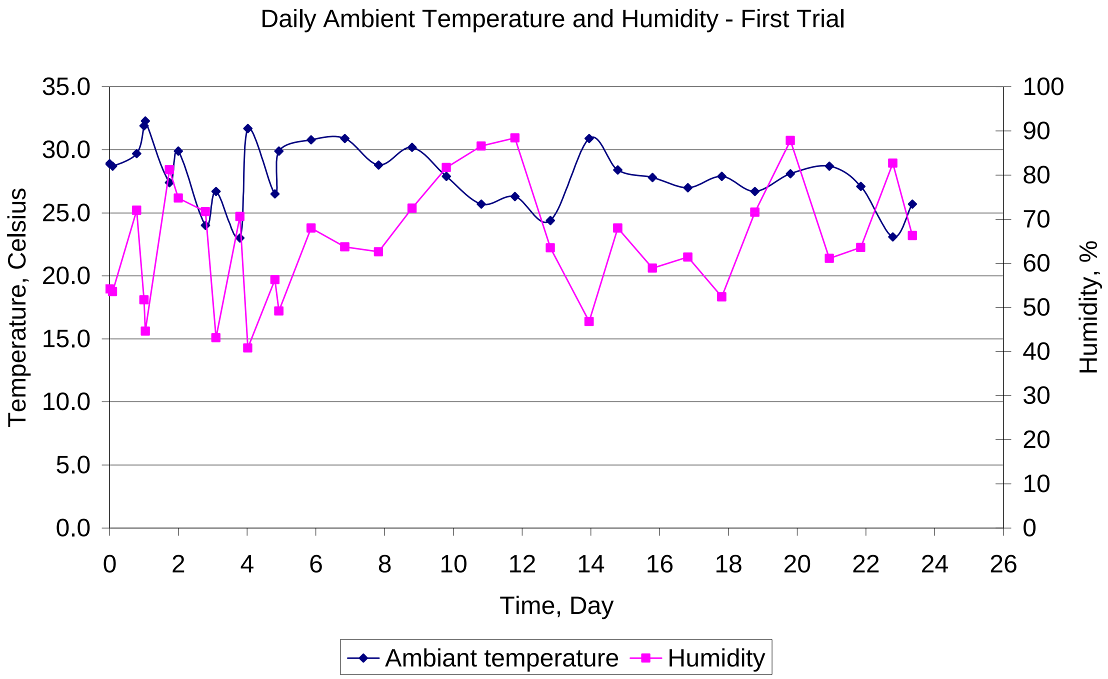


Figure E.3 Daily temperature and relative humidity in FTMSA during the first run. First run started from July 11th to August 4th. Average temperature and relative humidity during the 21 day run were 28 ºC and 64.7%.

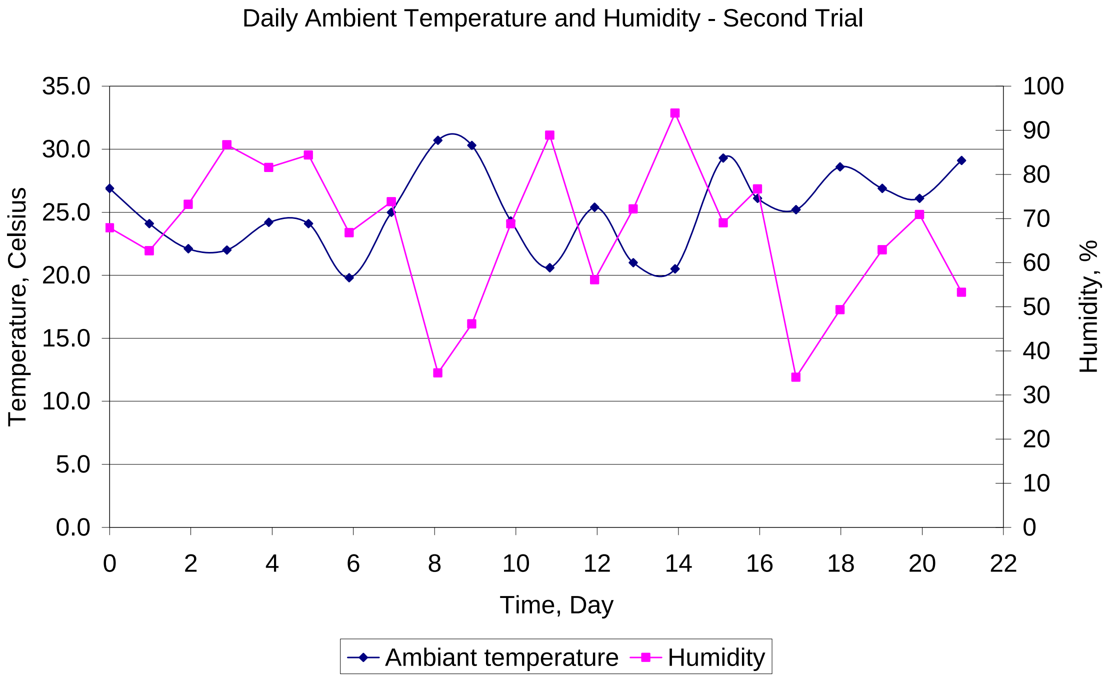
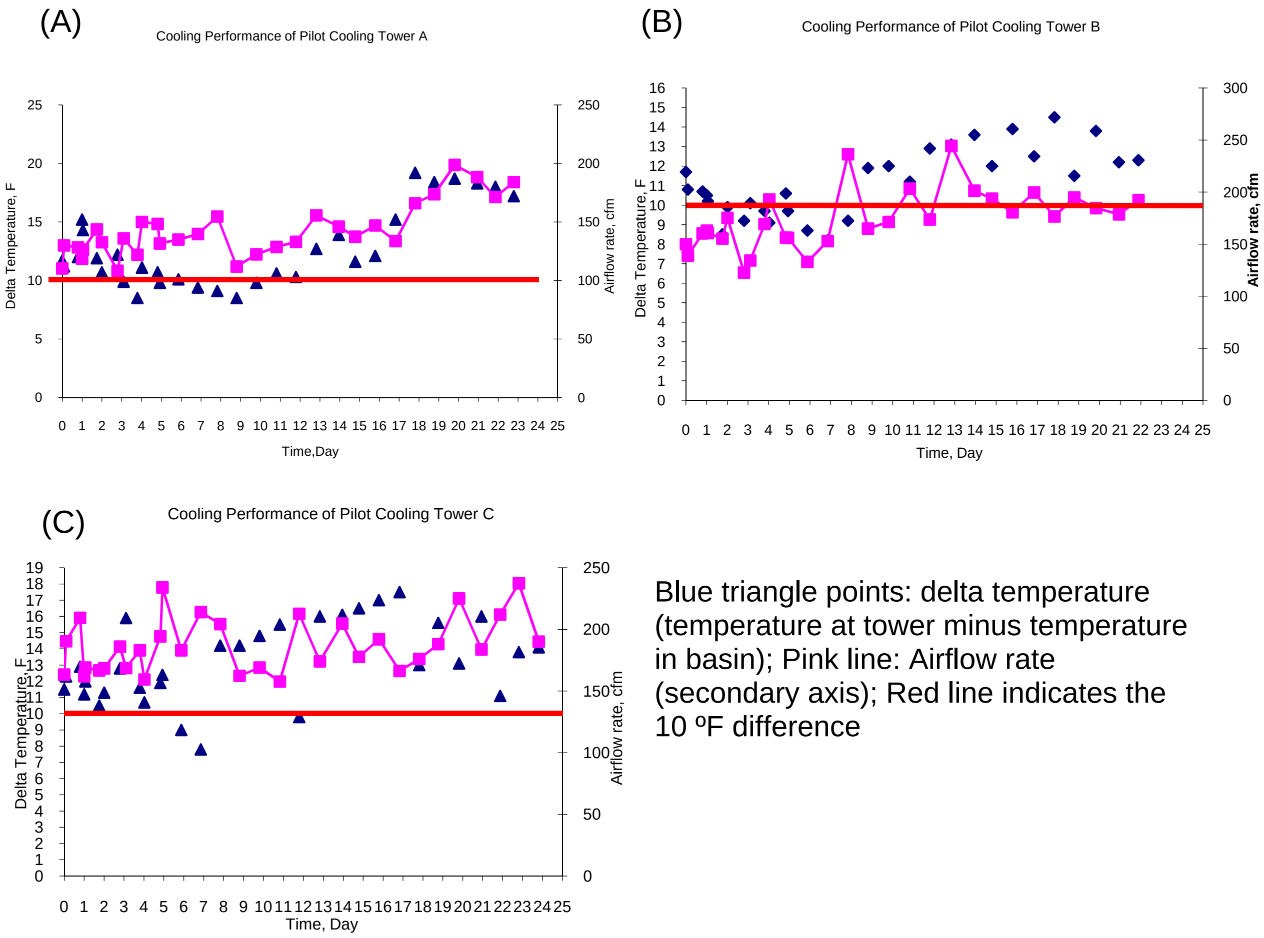


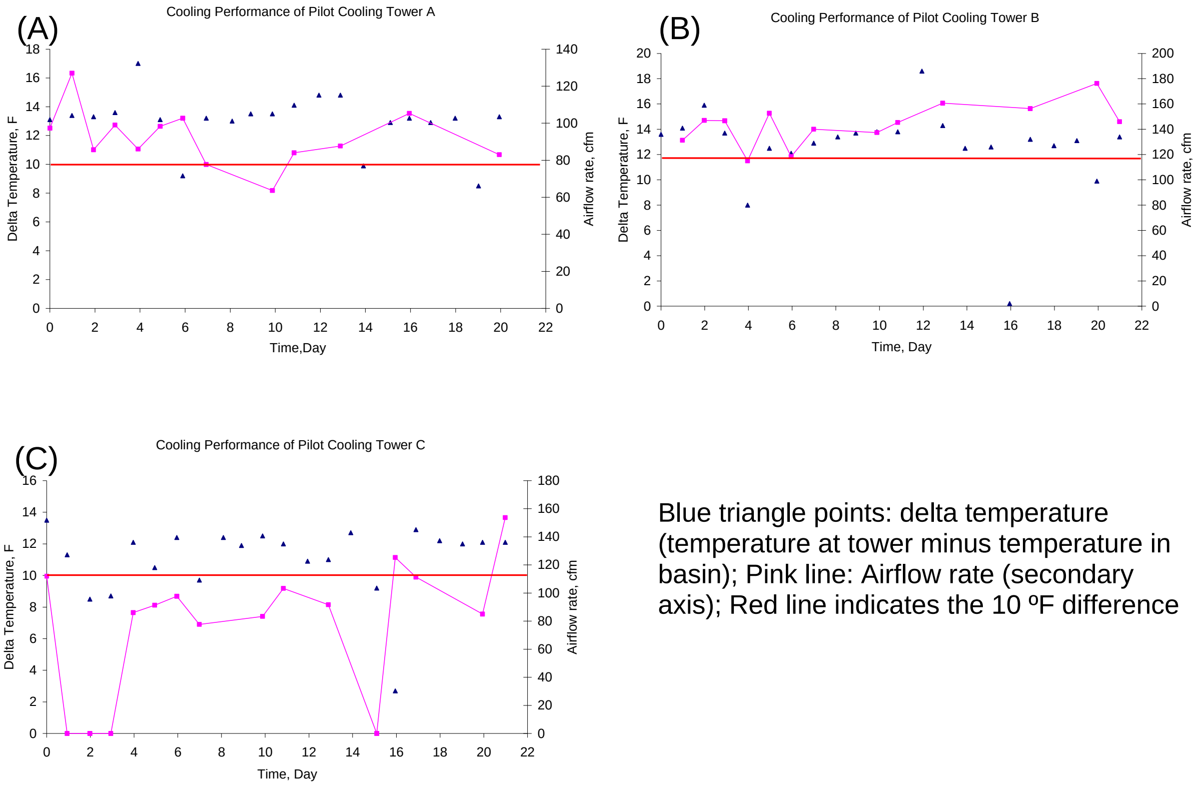
Figure E.4 Daily temperature and relative humidity in FTMSA during the second run. Second run started from August 11th to September 4th. Average temperature and relative humidity during the 21 day run were 26.1 ºC and 68%.

