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Global technologies for the removal of water scaling & water recovery - Department of Energy (DOE) USA

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Abstract

In this paper, we reported the current technologies of water scaling removal and also water recovery from the flue gases, which are funded by Department of Energy (DOE), USA. Globally, water resources are limited due to the climate change. The potential impacts of climate change is food and water shortages. In the 21st century, water shortages and pollution are expected to become more acute as populations grow and concentrate in cities. At present, the water stress increases over 62.0 ~ 75.8% of total water basin area and decreases over 19.7 ~ 29.0%. Many renewable energy sources demand secure water resources. Water is critical for successful climate change mitigation, as many efforts to reduce greenhouse gas emissions depend on reliable access to water resources. Water hardness is one of the major challenge to coal power plants. Department of energy (DOE) funded and encouraged for the development of advanced technologies for the removal of hardness of water (scaling) and also water recovery from the flue gases from coal power plants.

Key words : Water scaling, water recovery, coal-fired power plant, Waste water.

1. Introduction

Currently, 600 million people faces water scarcity. In future population growth rates up to 2.7 billion people may be living in either water scarce or water stressed conditions by 2025. Population growth, economy, energy and water all are interrelated and more significant to the sustainable society [1]. In the 21st century, the world faces a water crisis, both of quality and quantity, because by continuous population growth, industrialization, food production practices, increased living standards and poor water use strategies.

There are several sources for ground water pollution. The largest single use of water by industry is for cooling in thermal power generation. The heavy metals released into the atmosphere along with flue gases from coal power plants and then fall to earth as rain or snow. It affects the surface water and underground water quality.

Water is essential to thermoelectric power plants, used primarily for cooling. Using impaired water in place of fresh water is a potentially attractive solution to the problems of water scarcity and competing demands. As the population increases, good fresh quality water is much more needed for human use including growing food. Tertiary sewage treated water has been successfully used in many industrial applications.

Water usually falls as rain onto a land mass and then percolates through the layers of soil and rock, it gains hardness. This hardness is due to the rain passed over the rocks and Ca, Mg minerals dissolved

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in the water. The purity of makeup water is critical in maintaining steam quality and in limiting boiler blow down. Silica, iron oxide, calcium carbonate, and calcium sulphates can deposit on airfoils or blades and drastically reduce the power plant efficiency [2].

Water discharging from mines represents a large untapped resource for power plant cooling. Large power plants use thousands of gallons of water per minute for evaporative cooling to maintain their operations. This consumptive use often competes with other water uses such as navigation, drinking water and other industrial uses. Increased fresh water resource demand and environmental concerns related to power plant water use are driving the consideration of using alternate sources of water for thermoelectric generation. Suitable alternate water sources must be capable of providing large dependable quantities of flow; be thermally stable on a seasonal basis; and not cause different, but equally serious, environmental concerns compared to river water.

The use of impaired water is currently not very practical and cost effective, as the inferior water quality results in additional treatment requirements to address the high propensities of scaling, corrosion, and biofouling and to avoid adverse impacts to the environment. Depending on the impairment the treatment cost is prohibitively high because 1) the current separation technologies are inefficient, and 2) the scaling potential of the impaired waters is generally high and severely limits the number of cycles that can be achieved with current scale control technologies. Finally, any alternative water source must be legally developable and be economically competitive with traditional water sources. DOE focused more advanced cooling technologies in coal power plants to reduce use fresh water. Advanced cooling technologies are beneficial to improve performance and cost reduce cooling water blow down. Other option is recovery and reuse of flue gas water [3].

2. Strategy of Cooling and water recovery in coal-fired power plant and Scaling Removal Technologies-DOE Funding Projects:

2.1. The DOE project of Nalco Company is partnering with Argonne National Laboratory (ANL):

In this project to jointly develop advanced scale control technologies that will provide cost-effective solutions for coal based power plants to operate recirculating cooling water systems at high cycles using impaired waters. The overall approach is to use combinations of novel membrane separations and scale inhibitor technologies that will work synergistically, with membrane separations reducing the scaling potential of the cooling water and scale inhibitors extending the safe operating range of the cooling water system. The main objectives of this study to establish quantitative technical targets and develop calcite and silica scale inhibitor chemistries for high stress conditions including bench-scale testing to determine the feasibility of two membrane separation technologies (electrodialysis ED and electro deionization EDI) for scale minimization in additional novel scale inhibitor chemistries, develop selected separation processes, and optimize the integration of the technology components at the laboratory scale.

