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Surface Coating of Condenser Tubing and CO₂ Sparging for Preventing Fouling and Water Use Reduction

Jinyan Sun

**Thesis submitted to the
College of Engineering and Mineral Resources
at West Virginia University
in partial fulfillment of the requirements
for the degree of**

**Master of Science
In
Civil Engineering**

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Department of Civil and Environmental Engineering

**Morgantown, West Virginia
2010**

**Keywords: fouling, coating, condenser tubes, cooling tower, power plant
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ABSTRACT

Surface Coating of Condenser Tubing and CO₂ Sparging for Preventing Fouling and Water Use Reduction

Jinyan Sun

Fouling reduces heat transfer efficiency and increases the amount of water use, which result in lower energy production and increased fuel consumption in thermoelectric power plants. The current study was to investigate the effects of coating and CO₂ sparging on fouling prevention and cooling water use reduction. Bench-scale experiments were conducted to simulate the cooling system in power plants and to evaluate fouling rates on treated and untreated condenser tubes. Four bench-scale experiments (two without CO₂ sparging and two with CO₂ sparging) were performed. In each of those experiments, water from the Monongahela River (Morgantown, West Virginia) was used as cooling water and pumped through tested condenser tubes that placed inside a muffle furnace with a temperature of 450 °C. The cooling water was heated through the muffle furnace by about 10 - 15 °C and cooled down by a cooling tower, and then the water came back to a reservoir for recirculation. Fouling rates were evaluated by analyzing daily cooling water samples and fouling materials on the tested condenser tubes. In addition, morphology of fouling materials was investigated using a Scanning Electron Microscope (SEM).

The current study found that coating on the condenser tubes prevented fouling to some extent. This was supported by the results that concentrations of major metals on the surface of the coated tubes were generally lower than those on the uncoated tubes, especially the concentrations of calcium. Results from SEM displayed consistent evidence that more dense fouling materials on the uncoated tubes than those on the coated tubes. Comparisons of fouling rates between experiments with and without CO₂ indicated that CO₂ was effective in fouling control. Designing an integrated system incorporating surface coating and CO₂ sparging is expected to reduce water consumption, improve energy efficiency, and reduce economic loss in thermoelectric power plants.

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CHAPTER 1: INTRODUCTION

1.1 Background

Fouling is a problem in which accumulation of undesired materials on solid surfaces, such as these on heat exchangers. In the heat exchanger systems of thermoelectric power plants, fouling reduces heat transfer efficiency and increases the amount of water use, resulting in lower energy production and increased fuel consumption. In spite of decades of efforts, fouling control is still a severe problem for thermoelectric power plants.

Condenser fouling in power plants is also a major cause of economic loss. For example, it could cost as high as 0.25% of gross domestic product (GDP) in highly industrialized countries (Steinhagen et al.,1992). The total fouling-related cost in power plants can be attributed to the following aspects: high capital expense for oversized plants, energy losses due to decreased thermal efficiency and increased pressure drop, maintenance and cleaning, and loss of production (Epstein, 1983). The primary reason for higher energy consumption and low efficiency in power plants is the deterioration of heat transfer performance due to fouling (Herz et al. 2008). Furthermore, CO₂ production increases with increased fuel consumption adding greenhouse gas to the atmosphere of CO₂. It was estimated that one kilogram of CO₂ can be released into the atmosphere for each kilowatt-hour of electricity produced by burning the fossil fuel (Knox-holmes, 1993). The substantial increase in fuel consumption cost and the threat of climate change due to increased greenhouse gas emissions make prevention and control of fouling imperative. In addition, inefficient heat transfer due to condenser fouling results in high turbine back pressure, which reduces pressure difference between a boiler (turbine inlet)

and a condenser (turbine outlet). It is estimated that increasing the turbine back pressure by 0.1 inches of mercury can cost an extra \$ 100 million for US power generation stations (Atwood, 1980). Therefore, small improvement in the efficiency of power production can have significant effects on the economic cost and environmental impacts of fouling in thermal electric power plants.

In thermoelectric power plants, large quantities of fresh water are used for cooling each year. The need of freshwater for cooling in thermoelectric power plants is a major concern with the limited water resources in the nation. According to a recent United States Geological Survey (USGS) report, thermoelectric power plants accounted for 39% (136 BGD, Billion Gallons per Day) of total fresh water withdrawals in the nation in 2000, which ranks only slightly behind irrigation (i.e., 40%) (Hutson et al., 2004). Moreover, the 136 BGD fresh water withdrawal constituted 70% of the total water use (i.e., 195 BGD, including fresh and saline water) in thermoelectric power plants (Hutson et al., 2004). In a recirculating cooling water system, a portion of concentrated water (known as blow-down) resulting from evaporative losses needs to be discharged regularly from the cooling system to maintain a low concentration of mineral ions in the cooling water, and to prevent the buildup of minerals and particles on the condenser tubes. Therefore, additional water is needed to make up the water loss due to evaporation and blow-down. Nevertheless, elevated temperatures on the condenser tube surfaces can lower the solubilities of some minerals and salts (e.g., calcium carbonate, calcium sulfate, magnesium bicarbonate, magnesium sulfate, magnesium hydroxide, aluminum sulfate and some forms of silicon salts) (Morse, 1977; Stumm and Morgan, 1996; Lin, 1997). These minerals and salts precipitate on the condenser tube surfaces and form fouling,

which limit the number of cycles that the cooling water can be run through the cooling system. Cycle of concentration (COC) defined as the ratio of hardness of circulating water to that of the make-up water (Cho, 2006) is a very important factor for water use reduction in power plants. Low cycle of concentration is desired to minimize fouling, but high COC value is desired to reduce water use. Typically, reducing the cooling water use can be achieved by operating at a high COC if fouling could be effectively controlled.

1.2 Objectives

The main objective of this study is to reduce the potential of condenser tube fouling and makeup water use in thermoelectric power plants by surface coating of condenser tubes, and by water chemistry alterations of the cooling water. Coating of the condenser tubes was performed and tested for their effectiveness in preventing inorganic fouling. The potential of inorganic fouling on the condenser tube surfaces was examined by conducting bench-scale inorganic fouling experiments at elevated temperature conditions. Fouling rate, morphology, and chemical composition on both coated and un-coated condenser tubes were examined. In addition, similar experiments with CO₂ gas sparging in the cooling water were conducted to evaluate their effectiveness for reducing fouling. The CO₂ sparging was to lower the pH of the cooling water, which was expected to increase the solubility of fouling materials. Similarly, fouling rate, morphology, and chemical composition on both coated and un-coated condenser tubes were examined. Results from these experiments were compared between coated and uncoated condenser tubes with or without CO₂ sparging. Conclusions about reduction of condenser fouling and makeup water use were drawn from these results.

CHAPTER 2: LITERATURE REVIEW

2.1 Thermal electric power plants and cooling towers

Thermoelectric power plants including coal, oil, natural gas and nuclear power generation stations, rely on a fuel source (fossil or nuclear) to heat water into steam to drive a turbine. Power is generated by the turbine rotation which is driven by the pressure difference between a boiler (i.e., the turbine inlet) and a condenser (i.e., the turbine outlet). Exhausted steam from the turbine is condensed by cooling water in condenser tubes, and recycled to the boiler for reuse. The condenser is an important component in power plants and its main function is to remove the excess heat from exhausted steam, and transform the steam into liquid water. Therefore, the performance of the condenser tubes has a direct impact on efficiency of the plants. Condensers can be classified into surface condensers and direct contact condensers (Nageswara Rao and Venkateshan, 2001). Power plant condensers are usually surface condensers. Heat transfer in these condensers takes place between the vapor (i.e., the steam) and the cooling water separated by a wall (Nageswara Rao and Venkateshan, 2001). It is usually suggested that the flow rate of the cooling water is maintained to be 25 times greater than that of the steam (Feeley et al., 2005). The typical temperature rise of the cooling water in a thermal power plant is 15-25 °F. There are two types of cooling water systems: (1) once-through cooling system, and (2) recirculating cooling system. In the once-through cooling water system, the cooling water is directly pumped from the local water bodies, and discharged directly back to the original water sources after passing through the condensers. The once-through cooling system provides good cooling efficiency, but it has high water use

and renders some adverse effects such as thermal pollution on the water body if discharged without any treatment. In the more widely used recirculating cooling water system, the cooling water passes through the condensers, then is pumped to a cooling tower where excess heat is removed from the cooling water to the atmosphere by evaporation, and then the rest of the cooling water is recycled back to the condensers. Fig. 2.1 presented a typical recirculating cooling water system for a 650 megawatts (MW) coal-fired power plant. In a recirculating cooling water system, a portion of the concentrated cooling water that resulting from evaporative losses needs to be discharged regularly from the system (known as blow-down). This can maintain a low concentration of mineral ions in the cooling water and prevent buildup of minerals and particles in the cooling water. Therefore, makeup water is needed from the local water sources to replace evaporation loss and blow-down. The recirculating cooling system has relatively lower cooling efficiency and water use than those of the once-through cooling system.