Figures E.5 and E.6 show the temperature difference (cooling capacity) and airflow rate for all cooling towers and for both runs. In the first run, the temperature difference was not well maintained in first 10 days on CTA1, CTB1, and CTC1 and decreased below 10 ºF. Therefore, the airflow rate was increased up to 200 CFM to match target temperature difference. However, after 10 days the temperature differential started to increase regardless of airflow rate. The reasons for this increase in temperature differential include: 1) the setting of heat exchanger was increased because it was important to maintain the temperature at spray nozzles at 105 ºF, 2) the contact time of water in the heat exchanger increased because of a decrease in flowrate. In the second run, the temperature differences were much better controlled during the whole period on CTA2, and CTB2. However, CTC2 had several outliners because the axial fan was damaged and there was no airflow inside the cooling tower CTC2. The results indicate that the airflow rate plays an important role in controlling temperature difference.



Blue triangle points: delta temperature (temperature at tower minus temperature in basin); Pink line: Airflow rate (secondary axis); Red line indicates the 10 ºF difference

Figure E.5. Temperature differential across cooling towers and air flowrate during the first test.



Blue triangle points: delta temperature (temperature at tower minus temperature in basin); Pink line: Airflow rate (secondary axis); Red line indicates the 10 ºF difference

Figure E.6. Temperature differential across cooling towers and air flowrate during the second (the fan was broken on day 1~3 and day 14~15).

The airflow rate is measured by using anemometer at point X near the center of column close to the nozzle, point Y close to the wall, and point Z at the middle between points X and Y. Preliminary studies revealed that changing the fan speed only shifts the temperature difference instead of increasing the cooling capacity. Therefore, different fan speed settings were applied to all three towers to best meet desired temperature profile. Table E.1 shows the average airflow rate measured during first and second runs. In first run, most towers required higher airflow rate then design value. On contrary, in second run, all towers required lower airflow rate to maintain temperature difference.

The results are in accordance with the change of ambient temperature. The ambient temperature was 28 ºC and 24.8 ºC for first and second run respectively, while the ambient temperature used for cooling tower design is 26.1 ºC. This can explain why the airflow rate changed for different runs on the same cooling tower system.

Table E.1. Average Airflow rate in first and second run.

Airflow rate (CFM)	**Design**	**CTA**	**CTB**	**CTC**	**Ambient Temperature (ºC)**
First Run	150 (26.1)	142 ± 23	174 ± 28	187 ± 22	28
Second Run		95 ± 16	145 ± 16	117 ± 40	24.8

Besides the 10 ºF temperature differential across the tower, maintaining the temperature of water at spray nozzle at 105 ºF was required to simulate the real situation in the power generating facilities. Table E.2 summarizes the average water temperature at nozzle for all towers during both runs. During both runs, CTA and CTB could have water temperature at nozzle around 105 ºF. However, tower CTC had higher water temperature in both runs. During the second run, CTC had its exhausting fan broken twice and neither cold air is drawn into the column nor is hot air released into the atmosphere except through the convection.

Table E.2 Average water temperature at spray nozzle in first and second run.

Temperature of water at nozzle (ºF)	**CTA**	**CTB**	**CTC**
First run	105.2 ± 3.5	104.4 ± 1.5	107.2 ± 3.0
Second run	105.3 ± 2.9	105.8 ± 3.6	108.7 ± 6.3

Figures E.7 and E.8 show daily water temperature at nozzle during first and second run. The temperature of water at spray nozzle was maintained around 105 ^{o}F during the first run. During the second run, tower CTC had operational problems, such as broken fan on day 1 ~3 and day 14~15, which lead to changes in water temperature at the spray nozzle. Tower CTB was also influenced by broken fan problem on Day 4 and Day 16 (reduced heat output). As to tower CTA, the faulty solenoid valve caused the excess makeup water refill, thus causing the temperature drop in the second half run.

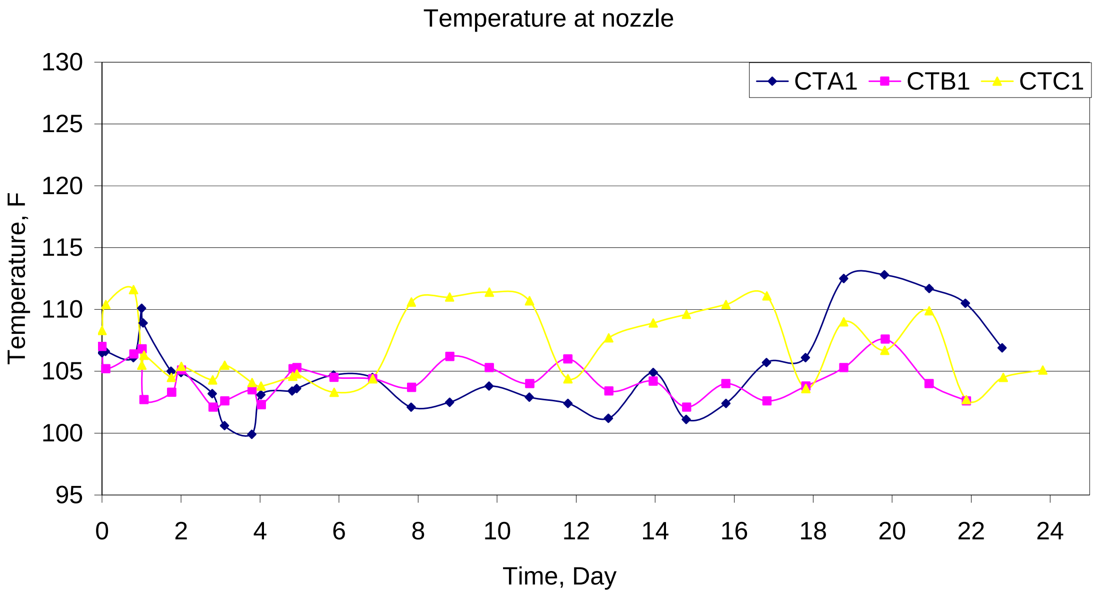


Figure E.7. Temperature of water entering nozzle for CTA1, CTB, and CTC1 in first run.

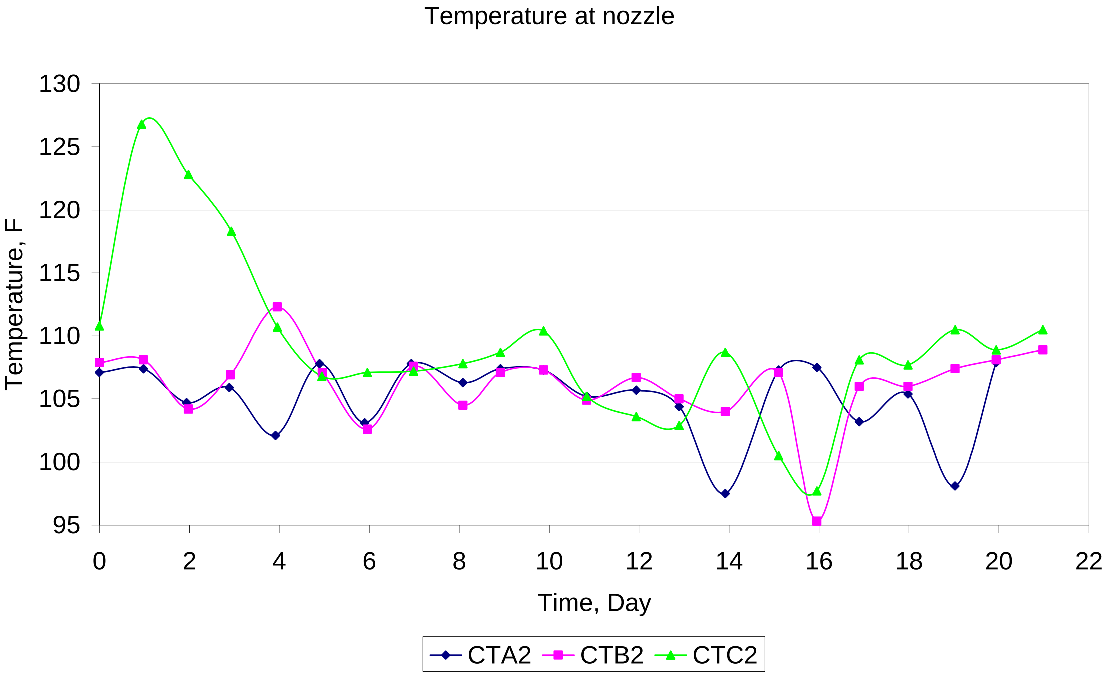


Figure E.8. Temperature of water entering nozzle for CTA2, CTB2, and CTC2 during the second run.

In summary, the operating procedure used in this study was adjusted in the field to fulfill the design criteria for pilot scale cooling towers. Temperature profile can be controlled by adjusting the airflow rate and heat input. In addition, the ambient temperature is equally important for cooling tower operation since it affects the airflow rate required to reach target temperature difference.

E.1.3 Makeup Water and Blowdown

The average daily water consumption rate is influenced by ambient temperature, temperature of water in the recirculating system, and airflow rate. Variations in these parameters will inevitably cause variations in daily water consumption.

The blowdown rate is controlled by the inline conductivity meter. When the conductivity of recirculating water exceeds the set point (in the case of municipal wastewater, set point was 4.8 mS/cm for the first run and 4 mS/cm for the second run), the conductivity meter will send the signal to open the solenoid valve and initiate blowdown, which will also trigger the influx of makeup water, until the conductivity reading drops below the set point.

