ELECTRIC POWER RESEARCH INSTITUTE

Case Studies to Evaluate FGD Wastewater Physical/Chemical Treatment Performance

3002001202

Case Studies to Evaluate FGD Wastewater Physical/Chemical Treatment Performance

3002001202

Technical Update, December 2013

EPRI Project Manager

P. Chu

ELECTRIC POWER RESEARCH INSTITUTE
3420 Hillview Avenue, Palo Alto, California 94304-1338 ▪ PO Box 10412, Palo Alto, California 94303-0813 ▪ USA
800.313.3774 ▪ 650.855.2121 ▪ askepri@epri.com ▪ www.epri.com

THE FOLLOWING ORGANIZATION, UNDER CONTRACT TO EPRI, PREPARED THIS REPORT:

CH2M HILL Engineers, Inc.

This is an EPRI Technical Update report. A Technical Update report is intended as an informal report of continuing research, a meeting, or a topical study. It is not a final EPRI technical report.

NOTE

For further information about EPRI, call the EPRI Customer Assistance Center at 800.313.3774 or e-mail askepri@epri.com.

ACKNOWLEDGMENTS

The following organization, under contract to the Electric Power Research Institute (EPRI), prepared this report:

CH2M HILL
155 Grand Avenue Suite 800
Oakland, CA 94612

Principal Investigator
D. Fink, P.E.

CH2M HILL
1100 112th Avenue NE Suite 500
Bellevue, WA 98004

Principal Investigator
C. Yeager, P.E.

CH2M HILL
1000 Abernathy Road Suite 1600
Atlanta, GA 30328

Principal Investigator
H. Suber, P.E.

This report describes research sponsored by EPRI.

EPRI would like to acknowledge the support of the organizations that were interviewed and provided sampling support and data included within this Technical Update.

This publication is a corporate document that should be cited in the literature in the following manner:

Case Studies to Evaluate Flue Gas Desulfurization Wastewater Physical/Chemical Treatment Performance. EPRI, Palo Alto, CA: 2013. 3002001202.

PRODUCT DESCRIPTION

This study focuses on physical/chemical wastewater treatment technologies used to remove trace metals from flue gas desulphurization (FGD) wastewater. The scope of this study includes FGD wastewater treatment for trace metals.

Background

The United States Environmental Protection Agency (EPA) is currently revising the Effluent Limitations Guidelines (ELGs) for the steam electric power generating industry. The Electric Power Research Institute (EPRI) provided comments on the draft ELG in September 2013.

Objectives

Physical/chemical treatment effectively removes trace metals in FGD wastewater. This study evaluates the potential for improving physical/chemical treatment systems to treat FGD wastewater—evaluating improved removal of a number of trace metals.

Approach

Case studies were compiled of interviews with FGD wastewater treatment plant managers and staff who have made improvements to their treatment systems by adding either additional equipment or chemicals to improve performance. The study also describes operational challenges and how they have been resolved. Treatability tests were conducted using samples from three plants. Treatability test results were compared to EPA data to evaluate representativeness to the industry and to proposed ELG trace metals limits.

Results

Jar tests included initial settling of solids, followed by treatment with ferric chloride (iron co-precipitation) and organosulfide addition. Overall, the results helped provide information on improved physical/chemical treatment for the various metals. Due to the small number of samples tested and the bench-scale nature of the tests, all results and conclusions should be considered preliminary. Much further research would be needed before any of the conclusions from the jar tests could be applied to an individual facility or to facilities in general.

Applications, Value, and Use

This report is written for managers at coal-fired power plants who are interested in learning about treatment technologies for the removal of trace metals from FGD wastewater.

Keywords

FGD
Flue gas desulphurization
Physical/chemical treatment
Wastewater

ABSTRACT

This study focuses on physical/chemical wastewater treatment technologies used to remove trace metals from flue gas desulphurization (FGD) wastewater. The scope of this study includes FGD wastewater treatment for trace metals. Case studies were compiled of interviews with FGD wastewater treatment plant managers and staff who have made improvements to their treatment systems by adding either additional equipment or chemicals to improve performance. The study also describes operational challenges and how they have been resolved. Treatability tests were conducted using samples from three plants. The tests included the addition of iron salts and organosulfide.

EXECUTIVE SUMMARY

Improved flue gas desulfurization (FGD) wastewater treatment will likely be required by the U.S. Environmental Protection Agency (EPA) under the proposed effluent limitation guidelines (ELGs) for the steam electric power generating point source category to remove and/or reduce trace metals from FGD wastewater that is discharged to surface waters from coal-fired power plants. The proposed ELGs were published in June 2013; the final rule is scheduled to be released in May 2014. This study focuses on physical/chemical wastewater treatment technologies used to remove trace metals from FGD wastewater. Previous Electric Power Research Institute (EPRI) research has focused on mercury and selenium removal from FGD wastewater [1-11]. EPA is currently reviewing comments submitted on the proposed ELGs for coal-fired power plants and will finalize the new regulations for ELGs based on what they determine to be best available technology (BAT) that is economically achievable.

For this project, case studies were compiled of interviews with FGD wastewater treatment plant managers and staff at seven facilities. Bench-scale testing was also conducted using FGD wastewater samples collected from three facilities. Each facility had a FGD scrubber on units firing eastern bituminous coal. Jar tests included initial settling of solids, followed by treatment with ferric chloride (iron co-precipitation) and organosulfide addition. Overall, the results helped provide information on improved physical/chemical treatment for the various metals. Additional testing is needed to focus on ways to improve metal removal at a given plant or to focus on a given set of metals. Due to the small number of samples tested and the bench-scale nature of the tests, all results and conclusions should be considered preliminary. Further research and larger scale pilot testing is needed before any of the conclusions from the jar tests could be applied to an individual facility or to facilities in general.

This report is written for managers at coal-fired power plants who are interested in learning about treatment technologies for the removal of trace metals from FGD wastewater.

CONTENTS

LIST OF FIGURES

LIST OF TABLES

ACRONYMS

As(III)	arsenite
As(V)	arsenate
BAT	best available technology economically achievable
ELGs	Effluent Limitations Guidelines
EPA	United States Environmental Protection Agency
EPRI	Electric Power Research Institute
ERG	Eastern Research Group, Inc.
FGD	flue gas desulfurization
gpm	gallons per minute
HCl	hydrochloric acid
mg/L	milligrams per liter
µg/L	micrograms per liter
ng/L	nanogram per liter
ppm	parts per million
Se(IV)	selenite
Se(VI)	selenate
SeCN	Selenocyanate
SO_2	sulfur dioxide
TSS	total suspended solids
TWF	toxic weighting factor

1
INTRODUCTION

Objectives

Physical/chemical treatment effectively removes trace metals in FGD wastewater. This study evaluates the potential for improving trace metals removal using physical/chemical treatment systems to treat flue gas desulfurization (FGD) wastewater.

Regulatory Background

The United States Environmental Protection Agency (EPA) is currently revising the Effluent Limitations Guidelines (ELGs) for the steam electric power generating industry. On April 19, 2013, EPA signed a notice of proposed rulemaking pertaining to revisions to the ELGs, which was published in the Federal Register on June 7, 2013. The final rulemaking is currently scheduled to be finalized by May 2014. The EPA plans to issue categorical ELGs based on best available technology economically achievable (BAT). The proposed BAT treatment technologies that EPA has cited in development of proposed ELGs for FGD wastewater are based on physical/chemical and biological treatment technologies. The focus of this report is the physical/chemical treatment technology.

EPA's proposed ELGs for FGD wastewater are shown in Table 1-1, and include limits for arsenic, mercury, selenium, and nitrate. The proposed selenium and nitrate-nitrite limits are based on using biological treatment technology for FGD wastewater treatment and are not anticipated to be removed by the physical/chemical treatment technology to the levels proposed in the ELGs.

Table 1-1
Draft ELG Discharge Permit Limits on FGD Wastewater

Parameter	Discharge Limits	
	Average Monthly	Daily Maximum
Arsenic, μg/L	6	8
Mercury, μg/L	0.119	0.242
Selenium, μg/L	10	16
Nitrate/Nitrite as N, mg/L	0.13	0.17

Source: EPA, 2013

Study Methods

To meet the objective of evaluating the potential to improve physical/chemical treatment of trace elements that might be regulated in the future, CH2M HILL interviewed facilities with FGD wastewater treatment systems and conducted treatability tests on FGD wastewater from three of these plants. CH2M HILL interviewed facility staff to evaluate how facilities have improved removal of trace elements at power plants using physical/chemical treatment. Seven facilities were interviewed to determine how modifications to design or operating conditions have improved physical/chemical treatment, to determine operational challenges that prevent facilities from meeting improved treatment conditions, and to evaluate historical data from facilities to determine the ability to remove trace metals. Three of the case study facilities provided FGD wastewater for further laboratory treatability testing to determine if improvements could be made to the physical/chemical treatment that would further reduce levels of trace elements in the wastewater.

Study Limitations

The study is limited by the number of facilities tested, the conditions at the time of sample collection, and by inherent limitations in representing full-scale treatment using bench-scale treatability testing. The number of samples or data points from each facility also limited the study. FGD wastewater is known from past EPRI studies [3-13] to be highly variable between plants and variable over time at a given plant. Therefore, the insights may not be applicable to FGD wastewater at all or even a majority of the plants.

2
CASE STUDIES OF PHYSICAL/CHEMICAL FGD WASTEWATER TREATMENT SYSTEMS

Effectiveness of Physical/Chemical Treatment

Most parameters are removed by physical treatment in ponds or chemical precipitation in a tank-based system. EPA calculated an average concentration from available data for untreated FGD water, settled FGD water, and chemical precipitation effluent in *Technical Development Document for the Proposed Effluent Limitations Guidelines and Standards for the Steam Electric Power Generating Point Source Category*. [13] As shown by these values (Table 2-1) and the calculated percent removal via settling or chemical precipitation treatment, a high percentage of the parameters, especially for parameters with high toxicity weighting factors such as mercury and arsenic, are removed over 99% by settled combined with chemical precipitation treatment. Table 2-2 lists all parameters removed over 99% by chemical precipitation with their EPA toxic weighting factors (TWF).