Fig. 2.1 Process flow schematic of a typical recirculating cooling water system

(Feeley et al., 2005).

2.2 Water use in power plants

Water is the major coolant in power plants. Excess heat is removed by passing the cooling water through heat exchangers. In thermoelectric power plants, large quantities of fresh water are used for cooling each year. For example, a 500 MW power plant would use about 300 million gallons per day for cooling and process requirement (Feeley et al., 2005). According to a recent United States Geological Survey (USGS) report, thermoelectric power plants accounted for 39% (136 Billion Gallons per Day or BGD) of total fresh water withdrawals in the nation in 2000, which was ranked only slightly behind irrigation (40%) (Hutson et al., 2004). Moreover, the 136 BGD fresh water withdrawal constituted to 70% of the total water use (i.e., 195 BGD, including fresh and

saline water) in thermoelectric power plants (Hutson et al., 2004). Fig. 2.2 showed the percentage of total U.S. fresh water withdrawals for different uses. As the population increases and associated economy develops, the increasing demand for electricity requires more water to meet these developments.

High chloride and hardness of sea water and brackish water limit their use for cooling because of water corrosion problem, which renders large use of fresh water for cooling. Huge and continuous fresh water loss from the cooling tower is also an important factor for large fresh water use. Specifically, water loss by spray accounts for 0.2% of total water use and about 1% of the cooling water is lost as water vapor for each 5 °C of cooling in a cooling tower (Pugh et al., 2004).

In addition, cycle of concentration (COC) is a very important factor for water use reduction in power plants. COC is defined as the ratio of hardness of circulating water to that of the make-up water (Cho, 2006). Low cycle of concentration is necessary for minimizing fouling, but high COC is desired to reduce water use. Typically, reducing the cooling water use can be achieved by operating at high COC value if fouling could be effectively controlled.

Fig. 2.2 U.S. freshwater withdrawal by category in 2000 (Feeley et al., 2005).

2.3 Fouling

Fouling is a problem in which accumulation of undesired materials on the heat transfer surfaces occurs. It reduces heat transfer efficiency and increases the amount of water use, resulting in lowered electricity production and increased fuel consumption. In an elevated temperature condition, solubilities of some minerals and salts (e.g., calcium carbonate, calcium sulfate, magnesium bicarbonate, magnesium sulfate, magnesium hydroxide, aluminum sulfate and some forms of silicon salts) become lower (Morse, 1977; Stumm and Morgan, 1996; Lin, 1997). These minerals and salts can precipitate on the condenser tubes. Even though make-up water is relatively soft, the hardness of the circulating water continues to increase with the continuous circulation of the cooling water due to evaporation. Heat exchanger fouling in general is a major economic problem

and it could cost as high as 0.25% of gross domestic product (GDP) in highly industrialized countries (Steinhagen et al., 1992). The total fouling-related cost can be attributed to: (1) high capital expense for oversized plants, (2) energy losses due to decreased thermal efficiency and increased pressure drop, (3) maintenance and cleaning, and (4) loss of production (Epstein, 1983).

Four epochs of fouling were presented by Somerscales in his review of fouling on heat transfer surfaces (1990). They are (1) before 1920 which was a period with observing and devising methods to control fouling, (2) 1920-1935 when measurement methods and representation of fouling were first formulated, (3) 1935-1945, fouling factor era, and (4) 1945-1979 when a scientific approach to understanding fouling gradually received attention.

The primary factor governing fouling in fresh water systems is the composition of the water, that is, the chemical, biological and particulate components dissolved or suspended in the water (Muller-steinhagen et al., 2009). Zhou and Ji (2006) investigated the composition of fouling in a power plant and silt was found to be the source of the fouling. They presented some chemical compositions of fouling occurred in a power plant in China.

The fouling encountered in freshwater systems can be categorized into five types listed below (Muller-steinhagen et al., 2009).

(1) Crystalline fouling (scale). Occurrence of crystalline fouling is due to deposition of crystals formed in the bulk fluid or formation of crystalline deposits on the surface itself. Crystalline fouling tends to be hard and difficult to remove. The key driving forces for the formation of the scale are concentration, temperature at the heat transfer surface,

bulk temperature, pH, ion pairs, heat flux and velocity. This type of fouling usually occurs at temperatures above 35 °C (Cross,1979).

Crystalline fouling usually occurs as a type of precipitation in condensation processes because of elevated operating temperatures of the systems. In aqueous systems, the general terms for crystallization fouling are “scaling” or “scale formation”. Most crystalline scaling issues are originated from inverse solubility salts, which have lower solubilities at increased temperature. The increased temperature resulted in supersaturated salt concentrations (Morse, 1977). Supersaturation is a prerequisite for crystallization fouling of normal solubility salts as well as inverse solubility salts. If the region of supersaturation occurs at the interface of tube surface and liquid, precipitation on the condenser surfaces is possible (Bott, 1997). On the other hand, if the supersaturation is not close to the condenser surfaces, crystals will form in the bulk solution and migrate to the condenser surfaces as particles to form a solid deposit (Bott, 1997). Usually, crystallization fouling is comprised of nucleation, growth, and re-crystallization steps. There are several special factors affecting inorganic fouling. Presence of gas bubbles (e.g., during boiling) would promote crystalline fouling while there is no relevance with the presence of biofouling (Sheikholeslami, 1999). Also, water quality parameters, such as pH, hardness, alkalinity, and CO₂ concentration are important in affecting fouling behavior and extent (Sheikholeslami, 1999). CO₂ loss from the solution (leading to pH increase) and temperature increase are the main reasons of inorganic fouling formation (Andritsos and Karabelas, 2003). As CO₂ escapes from the cooling water over operation time, the pH value of cooling water is usually greater than 8.0 (Andritsos and Karabelas, 2003). The water pH can affect the solubility of salts and surface hydrophilicity of

condenser tubes (Sheikholeslami, 1999). Alkalinity and hardness can affect concentrations of foulants while dissolved CO₂ influences calcium carbonate precipitation (Sheikholeslami, 1999). Crystal formation is usually increased by the presence of nuclei, which can be suspended solid impurities in solutions or sites on the heat exchanger surfaces (Sheikholeslami, 1999).

Scale strength is dependent on the composition of the scale (Morse and Knudsen 1977). It was found that scale with pure CaCO₃ was much stronger than the scale that comprised of substantial quantities of other crystalline components (Morse and Knudsen 1977).

Calcium carbonate and calcium sulfate are common predominant salts in inorganic fouling (Chong and Sheikholeslami, 2000). These salts have inverse solubility behavior where the solubility decreases with increasing temperature, and these salts deposit on heat exchanger surfaces when supersaturated (Chong and Sheikholeslami, 2000). The chemistry behind the most important inorganic fouling mechanism in cooling water is the precipitation of calcium carbonate (Snoeyink and Jenkins, 1982)

The above reaction does not occur even in a saturated condition because carbonate ions do not exist at room temperature condition, but rather in the form of bicarbonate, HCO₃⁻ (Cho, 2006). The dissociation of HCO₃⁻ needs extra energy from water. Thus, HCO₃⁻ dissociates into carbonate ions under elevated cooling water temperature, which provides sufficient energy, and results in the precipitation of CaCO₃ (Cho, 2006).

In addition to calcium carbonate and calcium sulfate, other common scale-forming compounds include calcium phosphate, magnesium hydroxide, carbonate, zinc

phosphate, iron hydroxides and silica which also occur naturally in water (Chinowski, 2003).

(2) Corrosion fouling. Corrosion and fouling are closely connected. Not only do surface deposits from corrosion form a corrosion fouling, but there are close interrelationships between scale, solid deposition, microbial growth and corrosion. Factors affecting corrosion include temperature, dissolved gases, dissolved solids, pH, water velocity, and the composition and nature of metallic surface attacked. For instance biofouling-causing corrosion is very severe on stainless steel parts in marine cooling water system (Kant, 2004). However, probability of this kind of corrosion is small on copper alloy tubes and is free on titanium tube.