The water consumption rate and blowdown rate were recorded by inline totalizers and the evaporation rate can be calculated by subtracting the blowdown rate from the water consumption rate. Data collected from the two filed tests are summarized in Table E.3. The average total makeup water consumption in the first run was 46.8 gallons/day, while average daily blowdown and evaporation were 8.5 gallons and 39.1 gallons, respectively. In the second run, the same towers had 56.1 gallons/day water consumption, 13 gallons/day blowdown, and 43.2 gallons/day evaporation.

Table E.3. Average daily water consumption rate, blowdown rate, and evaporation rate for all three towers during first and second runs.

First Run	**CTA1**	**CTB1**	**CTC1**
Daily Water Consuming rate (gallon/day)	43.6 ± 7.6	46.6 ± 6.6	50.2 ± 6.1
Daily Blowdown rate (gallon/day)	8.5 ± 3.4	9.3 ± 3.7	7.7 ± 4.0
Daily Evaporation rate (gallon/day)	36.2 ± 4.8	38.1 ± 4.7	42.9 ± 4.9
Second Run	**CTA2**	**CTB2**	**CTC2**
Daily Water Consuming rate (gallon/day)	54.3 ± 6.8	60.5 ± 11.1	53.6 ± 10.1
Daily Blowdown rate (gallon/day)	12.0 ± 4.0	14.1 ± 6.0	12.9 ± 5.0
Daily Evaporation rate (gallon/day)	42.2 ± 7.1	46.4 ± 8.4	40.7 ± 8.1

Figure E.9 and Figure E.10 show the daily water consumption and blowdown as well as cumulative water consumption and blowdown. During the first run, none of the cooling tower systems suffered mechanical breakdown. Tower CTA1 had first blowdown half a day later than others. Tower CTB1 had blowdown rate about 20 gallons/day on Day 16 without any mechanical failure.

During the second run, more abrupt changes in water consumption occurred because of system failure. Tower CTA2 had steady water usage rate until the blowdown solenoid valve broke on Day 17. Tower CTB2 had low blowdown value on Day 3 because of the faulty fan. Figure E.10 (A) shows CTB2 had no makeup water on Day 17, which may be caused by the clogged totalizer. Tower CTC2 had lower water consumption on Days 3 and 16 because the malfunctioning of the exhaust fan.

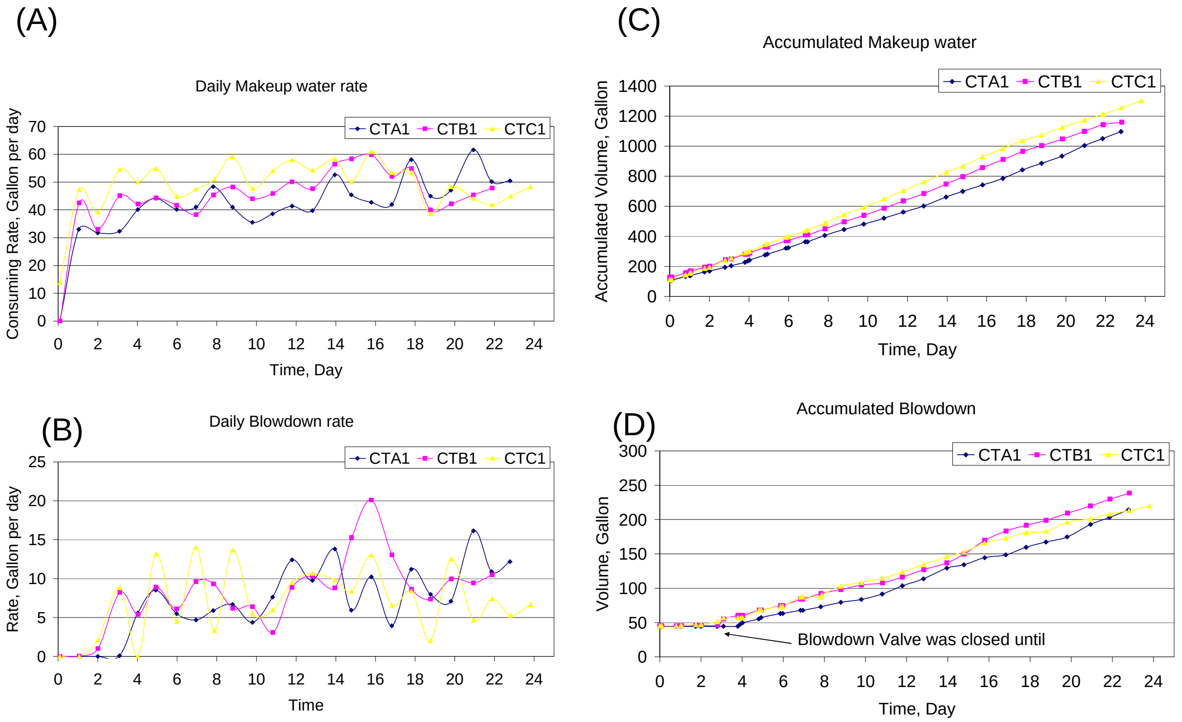


Figure E.9. Makeup water and blowdown during the first run: A) Daily makeup water rate, B) Daily blowdown rate, C) Cumulative makeup water volume, and D) Cumulative blowdown volume.

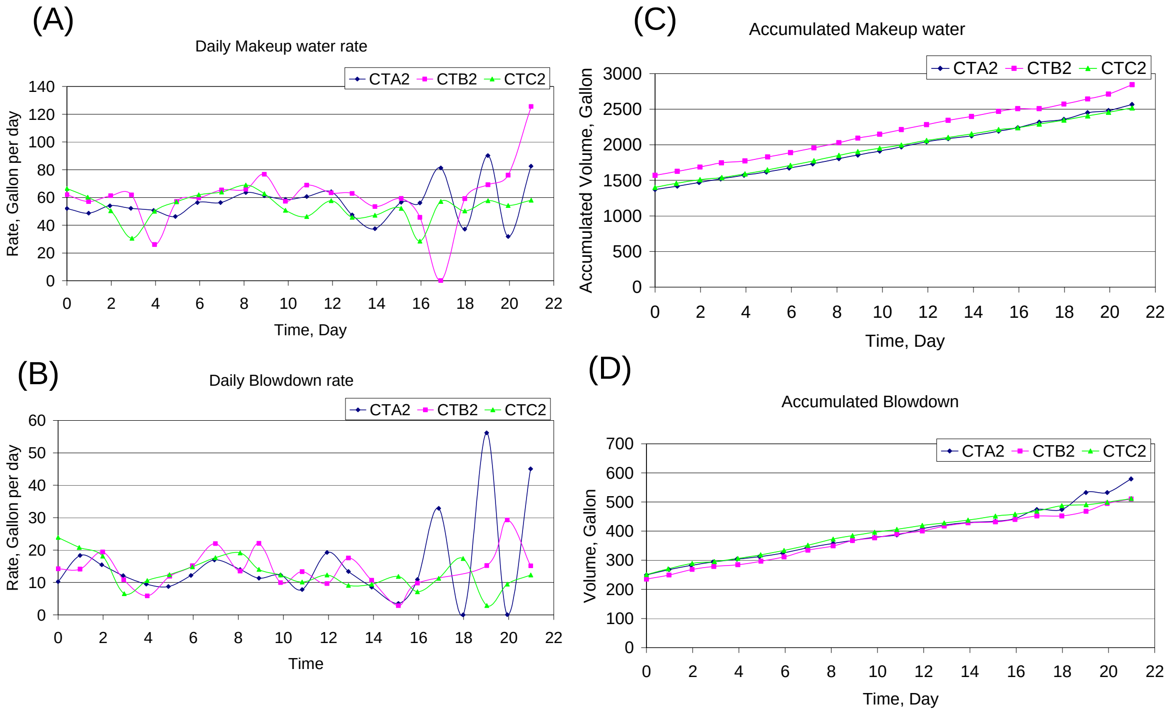


Figure E.10. Makeup water and blowdown during the second run: A) Daily makeup water rate, B) Daily blowdown rate, C) Cumulative makeup water volume, and D) Cumulative blowdown volume.

Generally, the characteristics observed for cooling towers in field correspond to that data collected in laboratory. Daily water evaporation rate is related to the water flowrate in the recirculating system. The slope of cumulative water consumption and blowdown curves are close to linear, which means the daily rates were steady most of the time. In addition, the performance of cooling towers would have been more stable without mechanical failures of solenoid valves and exhaust fans.

E.1.4 Cycles of Concentration in the Recirculating System Based on Conductivity

Conductivity of the makeup water was recorded daily with portable conductivity meter (Figure E.11) and the average conductivity was 1.02 ± 0.18 mS/cm for the first run. During the second run, the average conductivity was 1.05 ± 0.26 for secondary effluent and 0.97 ± 0.18 mS/cm for tertiary effluent.

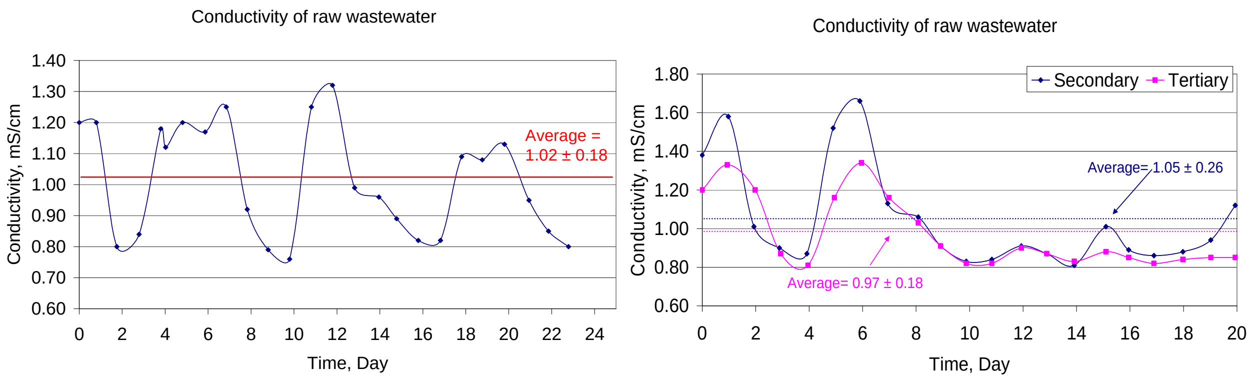


Figure E.11. Conductivity of makeup water. The average conductivity was 1.02 ± 0.18 mS/cm for the first run. During the second run, the average conductivity was 1.05 ± 0.26 for secondary effluent and 0.97 ± 0.18 mS/cm for tertiary effluent.