Municipal wastewater effluents have calcite and silica/silicate are two common minerals for using impaired waters. For reclaimed municipal wastewater effluents, calcium phosphate scaling can be an issue, especially in the co-presence of high silica. Coal fired power plants showed that the limited use and reuse of impaired waters is due to the formation of deposit caused by the presence of iron, high hardness, high silica and high alkalinity in the water. Appropriate and cost-effective inhibitors were identified and developed LL99B0 for calcite and gypsum inhibition and TX-15060 for silica inhibition. Nalco's existing dispersants HSP-1 and HSP-2 has excellent efficacy for dispersing Fe and Mn. ED and EDI were bench-scale tested by the CRADA partner Argonne National Laboratory for hardness, alkalinity and silica removal from synthetic make-up water and then cycled cooling water. Both systems showed low power consumption and 98-99% salt removal, however, the EDI system required 25-30% less power for silica removal.

The EDI system's performance was optimized and the length of time between clean-in-place (CIP) increased by varying the wafer composition and membrane configuration. The enhanced EDI system could remove 88% of the hardness and 99% of the alkalinity with a processing flux of 19.2 gal/hr/m2 and a power consumption of 0.54 kWh/100 gal water. The silica/silicate control approaches using chemical inhibitors include inhibition of silicic acid polymerization and dispersion of silica/silicate crystals. Long-term test of the EDI system and scale inhibitors was done at Nalco's cooling tower water testing facility, producing 850 gallons of high purity water (90+% salt removal) at a rate of 220 L/day and cooling tower runs were successfully completed by partially removing scaling ions (carbonate, hardness, and silica) and controlling fouling by using low level of scale inhibitors.

Electrodialysis (ED) and electro deionization (EDI) technology using for removing of bicarbonates, the optimization of cost and maximum reuse of water is to blend the two technologies. In the next section of the report developmental and work is reported, where some of the ions are partially removed from the impaired water and recycled to determine the scaling tendencies and maximize the impaired water reuse at the lowest cost.

One of the membrane systems being tested by Argonne for the removal of scaling components is resin wafer electro deionization (RW-EDI). EDI is an industrial process that incorporates ion exchange (IX) resin beads into an electro dialysis (ED) stack. ED is an electrically-driven membrane-based separations process. Commercial EDI systems are constructed by filling the diluate channel in an ED stack with loose ion exchange resin beads. Argonne has immobilized the loose IX resin beads with polyethylene resins to form a porous resin wafer (RW) material. A typical EDI system schematic is shown in Figure 1.

The RW-EDI platform enables in-situ pH control by using the water splitting reaction which eliminates or minimizes the need for acid or base additives. The RW-EDI platform provides flexibility in terms of membranes used and their configuration. Additionally, the wafer resin composition can be varied (anion excess, cation excess or equal amounts of anions and cations) to facilitate the removal of scaling components [4].

2.2. Scaling Control for Municipal Wastewater Used for Cooling:

Treated Mmunicipal secondary wastewater shows potential alternative to fresh water for power plant cooling tower makeup water, especially in arid regions.