(3) Biological fouling. One of the most important problems in managing cooling water system is biofouling. There are two types of biofouling: macro-biofouling and micro-biofouling. Macro-biofouling has to do with the deposition of macro organisms such as barnacles while micro-biofouling refers to the deposition of microorganisms such as bacteria, fungi, algae, protozoa, and viruses. Common factors affecting biofouling include dissolved oxygen (DO), temperature, velocity, materials of heat exchangers. DO must be above 3-4 mg/L for aerobic microorganism fouling to take place (Pugh et al., 2009). DO concentration in opening cooling water systems is usually 10-12 mg/L, which is a concentration that can easily cause biofouling place (Pugh et al., 2009). Biofouling tends to increase with temperature when the surface temperature is low. Growth of microorganism in cooling water systems ceases when the surface temperature is above 90 °C. Microorganism would probably die due to lack of oxygen and nutrients when the

velocity of the cooling water is very low or in stagnant. The optimal velocity for biological growth is 0.5-1.0 m/s (Muller-steinhausen et al., 2009). Possibility of biofouling in copper alloy condenser tubes is less than that on other materials because of toxicity of copper to bio-organisms (Kant, 2004).

(4) Particulate fouling (sludge). Most freshwater contains suspended solids that can deposit on the surfaces of the heat exchangers. Particulate fouling is typically easy to be removed by increasing fluid shear force. Factors affecting particulate fouling include flow velocity of cooling water, particle concentration, surface temperature, heat flux, and particle size. For example, high water velocity (e.g., > 1 m/s) can prevent particulate fouling. But, due to erosion, there is a maximum velocity that could be used (Cross, 1979).

(5) Chemical reaction fouling. Chemical reaction fouling mainly involves in organic material, even though it could involve both organic and inorganic materials.

In practice, fouling usually involves two or more above-mentioned fouling mechanisms. For instance, corrosion fouling is usually observed with precipitation fouling, particulate fouling, and biofouling. A series of factors that are important in affecting fouling are listed below (Muller-steinhausen et al., 2009).

(1) Surface temperature. The temperature at the interface between the cooling water and the heat exchanger surface is important for fouling formation. The relationships between the surface temperature and fouling rate varied with different fouling mechanisms (Fig. 2.3).

Fig. 2.3 Effect of surface temperature, T_w , on fouling rate R_f among different individual fouling mechanisms at a constant water velocity (Muller-steinhausen et al., 2009).

(2) Bulk temperature. Bulk temperature of the cooling water is also important and its influence depends on the mechanism of fouling. For example, biological growth increases with increase of bulk temperature at low temperature range, but could be inhibited at high temperatures. For normal-solubility salts, no fouling problem will be exhibited because solubility increases with temperature (Mukherjee, 1996). However, the reverse is true for inverse-solubility salts, which have decreased solubility with increasing temperature (Mukherjee, 1996). Rabas et al. (1993) compared the fouling rates of a plain tube and an enhanced tube based on long term field tests in power plant condensers using water from three different rivers. The results showed that the fouling resistance exhibited a strong dependence on cooling water temperature (Rabas et al., 1993).

(3) Water velocity. The effects of water velocity on fouling also vary with fouling mechanisms (Fig. 2.4). High velocity appears to lower all types of fouling. However, high velocities need increased pumping power and may result in erosion of condensers (Mukherjee, 1996). The ideal velocity is usually 1.5 – 2.1 m/s for liquid inside condenser tubes and 1.0 - 1.5 m/s for liquid outside the condenser tubes (Mukherjee, 1996).

Fig. 2.4 Effect of water flow velocity, V_a , on fouling rate R_f among various fouling mechanisms at a constant temperature.

(4) Oxygen concentration. The amount of oxygen in cooling water strongly affects corrosion fouling and biological fouling (Muller-steinhausen et al., 2009).

(5) Materials. Materials of the condenser tubes and upstream pipework play an important role in fouling. At present, materials of titanium alloys and stainless steel are commonly used for corrosion resistance (Gawlik et al., 1998). Springer (1980)

demonstrated an initially higher fouling rate with copper nickel than that with aluminum at a constant velocity.

(6) Solids. Fouling can be enhanced or inhibited by the presence of suspended solids, depending on the types of particulate materials (Sheikholeslami, 1999). Solids in the cooling water tend to deposit as a result of gravitational or intermolecular forces or serve as nucleation sites for crystallization and hence promote fouling. However, particles can have flushing effects on fouling and then reduce fouling (Sheikholeslami, 1999).

(7) Surface properties. Surface free energy is also an important factor affecting fouling. For example, low surface free energy materials such as polytetrafluoroethylene (PTFE) have the poorest adhesion on heat exchanger surface, and they could be easily removed. However, rough surfaces provide a shelter against removal of fouling by shear stress, and they can increase fouling rate (Sheikholeslami, 1999).

2.4 Anti-fouling methods

There are many approaches to prevent and control fouling.

(1) Chemical treatment. Chlorine is one of the most commonly used, cheapest and the excellent effective biocide. It acts as a strong oxidant in various chemical treatments. Due to biocide properties, chlorination is the most common chemically anti-biofouling method (Panchal et al., 1997). It was found that a continuous dose of 0.1 mg/L chlorine is satisfactory in most fouling control cases (Springer, 1980). It was reported that fouling development, quantity, composition, and transport properties can be affected by chlorination of cooling water (Nebot et al., 2006). However, continuous chlorine dosing is not allowed by stringent legislations. Furthermore, chlorine can cause corrosion to heat

exchangers, which is severe with differential aeration, increased temperature, lower pH, and lower velocity (Kant, 2004). As a result, some more environmentally friendly biocides, such as ozone and hydrogen peroxide, were proposed and tested (Bott, 2009). These chemicals have a relatively short life, and result in innocuous breakdown products after application. (Bott, 2009).

(2) Mechanical treatment. “Fresh” foulants (i.e., those deposited within 1-2 years) can be removed by hand, but this is extremely labor-consuming and can not be done to the level of “zero” remaining (Usachev, 2002). “Old” fouling that deposited for several years can be cleaned off using special mechanical instruments. Several self-cleaning designs and systems, such as sponge ball systems, the wire brush systems, and fluidized bed heat exchangers have been introduced into the anti-fouling field (Usachev, 2002). However, these mechanic treatments may create rough spots on condenser surfaces, which can in turn accelerate the fouling processes during subsequent operations.

(3) Heat treatment for biofouling control. The most frequently used biofouling control method at west coast power plants is heat treatment (Sommerville, 1986). Temperature rise in the circulating water can kill the attached fouling organisms and eventually remove these organisms from the cooling system. During the process of heat treatment, cooling seawater is heated by 100 to 110 °F and this temperature is maintained for a period of time from one to several hours (Sommerville, 1986).

(4) Anti-fouling designs of heat exchangers. Design of heat exchanger usually takes into account the decrease of heat transfer because of fouling and compensation from the increased heat transfer surface area. Well-designed cooling systems with anti-fouling and anti-corrosion features can minimize fouling and corrosion in cooling water systems.

Furthermore, materials with inherent anti-fouling properties are widely used in fouling control systems. The earliest recommended and most widely used antifouling materials are copper and some of its alloys (Abdul Azis et al., 2003).

(5) Anti-fouling paints and coatings. Anti-fouling paints and coating are the most cost effective ways to prevent fouling (Abdul Azis et al., 2003). Ease of manufacture, high speed, low cost application, reasonable duration and relative low costs are the advantages of coating (Abdul Azis et al., 2003).

2.5 Current understanding of fouling control

Fouling is an old problem in power plants, which poses many adverse effects. The accumulation of deposits on condenser tubes can reduce heat exchanger efficiency and consequently, the overall efficiency of power production with an incredible increase in fuel consumption and CO₂ emission. For every kilowatt-hour of fuel produced by fossil fuel, one kilogram of carbon dioxide could be released into the atmosphere (Knox-holmes, 1993). Therefore, small improvement in the efficiency of power production will have significant impacts on the cost and the environment. The substantial increase in energy costs and the threat of climate change due to CO₂ emission justify the need for fouling control. Coating is an effective way to prevent or mitigate fouling on condenser tubes. Coating of condenser tubes may prevent fouling and corrosion without losing heat transfer capacities, improve efficiencies, reduce cleaning maintenance costs, and extend capital equipment life (Woodruff, 2005). Tube coating is less expensive and less time-consuming than re-tubing. For example, tube coating usually costs less than one dollar a linear foot, which only accounts for 1/3 of re-tubing cost (Woodruff, 2005). It was also

reported that 100% solids epoxy coatings have long service lives time (e.g., 20+ years) and have been used to minimize or prevent corrosion on circulating water pipes in almost every industry in the world (Woodruff, 2005). Although the volume of condenser tubes is reduced by the coating, the increased flow rate of cooling water will compensate for coating thickness (Woodruff, 2005). Nair (1999) reviewed three kinds of toxic anti-biofouling coatings: (a) coatings based on copper and copper alloy system; (b) coatings containing active biocides; and (c) coatings with low surface free energy. He also reviewed another nontoxic foul-release coatings or low surface free energy coatings, which generally rely on the principal that adhesion of material to surface is weak when surface-free energy of the solid is low. The lower is the surface-free energy, the weaker is the adhesion (Nair, 1999).