The blowdown was controlled by the conductivity set point connected to the solenoid valve on the discharge pipe. For the first run, CoC 4 was defined as 4.8 mS/cm in the recirculating system. Figure E.12 shows the daily conductivity measured with portable conductivity during the first run. Figure E.12.(B) shows that the conductivity in CTB1 decreased dramatically after Day 15 since the blowdown control mechanism did not function correctly. On average, only tower CTB1 failed to maintain CoC 4 in the system for several days.

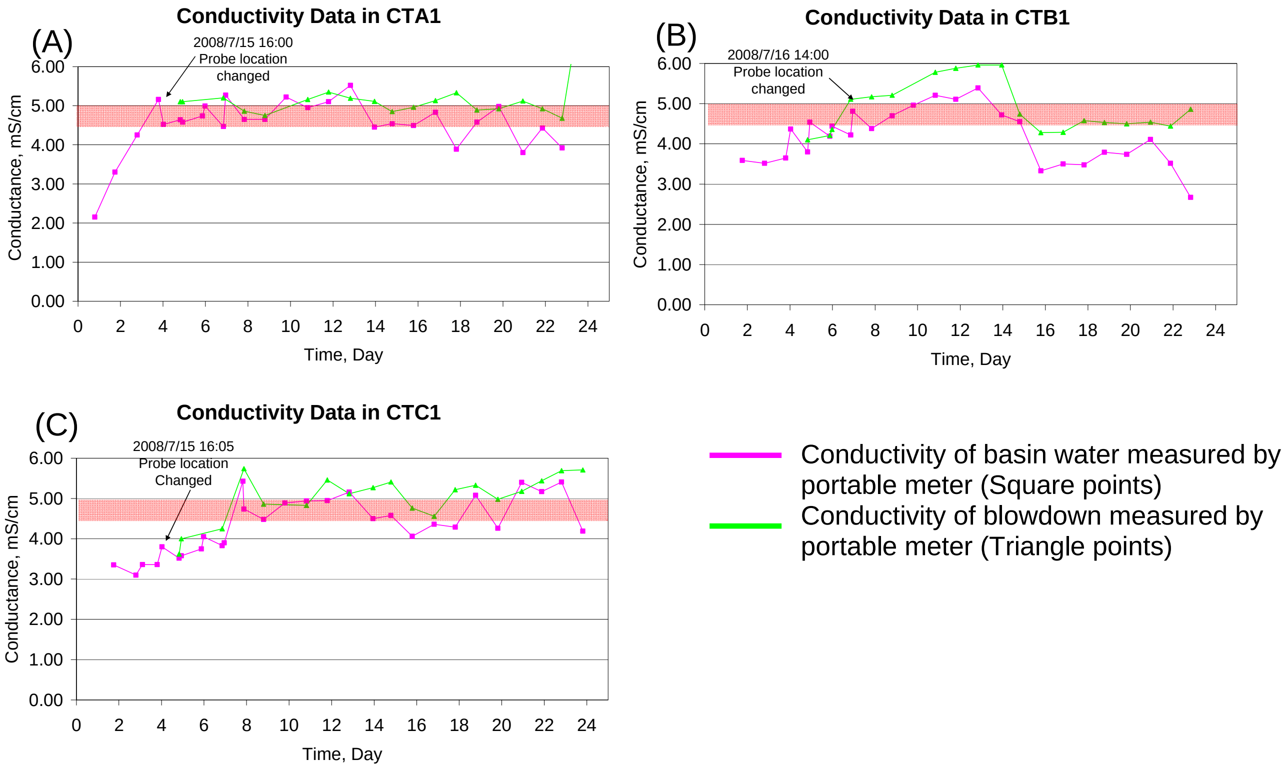


Figure E.12. Daily conductivity of recirculating water in cooling tower A, B, and C for the first run. Shaded area indicates the target 4 ~ 5 CoC range (4.5 ~ 5 mS/cm).

Figure E.13 shows the daily conductivity of recirculating water measured with portable conductivity meter during the second run. Towers CTB2 and CTC2 showed better control of CoC based on the conductivity of recirculating water. Tower CTA2 had higher conductivity during the first half of the test because of its better cooling capacity (Shown in Figure E.6 (A)). In the second half, tower CTA2 ran out of makeup water twice because the solenoid valve on the makeup water line did not function correctly.

Table E.4 summarizes the conductivity data during the two runs. The conductivity of raw wastewater, water in the basin, and blowdown were recorded daily and is shown as 21-day average. The last two columns show the calculated CoC based on different methods. CoC(1) is calculated by dividing the conductivity of blowdown by the conductivity of raw water. CoC(2) is calculated by dividing the conductivity of blowdown by the average makeup water conductivity (1.2 mS/cm for the first run and 1 mS/cm for the second run). The results in Table E.4. show that the CoC is well controlled in the range of CoC 4 ~5.

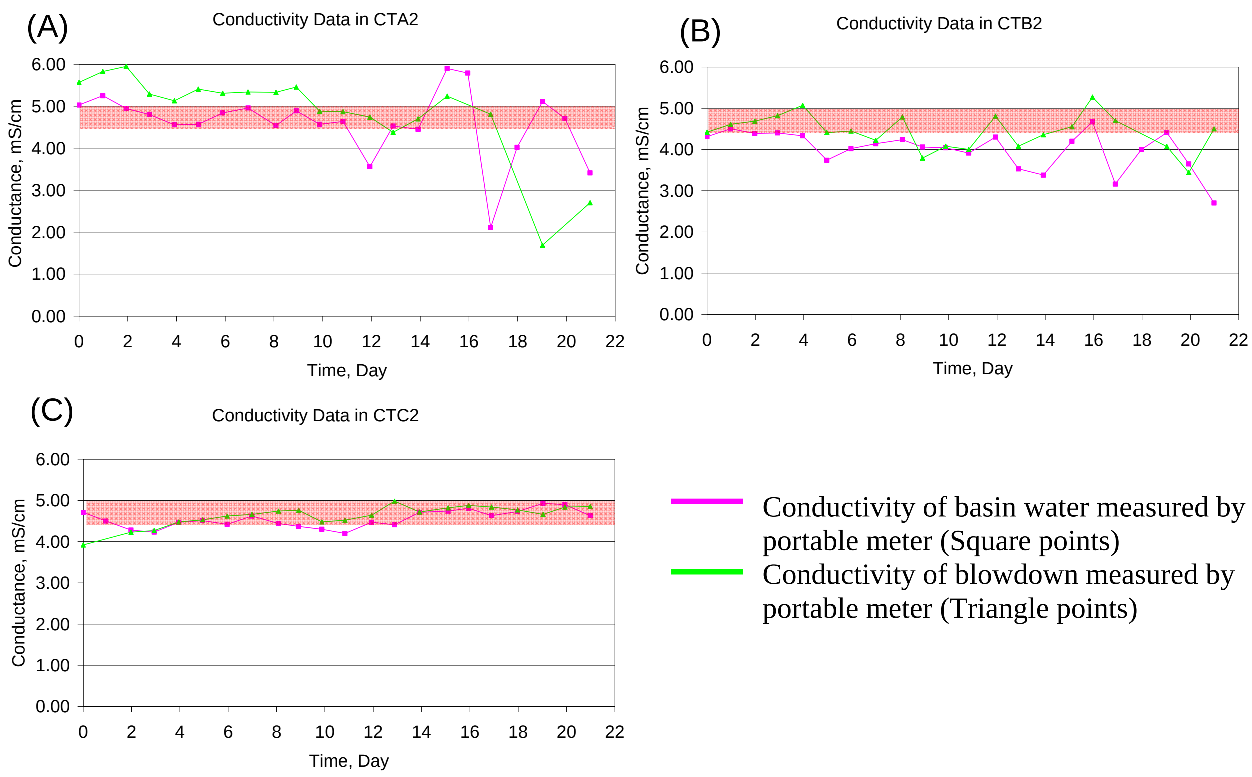


Figure E.13. Daily conductivity of recirculating water in cooling tower A, B, and C for the second run. Shaded area indicates the target CoC 4 ~ 5 range (4.5 ~ 5 mS/cm).

Table E.4. Conductivity measurement in CTA, CTB, and CTC for both runs and calculated CoC based on different methods.

	Conductivity	Raw	Basin	Blowdown	CoC (1)*	CoC (2)*
First Run	CTA1	1.02 ± 0.18	4.67 ± 0.44	5.30 ± 0.19	5.2	4.4
	CTB1		4.23 ± 0.70	4.87 ± 0.63	4.8	4.1
	CTC1		4.50 ± 0.59	4.67 ± 1.29	4.6	3.9
Second Run	CTA2	1.05 ± 0.26	4.82 ± 0.50	5.21 ± 0.42	5.0	5.2
	CTB2		4.07 ± 0.39	4.43 ± 0.43	4.2	4.4
	CTC2	0.97 ± 0.18	4.55 ± 0.21	4.63 ± 0.25	4.8	4.6

* The CoC is calculated by dividing conductivity of blowdown by conductivity of raw water.

** The CoC is calculated by dividing conductivity of blowdown by target conductivity value; 1.2 mS/cm for first run and 1 mS/cm for second run.

E.1.5 Cycles of Concentration in the Recirculating System Based on Blowdown Volume

Besides using conductivity to define CoC, the CoC can also be derived from dividing the average daily makeup water volume by total daily blowdown volume. Results are shown in Table E.5. Based on the volumetric comparison, the towers have slightly higher CoC than the target value (4-5) during the first run. CoC control during the second run was slightly better and closer to the target value.

Table E.5. CoC calculated using the volumetric method

	Tower	Water consuming rate (Gal/Day)	Blowdown rate (Gal/Day)	CoC
First Run	CTA1	43.6 ± 7.6	8.5 ± 3.4	5.1
	CTB1	46.6 ± 6.6	9.3 ± 3.7	5.0
	CTC1	50.2 ± 6.1	7.7 ± 4.0	6.5
Second Run	CTA2	54.3 ± 6.8	12.0 ± 4.0	4.5
	CTB2	60.5 ± 11.1	14.1 ± 6.0	4.3
	CTC2	53.6 ± 10.1	12.9 ± 5.0	4.2

In conclusion, the cooling towers were appropriately control to maintain CoC in a target range based on both the conductivity measurements and volumetric measurements of makeup and blowdown.

E.2. Pilot-scale cooling tower performance when using Passively treated acid mine drainage as makeup

E.2.1 Acid mine drainage collection and storage

After careful inspection of the St. Vincent College constructed wetlands AMD treatment site, it was decided to transport treated AMD water from the St. Vincent College wetlands to FTMSA. On September 30th 2008, treated AMD was collected from Cell # 5, St. Vincent College Wetland #3, Latrobe, PA where the discharge flow rate from the conduit was about one gallon per second. Hapchuk, Inc., PA was contracted to ship the water from the AMD site to FTMSA (Figure E.14).