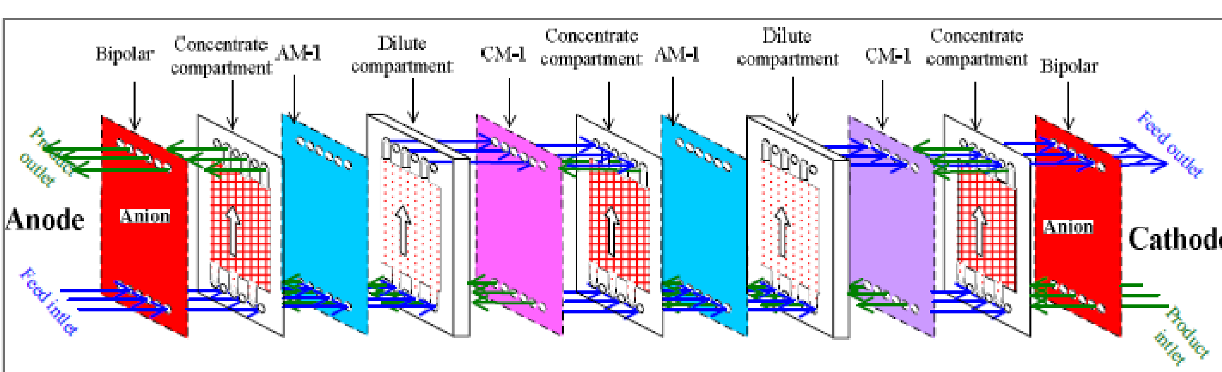

Figure 1: Schematic of the EDI system used for scaling ions removal

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 municipal wastewater (MWW) for cooling, scale layers formed on metal surfaces provided a certain degree of corrosion protection for the metal alloys was tested.

The chemistry of MWW cooling water at different cycles of concentration (CoC) was modeled using MINEQL+ version 4.5 [5,6], 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.

In this study 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. Circular discs made with stainless steel were inserted through sampling ports into the recirculating water to provide collect-

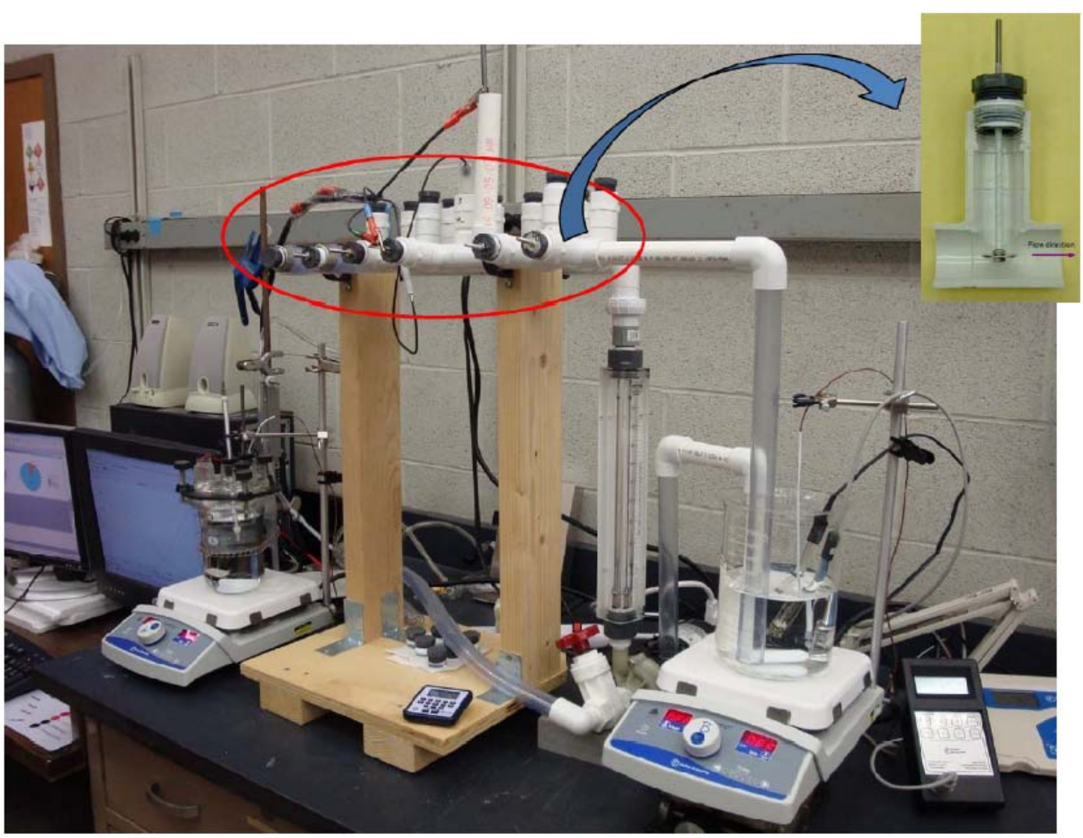

Figure 2. Bench-scale water recirculating system with inserted stainless steel circular discs for scale collection and subsequent mass gain measurement.

ing surfaces for scaling/deposition, as shown in Figure 2, 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.