Bott (2001) provided very useful insights for the design, operation and research issues associated with heat exchanger fouling, which are important for the studies of fouling control. An experimental program has been conducted by using eight clusters tubes with different conditions to investigate characteristics of the fouling and thermal performance at the Humboldt Bay Power Plant (Rabas and Elliott, 1993). The results showed that there was a continued increase of fouling resistance for the uncleaned tubes and a thermal performance reduction for new, distilled-water tubes at the initial stage (Rabas and Elliott, 1993).

Studies on fouling control can be divided into two areas: biological fouling and inorganic fouling.

(1) Biofouling

Biofouling in power plants is a serious problem. Condenser tubes are mostly affected by biofouling in the plants, which cause an overall decline in plant efficiency and great economic loss. It was estimated that reducing turbine back pressure by 0.1 inches of mercury (Hg) can save up to \$ 100 million for US power generation stations (Atwood, 1980). A 0.1 to 0.5 inches increasing of Hg in condenser back pressure is a common symptom of biofouling, which reduces the conversion efficiency of chemical energy (e.g., coal, oil, and nuclear fuel) into electrical energy (Knox-holmes, 1993). Coastal power plants that use seawater for cooling encounter numerous problems associated with marine fouling organisms. Fouling organisms, such as mussels and barnacles, can settle and grow in the seawater cooling system, cause blockage of condenser tubes and reduce the effective area, result in friction loss and water flow reduction. This biofouling problem can become deteriorating by the fact that cooling water temperature in the condenser tubes is close to the optimum temperature for maximum microbial growth. Nair (1999) reviewed some biofouling control methods in a review. There methods include toxic antifouling paint, nontoxic foul-release coatings, mechanical methods, flow control, heat treatment, and chemical biocides. Also, Jenner et al. (1998) presented some biofouling control methods: water filtration, cleaning, water velocity, heat treatment, paints and coatings, chemical treatments, and other physical treatment. Abdul Azis et al. (2003) reviewed marine macrofouling and categorized a few widely used fouling control technologies: antifouling paints and coatings, injection of biocides, marine bio-active compounds, materials of inherent anti-fouling properties, heat treatment, pulse-power devices, UV and nuclear radiation, scrubbing, and biological control. It was presented that about 5000 biological species have been involved in the fouling of equipment that

exposed to or immersed in water (Abdul Azis et al., 2003). Due to temperature sensitivity of marine organisms, warm water with temperature between 50-70 °C can kill nearly all organisms (Abdul Azis et al., 2003). Because of limitation in using chlorine as a biocide for biofouling control, alternative anti-fouling methods have been tested and a combination of in-service mechanical cleaning and chemical short dosages were suggested by Cristiani (2005). An in situ study was carried out to evaluate the evolution of fouling resistance and optimal chlorine dosage at a 550 MW power station (Nebot et al., 2006). The results showed that 0.2 ppm of residual chlorine concentration at cooling water discharge reduced 90% fouling, and this approach has been considered appropriate for prevention fouling. It also showed that the chlorination of cooling water had influences on the fouling development, fouling quantity, fouling composition and transport properties (Nebot et al., 2006). Kneo-holmes (1993) has initiated field trials to compare the efficiency of conventional chlorine dosing, copper dosing, copper and aluminium dosing and the combined copper/chlorine system on biofouling control. The results showed that the combination of very low concentrations of copper (5 ug /L) and chlorine (20ug/L) can work synergistically and are more effective than conventional chlorination or electrolytic copper dosing on biofouling control (Kneo-holmes, 1993). Pulsed acoustic waves were used by Mazzola et al. (1994) to remove and prevent biofouling. The results demonstrated that pulsed acoustic waves can prevent biofouling (Mazzola et al., 1994). Tests to evaluate the effectiveness of ozone on biofouling control as an alternative in a once-through cooling system have been conducted by Sugam et al. (1981). This study demonstrate that, although ozone was not as effective as chlorine, ozone was still capable of controlling fouling when dosed at >0.5 mg/L (Sugam et al.,

1981). However, this result can not be generalized because biofouling tends to be site-specific. Panchal et al (1997) have conducted some experiments to investigate the effectiveness of ultrasonic (US) and ultraviolet (UV) on biofouling control. US treatment is used for biofouling control by removing deposits from the condenser surfaces. UV radiation functions by photoinactivation or photostunning of the marine organisms to prevent their attachment to condenser surface. However, the results showed that biofouling could not be controlled with UV or US (Panchal et al, 1997). Nishimura et al. (1988) developed a new anti-fouling method by hydrogen peroxide with ferrous ion for a marine cooling water system. The results indicated that the chemicals hampered some organisms and prevented biofouling to some extent (Nishimura et al., 1988). A case study on interaction of biofouling and corrosion in Mar Del Plata power plant has been performed by Brankevich et al. (1990). This study demonstrated that stainless steel as a relatively corrosion resistant material is prone to colonize by microorganisms but copper-nickel surfaces can delay and reduce microfouling settlement because of toxic effects of copper ions (Brankevich et al., 1990).

(2) Inorganic fouling

For inorganic fouling, a physical model for fouling description was developed by Bohnet (1987) and experiments were carried out to verify the theoretical model. The results showed a satisfactory agreement on fouling factors between the physical model and the experiments (Bohnet, 1987). Herz et al. (2008) studied the fouling of an aqueous solution with inverse solubility behaviour on roughened stainless steel surfaces under convective heat transfers. The results showed that the heat transfer coefficient decreased with the roughness of tube surface and the fouling layer on rough surfaces has a stronger

adhesion than that on smooth surfaces (Herz et al., 2008). They also provided possible reasons for decreased heat transfer coefficient of roughened condensers: (1) increased heterogeneous nucleation rate; (2) reduction of local shear stress; and (3) reduced removal rate of the crystals (Herz et al., 2008). A study on calcium carbonate scale deposition on heat transfer surfaces was conducted by Hasson et al. (1968). A general model was developed from the study and the results showed that CaCO_3 scale deposition is diffusion controlled within the surface temperature range of 67-85 °C and Reynolds number range of 13,000-42,000 (Hasson et al., 1968). Gawlik et al. (1998) have conducted tests of polymer-based liner on carbon steel tubes in a highly aggressive brine environment and showed a fouling reduction of 15-19% compared to previous liner formulations. In another study, nearly 30 tests have been performed to evaluate the effectiveness of geometry and flow conditions on particulate fouling in plate heat exchangers (Thonon et al., 1999). The results indicated strong velocity effects and geometry effects on particulate fouling (Thonon et al., 1999). Pana-supamassadu et al. (2009) investigated the effectiveness of operating conditions on calcium carbonate fouling in a plate heat exchanger. The results indicated that high feed inlet velocity of cooling water reduced fouling rate significantly and the fouling tended to occur at the dead spot of low velocity (Pana-supamassadu et al., 2009). A study on high performance polymer coatings for carbon steel heat exchanger tubes in geothermal environments was carried out by Sugama et al. (2000). The results indicated that both PPS (polyphenylenesulfide) and PTFE (polytetrafluoroethylene)-blended PPS coatings can be treated as scale-free coatings (Sugama et al., 2000). Sugama et al. (2002) used a poly (phenylenesulfide) (PPS)-based system for carbon steel heat exchanger tubes in

geothermal environments. The system included PPS containing polytetrafluoroethylene (PTFE) as an anti-oxidant additive, silicon carbide (SiC) as a thermally conductive filler, and aluminum oxide-rich calcium aluminate (ACA) as an abrasive wear resistant filler. The results demonstrated that the PPS coating system adequately protected the tubes against the corrosion and had an excellent thermal stability (Sugama et al., 2002). In another study, Sugama and Gawlik (2002) evaluated the effectiveness of polyphenylenesulfide(PPS) and polytetrafluoroethylene(PTFE)-blended PPS in inhibiting silica scaling on carbon steel based tubes. The results showed that the PTFE-blended PPS had a high anti-silica fouling potential (Sugama and Gawlik, 2002). Also, PTFE was highly recommended by Zettler (2005) for industrial coating application because of their resistance to high temperature, chemical and organic solvents. Wang et al. (2004) studied the corrosion behavior and corrosion inhibition of 304 stainless steel (SS) coated with nano-sized Ti/silicone in an environment containing a solid NaCl and water vapor at 400-600°C. Results indicated that the corrosion of 304SS was inhibited efficiently by the coatings at 400-500°C (Wang et al., 2004). Effects of surface properties of corrugated heat exchanger plates on calcium sulfate crystallization fouling were investigated by Zettler (2005). It was concluded that proper heat transfer surface treatment may be an effective way to significantly reduce scale formation. For example, polish the surface of the heat exchanger plates have reduced fouling in the tests (Zettler, 2005).