Figure E.14. Collecting treated AMD effluent at St. Vincent College constructed wetlands. The outflow rate of AMD from the conduit was 1 gal/s. The 10-gal blue container was used to prevent sediments and debris from the bottom of the steam from entering the pipe.

About 7000 gallons of AMD was transported with two 4000 gal brand new industrial water tanker trucks and stored in a clean 8ft x 24ft x 8 ft metal roll-off steel tank with tarpaulin cover at the FTMSA site (Figure E.15). The inner surface of the tank was coated with a water-proof layer that prevented the interaction between AMD and steel. The tank was placed on an asphalt surface near the pilot-scale cooling towers and a transparent tube in the front of the tank was used to monitor the water level inside the tank. After placement of the AMD water in the tank at FTMSA, the water was allowed to settle for 2 days before being used for preliminary testing. Therefore, the original, passively-treated AMD water was subjected to additional sedimentation without chemical addition as pretreatment.

Figure E.15. The roll-off steel tank was placed on an asphalt surface next to the cooling towers at FTMSA. About 7000 gallons of treated AMD was stored and allowed to settle for 2 days before being used in the pilot-scale tests.

E.2.2 Water flowrate in the recirculating system

Target flowrate in the recirculating system was 3 GPM and the results shown on Figure E.16 indicate minor flow rate changes during the experimental run for all three towers. An inline flowmeter with range of 1~5 GPM (Acrylic Flowmeter, 7511212B-08, King Instrument Company, CA) was used to monitor the recirculating flowrate.

The flow meters were checked on Day 6 and Day 13 to ensure proper calibration and measurement. It was found that there was no significant change in flowrate on either Day 6 or Day 13 for all towers. No flow reduction due to deposition in the copper heating coil that was observed during the tests with municipal secondary effluent was detected in these test. In summary, the water flowrate in the recirculating system was well controlled and remained fairly constant.

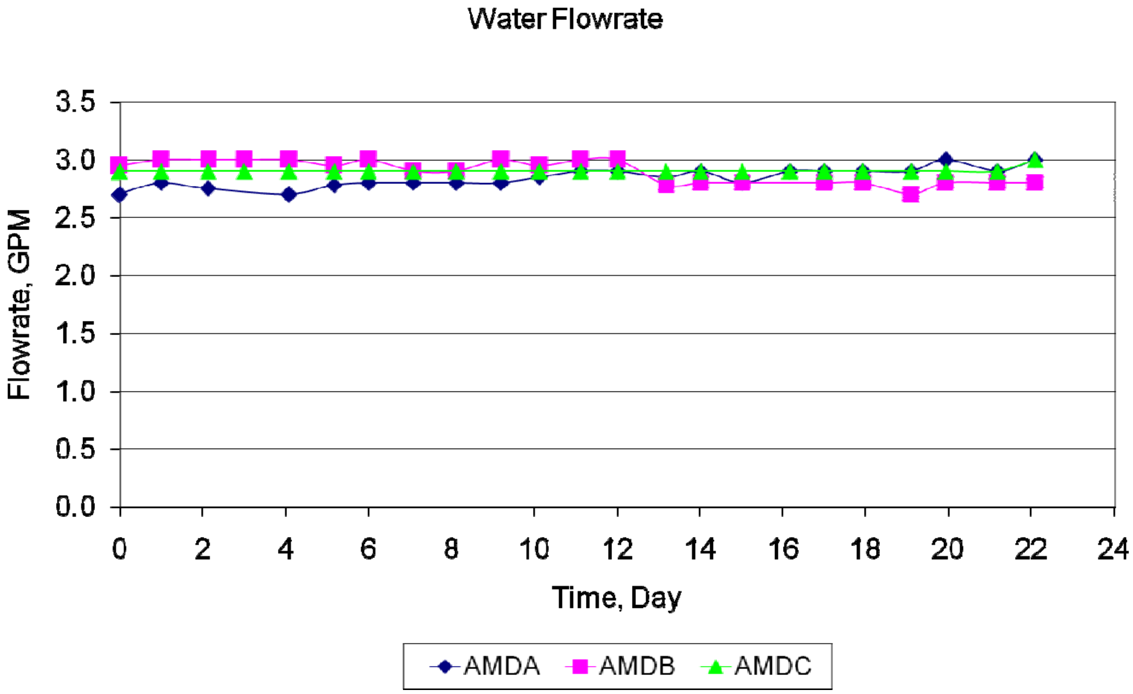


Figure E.16. Water flowrate during the pilot tests using treated AMD in FTMSA. Target flowrate is 3 GPM.

E.2.3 Temperature and Air Flowrate in the Cooling Towers

The ambient temperature used to design the cooling system was average summer temperature in Pittsburgh, which is 79 ºF (26.1 ºC). Figure E.17 shows the daily ambient temperature and relative humidity in FTMSA, Murrysville, PA during the period of the AMD runs. Because the AMD run started in the fall, the average ambient temperature was 13 ºC and the relative humidity was 56.1 %.

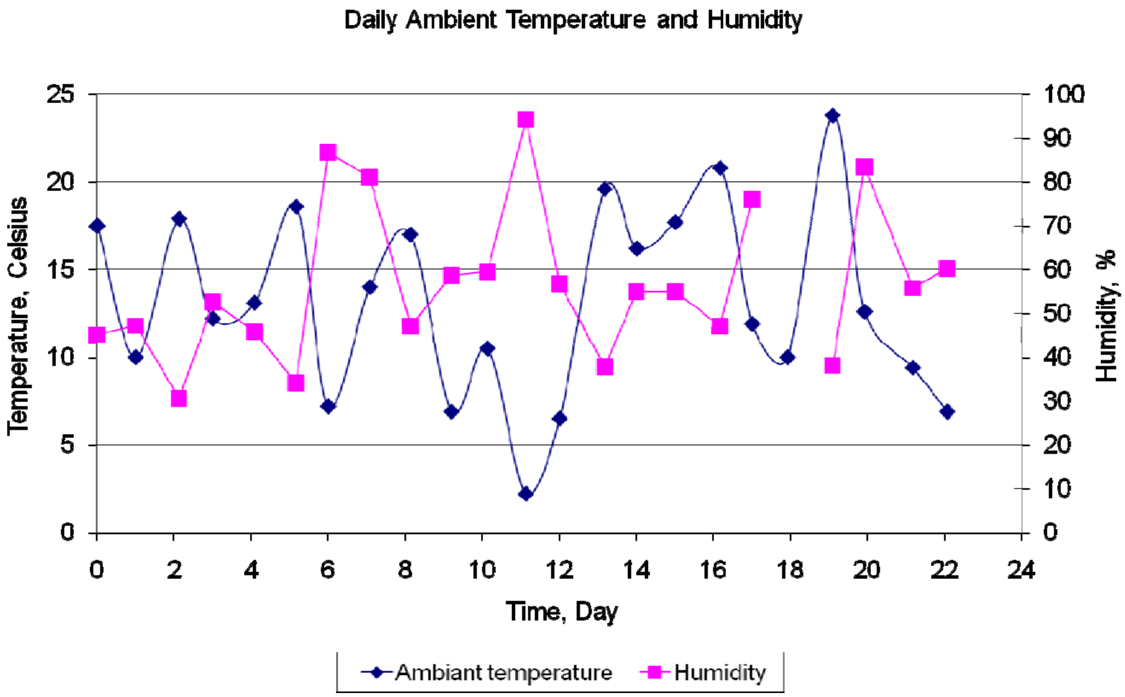
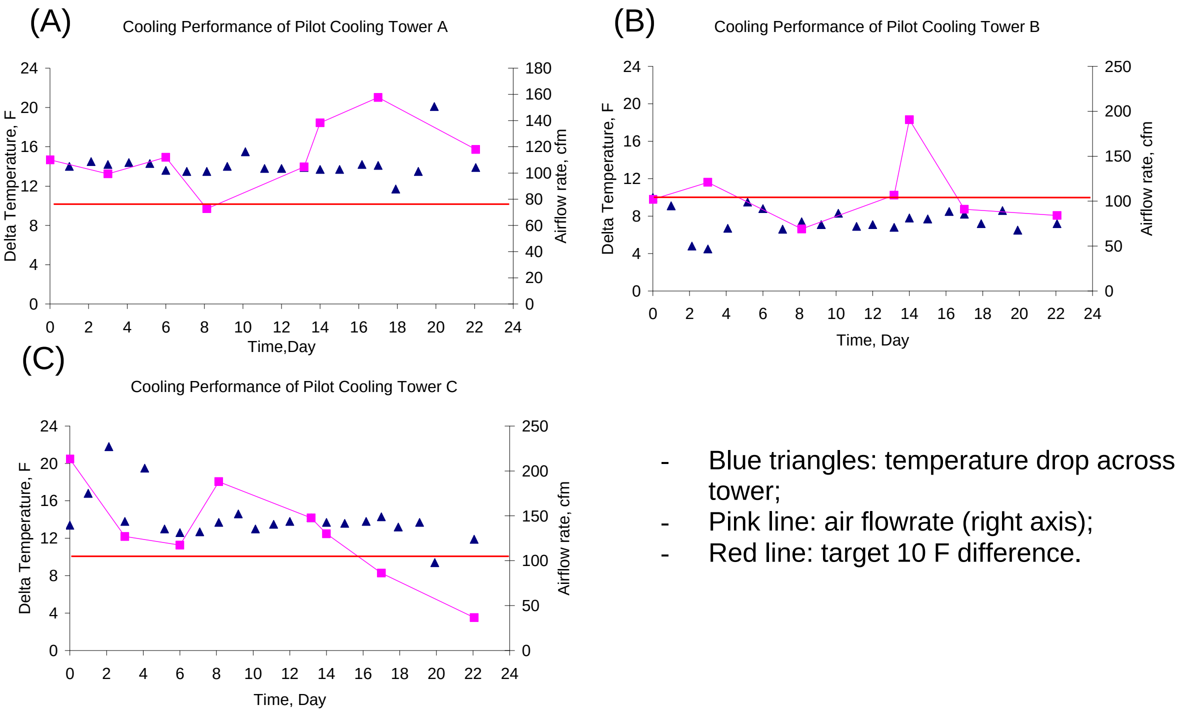


Figure E.17. Daily temperature and relative humidity in FTMSA during the AMD pilot tests. The final AMD run was conducted from October 18th to November 9th. Average temperature and relative humidity during the 25 day run were 13 ºC and 56.1%, respectively.

The measured ambient temperatures were much lower than the design temperature and the cooling efficiency was much better than expected. The cooling capacity of the tower is affected by the airflow rate and the temperature output of the heating element, and fine adjustment of the air flowrate and heating output were performed throughout the AMD run to maintain stable performance of the towers.