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., flow rate 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).

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 [7].

2.3. Cooling and water recovery in coal-fired power plant:

This project deals with an innovative water treatment technology that utilizes spark discharges in water for scale prevention. The key issue is how to precipitate and remove dissolved Ca ions in recirculating cooling water so that the calcium carbonate (CaCO3) scales can be avoided and COC can be increased. This study to develop technologies to reduce freshwater consumption in a cooling tower of coal-based power plant so that one could significantly reduce the need of make-up water. The specific goal was to develop a scale prevention technology based an integrated system of physical water treatment (PWT) and a novel filtration method so that one could reduce for the water blow down, which relation 30% of water losses approximately in a cooling tower. In this study investigated if a pulsed spark discharge in water could be used to remove deposits from the filter membrane. In this process included a pulsed power system and circulating water loop. The present experiments used artificially hardened water with hardness of 1,000 mg/L of $CaCO_3$ made from a mixture of calcium chloride ($CaCl_2$) and sodium carbonate (Na_2CO_3) in order to produce calcium carbonate deposits on the filter membrane. In the water spark was discharge and found to produce strong shockwaves in water, and the efficiency of the spark discharge in cleaning filter surface was evaluated by measuring the pressure drop across the filter over time.

The results showed that the pressure drop could be reduced to the value corresponding to the initial clean state and after that the filter could be maintained at the initial state almost indefinitely, confirming the validity of the present concept of pulsed spark discharge in water to clean dirty filter. The present study also investigated the effect of a plasma-assisted self-cleaning filter on the performance of physical water treatment (PWT) solenoid coil for the mitigation of mineral fouling in a concentric counter flow heat exchanger. The shockwaves produced by pulse-spark discharges in water to continuously remove scale deposits from the surface of the filter by using self-cleaning filters, thus keeping the pressure drop across the filter at a relatively low value. Artificial hard water was used in the present fouling experiments for three different cases: no treatment, PWT coil only, and PWT coil plus self-cleaning filter. Stinking resistances decreased by 59% to 72% for the combined case of physical water treatment coil plus filter compared with the values for without treatment cases.

The project will utilize spark discharges in water to precipitate dissolved mineral ions in circulating cooling water in a simulated laboratory cooling tower and continuously remove precipitated mineral salts using a self-cleaning filter. The system was constructed to examine the validity of pulsed electric fields for self-cleaning filters. The present system consisted of five parts: power supply, water filter, water tank with magnetic stirrer, peristaltic pump, and pressure-measuring unit. The schematic diagram of the self-cleaning system is shown in Fig. 3.

The spark discharged effectively to remove the calcium carbonate particles from a filter medium, another flow system was constructed to generate supersaturated water in calcium ions on a controlled laboratory set up. The test setup was a simulated cooling tower system as shown in Fig. 4. The setup had an approximately 1 ft-high cooling tower. The cooling tower system purpose was to circulate city-tap water and produce evaporating pure supersaturated water by using heated air. The tap water from the City of Philadelphia had an electric conductivity of 430 μ mho/cm and was circulated through a peristaltic pump and back to the tower. In cooling tower, hot air was constantly flowing for stimulate the vaporization of pure water. A conductivity controller monitored the conductivity of the circulating water until the water conductivity reached a supersaturated state [8].

