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Purification of Flue Gas Desulfurization Wastewater with Super Capacitor Radial Deionization

Behrang (Ben) Pakzadeh, Southern Research Institute, Cartersville, Georgia; Jay Wos, Southern Research Institute, Birmingham, AL; Jay Renew, Southern Research Institute, Cartersville, GA; Ken Cushing, Southern Research Institute, Birmingham, AL; Patrick Curran, Atlantis Technologies, Monarch Beach, CA; Richard Breckenridge, Electric Power Research Institute, Charlotte, NC; Jason (Xinjun) Teng, Southern Company Services, Birmingham, AL; Cassie Willingham, Georgia Power, Cartersville, GA; Dongxu Yan, Layne, Phoenix, AZ; Russell Mack, Boston, MA; John Hall, Layne, Lakeland, FL

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ABSTRACT

The US Environmental Protection Agency's effluent guidelines for steam electric power generating units will address stringent discharge limitations for mercury, selenium, arsenic, and nitrate/nitrite in flue gas desulfurization (FGD) wastewater. The Radial Deionization system (RDI^{TM}) from Atlantis Technologies may be applicable for FGD wastewater treatment. A 0.5 gpm pilot test was conducted at the Water Research Center at Plant Bowen in Georgia. The main objective was to evaluate the efficacy of the pilot RDI system in treating FGD wastewater.

INTRODUCTION

The use of Radial Deionization (RDI) treatment to remove high total dissolved solids (TDS) from flue gas desulfurization (FGD) wastewater and other power plant waste streams could provide significant cost and energy savings compared to conventional technologies used in plant cooling and make-up water systems. FGD wastewaters may contain up to 10,000 mg/L of total suspended solids (TSS) and up to 70,000 mg/L of TDS for those power plants that recirculate/recycle the FGD wastewater in their scrubber systems. The use of a radial deionization system such as the RDI process might prove beneficial to many power plants looking to process difficult-to-treat wastewater streams, including FGD wastewater, cooling tower blow down and other plant process streams. In addition, the RDI technology could provide separation of high TDS wastewater stream(s), allowing clean/processed water to be reused and the lower flow, concentrated wastewater stream(s) to be further processed utilizing a zero liquid discharge (ZLD) treatment or other type of disposal process.

Savings and efficiency improvements attainable through implementation of this type of technology in power plant wastewater systems may include:

- Enabling reuse of FGD blow down and/or other plant streams such as cooling tower blow down, reverse osmosis (RO) reject water and other currently unusable wastewater streams, thereby reducing make-up water requirements and overall water withdrawal from local resources.
- Establishing an innovative treatment process for water recovery in wastewater streams and water reuse in power plant systems such as cooling towers, thus improving overall water usage efficiency and water management optimization.
- Utilizing the RDI technology as a pretreatment step upstream of a thermal ZLD process, thereby minimizing the size of ZLD equipment required and thus reducing the capital and O&M costs associated with these conventional treatment systems, including evaporators and crystallizers.

RDI is an enhanced and modified version of capacitive deionization (CDI) technology (Atlantis Technologies Website, 2013; WaterTech, 2000; Dusenbury, 2003). CDI is an emerging desalination technology for removal of ionic impurities from waters. The Lawrence Livermore National Laboratory (LLNL), in Berkeley, California developed CDI in the late 1980s (RPSEA, 2009; Welgemoed, 2005). In CDI, water flows between anode and cathode electrodes applying a low electric field (1.0-1.7 Volt DC). Ions are adsorbed onto the oppositely charged electrodes. Several flat sheet electrodes stacked on top of each other provide numerous paths for water to flow through. The first CDI system that utilized aerogel electrodes was developed in the 1990s at the LLNL (Farmer et al., 1996; Welgemoed, 2005). Researchers have improved the efficiency of the CDI system through electrode adjustments or other parameters.