Figure E.18 shows the temperature difference (cooling capacity) and airflow rate for all cooling towers during the AMD run. During the AMD run, the target temperature profile across the tower changed from 105-95 F to 95-85 F because the cold weather prevented the maintenance of the original temperature profile. The temperature drop across Tower AMD-A and AMD-C were maintained slightly above 10 F. However, temperature drop across Tower AMD-B was below 10 F. Because there was no change in water flowrate, this behavior could not be explained by the scaling on the heat exchanger (Tower AMD-B received no antiscaling treatment). The most likely explanation is the heavy scaling on packing material, which is discussed in the next section.



- Blue triangles: temperature drop across the tower;
- Pink line: air flowrate (right axis);
- Red line: target 10 F difference.

Figure E.18. Cooling tower performance during the pilot tests with treated AMD. Towers A (AMD-A), and C (AMD-C) could maintain the temperature difference of 10 F. Tower B (AMD-B) had somewhat lower cooling capacity.

The airflow rate was measured using anemometer at point 1 near the center of column and close to the nozzle, point 2 close to the wall, and point 3 in the middle between points 1 and 2. Table E.6 shows the average airflow rate measured during first and second run with secondary effluent and during the experiments with AMD water. The air flowrate varied in accordance with the change in ambient temperature. The ambient temperature was 28 ºC and 24.8 ºC for first and second run respectively, while the ambient temperature used for cooling tower design was 26.1 ºC. However, during the AMD run, the ambient temperature was only 13.1 ºC. Comparing the results to the design temperature, the ambient temperature did affect the required air flow rate significantly.

Table E.6. Average air flowrate in the cooling towers during pilot tests with treated AMD

Airflow rate (CFM)	Design	Tower A	Tower B	Tower C	Ambient Temperature (ºC)
First Run	150 (26.1)	142 ± 23	174 ± 28	187 ± 22	28
Second Run		135 ± 16	145 ± 16	117 ± 40	24.8
AMD Run		100 ± 27	100 ± 37	131 ± 43	13.1

As stated earlier, the target temperature at the spray nozzle on top of the tower was reduced to 95 F and the target temperature in the basin was reduced to 85 F. Table E.7 summarizes the average water temperature at the nozzles of all three towers during the AMD run. Despite the increase in the heater output to the highest possible level, the temperature at the spray nozzle did not reach the target level (105 ºF). Figure E.19 shows the daily temperature of water at the nozzle during the run.

Table E.7. Average temperature of water at the nozzle during pilot tests with treated AMD

Temperature of water at nozzle (ºF)	AMD-A	AMD-B	AMD-C
AMD run	99.7 ± 4.2	96.7 ± 4.3	99.3 ± 4.8

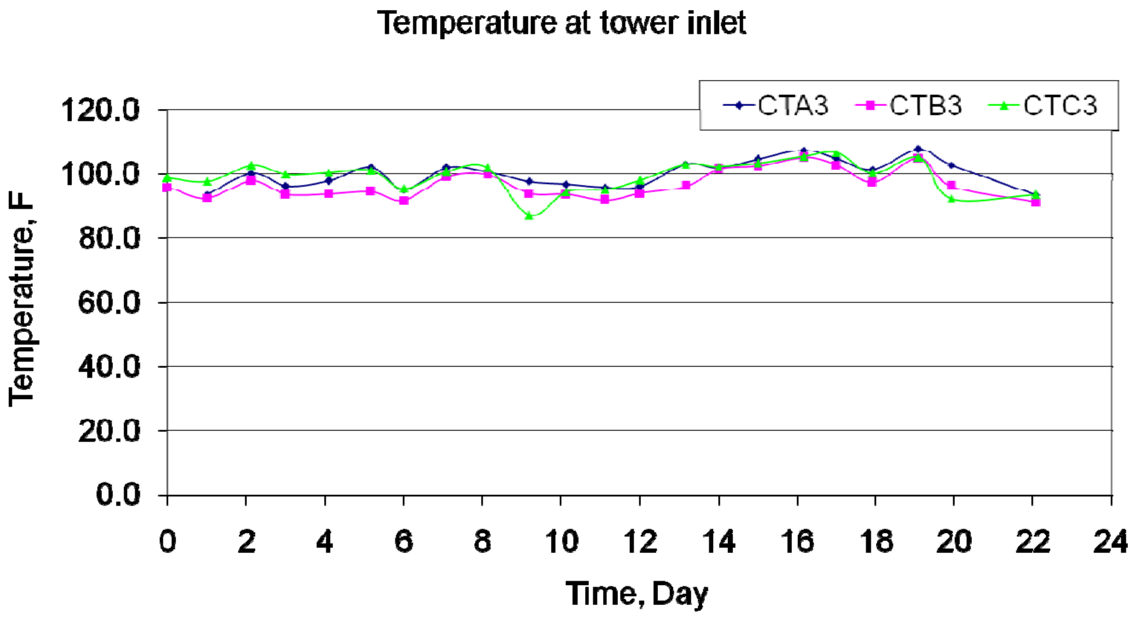


Figure E.19. Temperature of water at the nozzle for towers AMD-A, AMD-B, and AMD-C in pilot tests with treated AMD

In summary, the modified target range of temperature difference was accomplished by adjusting the air flowrate and heater setting. In addition, experimental results indicated that the ambient temperature was very important for cooling tower operation since it affects the air flowrate required to reach target temperature difference.

E.2.4 Makeup Water and Blowdown

The average daily water consumption rate was influenced by the ambient temperature, the temperature of water in the recirculating system, and air flowrate. The blowdown rate was controlled by adjusting the inline conductivity meter to acquire target daily blowdown volume. The objective in this project was to maintain CoC at 4~5. Therefore, the conductivity meter was adjusted manually to accomplish 10~12 gallons of blowdown daily since the average makeup volume was measured at about 50 gallons.

The makeup water supply and blowdown rate were measured by flow totalizers and recorded daily. Water usage during the pilot tests with treated AMD is summarized in Table E.8. The average water consumption, blowdown and evaporation in three cooling towers were 49.1 gal/day, 11.2 gal/day and 37.9 gal/day, respectively. These results show that the daily evaporation rate is lower in this test than during the two runs with treated municipal wastewater. This behavior can be explained by the significant decrease in ambient temperature and the consequent decrease in water temperature that was maintained in this run.

Table E.8. Average daily water consumption rate, blowdown rate, and evaporation rate for pilot tests with treated AMD

First Run	AMD-A	AMD-B	AMD-C
Daily Water Consuming rate (gallon/day)	48.7 ± 5.3	48.4 ± 4.4	51.8 ± 9.7
Daily Blowdown rate (gallon/day)	11.0 ± 3.2	11.7 ± 2.3	11.3 ± 3.8
Daily Evaporation rate (gallon/day)	38.3 ± 6.0	37.2 ± 5.5	41.0 ± 8.2

In general, the behavior of cooling towers operated with treated AMD was similar to the behavior observed in previous runs with secondary treated municipal wastewater. Blowdown volume control helped control the CoC in the tests with treated AMD since the base conductivity of the treated AMD was much higher than that of treated municipal wastewater. Comparing data derived from the AMD run to previous studies reveals that the daily water evaporation rate was closely related to the ambient temperature. In addition, the cold weather also forced the changes in control factors in this experiment.

E.2.5 Cycles of Concentration and Conductivity in the Recirculating System

Daily conductivity was recorded with portable conductivity meter. The average conductivity of makeup water was 1.92 ± 0.01 mS/cm and Figure E.20 shows daily conductivity of recirculating water in all three towers that was measured with portable conductivity meter. Figure (C) shows that the conductivity in AMD-C decreased dramatically after Day 2 and Day 11 because of excess blowdown. The conductivity of water in the system and blowdown measured by portable instrument are listed on Table E.9. The CoC calculated based on the conductivity measurements is also included in Table E.9.

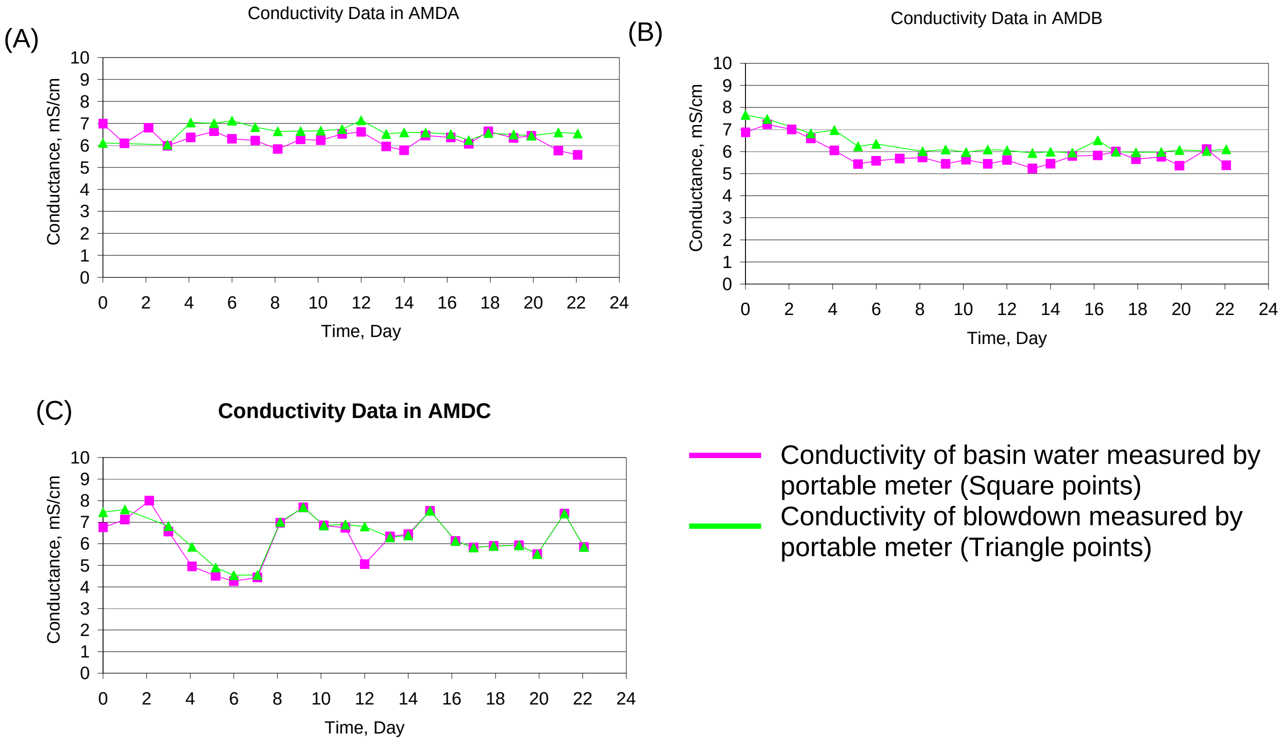


Figure E.20. Daily conductivity data in cooling towers A, B, and C for the pilot tests with treated AMD. The CoC was not controlled by the conductivity of water in the recirculating system because the base alkalinity and conductivity are high.