CHAPTER 3: CHARACTERIZATION OF FOULING ON INTERIOR SURFACE OF COATED AND UNCOATED CONDENSER TUBES

3.1 Materials and Methods

3.1.1 Preparation of condenser tubes

Stainless steel tubes (No. 304) purchased from McMSTER-CARR (Los Angeles, CA) were used as condenser tubes. Characteristics of these condenser tubes were presented in Table 3.1. Eight of these tubes were selected as control (i.e., uncoated tubes). Then, another eight tubes were selected and coated with SS-316, a siloxane-based coating material purchased from Superior Industries, Incorporated (Morris, MN), for rust and corrosion proof. The SS-316 coating material has a heat resistant property of up to 204 °C. For the surface coating (performed in the Department of Chemistry, WVU), the stainless tubes were thoroughly cleaned with distilled water and then rinsed with acetone, hexanes, and distilled water. The tubing was dried in an oven at 120 °C for 24 hours. The stainless steel tubing was mounted on a lathe with a rotation rate of 3 cycles per second. The aerosol can containing the paint was fitted with a 10" long and 1/16" in diameter stainless steel nozzle. The paint was sprayed onto the interior surface of the mounted stainless steel tubing through the two open ends. The excess paint was flushed out by applying three bursts of compressed air through the painted interior surface. The tubing was then allowed to cure for 24 hours. A visual examination of the coated interior surface indicated that a uniform thin layer of coating was formed.

3.1.2 Bench-scale experiments for fouling rate determination

A schematic diagram of experimental apparatus is shown in Fig. 3.1. It consists of a water tank, a pump, a cooling tower system, two coated and two uncoated condenser tubes, a tube muffle furnace, four thermal meters, and flow control valves (Fig. 3.1). It also includes a CO₂ cylinder in experiments with CO₂ sparging. Water from the Monongahela River (Morgantown, West Virginia) was used as cooling water in the current study. In order to improve the potential of fouling in the condenser tubes of the current experimental apparatus, the Monongahela River water (230 L) in each experiment was added with CaCl₂ (e.g., 0.73 g/L, equals to 200 mg Ca/L water) to enhance fouling. In addition, low cooling water velocity was used to accelerate the fouling rate and allow the collection of meaningful results in a short experimental period. Flow rate and temperature of the cooling water were maintained relatively constant during the whole experimental period for all experiments. A pH probe was calibrated before each experiment with standard buffer solutions at pH 4.0 and 7.0 at room temperature.

Four bench-scale experiments (e.g., $n=2$; experiment 1 and 2 are replicates without CO₂ sparging; experiment 3 and 4 are replicates with CO₂ sparging) were conducted using the water recirculation system and lasted for 10 days under a stable condition. In each of the experiments, the water was pumped through two coated and two un-coated condenser tubes which were placed inside a muffle furnace with a temperature of 450 °C. The cooling water was heated in the muffle furnace by around 10 ~15 °C and cooled down by the cooling tower, and then the water flowed back to the reservoir for recirculation. The velocity of the cooling water was about 0.04 m/s, which was a laminar flow with Reynolds Number 319 (< 2000). In the experiments with CO₂ sparging, CO₂

gas was added to the system through the cooling water inlet during the whole experimental period to maintain the pH of cooling water at about 6.0.

3.1.3 System monitoring, water sample collection and analyses

Temperature, pH, velocity and evaporation loss of cooling water were monitored daily. The daily operation conditions of the flowing system were recorded. Total suspended solids (TSS) in the cooling water were measured before and after operation of the flow system to estimate the fouling rates for each experiment. Replicate cooling water samples (i.e., $n=3$) were taken daily during the period of operation, and then stored at 4°C for analysis of anions (e.g., chloride, sulfate) and metals (e.g., Ca, Mg, Fe, Al). Standard methods were followed for chemical analyses of these cooling water samples (APHA, 1998).

3.1.4 Chemical and physical analyses of fouling materials

Tested condenser tubes were cut into small pieces (i.e., each piece has a length of 0.9 ft long) for fouling rate evaluation. Fouling materials inside the condenser tubes were dissolved by 1M HCl (pH=0) for 5 hours, and the concentration of major metal elements (e.g., Ca, Mg, Fe, Al) in the acid solution were measured using atomic absorption standard methods (APHA, 1998). In addition, morphology of fouling materials was investigated using a Scanning Electron Microscope (SEM).

3.2 Results from the experiments without CO₂ sparging (i.e., experiment 1 and 2)

3.2.1 Daily operation conditions of the recirculating system

Table 3.2 shows that the flow system for each of the experiments was stable in temperature, pH, water velocity, and evaporation loss of the cooling water.

3.2.2 TSS in the cooling water

In these experiments, the TSS increased from 2.40 to 10.50 mg/L (experiment 1), from 5.77 to 5.90 mg/L (experiment 2) respectively after the system operations (Table 3.3; Fig. 3.2).

3.2.3 Variations of major fouling components in the cooling water

In the experiment 1, chloride increased from 843 to 2372 mg/L, sulfate from 159 to 335 mg/L, calcium from 306 to 535 mg/L, and magnesium from 10 to 24 mg/L (Table 3.4; Fig. 3.3a-d) over the course of the experiment, respectively.

Similar to those in the experiment 1, chloride increased from 534 to 1420 mg/L, sulfate from 45.7 to 94.2 mg/L, calcium from 253 to 527 mg/L, and magnesium from 4.3 to 10.4 mg/L respectively (Table 3.4; Fig. 3.3a-d) in the experiment 2.

3.2.4 Major chemical constituents in the fouling materials

In the experiment 1, calcium concentrations were higher on the surface of the uncoated tubes (Table 3.5; Fig. 3.4a) than those on the coated tubes (Table 3.5; Fig. 3.4a) and on the blank (i.e., the unused stainless steel tube). Magnesium concentrations were higher on the surface of the uncoated tubes (Table 3.5; Fig. 3.4a) than those on the coated

tubes (Table 3.5; Fig. 3.4a) and on the blank (i.e., the unused stainless steel tube). Iron concentrations were higher on the surface of the uncoated tubes (Table 3.5; Fig. 3.4a) than those on the coated tubes (Table 3.5; Fig. 3.4a) and on the blank (i.e., the unused stainless steel tube). Aluminum concentrations were almost the same on the surface of the uncoated tubes (Table 3.5; Fig. 3.4a) and on the coated tubes (Table 3.5; Fig. 3.4a) but higher than those on the blank (i.e., the unused stainless steel tube).

In the experiment 2, calcium concentrations were higher on the surface of the uncoated tubes (Table 3.5; Fig. 3.4b) than those on the coated tubes (Table 3.5; Fig. 3.4b) and on the blank (i.e., the unused stainless steel tube). Magnesium concentrations were zero on the coated tubes (Table 3.5; Fig. 3.4b), uncoated tubes (Table 3.5; Fig. 3.4b), and on the blank (i.e., the unused stainless steel tube). Iron concentrations were lower on the surface of the uncoated tubes (Table 3.5; Fig. 3.4b) than those on the coated tubes (Table 3.5; Fig. 3.4b), but still higher than those on the blank (i.e., the unused stainless steel tube). Aluminum concentrations remained the same on both uncoated tubes (Table 3.5; Fig. 3.4b) and coated tubes (Table 3.5; Fig. 3.4b) but higher than those on the blank (i.e., the unused stainless steel tube).

3.2.5 Fouling from the SEM

The morphology of fouling materials on the coated tubes (Fig. 3.5a) and uncoated tubes (Fig. 3.5b) were presented.