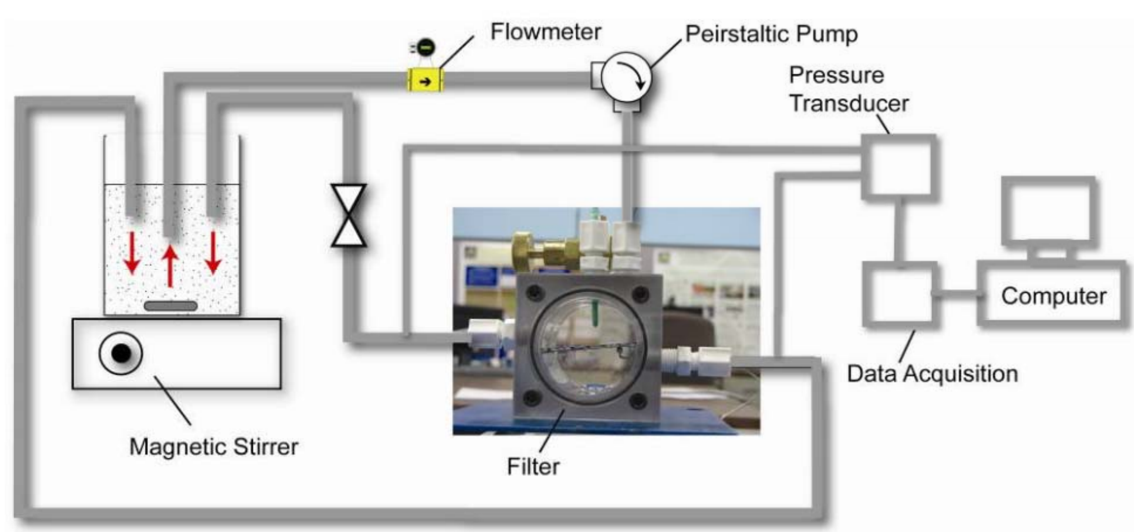

Figure 3. Schematic diagram of the self-cleaning filter system

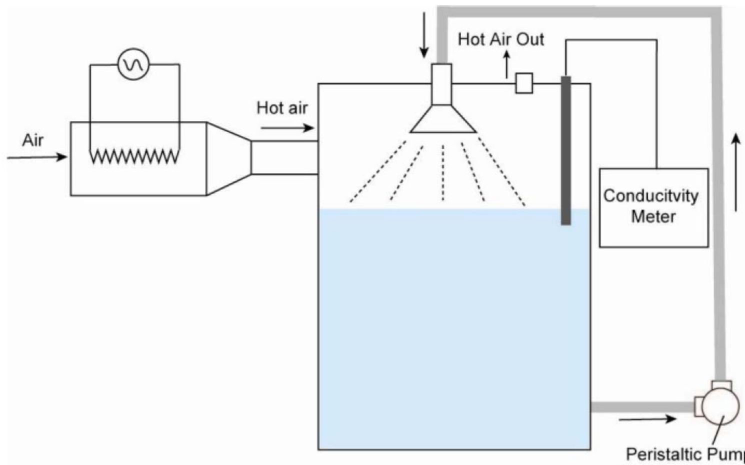

Figure 4. Sketch of a new test setup (a simulated cooling tower) to produce supersaturated water

2.3. Use of treated municipal waste water as power plant cooling system:

Treated municipal wastewater is a common, widely available alternative source of cooling water for thermoelectric power plants across the U.S. The biodegradable organic matter, carbonates, phosphates and ammonia-nitrogen in the treated wastewater pose challenges with respect to enhanced biofouling, corrosion, and scaling, respectively. The overall objective of this study was to evaluate the benefits and life cycle costs of implementing tertiary treatment of secondary treated municipal wastewater prior to use in recirculating cooling systems. The study comprised bench- and pilot-scale experimental studies with three different tertiary treated municipal wastewaters, and life cycle costing and environmental analyses of various tertiary treatment schemes. Sustainability factors and metrics for reuse of treated wastewater in power plant cooling systems were also evaluated [9].

The three tertiary treated wastewaters studied were: secondary treated municipal wastewater subjected to acid addition for pH control (MWW-pH); secondary treated municipal wastewater subjected to nitrification and sand filtration (MWW-NF); and treated secondary municipal wastewater subjected nitrification, sand filtration, and GAC adsorption (MWW-NFG).