Table E.9. Conductivity measurement in all towers for AMD run and calculated CoCs based on conductivity

	Tower	Specific Conductivity (mS/cm)			
		Makeup water	Basin	Blowdown	CoC*
AMD Run	AMD-A	1.92 ± 0.01	6.27 ± 0.36	6.62 ± 0.30	3.5
	AMD-B		5.86 ± 0.55	6.30 ± 0.51	3.3
	AMD-C		6.22 ± 1.08	6.37 ± 1.10	3.3

*The CoC is calculated by dividing conductivity of blowdown by conductivity of raw water.

The CoC for the AMD run can also be derived by dividing the total daily water consumption by total daily blowdown volume. Results of this calculation are shown in Table E.10. Because the blowdown volume was kept constant for all towers, the CoC of about 4 were maintained during the test. The CoCs derived from conductivity is included in this table of comparison. The reason for the difference in CoC calculated with the two methods is because of nonlinear behavior of conductivity measurement with highly concentrated AMD water. Therefore, the CoC calculated based on the volumetric measurements represents a true value for this test.

Table E.10. CoC calculated with volumetric method for tests with treated AMD

	Tower	CoC based on volume	CoC based on conductivity
AMD Run	AMD-A	4.4	3.5
	AMD-B	4.1	3.3
	AMD-C	4.6	3.3

APPENDIX F: The Influence of Municipal Wastewater Organic Matter on Copper and Mild Steel Corrosion

F.1 Introduction

Dissolved organic matter in water has been found to influence copper corrosion by-product release (Edwards and Sprague, 2001; Broo et al., 1998) and copper corrosion rate (Rehring and Edwards, 1996; Edwards and Sprague, 2001) in drinking water systems. The increased byproduct release is due to complex formation, and colloid mobilization/dispersion (Edwards and Sprague, 2001). During stagnant condition, organic matter, in contrast, can reverse the copper dissolution process through Cu(I) re-deposition stimulated by oxygen removal caused by enhanced microbial processes and through sorption to pipe surface (Edwards and Sprague, 2001). However, another study showed that after one night of stagnation, copper corroded more in the presence of organic matter (Broo et al., 1999). The presence of organic matter also negatively affects copper corrosion protection by orthophosphate in soft water (Li et al., 2004).

It was found that organic matter decreased mild steel corrosion rate in sea water, suggesting that forms iron-organic matter complexes which passivate the mild steel metal surface and inhibits mild steel corrosion in the sea water (Bhosle and Wagh, 1992). Another study showed that the presence of organic matter decreased corrosion rate of iron in drinking water distribution systems (Broo et al., 1999).

Organic matter was also found to increase lead leaching and corrosion rate in drinking water distribution systems (Korshin et al., 2000, 2005).

Overall, the corrosion of metal alloys is influenced by the presence of organic matter. However, its influence depends on pH (Rehring and Edwards, 1996) and flow conditions (Edwards and Sprague, 2001; Broo et al., 1999). Since most previous studies focused on drinking water systems, the organic matter doses in those studies were low (generally less than

16 ppm TOC). However, in cooling water systems using secondary treated municipal wastewater, the concentration of TOC can reach 120 ppm (FTMSA secondary wastewater at CoC 4). Furthermore, organic matter in municipal wastewater will have different properties than natural organic matter in drinking water systems. Thus, the influence of high organic matter concentration from municipal wastewater on the corrosion of metal alloys needs to be investigated.

Several chemicals have been used for municipal wastewater organic matter surrogates: 1) glucose, acetate, peptone, meat extract (An et al., 2009), 2) meat extract, sucrose, (Pons et al., 2009), 3) acetate (Kimura et al, 2009; Chowdhury et al., 2008; Bernat and Wojnowska-Baryla, 2007), 4) glucose (Naghizadeh et al., 2008; Holakoo et al., 2007; Sen and Demirer, 2003), 5) peptone, yeast extract (Bajaj et al., 2008), 6) peptone, meat extract, urea (Kositzi et al., 2004), 7) acetate and glucose (Dangcong, 2001).

In this study, acetate and glucose were used as surrogates for municipal wastewater organic matter in treated secondary wastewater. Electrochemical methods (polarization resistance method and potentiodynamic polarization method) were utilized to study the influence of acetate and glucose on the corrosion rates and anodic and cathodic corrosion behaviors of metal alloys.

F.2 Materials and methods

F.2.1 Synthetic wastewater preparation

Synthetic wastewater was prepared to simulate pH, alkalinity, and total dissolved solids of cooling water consisting of secondary treated municipal wastewater at four cycles of concentration. The synthetic wastewater was prepared with NaCl 1,170 ppm, $NaHCO_3$ 504 ppm, and pH 8.8.

F.2.2 Metal alloy pre-exposure treatment

The copper (UNS C10100) and mild steel (UNS G10180) specimens tested were cylinder-shaped, 0.95 cm in diameter obtained from McMaster-Carr (Cleveland, OH). Prior to being exposed to synthetic wastewater, they were wet polished with SiC paper to a 600 grit surface finish, dried, degreased with acetone, rinsed in distilled water, and then immersed into synthetic wastewater.

F.2.3 Corrosion cell

The corrosion cells used for electrochemical studies were glass reactors with volume of 1 L, as shown in Figure X-1. A three electrode system was employed with copper or mild steel specimen as a working electrode, graphite as a counter electrode, and saturated calomel electrode as a reference electrode in a Luggin capillary probe. The synthetic wastewater was aerated by purging air into the solution. The temperature of the water was kept at room temperature (25 ± 1 °C).

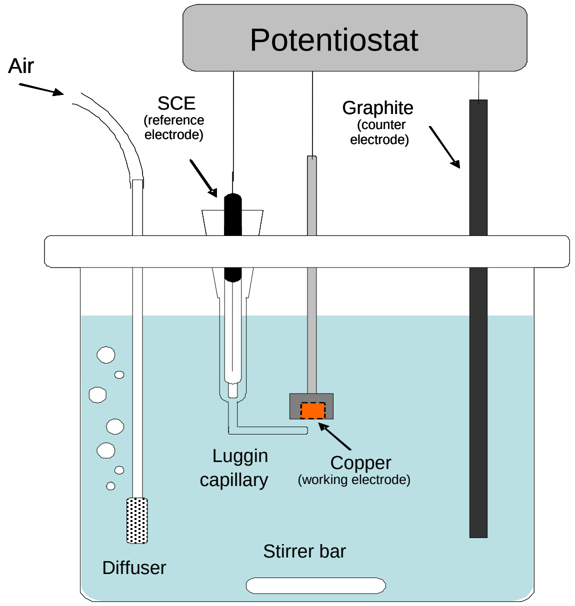


Figure F-1 Corrosion cell for electrochemical potentiodynamic polarization and polarization resistant studies.

F.2.4 Instrumentation

A PGSTAT100 potentiostat (ECO CHEMIE, the Netherlands) was used for electrochemical potentiodynamic polarization and polarization resistance measurements.

F.2.5 Potentiodynamic polarization study

Potentiodynamic polarization was conducted to study the anodic and cathodic behaviors of mild steel and copper electrodes in the presence of glucose and acetate. This method applies potential dynamically over a wide range relative to an electrode to acquire a polarization curve (potential vs. current) of the electrode in a particular aqueous system. The positive-potential (positive potential relative to the open circuit potential of the copper electrode) part of the polarization curve gives information about the anodic reaction (oxidation) of the electrode. The negative-potential part gives information about the cathodic reaction (reduction) of the electrode. By comparing the polarization curves derived from similar aqueous systems with a parameter varied, the influence of the parameter on open-circuit potential, corrosion current density, anodic reaction, and cathodic reaction can be determined.

A one-liter volume corrosion cell was used to contain the synthetic wastewater. A copper or mild steel cylinder specimen acting as a working electrode was embedded in epoxy giving an exposure surface area of 0.71 cm^2. Several conditions were tested in the potentiodynamic polarization study for copper and mild steel electrode.

In each test, the copper or mild steel electrode was immersed in the corrosion cell containing synthetic wastewater with or without glucose/acetate addition. One hour after the electrode immersion, potentiodynamic polarization was performed. Potentiodynamic polarization scan was performed from -250 mV to 250 mV v.s. SCE at a scan rate of 0.3 mV/s.

F.2.6 Polarization resistance study

Polarization resistance was conducted to study the corrosion resistance of copper in the presence of acetate and glucose. The polarization resistance method can be used to determine semi-continuously instantaneous corrosion rate of the electrode (Lu et al., 1994). The method involves applying a very small range of potential to a working electrode. Unlike the potentiodynamic polarization method which employs a wide range of potential, the small applied potential of the polarization resistance method doesn't change the surface property of the electrode, making semi-continuous monitoring possible. Polarization resistance is defined as the slope of the polarization curve at open-circuit potential. It is inversely proportional to instantaneous corrosion rate. The proportionality factor can be determined by combining the polarization resistance method and the gravimetric weight loss method.

A two-liter corrosion cell was used to contain the synthetic wastewater. A copper cylinder with exposure surface area of 24.7 cm^2 was used in this study.

In each test, polarization resistance measurement was performed semi-continuously for two days. All chemicals added were maintained at target concentration levels. Polarization resistance scan was performed from -30 mV to +30 mV with respect to the corrosion potential at a scan rate of 0.3 mV/s.

F.3 Results and discussions

F.3.1 Potentiodynamic polarization study

Figure F-2 shows the results of potentiodynamic polarization experiments with a copper electrode immersed in synthetic wastewater with the addition of acetate or glucose. It can be seen that glucose of 500 ppm had no influence on the potentiodynamic behavior of the copper electrode, while sodium acetate of 500 ppm significantly retarded the anodic reaction at the electrode potential higher than 0.5 V.