In CDI, a large number of stacked electrode pairs are required to desalinate high TDS waters because this system is operated at low voltages (1.2-1.7 V). The capital costs for such a system are very high and using the CDI process is cost prohibitive. Furthermore, in conventional CDI, the separation of pure and brine streams is less than ideal and the possibility of cross contamination of the pure water with brine is an issue. In addition, the capacities of the stacked capacitors are limited and there is a need for a multi-stage process (Dermentzis et al., 2009). To overcome these drawbacks of CDI, RDI was developed.

The RDI technology can deionize water streams with high total dissolved solids (TDS) utilizing a super capacitor based system. The super capacitor based system can handle low solubility species such as calcium and barium sulfate, high TDS streams such as produced/flowback water and reverse osmosis (RO) reject, and high TDS streams from acid mine drainage (Atlas and Wendell, 2007; Christen, 2006). The RDI device is specifically designed to remove large quantities of ions and isolate the clean and concentrated wastewater streams. The RDI system can desalinate industrial wastewater for up to 75% less cost than existing technologies such as brine concentrators, and RO. For some streams, the concentrated reject is the desired product. In such applications, the generated brines may have concentrations 10 to 20 times greater than the incoming solution concentrations.

For operation of the RDI unit, a wastewater containing dissolved solids (salt) is passed between two oppositely charged super capacitors (electric double layer capacitors, or EDLC). As the wastewater passes through the dielectric spacer, charged ions are adsorbed by the oppositely charged capacitor layers. The ions flow through a charge specific membrane coating prior to their adsorption to the electrode. Figure 1 presents the purification process when anions and cations are adsorbed onto the carbon electrodes.

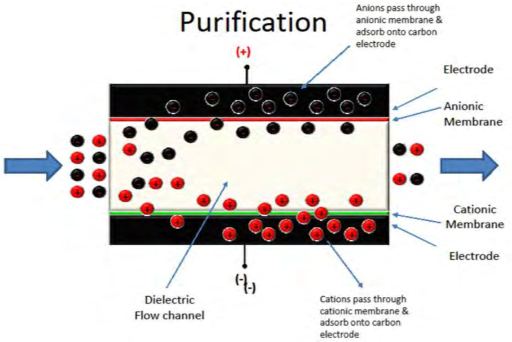

Figure 1. RDI Purification process

When the capacitors have filled with ions, the polarity is reversed and the ions are discharged back into the dielectric spacer and removed from the system. A three-way valve is situated at the outlet of the device(s) which directs the discharged ions away from the previously cleaned process stream. Figure 2 shows the RDI Rejection Process. Typical cycle times range from 2 to 40 minutes depending on the TDS concentrations of the wastewater being processed.

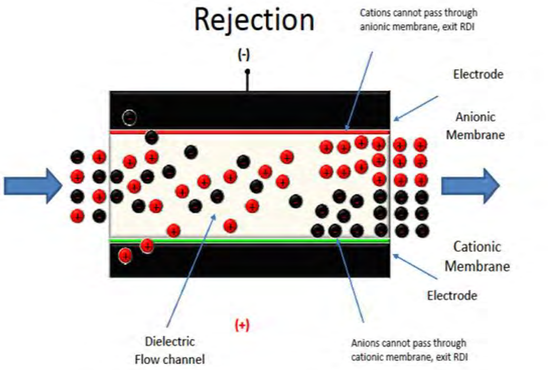

Figure 2. RDI Rejection Process

The current project was a test to verify the applicability of this system for FGD wastewater treatment. The current research program was funded by the Electric Power Research Institute (EPRI). The program was a three-month demonstration project. A small pilot RDI unit with a capacity of 0.5 gpm was tested at the Water Research Center (WRC) located at Georgia Power Company's Plant Bowen in Cartersville, GA. Specifically, the objectives of the project were to:

- Assess, via pilot tests at the WRC, the RDI system's performance, particularly related to water quality produced and its potential reuse in the power plant. The pre-demonstration tests also served to assess the following parameters over the operational period:
    - Process efficiency
    - Extent of fouling
    - Performance degradation
- Optimize the RDI unit for FGD wastewater treatment