Table 2-1
EPA's Average Effluent Pollutant Concentration for FGD Surface Impoundments

Analyte	Untreated FGD Water (ug/L)	Settled FGD Water (ug/L)	Percent Removed	CP Effluent (ug/L)	Percent Removed
Aluminum	332,000	2,080	99 %	155	100%
Antimony	22	13	41%	5	77%
Arsenic	489	7	99%	4.5	99%
Barium	2,850	303	89%	163	94%
Beryllium	17	2	88%	1	94%
Cadmium	159	112	30%	3.8	98%
Calcium	3,250,000	2,050,000	37%	2,330,000	28 %
Chloride	7,740,000	7,320,000	5%	8,940,000	NR
Chromium	1,300	18	99%	9.1	99%
Cobalt	310	183	41%	10	97%
Copper	784	21	97%	2	100%
Iron	764	1,510	NR	127	83%
Lead	323	5	98%	1	100%
Manganese	107,000	93,100	13%	13,600	87%
Mercury	411	6	99%	0.17	100%
Molybdenum	313	125	60%	215	31%
Nickel	1,880	878	53%	5.6	100%
Nitrate/Nitrite	74,900	67,300	10%	67,300	10%
Selenium	4,490	1,110	75%	455	90%
Silver	9	1	89%	1	89%
Sodium	275,000	276,000	NR	420,000	NR
Sulfate	8,140,000	1,240,000	85%	5,980,000	27%
Thallium	27	13	52%	8.6	68%
Tin	184	100	46%	100	46%
Titanium	4,840	27	99%	10	100%
Vanadium	1,450	16	99%	15	99%
Zinc	5,380	1,390	74%	18	100%
Ammonia	6,350	NA	NA	8,120	NR
Boron	291,000	243,000	16%	279,000	4%
Magnesium	3,630,000	3,370,000	7%	3,340,000	8%
Cyanide	764	1,190	NR	1,190	NR

Notes:
NA – Not available; NR – No removal; Source: EPA, 2013; Table 6-3, 10-3, and 10-4

Table 2-2
Parameters with greater than 99 Percent Removal by Chemical Precipitation

Analyte	EPA Toxic Weighting Factor	Untreated FGD Water (ug/L)	Settled FGD Water (ug/L)	Percent Removed	CP Effluent (ug/L)	Percent Removed
Aluminum	0.064691	332,000	2,080	99 %	155	100%
Arsenic	4.041333	489	7	99%	4.5	99%
Chromium	0.075697	1,300	18	99%	9.1	99%
Copper	0.634822	784	21	97%	2	100%
Lead	2.24	323	5	98%	1	100%
Mercury	117.118	411	6	99%	0.17	100%
Nickel	0.108914	1,880	878	53%	5.6	100%
Titanium	0.029319	4,840	27	99%	10	100%
Vanadium	0.035	1,450	16	99%	15	99%
Zinc	0.046886	5,380	1,390	74%	18	100%
Notes: Source: EPA, 2013; Table 6-3, 10-3, and 10-4						

State of the Technology for FGD Wastewater Physical/Chemical Treatment

Figure 2-1 shows a typical FGD wastewater physical/chemical treatment system. Typically, a FGD wastewater treatment plant that employs chemical precipitation includes the following unit processes: equalization, desaturation, clarification, and chemical addition. Plants that require additional metals polishing may also include filtration to remove solids that pass through the clarifier. Plants that have high influent solids may require two clarifiers – the primary to remove the bulk of solids, the second to remove metals precipitated. Previous EPRI reports have focused on FGD wastewater management options for these unit processes, including design and operational considerations [1-11].

As part of this study, plant staff were interviewed to determine how they have improved their FGD wastewater physical/chemical treatment systems to understand design and operational considerations better to improve physical/chemical treatment.

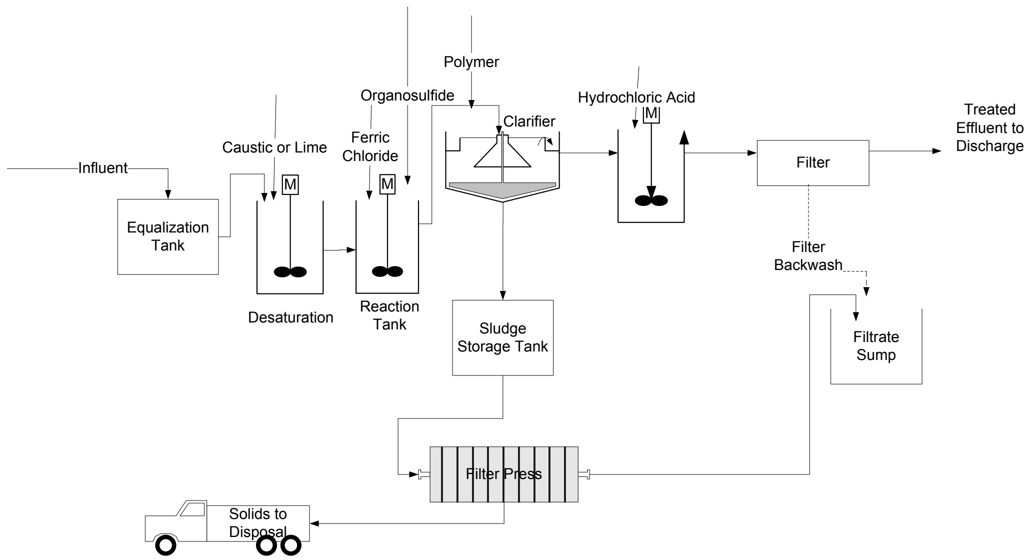

Figure 2-1
FGD Wastewater Treatment System Process Flow Diagram

Chemical Precipitation

Chemical precipitation may include addition of iron, polymers, acids or bases and sulfide compounds to improve precipitation. Trace elements precipitate at varying pHs. In this study, chemical precipitation through pH adjustment, iron co-precipitation, and organosulfide addition was evaluated both with plant historical data and with treatability testing.

Chemical precipitation can be used to help remove trace metals present in dissolved form or as small particles that would otherwise not be removed by settling or filtration alone. Metals are present in wastewater in either particulate or soluble form. Although some process wastewater treatment facilities may only require removal of suspended solids, adding the capacity for chemical precipitation may be needed to meet present or future discharge permit limits. A chemical precipitation system generally consists of a chemical feed system, mix tank, and mixer.

Iron Co-precipitation

In the iron co-precipitation process, a bulk iron hydroxide compound is formed that precipitates with the addition of an iron source such as ferric chloride. Other ions in solution adsorb to the bulk compound and are co-precipitated. Iron is added for precipitation of metals and for coagulation of suspended solids. The following is the simplified chemical equation to represent this reaction.

$$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_{3(solid)} + 3H^+ \qquad \text{(Eq. 2-1)}$$

Dissolved metals concurrently adsorb and precipitate with the ferric hydroxide solid developed during this reaction. Heavy metals form their insoluble hydroxide products and attach to the highly charged, relatively dense ferric hydroxide precipitate. Ferric chloride is a common coagulant used to remove suspended particulate material in wastewater. An advantage of using ferric chloride over other coagulants for suspended solids removal is that the ferric hydroxide solid that is formed also binds and precipitates dissolved metals. Optimal bulk iron hydroxide formation and manipulating the pH can enhance treatment performance.

Organosulfide Addition

When metals removal is required to levels below those that can be met using iron co-precipitation and filtration, organosulfide metals precipitation can be used to help remove many trace metals. Organosulfide addition is typically used to enhance mercury removal in power plant wastewater. Organosulfide compounds are polymers that bond with cationic metals and are used to counter the solubility of mercury and other cationic metal chloride complexes, and form precipitates of mercury that can be removed. Polymer addition may be needed after organosulfide precipitation to enhance flocculation. Various organosulfides are available from numerous vendors (e.g. Nalco's Nalmet-1689, Evonik's TMT-15, and GE's MetClear MR2405). Organosulfides are used at numerous power plants for mercury removal from FGD wastewater. Organosulfides are typically ineffective at removing anions from solution.

Clarification

Clarifiers are used to settle solids in wastewater. Wastewater should flow by gravity to a clarifier so that solids formed by coagulation and flocculation are not sheared by pumping into smaller particles that are less likely to settle. Traditional circular clarifiers are equipped with a mechanism and flocculation zone. The clarifier mechanism is equipped with rake arms used to remove settled solids. The flocculator provides gentle mixing of the solids and polymer to promote particle growth to enhance settling of the solids. The flocculated mixture passes below the skirt of the flocculation zone and enters the clarification zone. Solids settle to the conical, sloped bottom of the clarifier, clarified liquid rises to the top, and exits as overflow from the clarifier. Clarifier types other than circular clarifiers are also in use in FGD wastewater treatment, including those that have packs of inclined plates to increase effective surface area.

Clarifier performance can be enhanced by adding polymers. Polymer is often used to help coagulate solids before clarification. It is therefore prudent to include a flocculation well in the primary clarifier and to provide the ability to add polymer at this point. Polymer doses vary widely based on the type of polymer and the water chemistry. Polymer may be added to the mix tank effluent pipe to provide initial mixing in the gravity line to the clarifier.

Additional information on clarifier design and operation is included in a past EPRI document.[3]

Filtration

Filtration is used to remove total suspended solids (TSS) and heavy metals in particulate form. Filtration will typically not be used in process wastewater applications unless metals limits cannot be met with chemical precipitation and clarification. Sand filters can typically reduce FGD wastewater TSS to below 10 parts per million (ppm) and generally remove solids that are 5 micron or larger. Additional membrane technologies, such as microfiltration, ultrafiltration, nanofiltration, or reverse osmosis could also be used to remove smaller solids particles from process wastewater; however these technologies have not been commercially applied to FGD wastewater and there are significant concerns with potential scaling.