Tertiary treatment was determined to be essential to achieve appropriate corrosion, scaling, and biofouling control for use of secondary treated municipal wastewater in power plant cooling systems. The ability to control scaling was significantly enhanced with tertiary treated wastewater compared to secondary treated wastewater. MWW-pH treated water (adjustment to pH 7.8) was effective in reducing scale formation, but increased corrosion and the amount of biocide required to achieve appropriate biofouling control. Corrosion could be adequately controlled with tolytriazole addition (4-5 ppm TTA), however, which was the case for all of the tertiary treated waters. For MWW-NF treated water, the removal of ammonia by nitrification helped to reduce the corrosivity and biocide demand. Also, the lower pH and alkalinity resulting from nitrification reduced the scaling to an acceptable level, without the addition of anti-scalant chemicals. Additional GAC adsorption treatment, MWW-NFG, yielded no net benefit. Removal of organic matter resulted in pitting corrosion in copper and cupronickel alloys. Negligible improvement was observed in scaling control and biofouling control. For all of the tertiary treatments, biofouling control was achievable, and most effectively with pre-formed monochloramine (2-3 ppm) in comparison with NaOCl and ClO2.

Life cycle cost (LCC) analyses were performed for the tertiary treatment systems studied experimentally and for several other treatment options. A public domain conceptual costing tool (LC3 model) was developed for this purpose. MWW-SF (lime softening and sand filtration) and MWW-NF were the most cost-effective treatment options among the tertiary treatment alternatives considered because of the higher effluent quality with moderate infrastructure costs and the relatively low doses of conditioning chemicals required.

Life cycle inventory (LCI) analysis along with integration of external costs of emissions with direct costs was performed to evaluate relative emissions to the environment and external costs associated with construction and operation of tertiary treatment alternatives. Integrated LCI and LCC analysis indicated that three-tiered treatment alternatives such as MWW-NSF and MWW-NFG, with regular chemical addition for treatment and conditioning and/or regeneration, tend to increase the impact costs and in turn the overall costs of tertiary treatment. River water supply and MWW-F alternatives with a single step of tertiary treatment were associated with lower impact costs, but the contribution of impact costs to overall annual costs was higher than all other treatment alternatives. MWW-NF and MWW_SF alternatives exhibited moderate external impact costs with moderate infrastructure and chemical conditioner dosing, which makes them (especially MWW-NF) better treatment alternatives from the environmental sustainability perspective since they exhibited minimal contribution to environmental damage from emissions.

The study employed bench-scale recirculation water systems and for testing of various chemical control schemes for corrosion, scaling, and biofouling in systems using different tertiary treated municipal wastewaters. Initial bench-scale experiments included batch-reactor experiments for performance evaluation of different scaling inhibitors and biocides. An experimental setup was prepared for scaling studies on a heated surface. A synthetic wastewater recipe was formulated for different types of tertiary treated municipal wastewaters having constituent concentrations similar to that at four cycles of concentration, a usual concentration of recirculating cooling waters in power plant cooling systems.

The bench-scale recirculating water system consisted of a centrifugal pump, a water bath on hot-