3.3 Discussion for the experiments without CO₂ sparging (i.e., experiment 1 and 2)

The current study found that coating on the condenser tubes prevented fouling to some extent. During the 10-day experimental period, the system had stable operation conditions (e.g., temperature, pH, water velocity, and evaporation loss of the cooling water) in both of the two experiments (Table 3.2 a-b). This assured the reliable comparisons of the fouling results between the coated and uncoated test tubes.

In these experiments, TSS concentrations in the cooling water increased after the system operation (Table 3.3; Fig.3.2). These results indicate that the solids in the cooling water became concentrated due to evaporation loss. Consequently, the fouling potential will increase due to these concentrated solids in the cooling water. This was supported by other studies that crystallization fouling rate is significantly affected by the presence of suspended particles in the cooling water (Bansal et. al, 1997).

Detailed analysis of these solids in the cooling water further strengthened this point of view. In both experiments (i.e., experiments 1 and 2), concentrations of major fouling components (e.g., chloride, sulfate, calcium and magnesium) increased in the cooling water after the system operations (Table 3.4; Fig. 3.3). Concentrated salts from these metals and anions increased the precipitation potentials on the surface of the condenser tubes. During the condition of elevated temperatures (e.g., heating the cooling water by the oven in the current experiments), chemical precipitates such as calcium carbonate, calcium chloride, calcium sulfate, magnesium carbonate, magnesium chloride, magnesium sulfate, and aluminum sulfate have lower solubilities (Morse, 1977; Stumm and Morgan, 1996; Lin, 1997). However, the concentrations of aluminum and iron only

had slight variations. This may result from the lower concentrations of aluminum and iron than those of calcium and magnesium in the cooling water.

In response to concentrated TSS, anions, and metals in the cooling water, fouling was observed on the surface of the condenser tubes. This was supported by the results that concentrations of all the major metals (except magnesium in the experiment 2) were higher on the surface of the experimental tubes (i.e., the coated and uncoated) than that on the blank.

Further, coating on the condenser tubes reduced fouling in the current experiments. This was supported by the results that concentrations of major metals on the surface of the coated tubes were generally lower than those on the uncoated tubes, especially the concentrations of calcium, which was the major component of the make-up water. Mean calcium concentrations on the surface of the uncoated tubes were two and four times higher than those on the coated tubes in the experiments 1 (i.e., 0.20 mg/in² on the uncoated tubes and 0.10 mg/in² on the coated tubes) and 2 (i.e., 0.02 mg/in² on the uncoated and 0.005 mg/in² on the coated tubes) respectively. Based on these short-term and small scale experiments, these magnitudes of fouling preventing on the coated tubes indicated the efficiency of coating in the current study. The possible reasons for slightly inconsistent results of other metals between the two experiments may result from lower concentrations in the cooling water and no additions of these metals in the make-up water.

3.4 Results from the experiments with CO₂ sparging (i.e., experiment 3 and 4)

3.4.1 Daily operation conditions of the recirculating system

Table 3.6 shows that the flow system for each of the experiments was stable in temperature, pH, water velocity, and evaporation loss of the cooling water.

3.4.2 TSS in the cooling water

In these experiments, the TSS decreased from 3.77 to 3.57 mg/L (experiment 3), from 6.13 to 4.70 mg/L (experiment 4) respectively after the system operations (Table 3.7; Fig. 3.6).

3.4.3 Variations of major fouling components in the cooling water

In the experiment 3, chloride increased from 453 to 1120 mg/L, sulfate from 34 to 90 mg/L, calcium from 417 to 649 mg/L, and magnesium from 6.60 to 9.61 mg/L (Table 3.8; Fig. 3.7 a-d) over the course of the experiment, respectively.

Similar to those in the experiment 3, chloride increased from 452 to 1080 mg/L, sulfate from 63.2 to 83.0 mg/L, calcium from 315 to 601 mg/L, and magnesium from 4.53 to 9.83 mg/L (Table 3.8; Fig. 3.7 a-d) respectively in the experiment 4.

3.4.4 Major chemical constituents in the fouling materials

In the experiment 3, calcium concentrations were lower on the surface of the uncoated tubes (Table 3.9; Fig. 3.8 a) than those on the coated tubes (Table 3.9; Fig. 3.8 a) but still higher than those on the blank (i.e., the unused stainless steel tube). Magnesium concentrations were lower on the surface of the uncoated tubes (Table 3.9; Fig. 3.8 a) than those on the coated tubes (Table 3.9; Fig. 3.8 a) and was the same as those on the blank (i.e., the unused stainless steel tube). Iron concentrations were lower on the surface of the uncoated tubes (Table 3.9; Fig. 3.8 a) than those on the coated tubes (Table 3.9;

Fig. 3.8 a) but still higher than those on the blank (i.e., the unused stainless steel tube t). Aluminum concentrations were lower on the surface of the uncoated tubes (Table 3.9; Fig. 3.8 a) than on the coated tubes (Table 3.9; Fig. 3.8 a) but still higher than those on the blank (i.e., the unused stainless steel tube).

In the experiment 4, calcium concentrations were the same on both uncoated tubes and coated tubes (Table 3.9; Fig. 3.8 b) but still higher than those on the blank (i.e., the unused stainless steel tube). Magnesium concentrations were zero on the uncoated tubes, coated tubes (Table 3.9; Fig. 3.8 b), and on the blank (i.e., the unused stainless steel tube). Iron concentrations were lower on the surface of the uncoated tubes (Table 3.9; Fig. 3.8 b) than those on the coated tubes (Table 3.9; Fig. 3.8 b) and but still higher than those on the blank (i.e., the unused stainless steel tube). Aluminum concentrations were lower on the surface of the uncoated tubes (Table 3.9; Fig. 3.8 b) than those on the coated tubes (Table 3.9; Fig. 3.8 b) but still higher than those on the blank (i.e., the unused stainless steel tube).

3.4.5 Fouling from the SEM

The morphology of fouling materials on the coated tubes (Fig. 3.9a) and uncoated tubes (Fig. 3.9b) were presented.

3.4.6 Major fouling components on the coated tubes without CO₂, uncoated tubes without CO₂, coated tubes with CO₂, uncoated tubes with CO₂.

Calcium concentrations in the experiments without CO₂ (mean = 0.050 mg/in² on the coated tubes; mean = 0.11 mg/in² on the uncoated tubes; Table 3.10; Fig. 3.10) were

higher than those in the experiments with CO₂ (mean = 0.04 mg/in² on the coated tubes; mean = 0.002 mg/in² on the uncoated tubes; Table 3.10; Fig. 3.10). Magnesium concentrations in the experiments without CO₂ (mean = 0.000 mg/in² on both coated tubes and uncoated tubes; Table 3.10; Fig. 3.10) were lower than those in the experiments with CO₂ (mean = 0.002 mg/in² on the coated tubes; mean = 0.000 mg/in² on the uncoated tubes; Table 3.10; Fig. 3.10). Iron concentrations in the experiments without CO₂ (mean = 0.144 mg/in² on the coated tubes; mean = 0.150 mg/in² on the uncoated tubes; Table 3.10; Fig. 3.10) were higher than those in the experiments with CO₂ (mean = 0.124 mg/in² on the coated tubes; mean = 0.092 mg/in² on the uncoated tubes; Table 3.10; Fig. 3.10). Aluminum concentrations in the experiments without CO₂ (mean = 0.002 mg/in² on the coated and uncoated tubes; Table 3.10; Fig. 3.10) were lower than those in the experiments with CO₂ (mean = 0.006 mg/in² on the coated tubes; mean = 0.003 mg/in² on the uncoated tubes; Table 3.10; Fig. 3.10).

3.5 Discussion for the experiments with CO₂ sparging (i.e., experiment 3 and 4)

The current study found that CO₂ sparging in the cooling water prevented fouling to some extent. During the 10-day experimental period, the system had stable operation conditions (e.g., temperature, water evaporation loss, pH, and water velocity) in both of the two experiments (Table 3.6). This allowed the reliable comparisons of the fouling results between the coated and uncoated tubes with CO₂ sparging, and between the experiments with CO₂ sparging (i.e., experiment 3 and 4) and without CO₂ sparging (i.e., experiment 1 and 2).

In these experiments, the TSS concentrations in the cooling water decreased after the system operations (Table 3.7; Fig. 3.6). These results were inconsistent with those in the experiments 1 and 2 where TSS increased after the system operations. One possible reason is that the solubility of solids in the cooling water was increased by the addition of CO₂ gas. Consequently, the fouling potential was reduced due to increased solubility of solids in the cooling water.