EXPERIMENTAL

In order to evaluate the effectiveness of the RDI technology when applied to FGD wastewater, a small pilot unit (0.6 gpm or 2,200 mL) was tested for a three-month period at the Water Research Center (WRC). FGD wastewater had to be pretreated prior to entering the RDI unit. Total suspended solids (TSS) were removed and the wastewater was processed through a 1 micron filter. The iron concentration of the inlet wastewater to the RDI unit was maintained below 1 mg/L. Two pretreatment options were used to achieve the inlet TSS and iron limits: (1) conventional aeration and clarification and (2) conventional aeration and membrane filtration. The experimental test plan for RDI pilot unit is presented next followed by the experimental test plan for the Layne Christensen MOS pretreatment option.

RDI PERFORMANCE - FGD wastewater characteristics vary with power plant operations. FGD wastewater with a TDS of approximately 5,100 mg/L was utilized for the tests. Three streams were monitored including influent, effluent, and generated waste brine. The following characteristics were analyzed in the influent, effluent, and generated waste brine:

- Metals with ICP-MS per USEPA Method 200.7
- Total iron with DR 6000TM UV-Vis Spectrophotometer Method 8008
- Ferrous iron with DR 6000TM UV-Vis Spectrophotometer Method 10229
- pH; Method EPA 150.2
- Conductivity with HQ14d Portable Conductivity Meter and IntelliCAL™ CDC401 probe
- TSS and TDS; Method ASTM D5907-03

<u>Efficacy of the RDI for Removing Selenium, Mercury, and TDS</u> The objective of these tests was to evaluate the efficacy of the pilot unit for removing selenium and mercury from FGD wastewater down to (or equivalent to) drinking water specifications/limitations for mercury and selenium. The purification and rejection flow rates were 0.05 gpm (200 mL/min). The purification and reject periods were 10 minutes and 22 minutes, respectively. The FGD wastewater was pumped only for three minutes during the reject time. Therefore, the reject brine volume was 0.16 gal (600 mL). In each cycle, the pure water volume was 0.53 gal (2 L). The pure water volume and reject water volume were 70% and 30% of total treated water volume, respectively. Water was passed through the RDI four times to meet the drinking water specifications/limits for mercury and selenium.

<u>Optimization Tests</u> The goal was to optimize unit parameters to maximize TDS removal from FGD wastewater. Flow rates of 0.03 gpm (107-110) mL/min were used for four optimization tests with various set points.

PRETREATMENT FOR THE RDI - FGD wastewater had to be pretreated for TSS and iron removal prior to the RDI unit. Two options were utilized. These included a standard aeration/settling/filtration system (Option 1) and a Membrane Operation System (MOS) (Option 2). These are discussed in more detail below.

<u>Pretreatment Option 1 – Standard Aeration/Settling/Filtration</u> A flow diagram for the system is shown in Figure 3. The blue line shows the flow path for this standard pretreatment process. The equipment at the WRC is shown in the photograph in Figure 4. FGD wastewater was initially fed into a 2,000 gallon settling tank. FGD wastewater was aerated in this tank to remove ferrous (Fe^{2+}) ions from the solution.

In this process, the iron in the ferrous form was oxidized to iron in the ferric (Fe^{3+}) state which is insoluble at pH (6-8) of the wastewater. After aeration, the FGD wastewater remained in the settling tank undisturbed to separate out solids from the liquid. The supernatant was gravity fed to the second settling tank for furthur solids removal.