Case Studies

In order to gather information regarding the treatment of FGD wastewater using physical/chemical methods, staff from seven coal-fired power plants were interviewed regarding the design of their FGD wastewater treatment system, the performance it achieves, and operational challenges they have encountered while treating FGD wastewater. The following summarizes the information gathered during the interviews. The sites are named only by identifiers to provide anonymity. Power plants, in some cases, provided their site data. EPRI reviewed the analytical methods used by the facilities to confirm that these methods were consistent with methods used by EPRI in previous studies and methods used by EPRI to analyze samples during treatability testing conducted with samples from three of these power plants. Analytical methods used by most facilities for trace metals analysis were typically EPA Method 200.8 or Method 1631 for low-level mercury.

It should be noted that the case study plants varied in what metals they were targeting for removal. Some plants are only regulated for TSS and pH, others have limits just on the FGD treatment system effluent and final outfall, and some (most of the case studies) have limits applied on their final effluent, which combines FGD water along with other waters. This is an important consideration in evaluating the concentrations of the pollutants treated. If a facility is not targeting a certain metal, the concentrations of that metal in the effluent may not be as low as the system can treat. In other words, in some cases removal of a metal is a byproduct of the targeted pollutant removal. During the interviews, the plants' discharge permits and limits were discussed. As shown in Table 2-3, most plants had compliance points at combined outfalls. Table 2-3 provides a brief summary of the sites surveyed and basic information regarding their operations.

Table 2-3
Summary of Plants Interviewed

	PC1	PC2	PC3	PC4	PC5	PC6	PC7
FGD Type	Limestone Forced oxidation	Limestone Forced oxidation	Limestone Forced oxidation	Limestone Forced oxidation	Limestone Forced oxidation	Limestone Forced oxidation	Limestone Forced oxidation
FGD Wastewater Treatment System Online	2009	2009	2007	2007	2009	1984 (chemical precipitation 2000)	2007
Coal Type	Bituminous, Subbituminous	Bituminous	Bituminous	Bituminous	Bituminous, Subbituminous	Bituminous	Bituminous
Current Monitoring Location	Limits at FGD wastewater treatment effluent	Limits at Final Outfall	Limits at Final Outfall, after FGD mixed with other water	Limits at Final Outfall, after FGD mixed with other water	Limits at Final Outfall, after FGD mixed with other water	Limits at Final Outfall, after FGD mixed with other water	Limits at Final Outfall, after FGD mixed with other water
Numeric NPDES Limits for Trace Elements	Be, Cu, Hg, Pb, Se, Ag	Cu, Pb	Hg, Se	Se, Fe	Al, As, Fe, Mg, Hg, Se	Se, Hg, Ag	None (monitor and report only)
FGD wastewater source	Primary or secondary hydrocyclones overflow	Secondary hydrocyclones overflow	Primary hydrocyclones overflow	Primary hydrocyclones overflow	Primary hydrocyclones overflow	Primary hydrocyclones overflow	Secondary hydrocyclones overflow
Design Flow Rate	500 gpm	500 gpm	360 gpm	650 gpm	330 gpm	400 gpm	200 gpm
Typical Flow Rate	75 gpm	230 gpm	140 gpm	557 gpm	200 gpm	Batch operation: Typical day is 18 batches, each 25,000 gallons = 312 gpm	75-150 gpm
Typical Influent TSS	5-6%	1-2%	3-5%	1%	Data not obtained	8%	Data not obtained
Typical Chlorides	12,000 mg/L	Data not obtained	Data not obtained	6,000 mg/L	Data not obtained	15,000 mg/L	Maximum 12,000 mg/L

Table 2-3
Summary of Plants Interviewed

	PC1	PC2	PC3	PC4	PC5	PC6	PC7
Iron and organosulfide?	Both	Both	Both	Both	Both	Iron only	Organosulfide only
Filter?	Yes, Sand	Yes, Sand	No	No	No	Yes, Sand	No

Site PC1

The Site PC1 facility used to be a base load plant, but now the unit operates much less frequently. Site PC1 uses bituminous and Powder River Basin coal. It has a limestone forced-oxidation FGD system for sulfur dioxide (SO_2) removal from flue gas. The FGD wastewater produced contains a maximum of 5.5 percent solids and 12,500 ppm of chlorides.

The Site PC1 FGD system has a maximum design flow rate of 500 gallons per minute (gpm). The scrubber system is equipped with secondary hydrocyclones but these hydrocyclones have had operational issues and as a result have not operated consistently. The system operates under a permit that limits flow to 160 gpm or less. The system is typically operated as a low flow continuous system (as low as 75 gpm) but is also operated as a batch system on occasion. Figure 2-2 presents a process flow diagram of the Site PC1 FGD wastewater treatment system.

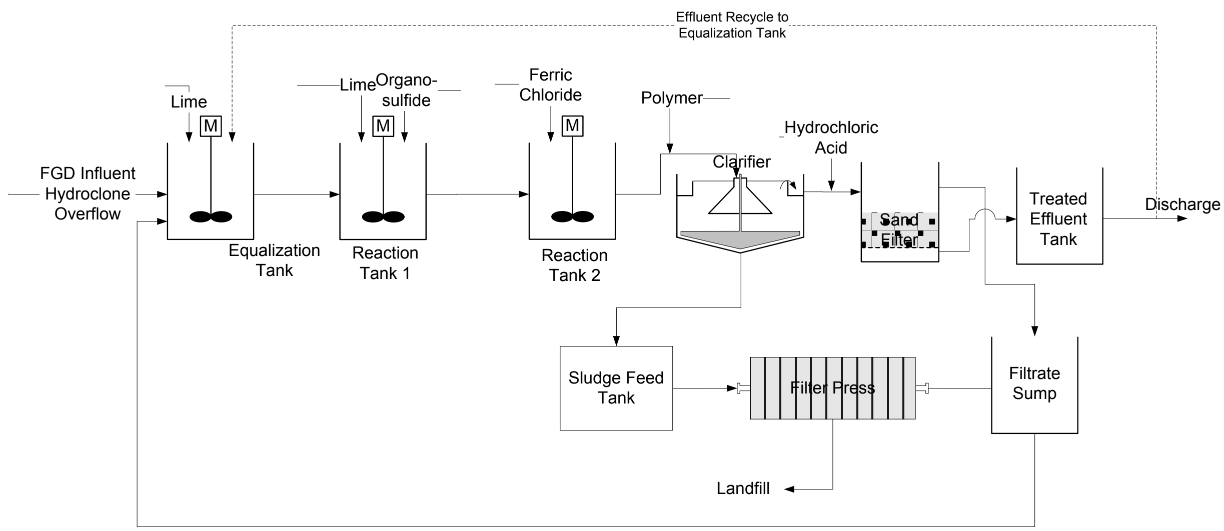

Figure 2-2
Site PC1 FGD Wastewater Treatment System Process Flow Diagram

Overflow from the hydrocyclones flows to the FGD wastewater treatment system equalization tank. The equalized FGD wastewater is then chemically treated for desaturation using lime to pH of 8.9. Ferric chloride is added at a dosage of 100 to 150 ppm for metals removal and coagulation. Organosulfide (Nalmet-1689) is added at a dosage of 12 ppm for mercury and divalent metals removal. Site PC1 also adds a polymer for flocculation prior to solids removal in the solids contact clarifiers. Clarifier underflow is dewatered using a plate and frame press.

Effluent from the clarifier is filtered in a traditional sand filter and then discharged with other flows. Site PC1 has an internal monitoring point at the FGD discharge point with discharge limits for metals listed in Table 2-3.

Treatment Achieved

Site PC1 collects weekly data for their internal outfall from the FGD wastewater system. Table 2-4 presents data for selected parameters collected from July 2009 to October 2011. The median value was based on detected results. Trace elements except for mercury were analyzed using EPA Method 200.7. Mercury was analyzed using Method 245.2.

Table 2-4
Site PC1 Historic FGD Effluent Metals Data

Parameter	Units	Number of Samples	Median	Max
Aluminum	mg/L	121	0.126	1.331
Arsenic	mg/L	149	0.010	0.241
Beryllium	mg/L	120	0.000	0.0006
Boron	mg/L	121	188	319.6
Cadmium	mg/L	155	0.002	0.0225
Chromium	mg/L	142	0.005	0.0374
Copper	mg/L	129	0.004	0.0491
Iron	mg/L	121	0.105	1.01
Lead	mg/L	126	0.002	0.0466
Manganese	mg/L	163	2.7	3110
Mercury	µg/L	162	0.061	3.4
Nickel	mg/L	120	0.014	0.262
Selenium	mg/L	170	0.527	1.49
Silver	mg/L	119	0.002	0.0187

When compared to the proposed limits in the draft ELG, PC1's FGD treatment system effluent would not consistently meet the limitations for arsenic and mercury.

PC1's FGD wastewater treatment is focused on the removal of metals and is operated to focus on metals removal. The historic effluent values for eight metals was plotted to evaluate the level of consistency achieved by their wastewater treatment system. Figures 2-3 through 2-10 present the historic effluent data for PC1.