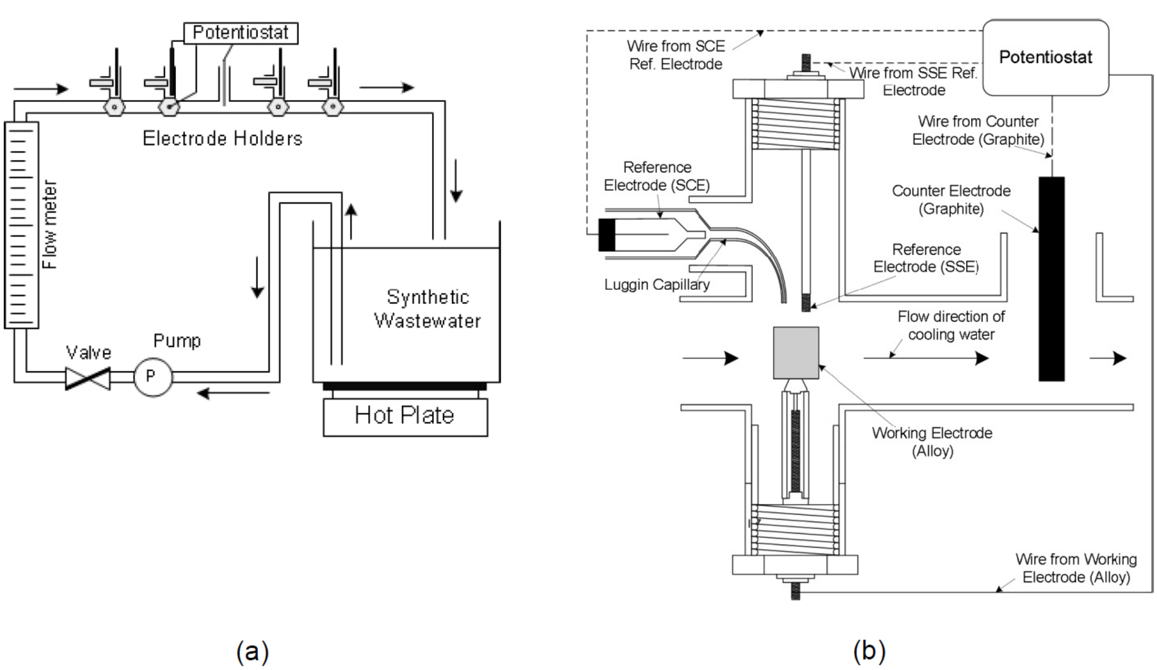

Figure 5. Schematic diagrams of (a) bench-scale recirculating system, (b) metal alloy specimen holder and ports for counter electrode and reference electrodes in the bench scale recirculating system.

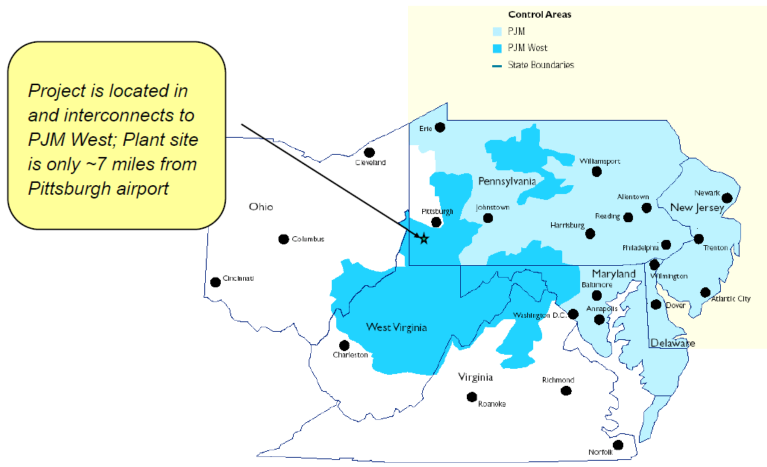

Figure 6. Project location.

plate (to control the water temperature) and a 1.91 cm (0.75 in) nominal diameter PVC pipe circulation system with a pipe rack to hold different electrodes. Design of the pipe rack holder was modified to accommodate two different reference electrodes shown in Figure. 5a. The pipe rack system included four tee-sections into which alloy specimen holders were mounted. Each tee-section was connected to another tee section, which accommodated two different reference electrodes in Figure. 5b, for side by side polarization resistance measurement. Temperature of the recirculating water was maintained at 40°C in the bench scale system to simulate the temperature of cooling water in the pilot-scale recirculating cooling water systems [10]. Flow rate through the system was maintained at 11.4 L/min (3 gpm) to achieve flow velocity of 0.66 m/s (2.18 ft/s) and Reynolds number of 1.9x10^4.

The bench-scale recirculating systems to incorporate a heated cartridge, which will be used to simulate the heat exchanger tubing surface in mineral scaling investigation. The design principle for the new system is taken from ASTM Standard Test Method for Determination of Corrosion and Fouling Tendency of Cooling Water under Heat Transfer Conditions (ASTM D 4778-05)

2.4. Assessing the Efficacy of Using Mine Water for Thermoelectric Power Generation:

Thermoelectric power plants use large volumes of water for condenser cooling and other plant operations. Traditionally, this water has been withdrawn from the cleanest water available in streams and rivers. However, as demand for electrical power increases it places increasing demands on freshwater resources resulting in conflicts with other off stream water users. The main objectives of this project were to develop and demonstrate a user friendly computer based design aid for assessing the costs, technical and regulatory aspects and potential environmental benefits for using mine water for thermoelectric generation. The framework provides a systematic process for evaluating the hydrologic, chemical, engineering and environmental factors to be considered in using mine water as an alternative to traditional freshwater supply [11].