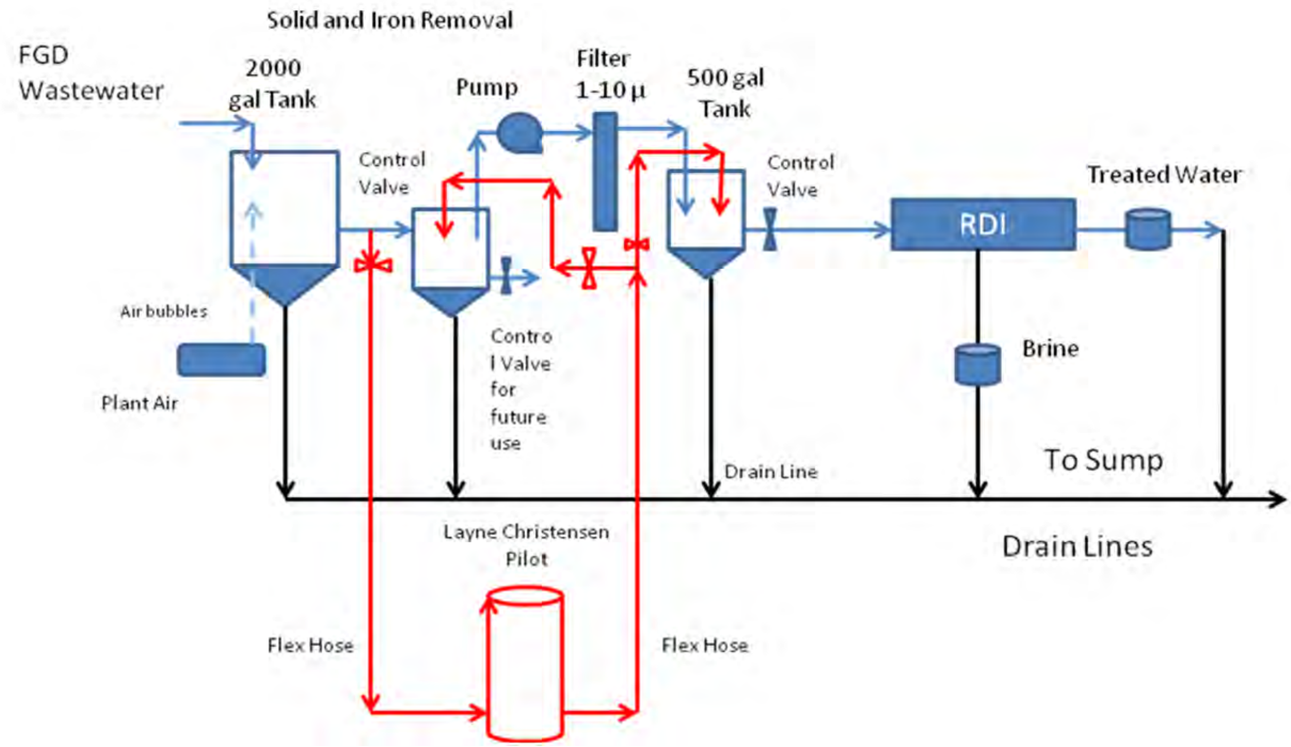

Figure 3. RDI Pretreatment Options

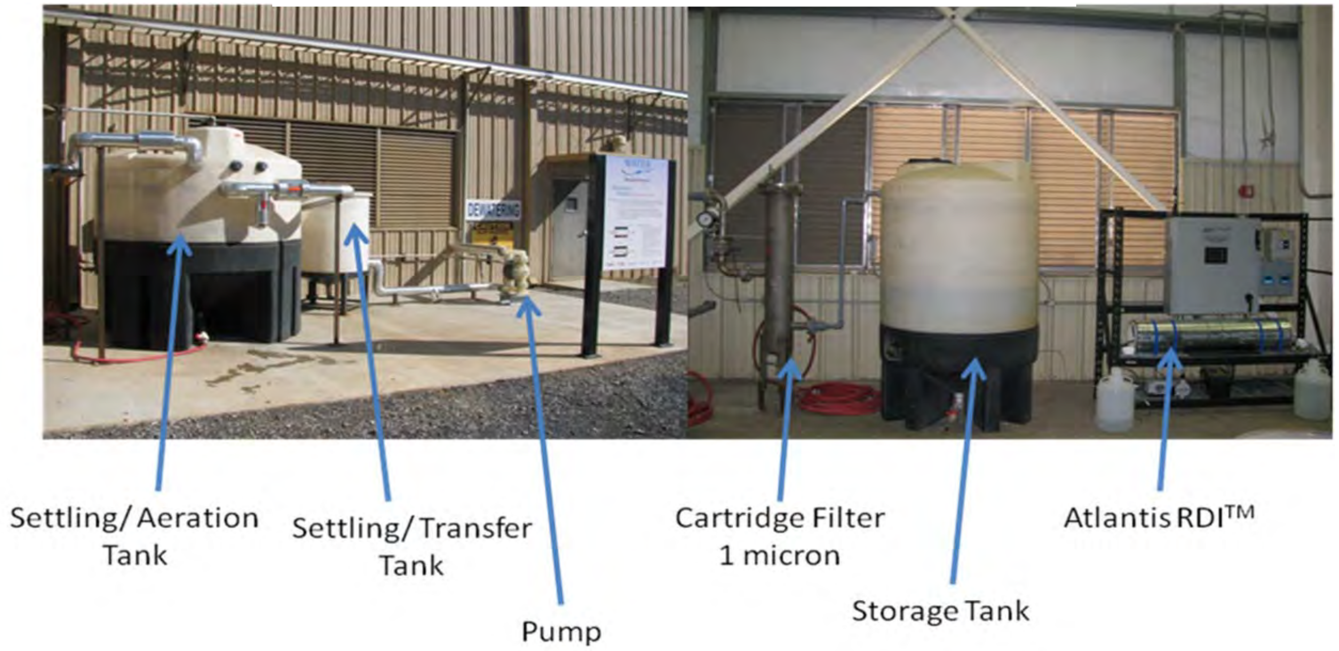

Figure 4. Pretreatment Option 1 – Aeration/Settling/Filtration

<u>Pretreatment Option 2 – Membrane Operation System (MOS)</u> An alternative pretreatment technique to conventional sedimentation and aeration settling processes for removing suspended solids from the FGD wastewater (i.e. Option 1) is to use a membrane system, such as the Membrane Operation System (MOS) shown in Figure 5.

As a potential alternative pretreatment technique to conventional sedimentation and aeration settling processes, the MOS was utilized to remove TSS from the FGD wastewater prior to entering the RDI system. TSS and turbidity were measured in the influent and effluent of the MOS to determine the efficacy of this system in removing TSS from the FGD wastewater.

Figure 5. Membrane Operation System (MOS) Pilot Unit using POREFLON Membrane.

TDS, conductivity, and pH of the influent and effluent were monitored to investigate the effect of the MOS on these parameters. The following methods were used for the measurements:

- TSS and TDS; Method ASTM D5907-03
- pH; Method EPA 150.2
- Conductivity with HQ14d Portable Conductivity Meter and IntelliCAL™ CDC401 probe
- Turbidity; EPA Method 180.1

The MOS utilizes POREFLON hollow fiber membranes. This fiber has six times the tensile strength of polyvinylidene fluoride (PVDF) fibers. The high tensile strength helps resist leaks and failures that often result from mechanical damage, providing a longer lasting and lower maintenance membrane. POREFLON can operate in environments up to 50˚C (122 ˚F). The membrane fibers have a nominal pore size of 0.2 microns. POREFLON is stable against all acids, alkaline solutions, oxidizers and solvents with a pH range from 0-14. The POREFLON hydrophilic properties eliminate the preparation needed to get the membrane in service. The membrane can be shipped and stored dry. This feature significantly lightens the weight of the elements for easy storage, handling and shipping.

Performance tests were conducted with the MOS. The duration of each test was approximately eight hours. The following parameters were measured in the influent and effluent of the MOS system: TSS, turbidity, pH, TDS, and conductivity. Flow rate, backwash flow rate, static membrane pressure, and trans-membrane pressure at minute 1 (TMP1) and minute 29 (TMP29). The membrane was operated with 30 minutes filtration and 1.5 minutes backwash, relax, and cleaning cycles.