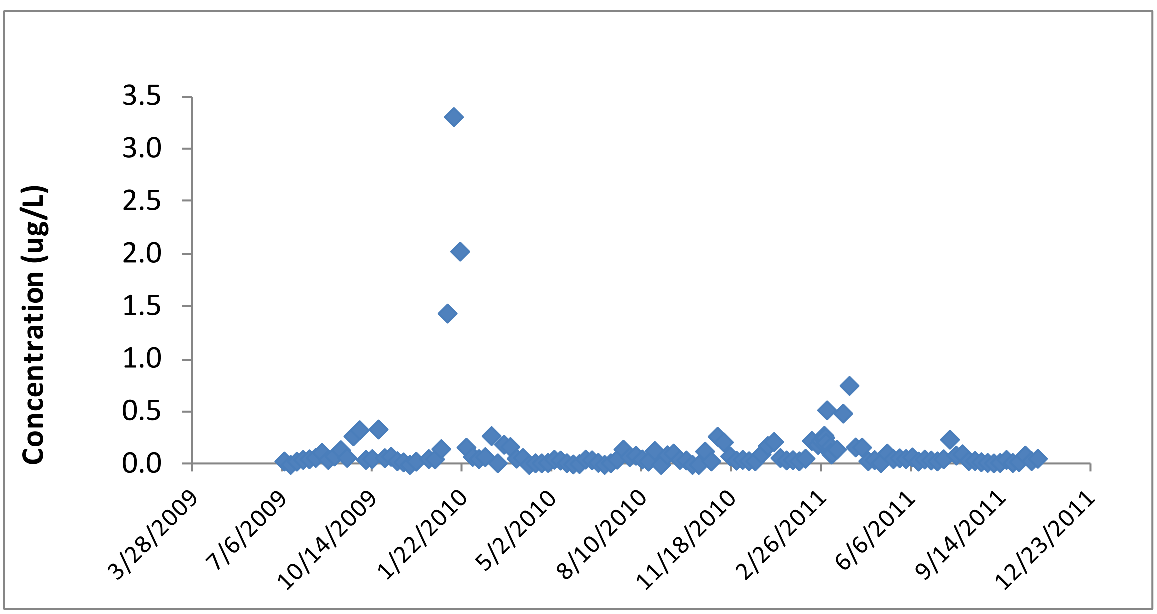

Figure 2-3
Site PC1 FGD Wastewater Treatment System Effluent Mercury Concentration

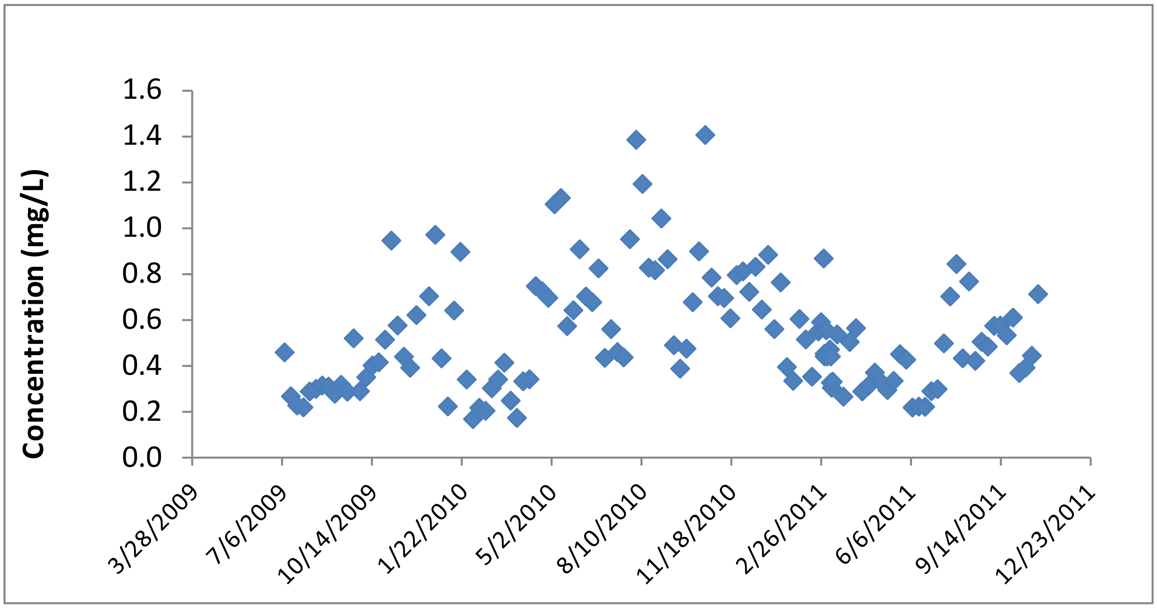

Figure 2-4
Site PC1 FGD Wastewater Treatment System Effluent Selenium Concentration

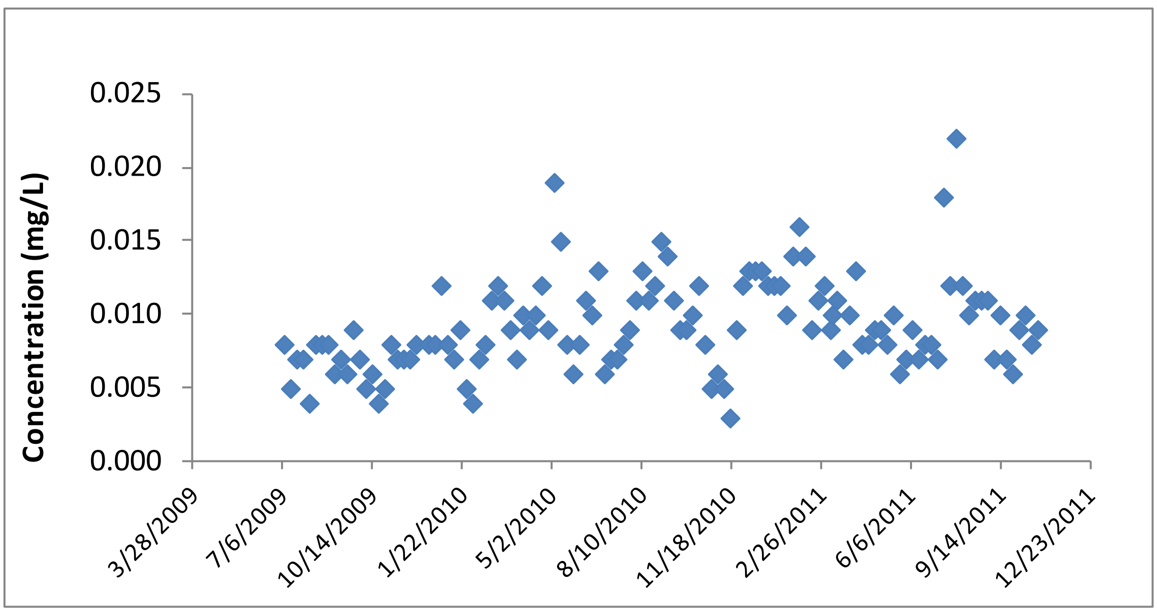

Figure 2-5
Site PC1 FGD Wastewater Treatment System Effluent Arsenic Concentration

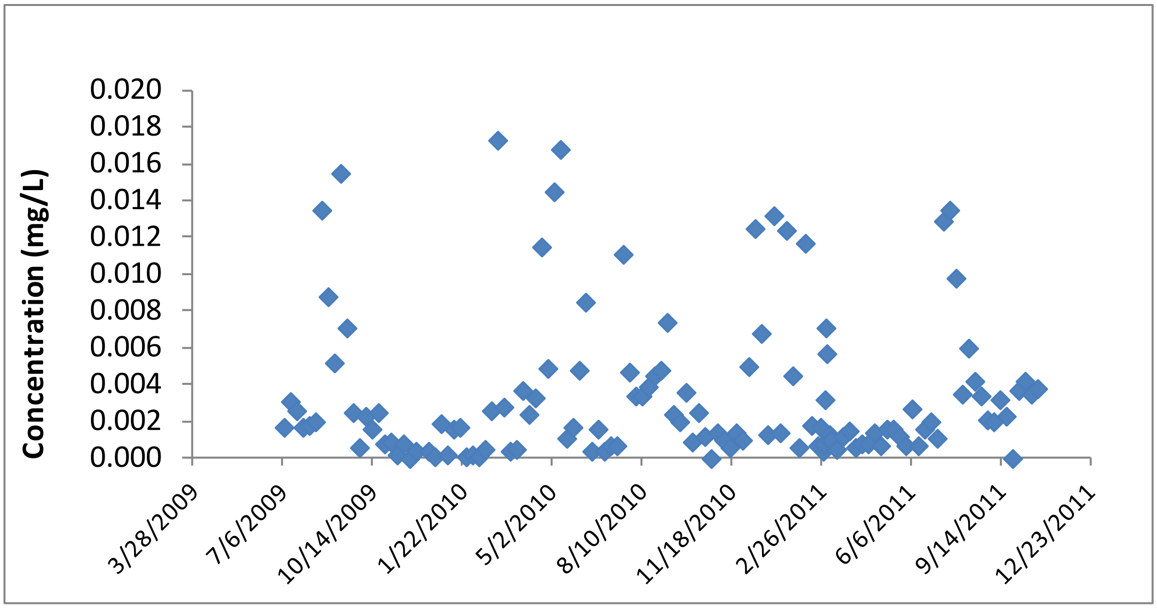

Figure 2-6
Site PC1 FGD Wastewater Treatment System Effluent Cadmium Concentration

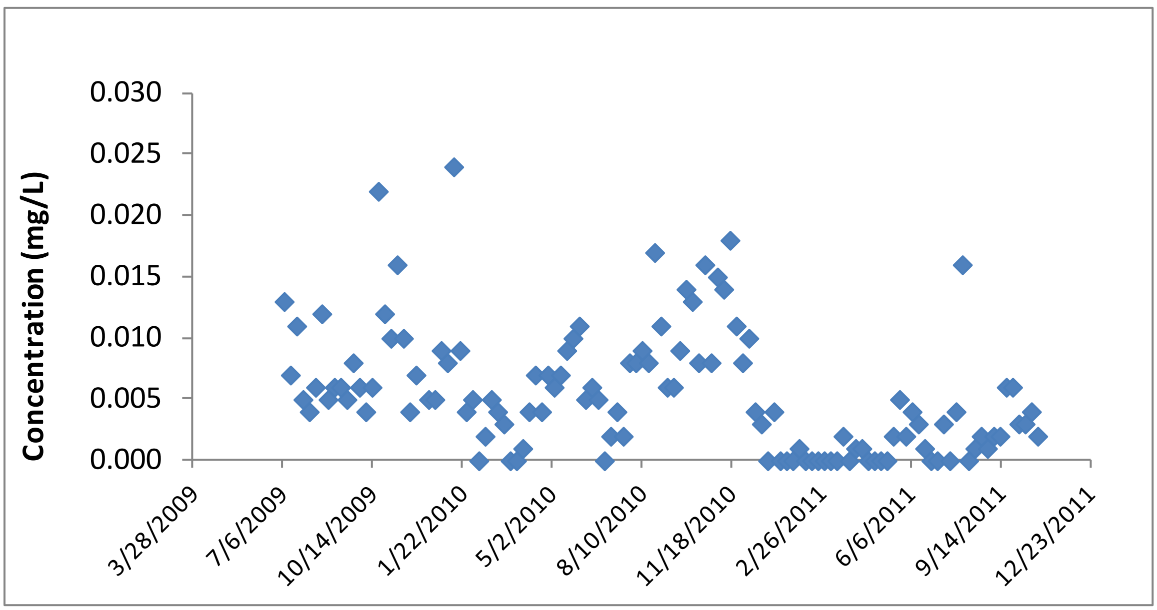

Figure 2-7
Site PC1 FGD Wastewater Treatment System Effluent Chromium Concentration