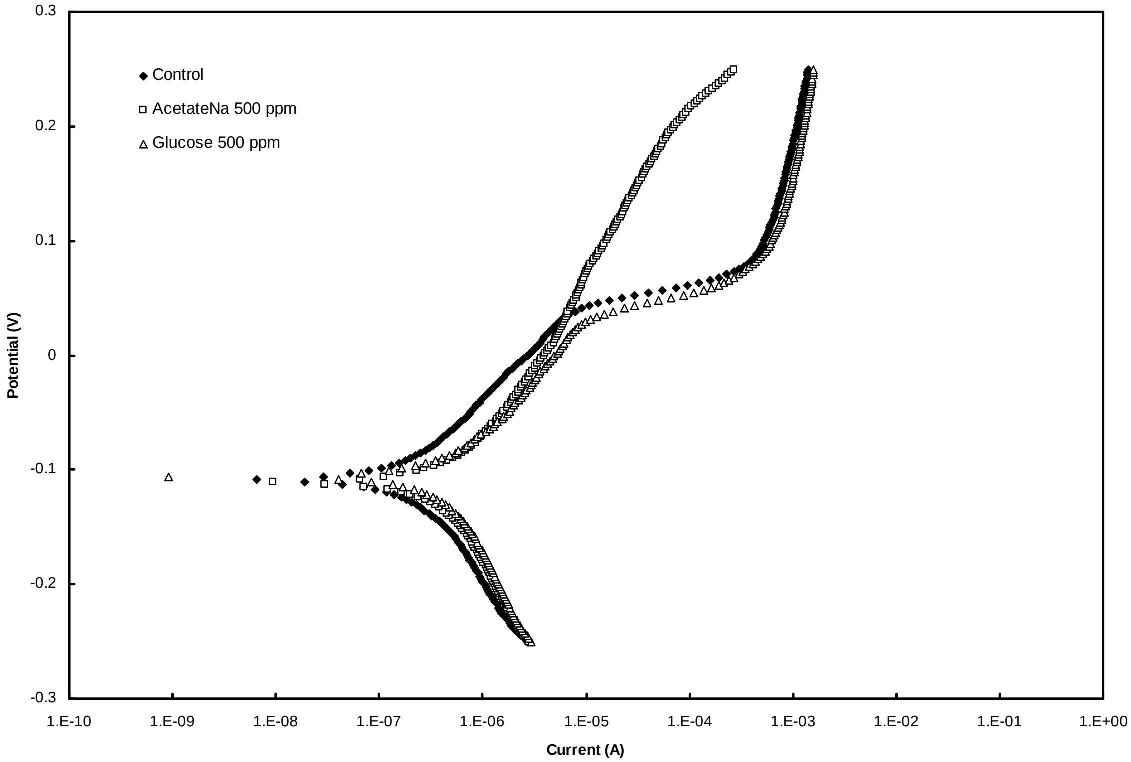


Figure F-2 Potentiodynamic polarization curves of copper electrode immersed in synthetic wastewater with the addition of acetate or glucose at 500 ppm. The potentiodynamic polarization was performed after 1 hour copper electrode immersion. The solution was aerated, stirred, and kept at room temperature and pH 8.75 ± 0.05. The results show that a significant corrosion inhibition was found when higher potential was applied in the case of acetate addition. The inhibition effect was probably due to acetate-copper surface complex formation which passivated copper surface (Kilincceker and Galip, 2008, 2009; Kilincceker, 2009).

Figure F-3 shows the results for experiments with the mild steel electrode. It was found that both glucose and acetate had no influence on the overall corrosion behavior of mild steel.

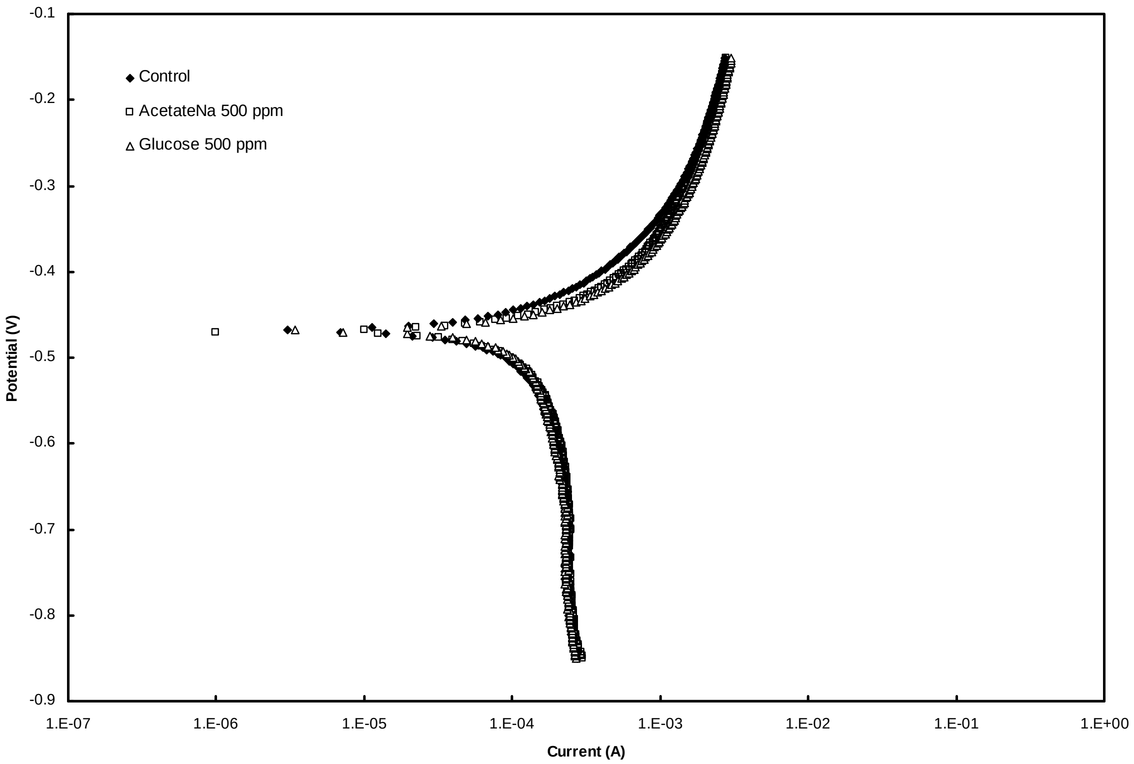


Figure F-3 Potentiodynamic polarization curves of mild steel electrode immersed in synthetic wastewater with the addition of acetate or glucose at 500 ppm. The potentiodynamic polarization was performed after 1 hour copper electrode immersion. The solution was aerated, stirred, and kept at room temperature and pH 8.75 ± 0.05. The results show that acetate and glucose didn't affect the corrosion of mild steel.

Overall, only acetate was found to influence of corrosion behavior of the copper electrode. The formation of acetate-copper surface complexes on the copper alloy might be responsible for the observed lower corrosion rate in the presence of acetate (Kilincceker and Galip, 2008, 2009; Kilincceker, 2009).

F.3.2 Polarization resistance study

Figure F-4 shows the instantaneous corrosion rate measurements made for a copper electrode in synthetic municipal water under the influence of acetate and monochloramine. It can be seen that whether monochloramine was present or absent, the presence of acetate effectively inhibited the corrosion of copper. The inhibition effect was more significant in the presence of monochloramine. In the absence of monochloramine, the corrosion rates were similar initially.

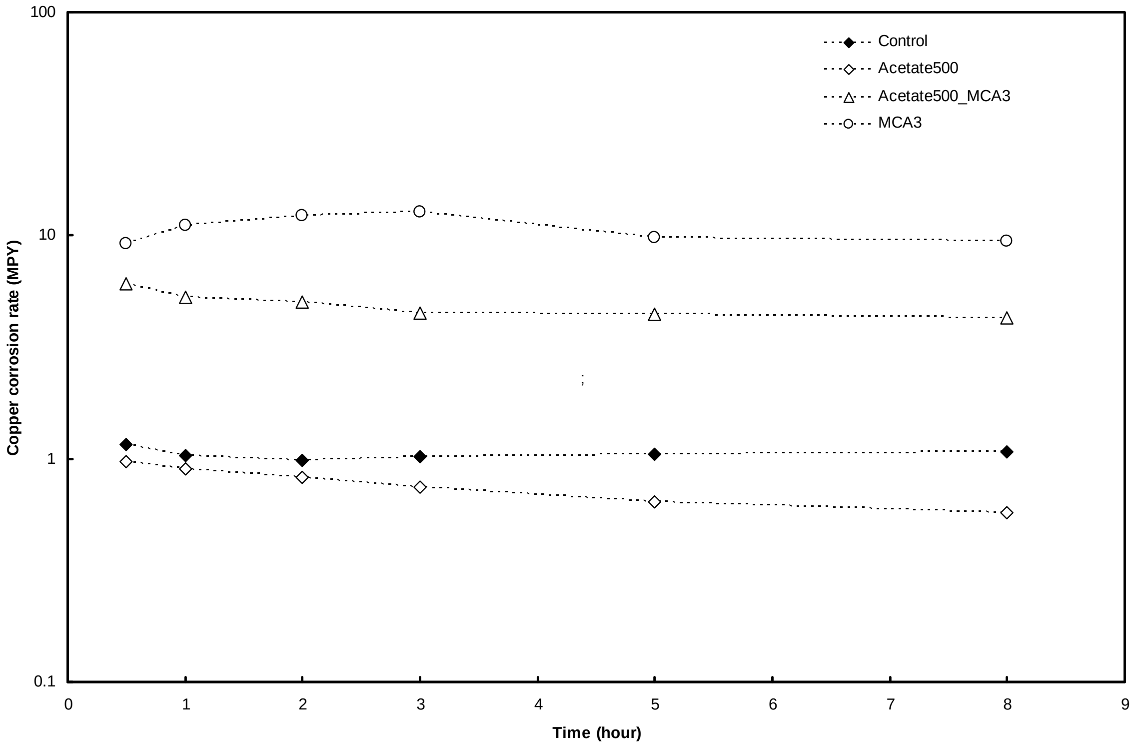


Figure F-4 Instantaneous corrosion rate vs. time of copper measured by polarization resistance method in the presence/absence of acetate (500 ppm as sodium acetate) and monochloramine (MCA, initial dose of 3 ppm as Cl_2). In general, copper corrosion rates were lower in the presence of acetate in both cases of MCA presence and MCA absence. In the case of MCA absence, copper corrosion rates were similar initially but differed significantly as time passed. This might be due to the time needed for acetate-copper surface complex formation to passivate the copper surface (Kilincceker and Galip, 2008, 2009; Kilincceker, 2009). In the case of MCA presence, copper corrosion rate in the absence of acetate was always significantly higher than the case when acetate was present. The presence of MCA leveled the potential, causing higher copper dissolution, and perhaps accelerating acetate-copper surface complex formation to passivate copper surface, as supported by the conclusion drawn from Figure F-2.

Overall, the presence of acetate can inhibit copper corrosion, probably due to acetate-copper complex formation, which might passivate the copper surface and reduce corrosion rate. The passivation effect was more obvious with the increase of immersion time, since time might be needed for acetate copper complex to form a passivation layer. The presence of monochloramine apparently enhanced copper dissolution and accelerated the passivation.

F.4 Summary and Conclusions

In this study, acetate and glucose were chosen to simulate organic matter in secondary treated municipal wastewater. The influence of acetate and glucose on copper and mild steel corrosion was investigated. It was found that acetate and glucose had no influence on the corrosion of mild steel. Glucose had no influence on copper, but acetate slowed copper corrosion. It was hypothesized that formation of acetate-copper surface complexes on the copper alloy was responsible. The complexes might passivate copper surface and inhibit copper corrosion. When higher potential was applied, the passivation effect was even more significant, as evidenced by the results from applying higher anodic potential. Adding monochloramine appeared to enhance copper dissolution and thus accelerate acetate copper complex formation and passivation.

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