The influent and effluent streams were sampled at various filtration cycles. The influent TSS concentration was manipulated by introducing compressed air inside the clarifier and adjusting valves to vary the residence time of the wastewater in the tank. Increased air flow in the clarifier caused higher mixing and higher TSS values. The MOS is a microfilter (MF) with 0.2 micron pore size diameter. The MF only removes suspended solids from water. TSS and turbidity of the influent and effluent were monitored to determine the efficacy of MOS in removing solids from FGD wastewater with varying TSS concentrations. Six different samples were collected during the filtration cycles. Flow rates were between 1.14 and 1.18 gpm. The backwash flow rate was 2.42 gpm.

FGD WASTEWATER CHEMISTRY - The FGD wastewaters utilized for examining MOS had a TSS content varying between 50 mg/L – 4,600 mg/L. FGD wastewater was filtered using 0.2 µm MOS filter prior to entering the RDI system. Iron concentrations were monitored during all experiments.

The average TSS of the RDI influent was approximately 3 mg/L and varied between non-detectable and approximately 7.9 mg/L. All total iron levels were below 0.18 mg/L. The conductivity of the FGD wastewater varied between 2,450 µS/cm and 10,250 µS/cm with an average conductivity of 6,250.

FGD wastewater is mainly composed of calcium, magnesium, chloride, and sulfate. Figure 6 presents common anion and cation concentrations in FGD wastewater. Typically, FGD wastewater is composed of 89% calcium, 9% magnesium, and 2% other cations. The FGD wastewater contained 67% chloride, 31% sulfate, and 2% other anions. Metals or other contaminants comprise approximately 2-4% of the FGD wastewater.

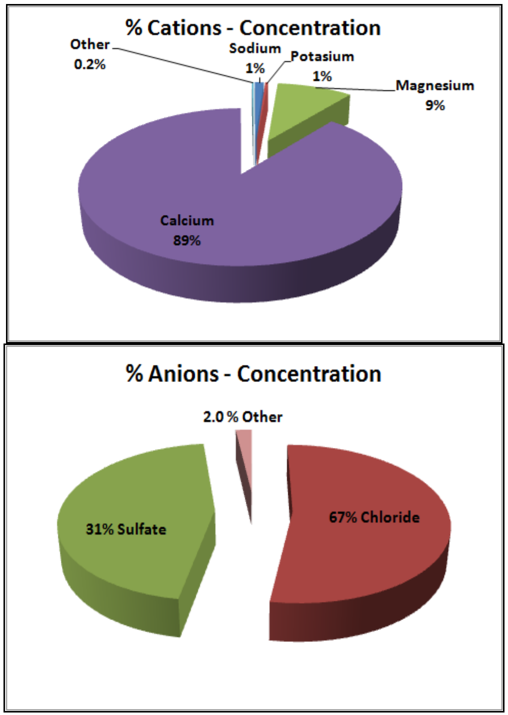

Figure 6. Typical anion and cation concentrations of FGD wastewater

RESULTS

RDI PERFORMANCE

Efficacy of the RDI for Removing Selenium, Mercury, and TDS The objective of this test was to evaluate the efficacy of the RDI for removing selenium, mercury, and other contaminants to achieve the EPA's drinking water maximum contaminant levels (MCLs) for mercury (2 µg/L) and selenium (50 µg/L). In this test, the FGD wastewater was passed through the unit four times. For each pass, the water recovery was 70% and the percent total TDS removal was calculated and is presented in Figure 7. The percent TDS removal for Pass 1 was 31.5%. The percent TDS removal decreased from 31.5% in Pass 1 to 10.3% in Pass 2 and 25.4% in Pass 3. However, the TDS removal increased from 31.5% in Pass 1 to 46.5% in Pass 4.