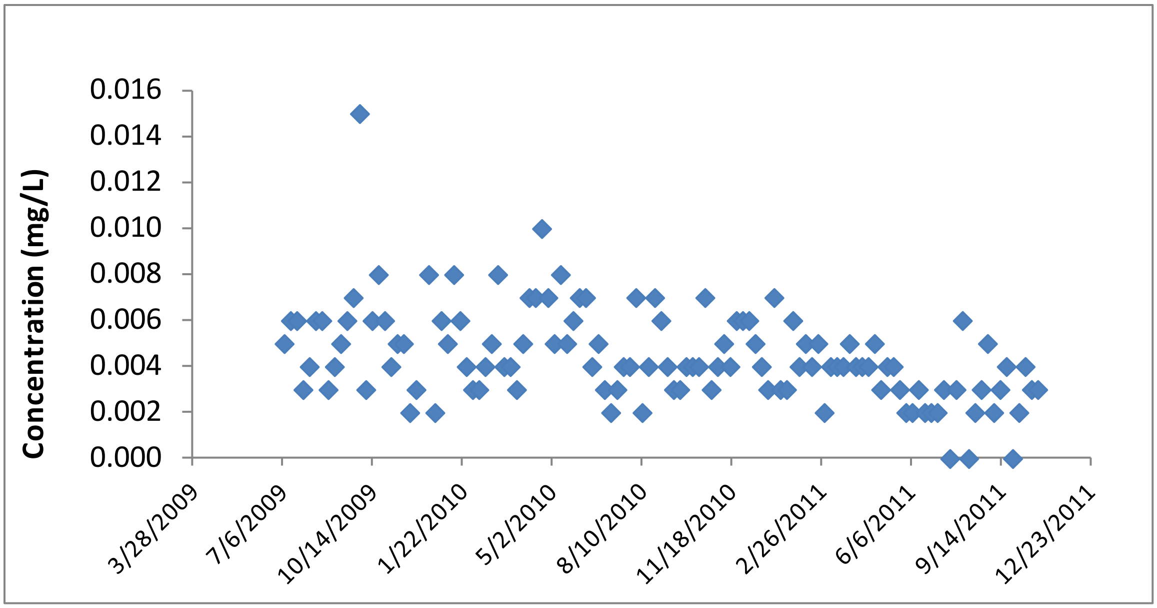

Figure 2-8
Site PC1 FGD Wastewater Treatment System Effluent Copper Concentration

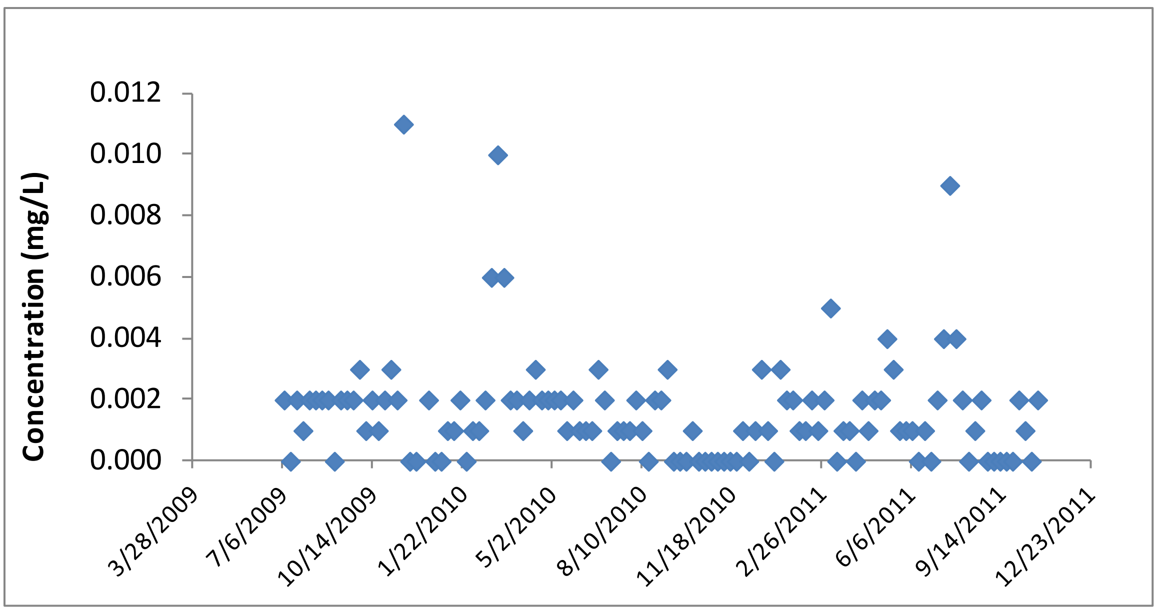

Figure 2-9
Site PC1 FGD Wastewater Treatment System Effluent Lead Concentration

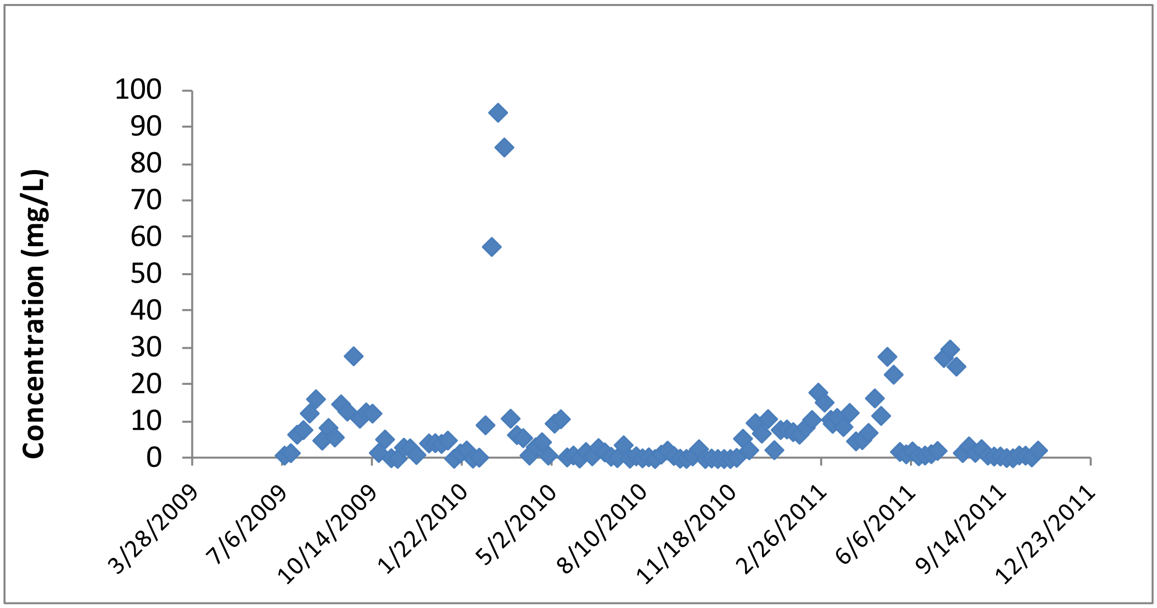

Figure 2-10
Site PC1 FGD Wastewater Treatment System Effluent Manganese Concentration

The data plots indicate that despite a focus on the removal of metals, PC1's metals removal concentrations are variable. The data show periodic spikes in concentrations for most metals. Interestingly, the spikes in concentration are not necessarily consistent across metals. For instance, the highest selenium concentration occurred on October 19, 2010. However, on the same date, mercury, lead, manganese, copper, and cadmium all exhibit relatively low concentrations in the FGD wastewater effluent.

This indicates that the physical/chemical treatment process was functioning properly during this time period, but that influent variability and/or other factors resulted in spikes despite treatment. This indicates that even a facility that uses physical/chemical treatment focused on metals removal to treat FGD wastewater can have discharge variability. However, for a limited data set provided for mid-2010, the physical/chemical treatment process achieved nearly 100 percent removal for arsenic, cadmium, copper, lead, manganese, selenium, and zinc.

Lessons Learned

Operational challenges for PC1's FGD wastewater treatment system include the following:

- Despite desaturation and chemical treatment using anti-scalants, the FGD wastewater still has very high scaling potential. Site PC1's hydrochloric acid (HCl) feed system to control the wastewater pH prior to the filtration process was undersized. The pH entering the filters was too high resulting in scaling of the filter media. To prevent the scaling problems in the filters, the size of the HCl feed system pumps was increased. In addition, a scale inhibitor was added to help increase media life in the sand filters.
- Biogrowth is a problem in both the clarifier and the sand filter. Biogrowth in the clarifiers carries over to the filters resulting in fouling and increased backwashes. PC1 is testing biocide addition to reduce biogrowth in the system. Biocides may be needed to help control the biogrowth; however, these chemicals should be carefully considered before use. Some

biocides could result in effluent toxicity while others could contribute to effluent metals concentrations.

- PC1 has two solids contact clarifiers that are designed to operate in parallel; however, PC1 typically operates only one of them at a time. This is because at lower flow rates, it is difficult to keep good solids blankets in both clarifiers. Operating with one clarifier allows for a thicker solids blanket, which prevents bed collapse, which can result in dispersed solids in the effluent. The use of a single clarifier results in a higher solids concentration in the waste sludge and promotes better operation of the solids handling system.

Site PC2

Site PC2 burns bituminous coal and uses a limestone forced oxidation FGD to remove SO_2 from the flue gas. Site PC2's FGD wastewater treatment system was brought online in 2009. The system has a maximum design flow rate of 500 gpm. The system typically operates with one train at approximately 230 gpm. Figure 2-11 presents a process flow diagram of PC2's FGD wastewater treatment system.