Similar to the results in the experiments 1 and 2, concentrations of major fouling components (e.g., chloride, sulfate, calcium and magnesium) increased in the cooling water after the system operations in the experiments 3 and 4 (Table 3.8; Fig. 3.7). These increased concentrations of major anions and metals were resulted from the concentrated process of the cooling water (i.e., water loss from the evaporation).

However, concentrations of calcium (the major component of the make-up water) on the surface of the tested tubes were significantly lower in experiments with CO₂ (i.e., experiment 3 and 4) than those without CO₂ (i.e., the experiments 1 and 2) (Table 3.10; Fig. 3.10). This result indicates that the addition of CO₂ to the system has reduced fouling rate on the condenser tubes. In the CO₂ treatments, coated tubes even had slightly higher concentrations of calcium than those on the uncoated tubes. It seems the addition of CO₂ outcompeted the effects of coating on fouling control in the current study. But based on these short-term and small scale experiments, the current study detected the efficiency of CO₂ sparging in fouling prevention.

CHAPTER 4: CONCLUSIONS & APPLICATIONS

Coating of condenser tube and CO₂ sparging were tested for their effectiveness on preventing fouling and water use reduction in thermal electric power plants in this study. The study found that coating on the condenser tubes prevented fouling to some extent. This was supported by the results that concentrations of major metals on the surface of the coated tubes were generally lower than those on the uncoated tubes, especially the concentrations of calcium, which was the major component of the make-up water.

Results from comparisons of fouling materials on tested tubes between experiments with and without CO₂ demonstrated that the addition of CO₂ to the system has reduced fouling rate on the condenser tubes statistically significantly. The concentrations of calcium (the major component of the make-up water) on the surface of the tested tubes were significantly lower in experiments with CO₂ sparging than those in experiments without CO₂ sparging.

However, no synergistic effects of coating and CO₂ have been observed in the study. In the CO₂ treatments, coated tubes had slightly higher concentrations of calcium than uncoated tubes. It seems the addition of CO₂ outcompeted the effects of coating on fouling control in the study.

Coating on the condenser tubes and CO₂ sparging in the cooling water in thermoelectric power plants can reduce fouling rate, resulting in water use reduction, energy efficiency improvement, and economic cost decreasing during power generation. Further experiments are needed to test the interactive effects between coating and CO₂ sparging on fouling control in power plants. Designing an integrated system which

includes coating and CO₂ sparging is expected reduce water consumption, improve energy efficiency, and reduce economic loss in thermoelectric power plants.

Table 3.1 Characteristics of the condenser tubes

Category	Characteristics
Material	type 304/304L stainless steel
Length	24 inch
Shape	structural tubes
Structural tube type	plain round
Structural tube tolerance	standard
Outside diameter	3/8 inch (.375 inch)
Inside diameter	.319 inch
Wall thickness	.028 inch

Table 3.2 Daily operation conditions of the flowing system in the experiments1 and 2

Experiment 1

Date	Water Temperature (°C)						Flow rate (m/s)				Water loss (L/day)
	Before heating	After cooling	tube 1 (un-1)	tube 2 (un-2)	tube 3 (c-1)	tube 4 (c-2)	tube 1 (un-1)	tube 2 (un-2)	tube 3 (c-1)	tube 4 (c-2)	
9/17/09	23.9	26.1	34.0	35.7	35.2	35.5	0.03	0.06	0.03	0.04	0
9/18/09	25.8	27.3	38.5	36.8	38.5	37.8	stable	stable	stable	stable	16
9/19/09	27.6	28.8	39.2	37.0	39.4	39.0	stable	stable	stable	stable	15
9/20/09	27.2	28.1	38.9	37.2	39.0	38.8	stable	stable	stable	stable	15
9/21/09	27.1	28.3	39.2	37.0	39.1	38.9	stable	stable	stable	stable	13
9/22/09	27.8	28.9	39.7	37.4	39.6	39.6	stable	stable	stable	stable	14
9/23/09	27.8	28.8	39.7	38.2	39.8	39.8	stable	stable	stable	stable	12
9/24/09	28.1	29.0	39.8	38.5	39.3	40.2	stable	stable	stable	stable	15
9/25/09	27.7	28.5	40.1	38.5	38.9	40.0	stable	Stable	stable	Stable	13
9/26/09	27.5	28.3	40.0	38.5	39.0	40.1	stable	stable	stable	Stable	12
9/27/09	26.2	27.8	39.0	38.4	39.1	40.3	stable	stable	stable	stable	12

Experiment 2

Date	Water Temperature (°C)						Water Loss (L/day)	pH
	Before heating	After cooling	Tube 1 (c-1)	Tube 2 (c-2)	Tube 3 (un-1)	Tube 4 (un-2)		
11/04/09	22.70	22.7	22.7	22.7	22.7	22.7	0	7.3
11/05/09	27.50	28.3	39.1	40.3	37.9	37.3	12.5	7.1
11/06/09	28.20	29.4	39.2	41.0	38.0	37.6	12.5	7.5
11/07/09	28.1	29.0	38.0	41.0	37.6	37.5	12.5	6.9
11/08/09	28.3	29.6	38.3	41.4	38.1	37.8	12.5	7.4
11/09/09	28.4	29.3	38.2	41.8	38.0	38.0	12.5	7.3
11/10/09	28.7	29.9	38.4	41.9	38.5	38.4	12.5	7.2
11/11/09	27.8	29.0	38.5	42.4	38.0	38.0	12.5	7.5
11/12/09	27.8	29.3	38.7	42.0	38.1	38.2	12.5	7.1
11/13/09	28.1	29.2	39.0	42.4	38.2	38.6	12.5	7.6

Note: “un” represents uncoated, “c” represents coated. The flow rate in the experiment 2 was the same as that in the experiment 1 (Reynolds Number = 319).

Table 3.3 Total suspended solids (TSS) in the cooling water before and after operation of the flowing system in the experiments 1 and 2

Experiment 1

Period	Date	Replicates	Filtered volume (L)	TSS (mg/L)	Mean
Before operation	09/17/09	1	2	2.35	2.40
		2	2	2.40	
		3	2	2.42	
After operation	09/27/09	1	2	10.80	10.50
		2	2	10.30	
		3	2	10.50	

Experiment 2

Period	Date	Replicates	Filtered volume (L)	TSS (mg/L)	Mean
Before operation	11/4/09	1	1	6.70	5.77
		2	1	5.60	
		3	1	5.00	
After operation	11/13/09	1	1	5.40	5.90
		2	1	6.20	
		3	1	6.10	

Table 3.4 Concentration (Mean; n=3) of anions and metals in the cooling water during the monitoring period in the experiments 1 and 2

Experiment 1

Date	Cl ⁻ (mg/L)	SO ₄ ²⁻ (mg/L)	Ca (mg/L)	Mg (mg/L)	Fe (mg/L)	Al (mg/L)
9/17/09	843	159	306	10	0.06	0.10
9/18/09	1066	158	299	11	0.05	0.06
9/19/09	1115	180	321	12	0.06	0.12
9/20/09	1168	192	319	14	0.06	0.13
9/21/09	1176	203	318	14	0.05	0.19
9/22/09	1240	217	364	14	0.06	0.15
9/23/09	1437	229	382	15	0.08	0.11
9/24/09	1447	242	399	15	0.07	0.06
9/25/09	1657	263	487	19	0.05	0.25
9/27/09	2372	335	535	24	0.05	0.17

Experiment 2

Date	Cl ⁻ (mg/L)	SO ₄ ²⁻ (mg/L)	Ca (mg/L)	Mg (mg/L)	Fe (mg/L)	Mn (mg/L)
11/4/09	534	45.7	253	4.3	0.05	0.02
11/5/09	637	47.6	270	4.8	0.02	0.00
11/6/09	682	52.6	300	5.4	0.01	0.00
11/7/09	781	55.9	307	5.6	0.00	0.00
11/8/09	842	47.6	310	5.8	0.02	0.00
11/9/09	946	56.7	333	6.2	0.27	0.00
11/10/09	1028	60.6	340	6.6	0.00	0.00
11/11/09	1150	69.2	380	7.4	0.02	0.02
11/12/09	1350	74.8	430	8.5	0.00	0.00
11/13/09	1420	94.2	527	10.4	0.02	0.02

Table 3.5 Metal concentrations (Mean; n=2) in fouling material on the coated and uncoated tubes in the experiments 1 and 2

Treatment		Ca (mg/in ²)	Mg (mg/in ²)	Fe (mg/in ²)	Al (mg/in ²)
Exp.1	Coated	0.096	0.001	0.149	0.002
	Uncoated	0.195	0.002	0.178	0.002
Exp.2	Coated	0.005	0.000	0.139	0.002
	Uncoated	0.020	0.000	0.120	0.002
Blank		0.000	0.000	0.039	0.001

Note: Exp.1 = experiment 1; Exp. 2 = experiment 2. Blank is an unused condenser tube.