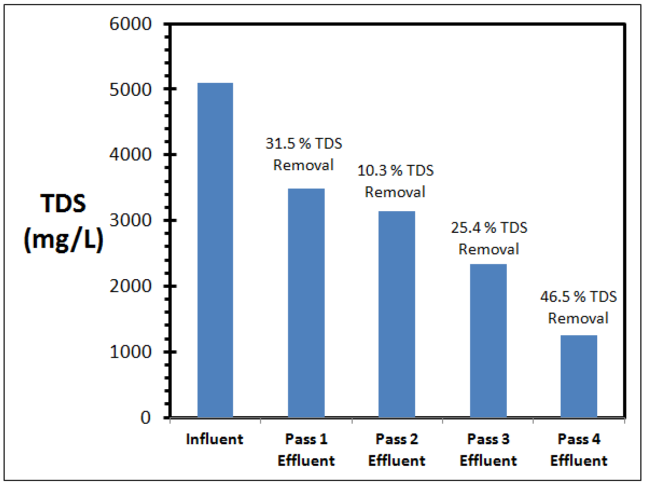

Figure 7. TDS and Percent TDS Removal for each Pass

The cumulative percent total TDS removal for all four passes (i.e. Pass 1 through Pass 4) was 75.5%. After passing the FGD wastewater through the RDI cylinder four times (i.e. Pass 1 through Pass 4), the final Pass 4 effluent selenium and mercury concentrations were 19 µg/L (<50 µg/L) and 0.866 µg/L (<2 µg/L), respectively (Table 1).

Table 1. Influent and Pass 4 – Effluent Characteristics

Parameter	Influent (µg/L)	Effluent (µg/L)	[1]MCL (µg/L)
Selenium	137	19	50
Mercury	4.1	0.866	2
TDS	5,094	1,249	n.a.

[1] Drinking Water Maximum Contaminant Level

These results indicate that the RDI may be used to process FGD wastewater to achieve EPA's drinking water MCLs for mercury (2 µg/L) and selenium (50 µg/L). However, a series of optimization tests is needed to confirm these initial findings and substantiate these results/observations.

Optimization Tests The purpose of these tests was to optimize the system parameters in order to increase the efficiency or effectiveness of the RDI system in removing TDS from FGD wastewater.

Based on the tests mentioned above, the highest removal efficiency was achieved/observed at the lowest flow rate. Therefore, flow rates of 107-110 mL/min (~0.03 gpm) were used for the optimization tests. In previous tests, the flow rate of 0.03 gpm (108 mL/min) resulted in total TDS removal values between 30.8% and 51.2%. In this test, the efficiency or effectiveness of the system in removing TDS from FGD wastewater with a TDS of 5,094 mg/L was improved from 30.8% to 62.2%. However, during the tests, a system leak was observed and the testing was discontinued. This concluded the demonstration trial of the RDI at the WRC, since the unit had to be sent back to the manufacturer for repair.

The vendor estimated that the capital expenditure (Capex) for a 100 gpm system, excluding pre-treatment and installation, would be approximately $1,000,000-$1,500,000, the maintenance would be approximately $30,000/yr-75,000/yr, and the total operational expenditure (Opex) including maintenance, energy use, and chemicals would be approximately $2-$3 per kgal depending on the water characteristics. Energy usage of this system would be approximately 20 - 50 Kw.hr/kgal.

MOS PERFORMANCE - The MOS was utilized to remove suspended solids from the FGD wastewater prior entering the RDI system. Figure 8 illustrates the TSS and turbidity versus date and time for MOS Performance Test for the influent and effluent wastewater of MOS when treating FGD wastewater. In this test, the TSS and Turbidity in MOS influent increased from 1,018 mg/L and 610 NTU to 4,465 mg/L and 834 NTU, respectively. The effluent TSS was below 19 mg/L and in some cases the TSS in the effluent was non-detectable (~0). The turbidity of effluent was below 0.153 NTU and the MOS effluent was visually clear. Approximately 550 gallons of wastewater were treated during this test.