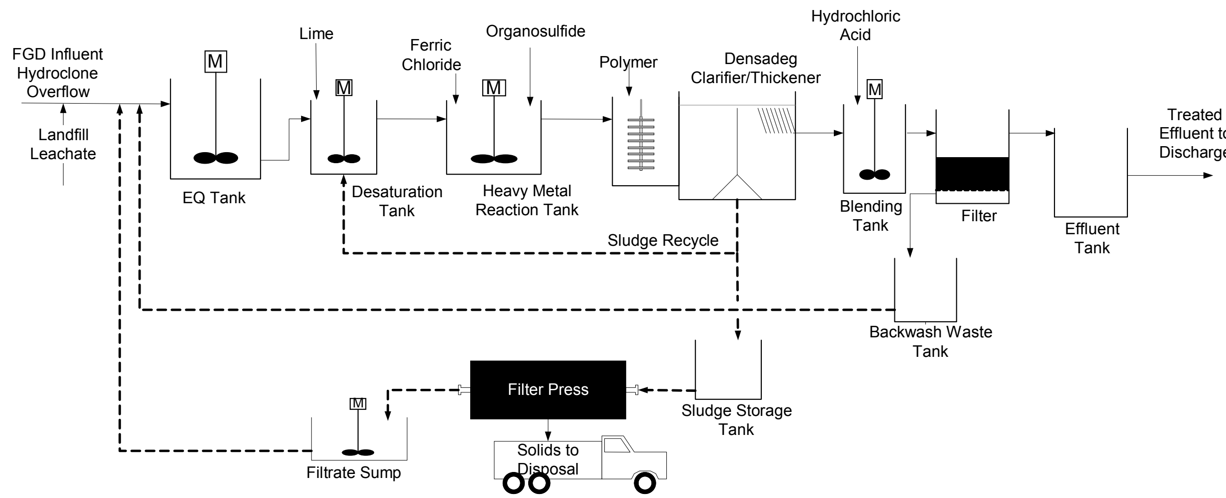

Figure 2-11
Site PC2 FGD Wastewater Treatment System Process Flow Diagram
Note -PC2 currently bypasses the backwash waste tank and pumps backwash directly to the EQ Tank

Hydrocyclone overflow (which consists of 1 to 2 percent TSS) is stored in an equalization tank. The equalized FGD wastewater is pumped to a desaturation tank where lime is added to raise the pH to 8.2. The desaturated wastewater then overflows to the heavy metals reaction tanks where 80 ppm ferric chloride is added for metals removal and solids coagulation. The reaction tank effluent flows to a clarifier (Infilco Degremont's Densadeg high-rate clarifier) where 2 ppm of organosulfide (TMT-15) and a polymer are added. The solids from the Densadeg are recycled to the desaturation tanks. Waste solids are dewatered using a plate and frame filter press.

The clarified wastewater is stored in a blending tank. An HCl feed system is used to adjust the pH as needed before sand filtration. The filtered water is stored in an effluent tank and then discharged.

Treatment Achieved

The only metals the site currently has discharge limitations for are copper and lead, and these limits are met without specific efforts focused at their treatment. Site PC2 provided historic FGD effluent data from January 2011 to May 2012. Selected parameters are presented in Table 2-5.

Table 2-5
Site PC2 Historic FGD Effluent Metals Data

Parameter	Units	Number of Samples	Median	Max
Aluminum	mg/L	17	<2.5	2.5
Antimony	mg/L	17	<0.5	0.50
Arsenic	mg/L	17	<0.25	0.25
Boron	mg/L	17	378	471
Cadmium	mg/L	17	0.03	0.05
Chromium	mg/L	17	<0.13	0.13
Copper	mg/L	72	<0.25	0.25
Iron	mg/L	17	<1.5	1.7
Lead	mg/L	72	<0.15	0.58
Mercury	µg/L	17	1.1	87
Molybdenum	mg/L	17	<0.5	0.50
Nickel	mg/L	17	0.54	1.50
Selenium	mg/L	17	<0.5	0.50
Thallium	mg/L	17	<0.5	0.50
Zinc	mg/L	17	0.25	0.78

Most of the metals analyses performed on Site PC2's effluent were performed at detection limits greater than the draft ELG limits. However, based upon the maximum values seen in the data set, Site PC2 would not currently meet the draft ELG limitations for arsenic or mercury.

Lessons Learned

Operational challenges for PC2's FGD wastewater treatment system have included:

- Although originally designed for solids recirculation, Site PC2 has halted the return of solids from the Densadeg to the desaturation tank. Sludge handling can be challenging and has required particular attention to proper operation and maintenance.
- Site PC2 has also bypassed the backwash holding tank for their system. The piping is prone to clogging. The backwash is now pumped directly to the equalization tank.

Site PC3

The Site PC3 FGD wastewater treatment system has a maximum design flow rate of 360 gpm, but currently operates at a flow of approximately 140 gpm. The FGD scrubber is a limestone forced oxidation system. A process flow diagram of the Site PC3 FGD wastewater treatment system is presented in Figure 2-12.

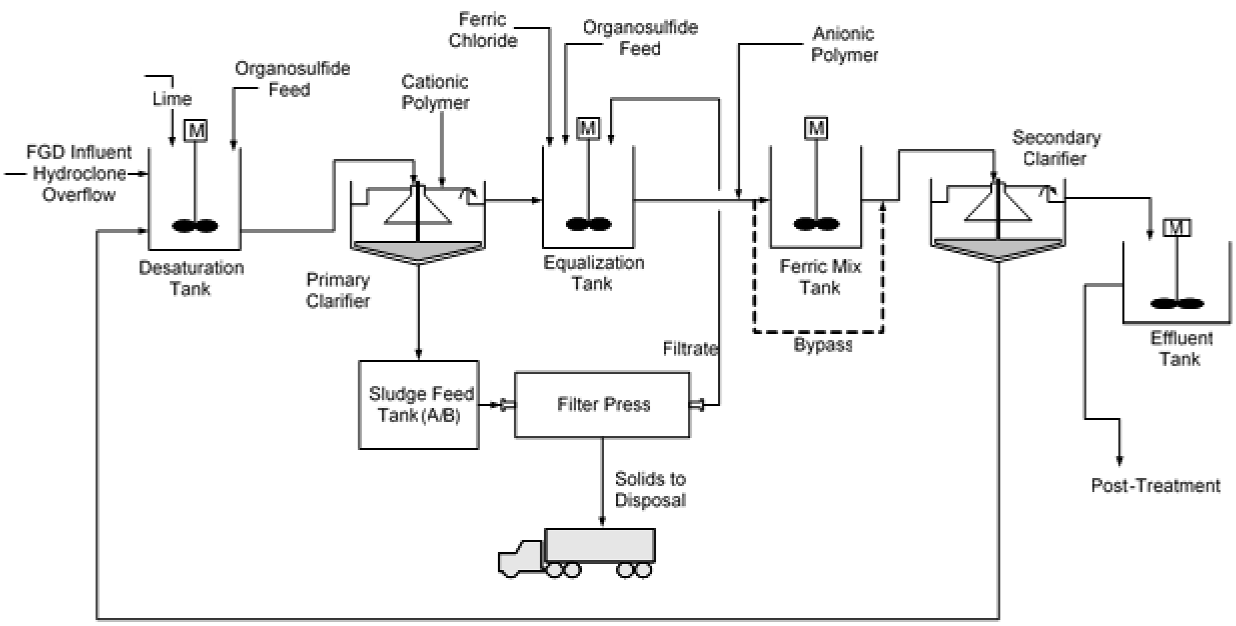

Figure 2-12
Site PC3 FGD Wastewater Treatment System Process Flow Diagram

The system operates continuously, receiving secondary hydrocyclone overflow. Solids returned from the secondary clarifier underflow are combined with the FGD wastewater in the desaturation tank to improve the performance of the precipitation process. Lime is added to the desaturation tank to achieve pH 8.5 and 25 ppm of organosulfide (MetClear) is added to the same tank to remove mercury and divalent metals during the desaturation process. A polymer is added to coagulate the particles as the water flows to the primary clarifier. Solids removed from the clarifier are dewatered using a plate and frame filter press. The primary clarifier overflow is stored in an equalization tank.

The desaturated FGD wastewater is dosed with ferric chloride (20 ppm maximum) and organosulfide (50 ppm) in the equalization tank for additional metals removal. The wastewater receives an additional dose of anionic polymer for flocculation as it flows to the ferric chloride mix tank and then into the secondary clarifier. The clarified wastewater flows to an effluent tank and is then fed to a biological treatment system for selenium removal (GE ABMet®). Effluent from the biological treatment system flows to treatment ponds where it is combined with other flows for discharge.

Treatment Achieved

Site PC3 has permit limits at the plant's final outfall (which contains FGD and other wastewater streams), but they do not have limits on the discharge of the FGD system. Therefore, they collect limited data on their FGD wastewater treatment system. The focus of the plant's overall treatment system is solids removal. However, selenium limitations on the final outfall have required the addition of biological treatment after physical/chemical treatment. Reducing selenium before the biological treatment is therefore desirable. Site PC3 provided their selenium data (prior to biological treatment) from January 2012 to June 2012. The data are presented in Table 2-6.

Table 2-6
Site PC3 Historic FGD Physical/Chemical Effluent Metals Data

Parameter	Selenium (mg/L)
Number of Samples	5
Median	0.279
Max	0.311

The data shows that the physical/chemical FGD wastewater treatment system is not removing selenium below the draft ELG limits. This is expected because this plant has a forced oxidation scrubber, so the selenium is likely selenate, which is not typically removed by physical/chemical treatment.