A field investigation and case study was conducted for the proposed 300 MW Beech Hollow Power Plant located in Champion, Pennsylvania shown in Fig. 6. The field study based on previous research conducted by NMLRC identified mine water sources sufficient to reliably supply the 2-3,000gpm water supply requirement of Beech Hollow. A water collection, transportation and treatment system was designed around this facility. Using this case study a computer based design aid applicable to large in-

Figure 7. (a) H-Flume at the Primrose discharge, (b) H-Flume at the Hopper discharge

dustrial water users was developed utilizing water collection and handling principals derived in the field investigation and during previous studies of mine water and power plant cooling.

This study evaluates the potential economic and environmental benefits of using mine water at the proposed Beech Hollow Power Project. As originally proposed this study was intended to be developed and integrated into the engineering and construction of the power plant. However, due to the recession and resulting difficulty with financing development of the Beech Hollow project has been delayed. As proposed, Beech Hollow consists of the design, construction, and operation of an approximately 320 MW coal waste-fired power generation facility to be located in Robinson Township, Washington County, Pennsylvania. The project will generate approximately 288 MW of electrical energy for sale into the grid. Project fuel will consist of approximately 37.5 million tons of bituminous waste coal material ("gob") in place on 600 acres adjacent to the project site. The bituminous coal waste material represents the waste product from coal cleaning and processing operations conducted at the site for a period of in excess of 50 years. Coal Combustion Byproducts (CCB) generated from the combustion of the waste coal will be beneficially used in the reclamation of the permitted area adjacent to the project site and other unreclaimed mine lands in the area. Numerous mine water sources exist within, or just outside of a five mine radius of the proposed Beech Hollow Power Plant.

The locations of these discharges were identified using published reports on mine discharges in the area, combined with field reconnaissance. Of the 49 discharges identified in the study, six were selected for in depth study. Four of these discharges, JB-1, Primrose, McDonald, and Hopper are classified as high volume discharges as shown in Fig. 7. These two discharges were monitored that are low volume sources. These discharges are North Branch and Seabright. Because power plants require large volumes of cooling water, the focus of this investigation is on the larger discharges.

The framework will facilitate the use of mine water for thermoelectric generation, reduce demand on freshwater resources and result in environmental benefits from reduced emissions and abated mine discharges. Using mine water from the five mines in the example problem the amount of additional electricity generated is calculated to be 10,003,508.48 Kwh/yr which is equal to $630,221.03 based on an electricity rate of $0.063 /kwh. The avoided emissions from this site are 10,210 t/yr of carbon dioxide, 357 t/yr of sulfur dioxide, 143 t/yr of NOx and 3.48 lb/yr of mercury. The cost of building the water collection and treatment system is $11,110,189.51 with an estimate cost of operation of $618,829.32.

This translates into a water acquisition cost of $518.93/ million gallons compared to a cost of $3,000.00 per million gallons from the municipal water supply.

The use of constant cool makeup water to a power plant has numerous advantages. The principle advantage is that the power plant is able to generate more electricity without increasing its burn rate or derating the unit during hot humid summer days. This also has a number of secondary advantages including reduced coal consumption resulting in reduced emissions of CO_2, SOX, NOx, and mercury.

3. Conclusions:

The Department of Energy (DOE) has been continuously focused on the energy-water nexus. The DOE's National Laboratories funded to the development of water hardness removal technologies particularly in the coal power plants. DOE's laboratories are considered innovative, highly-effective and accessible techniques for removing the water hardness levels and also the research and development (R&D) solutions that will help to resolve water security issues. As the population grows and demand electricity and water increase, power plants located in some parts of the country will find it increasingly difficult to obtain the large quantities of water needed to maintain operations. Most of the water used in a coal power plants are used for cooling, and department of energy (DOE) has been focusing on possible technologies to control the amount of fresh water consumed for cooling purpose. The department of energy (DOE) is also evaluated the technologies on the recovery of usable water, such as, water produced from oil and gas extractions, mine water, and water contained in boiler flue gases.

Acknowledgements

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