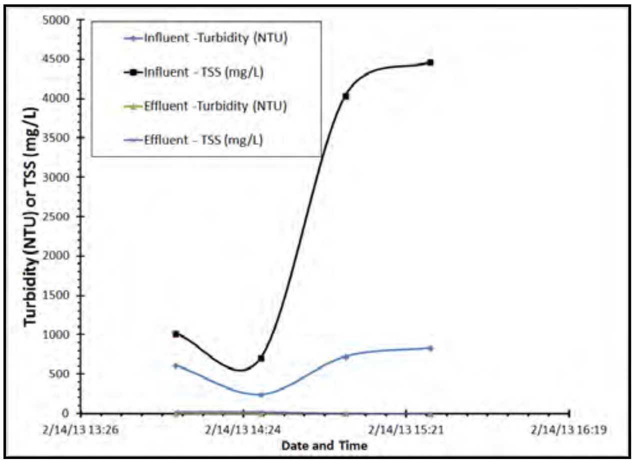

Figure 8. MOS Performance Test - TSS and turbidity in the influent and effluent of MOS

The static membrane pressure varied between 1.8-1.9 psi, while the transmembrane pressure at minute 1 (TMP1) and transmembrane pressure at minute 29 (TMP29) stabilized in the range of 0.8-0.9 psi. These results indicate virtually no pressure build up was observed during operation, but the test period was too short to provide substantial/meaningful membrane data to establish chemically enhanced backwash (CEB) cleaning frequency. A longer term test is needed to produce conclusive membrane data. In general, when the influent TSS was not varied, the effluent TSS was consistent and lower than 10 mg/L. Negligible differences were observed between influent and effluent pH and conductivity.

In summary, MOS was operated for approximately fifty hours and the TMP remained below 0.9 psi and no chemical cleaning was required. The test results look promising, but the duration of experiments was very short. More research is needed to produce conclusive membrane data to evaluate the long-term performance of membrane system for FGD wastewater treatment.

CONCLUSIONS

For the RDI unit tested, the highest TDS removal efficiency was achieved at the lowest flow rate. Lower flow rates translate to lower salt loadings, thereby increasing the ability of the unit to adsorb a larger portion of the salt loading. Higher flow rates translate to higher salt loadings; therefore, more ions were adsorbed on the capacitors and then subsequently rejected into the brine. This resulted in higher brine TDS concentrations at higher flow rates.

The results indicate the RDI may be applicable for treating FGD wastewater depending on its economics, however, the desired effluent limits should be considered in the design of any future unit (i.e. surface area and quantity of capacitors). No economical feasibility assessment was performed in this research.

In order to meet the EPA's drinking water maximum contaminant levels (MCLs) for mercury (2 µg/L) and selenium (50 µg/L) in the effluent, the FGD wastewater was passed through the RDI unit four times. The TDS of the treated FGD wastewater was 5,094 mg/L, but some FGD wastewaters may contain higher TDS concentrations, which mean they may require greater surface area and more capacitors. More research is needed to determine the water recovery for a unit with multiple capacitors.

A series of research and development tests were performed to improve the efficiency of the RDI system for FGD wastewater treatment. The TDS removal efficiency of the system achieved with the initial set points was 30.8% at a flow rate of 0.03 gpm. The final TDS removal efficiency achieved was more than 62.2% when treating FGD wastewater with a TDS of 5,094 mg/L.

The MOS membrane pilot tested at the WRC had a flow rate of approximately 1.2 gpm and a membrane surface area of 64.58 ft^2. The design flux rate of 26.3-27.0 GFD was calculated for this operation. The influent FGD wastewater contained TSS of 55 to 4,465 mg/L and turbidity of 17.2 to 834 NTU. Total suspended solids (TSS) were successfully removed using the MOS pilot and the effluent TSS and turbidity were below 19 mg/L and 0.206 NTU, respectively. The removal efficiently of 87.1-100% was achieved and the effluent water was visually clear. The equipment was used for the duration of approximately 50 hours. The TMP was below 0.9 psi and no chemical cleaning was required. Based on the experiments conducted and the data observed, performance of the MOS is promising, but more research is needed to determine the economics of the process.

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