Table 3.6 Daily operation conditions of the flowing system in the experiments 3 and 4

Experiment 3

Date	Water Temperature (°C)						Water Loss (L/day)	pH
	Before heating	After cooling	Tube 1 (C-1)	Tube 2 (C-2)	Tube 3 (un-1)	Tube 4 (un-2)		
1/12/10	10.6	11.3	21.0	21.3	21.0	21.7	0	6.0
1/13/10	25.9	28.5	43.6	40.1	41.9	38.6	8	6.0
1/14/10	25.7	28.8	37.3	38.5	38.6	39.3	11	5.6
1/15/10	26.7	28.6	39.3	39.6	38.0	39.3	12	6.0
1/16/10	27.0	28.8	45.2	38.2	39.8	40.5	10	5.7
1/17/10	26.6	28.5	43.6	38.1	38.9	40.7	12	6.0
1/18/10	26.3	28.0	40.9	39.0	38.0	41.0	11	5.9
1/19/10	26.1	28.1	41.7	39.7	40.3	41.0	12	6.0
1/20/10	26.4	28.6	40.2	42.7	41.0	43.4	12	6.0
1/21/10	26.3	28.3	42.2	41.7	40.6	38.3	12	5.7
1/22/10	26.3	28.3	38.2	42.0	44.7	39.9	11	5.8

Experiment 4

Date	Water Temperature (°C)						Water Loss (L/day)	pH
	Before heating	After cooling	Tube 1 (c-1)	Tube 2 (c-2)	Tube 3 (un-1)	Tube 4 (un-2)		
1/28/10	20.3	27.0	34.4	30.6	33.7	32.0	0	5.8
1/29/10	29.0	31.0	39.6	39.8	40.0	40.2	13	5.8
1/30/10	29.0	31.1	40.4	41.5	41.6	43.0	12	6.3
1/31/10	29.3	31.4	40.6	42.5	43.0	44.2	11	5.6
2/1/10	29.5	31.8	41.3	44.3	43.5	44.7	12	5.8
2/2/10	29.5	31.6	41.9	45.2	44.1	45.5	12	6.0
2/3/10	29.2	32.0	42.4	46.1	44.5	44.1	11	6.2
2/4/10	30.2	31.6	44.2	46.0	45.4	46.2	12	5.7
2/5/10	30.7	32.3	43.9	41.3	46.3	42.0	12	5.8
2/6/10	30.2	32.0	44.5	43.0	47.5	42.3	12	6.2
2/7/10	29.6	31.9	45.3	44.4	48.0	43.5	11	6.4

Note: ‘un’ represents uncoated, ‘c’ represents coated. The flow rate in the experiment 3 and experiment 4 were the same as that in experiment 1 (Reynolds number = 319).

Table 3.7 Total suspended solids (TSS) in the cooling water before and after operation of the flowing system in the experiments 3 and 4

Experiment 3

Period	Date	Replicates	Filtered volume (L)	TSS (mg/L)	Mean
Before operation	1/12/2010	1	1	3.80	3.77
		2	1	3.80	
		3	1	3.70	
After operation	1/22/2010	1	1	3.50	3.57
		2	1	3.60	
		3	1	3.60	

Experiment 4

Period	Date	Replicates	Filtered volume (L)	TSS (mg/L)	Mean
Before operation	1/28/2010	1	1	6.20	6.13
		2	1	6.30	
		3	1	5.90	
After operation	2/8/2010	1	1	4.50	4.70
		2	1	4.60	
		3	1	5.00	

Table 3.8 Concentrations (Mean; n=3) of anions and metals in the cooling water during the monitoring period in the experiments 3 and 4

Experiment 3

Date	Cl ⁻ (mg/L)	SO ₄ ²⁻ (mg/L)	Ca (mg/L)	Mg (mg/L)	Fe (mg/L)	Al (mg/L)
1/12/10	453	34	417	6.60	0.18	0.03
1/13/10	525	39	430	6.50	0.20	0.00
1/14/10	582	42	472	7.24	0.23	0.18
1/15/10	609	44	456	7.28	0.13	0.00
1/16/10	629	52	515	7.94	0.15	0.06
1/17/10	644	54	476	7.65	0.18	0.15
1/18/10	719	54	557	8.96	0.16	0.02
1/19/10	828	61	580	8.59	0.14	0.04
1/20/10	929	72	639	9.70	0.09	0.05
1/21/10	1005	80	647	10.47	0.14	0.08
1/22/10	1120	90	649	9.61	0.09	0.04

Experiment 4

Date	Cl ⁻ (mg/L)	SO ₄ ²⁻ (mg/L)	Ca (mg/L)	Mg (mg/L)	Fe (mg/L)	Al (mg/L)
01/28/10	452	63.2	315	4.53	0.29	0.25
01/29/10	496	68.4	362	4.48	0.14	0.20
01/30/10	524	72.5	378	4.87	0.12	0.26
01/31/10	556	73.9	400	5.77	0.11	0.23
02/01/10	639	77.2	410	5.90	0.20	0.19
02/02/10	690	81.5	414	6.59	0.17	0.24
02/03/10	744	80.6	448	6.90	0.18	0.24
02/04/10	831	80.6	467	6.83	0.12	0.36
02/05/10	868	81.2	468	8.21	0.14	0.29
02/06/10	945	81.6	547	9.39	0.15	0.27
02/07/10	1080	83.0	601	9.83	0.13	0.26

Table 3.9 Metal concentrations (Mean; n = 2) on the surface of the coated and uncoated tubes in the experiments 3 and 4

Treatment		Ca (mg/in ²)	Mg (mg/in ²)	Fe (mg/in ²)	Al (mg/in ²)
Exp.3	Coated	0.079	0.003	0.122	0.005
	Uncoated	0.002	0.000	0.092	0.003
Exp.4	Coated	0.002	0.000	0.126	0.008
	Uncoated	0.002	0.000	0.092	0.003
	Blank	0.000	0.000	0.039	0.001

Note: Exp.3 = experiment 3; Exp. 4 = experiment 4. Blank is an unused condenser tube.

Table 3.10 Metal concentrations (Mean; n=4) on the surface of the coated tubes without CO₂, uncoated tubes without CO₂, coated tubes with CO₂, and uncoated tubes with CO₂

Treatment	Ca (mg/in ²)	Mg (mg/in ²)	Fe (mg/in ²)	Al (mg/in ²)
coated without CO ₂	0.050	0.000	0.144	0.002
uncoated without CO ₂	0.107	0.000	0.150	0.002
coated with CO ₂	0.040	0.002	0.124	0.006
uncoated with CO ₂	0.002	0.000	0.092	0.003

Fig. 3.1 Schematic diagram of the experimental apparatus without CO₂ sparging

Figure 3.2 Concentrations (mean) of total suspended solids (TSS) in the cooling water before and after the system operations in the experiments 1 and 2.

(a)

(b)

(c)

(d)

Fig. 3.3 Variations of (a) chloride, (b) sulfate, (c) calcium, and (d) magnesium in the cooling water during the monitoring period in the experiments 1 and 2

Fig. 3.4 Concentrations of calcium, magnesium, iron, and aluminum on the surface of the coated and uncoated tubes during the monitoring period in the (a) experiment 1 and (b) experiment 2.

Fig. 3.5 SEM micrograph of fouling on the surface of the (a) coated and (b) uncoated condenser tubes without CO₂ sparging

Figure 3.6 Concentrations (mean) of total suspended solids (TSS) in the cooling water before and after the system operations in the experiments 3 and 4.

(a)

(b)

(c)

(d)

Fig. 3.7 Variations of (a) chloride, (b) sulfate, (c) calcium, and (d) magnesium in the cooling water during the monitoring period in the experiments 3 and 4

Fig. 3.8 Concentrations of calcium, magnesium, iron, and aluminum on the surface of the coated and uncoated tubes during the monitoring period in the (a) experiment 3 and (b) experiment 4.

(a)

(b)

Fig. 3.9 SEM micrograph of fouling on the surface of the (a) coated and (b) uncoated condenser tubes with CO₂ sparging

Fig. 3.10 Concentrations of calcium, magnesium, iron, and aluminum on the surface of the coated tubes without CO₂, uncoated tubes without CO₂, coated tubes with CO₂, uncoated tubes with CO₂ during the monitoring period.

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