Lessons Learned

The following are operational challenges cited by plant staff:

- Due to the high concentrations of solids, the feed lines to the ferric chloride mix tank have a history of clogging. Site PC3 has chosen to bypass the ferric chloride mix tanks in order to avoid hydraulic problems and clogging. Instead, ferric chloride and organosulfide are added to the equalization tank after the primary clarifier, which acts as a mix tank for the chemical precipitation reactions.
- In addition, because of the high solids concentrations, Site PC3 has had trouble with filter press feed pump failure. The high solids tend to cause problems with rotors and other pump components. Site PC3 has used progressive cavity pumps, recessed impellor pumps, and electric diaphragm pumps. They have had issues with each pump style. Rotary lobe pumps are currently being evaluated as a possible replacement pump.

Site PC4

Site PC4 burns bituminous coal and uses a limestone forced oxidation scrubber to remove SO_2 from the flue gas. The FGD wastewater treatment system has a maximum design flow rate of about 650 gpm. The FGD wastewater generated is typically 1 percent TSS and has a chloride concentration of roughly 6,000 ppm. Figure 2-13 presents a process flow diagram of Site PC4's FGD wastewater treatment system.

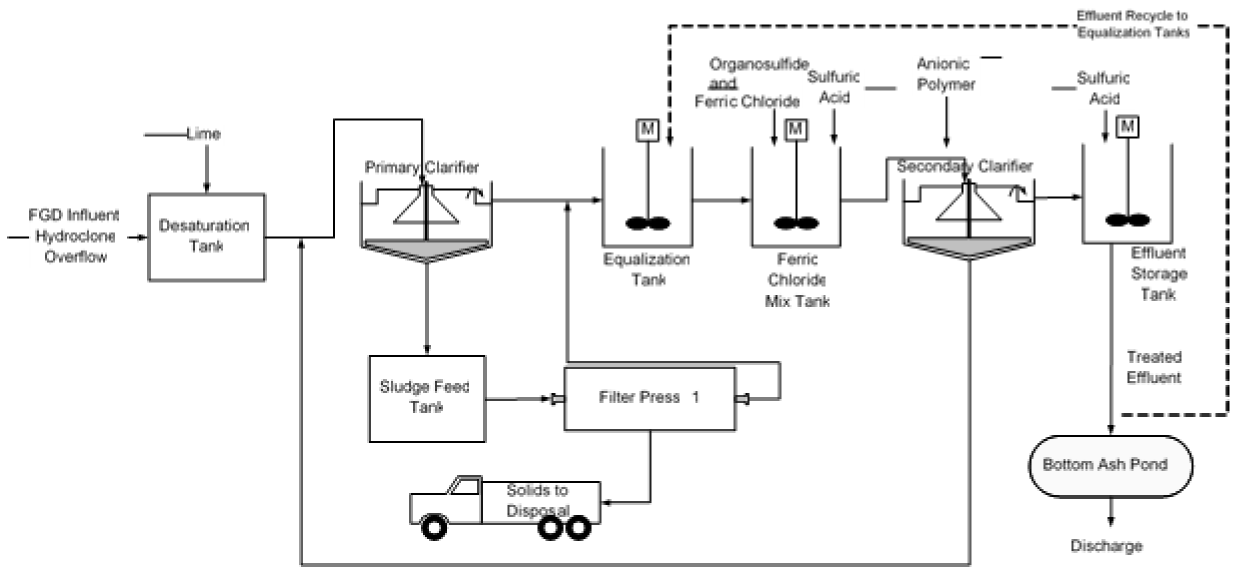

Figure 2-13
Site PC4 FGD Wastewater Treatment System Process Flow Diagram

Site PC4's FGD overflow from hydrocyclones is collected in a desaturation tank where lime is added to a pH set point of 8.6 for solids precipitation, including metal hydroxides formed under alkaline conditions. After pH adjustment, the FGD wastewater flows into the primary clarifier for solids removal.

The desaturated FGD wastewater is equalized and then treated with 36 ppm of Nalmet-1689 organosulfide and 50 ppm of ferric chloride for the additional removal of metals. Sulfuric acid and anionic polymer are used for minor pH adjustments and improved flocculation particle formation, respectively. Solids are removed through secondary clarification. Solids from primary and secondary clarification are dewatered using filter presses. The clarifier effluent is discharged to bottom ash ponds and eventually the wastewater system outfall. A chemical supplier performed jar tests to improve the removals of solids and metals in the FGD wastewater treatment system by adjusting the ferric chloride and organosulfide dosages.

Treatment Achieved

Site PC4 is not regulated at the effluent of the FGD treatment system, but rather at a combined outfall, which includes additional low volume flows and bottom ash pond effluent. The final outfall has limits for mercury, selenium, aluminum, and iron. Additional parameters must be monitored, but do not have permit limitations. Site PC4 does periodically collect samples at the discharge of its FGD wastewater treatment system. Site PC4 provided FGD effluent data collected from January 2010 to September 2011 for use in this report. A summary of the data for selected parameters is presented in Table 2-7.

Table 2-7
Site PC4 Historic FGD Effluent Metals Data

Parameter	Units	Number of Samples	Median	Max
Aluminum	mg/L	13	0.105	0.332
Arsenic	mg/L	13	0.007	0.011
Iron	mg/L	13	0.94	1.77
Magnesium	mg/L	13	1660	1900
Mercury	ng/L	46	749	5850
Selenium	mg/L	13	0.088	0.156

Effluent values were compared to the proposed ELG limits to evaluate the efficacy of physical/chemical treatment at this plant to meet these discharge levels. The comparison indicates that, as it currently operates, the Site PC4 FGD wastewater treatment system is not consistently able to meet the draft ELG arsenic limits, and does not meet the draft ELG limits for mercury. PC4 monitors mercury concentrations more frequently than other parameters, using low-level detection EPA Method 1631. PC4 provided data for 46 samples. Figure 2-14 illustrates the variability in the data over time.

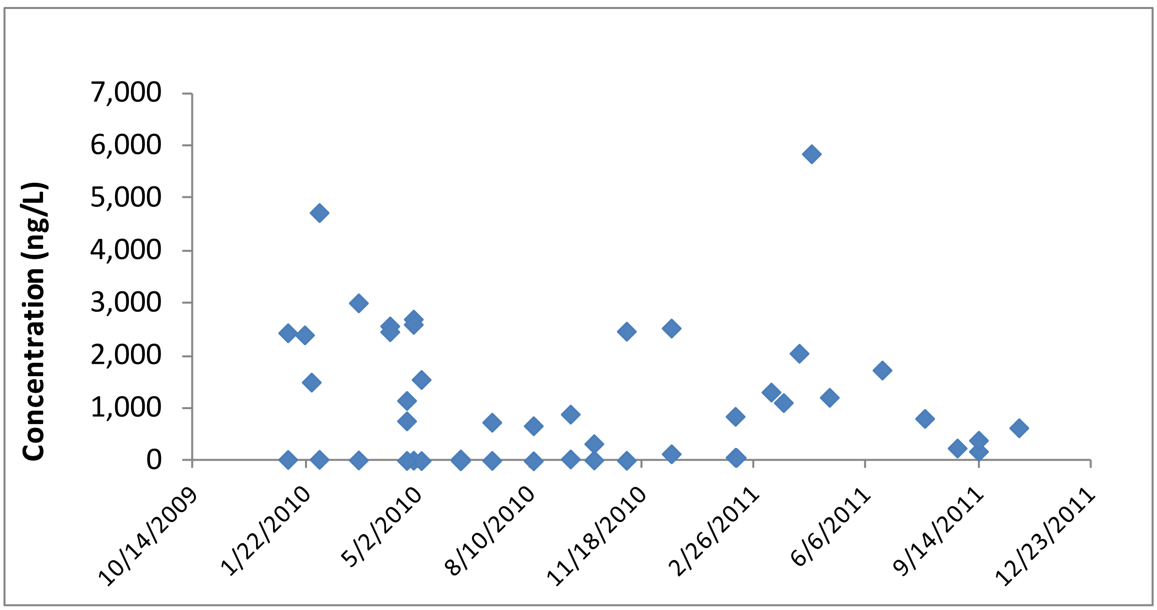

Figure 2-14
Site PC4 FGD Wastewater Treatment System Effluent Mercury Concentration

Historic mercury data indicates that, as with PC1, the PC4 effluent concentrations are somewhat variable despite treatment.

Lessons Learned

During the interview with Site PC4 representatives, they reviewed operational and equipment changes that have been instituted since the design and the commission of the treatment system. The main lessons learned by Site PC4 operators are as follows:

- Site PC4 had trouble with short-circuiting across the desaturation tank. To prevent this, dip tubes were installed in the desaturation tank to improve contact time with the lime.
- The anionic polymer is added directly to the secondary clarifier, which has caused mixing issues. Relocating the polymer addition point to an inline location is being pursued to promote better mixing with the FGD wastewater.
- The system was designed for solids to be recycled from the secondary clarifier underflow to upstream of the clarifier. This was included in the design to help improve settling, dewatering, and promote metals removal and improve treatment. However, recycling solids resulted in pumping problems and clarifier loading issues. Therefore, Site PC4 has chosen not to recycle solids in its FGD treatment system.

Site PC5

Site PC5 burns bituminous and sub-bituminous coal. The flue gas is scrubbed using a forced oxidation limestone FGD system generating a purge stream with approximately 5.5 percent solids and 12,500 ppm of chlorides. Site PC5 is typically a base-load plant but recent operation has been more peaking due to market factors. This change in plant availability may affect the consistency of the wastewater from the FGD.

The FGD wastewater system was brought online in late 2009. It treats water from the FGD's primary hydrocyclones. The FGD wastewater treatment system has a maximum design flow rate of 330 gpm but currently operates at an average of approximately 200 gpm. Figure 2-15 presents a process flow diagram of the FGD wastewater treatment system.

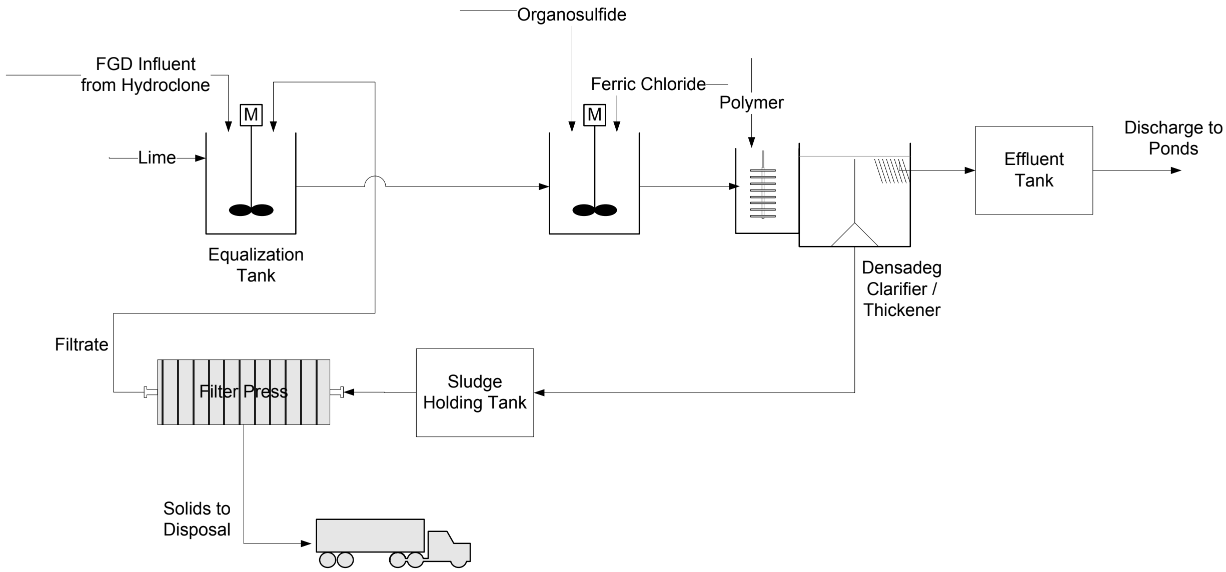

Figure 2-15
Site PC5 FGD Wastewater Treatment System Process Flow Diagram

The system operates as a batch system. FGD wastewater is collected in the system equalization tank. When sufficient volume is collected, the wastewater is treated using lime to pH of 8 for desaturation. Then 100 ppm of ferric chloride is added for coagulation and metals removal, and 20 ppm of organosulfide (Nalmet-1689) is added for mercury and divalent metals removal.

Site PC5 also adds polymers to promote flocculation for better solids removal. Solids removal occurs in a Densadeg high-rate clarification system. The solids removed by the Densadeg are dewatered using a plate and frame filer press. The effluent from the FGD wastewater treatment system is discharged to a pond that receives other flows from the facility. There are no limits on the FGD wastewater before it mixes with other wastewater. Because of this discharge scenario, Site PC5 does not currently monitor the FGD effluent. Site PC5 has numeric limits at the final outfall, after FGD wastewater is mixed with other waters.

Lessons Learned

During the interview, Site PC5 representatives identified the following challenges with their FGD wastewater treatment system:

- The Densadeg works well to increase the density of the sludge before dewatering. In some cases, water has to be added to dilute the thickened sludge for pumping to the dewatering system. The sludge pumps for the system have been an issue due to the high solids concentration and abrasiveness. Originally, screw progressive cavity pumps were used to pump the solids, but these pumps have been replaced with recessed impellor centrifugal sludge pumps to reduce wear and tear on the pumping system.
- Site PC5 is controlling to pH 8.0 due to limitations of the acid pumping system. This indicates that chemical pumping systems should be sized carefully to provide a range of chemical feed rates for a variety of system flows. Turn up and turn down ratios of the chemical feed system should be carefully assessed before selection to maintain maximum flexibility in the treatment system.

Site PC6

The Site PC6 treatment system was built in 2000 and burns bituminous coal. It uses a batch system to treat FGD purge wastewater from its forced oxidation limestone scrubber. Figure 2-16 presents a process flow diagram of the Site PC6 FGD wastewater treatment process.

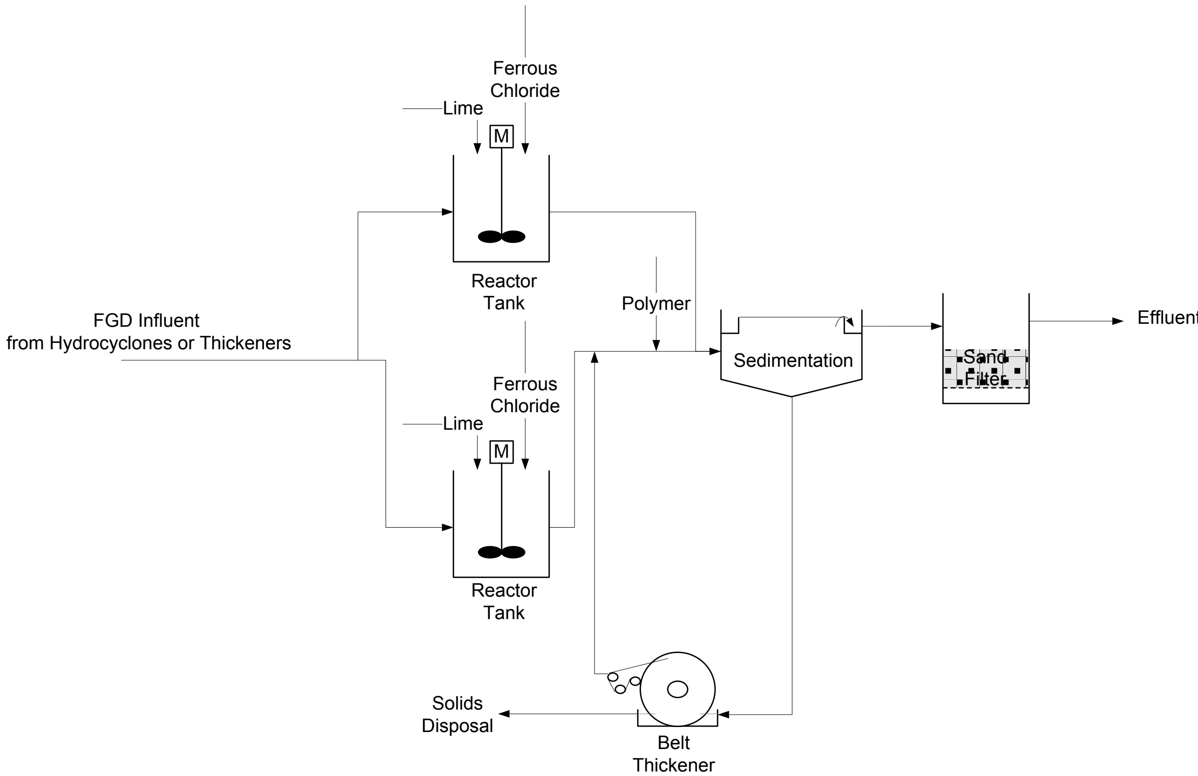

Figure 2-16
Site PC6 FGD Wastewater Treatment System Process Flow Diagram

The FGD wastewater is stored in a thickener that overflows to one of two batch treatment tanks. One tank (25,000 gallons) is filled while the other processes wastewater. Once a batch tank is filled, lime is added to a pH of 8 to 8.4. After the target pH is reached, ferrous chloride is added volumetrically (275-325 gallons per 25,000-gallon batch) to remove selenate and metals by reduction and subsequent adsorption from the wastewater. PC6 treats approximately 18 batches per day.

Following chemical treatment, the batch is discharged to a tank for settling with a 3-day retention time. The tank does not contain traditional clarifier internals. Solids settled in the tank are pumped from the bottom of the tank to a vacuum filter for dewatering. Fly ash is added to the dewatered solids for stabilization and then landfilled. The sedimentation tank overflows to a sand filter. The filtered water is collected in a treated water tank. The treated water is combined with other plant flows for discharge.

Treatment Achieved

Site PC6 conducts periodic sampling of its FGD wastewater effluent. The focus of the treatment is to remove selenium from the FGD wastewater. The plant operators provided effluent metals data for samples collected from January 2012 to September 2012. Table 2-8 presents selected effluent data. Mercury was analyzed using low-level detection EPA Method 1631.

Table 2-8
Site PC6 Historic FGD Effluent Metals Data

Parameter	Units	Number of Samples	Median	Max
Arsenic	mg/L	4	0.006	0.008
Beryllium	mg/L	4	0.0001	0.0003
Cadmium	mg/L	4	0.0002	0.0004
Chromium	mg/L	4	0.001	0.003
Copper	mg/L	4	0.001	0.005
Iron	mg/L	4	0.002	0.002
Mercury	µg/L	159	0.732	3.7
Nickel	mg/L	4	0.004	0.017
Lead	mg/L	9	0.001	0.003
Selenium	mg/L	4	0.035	0.057
Silver	mg/L	4	0.0001	0.0003
Zinc	mg/L	4	0.003	0.013

When compared with the proposed ELG limits, Site PC6 appears to comply with arsenic. Mercury is consistently present at levels higher than the draft ELG limits.

Lessons Learned

During the interview, Site PC6's operators discussed operational challenges that they have commonly faced during the operation of their system and how these issues were addressed.

- Site PC6 focuses on selenium removal. Site PC6 monitors its influent chloride levels and has found that their removal efficiencies are reduced when the FGD chloride levels are greater than 18,000 milligrams per liter (mg/L) chloride. They target 15,000 mg/L chlorides and typically achieve 90 percent selenium removal at these chloride levels. Increasing chlorides to 18,000 mg/L reduces the selenium removal to 60 percent at Site PC6. This may be because increasing chlorides could be a result of increased detention time within the scrubber resulting in concentrating up selenite, which means there would be higher influent selenate in the FGD wastewater influent to the treatment plant.
- The media filter used at Site PC6 originally contained anthracite and sand. Due to issues with flow pathways and short-circuiting, the anthracite was removed and now operates as a sand filter.

Site PC7

Site PC7 burns bituminous coal. The flue gas is scrubbed using a forced-oxidation limestone unit. The unit produces an FGD wastewater stream with a maximum chloride concentration of 12,000 mg/L. The FGD wastewater system treats secondary hydrocyclone overflow. The system is designed to treat 200 gpm but typically operates at approximately 175 gpm. A process flow diagram of the system is presented in Figure 2-17.

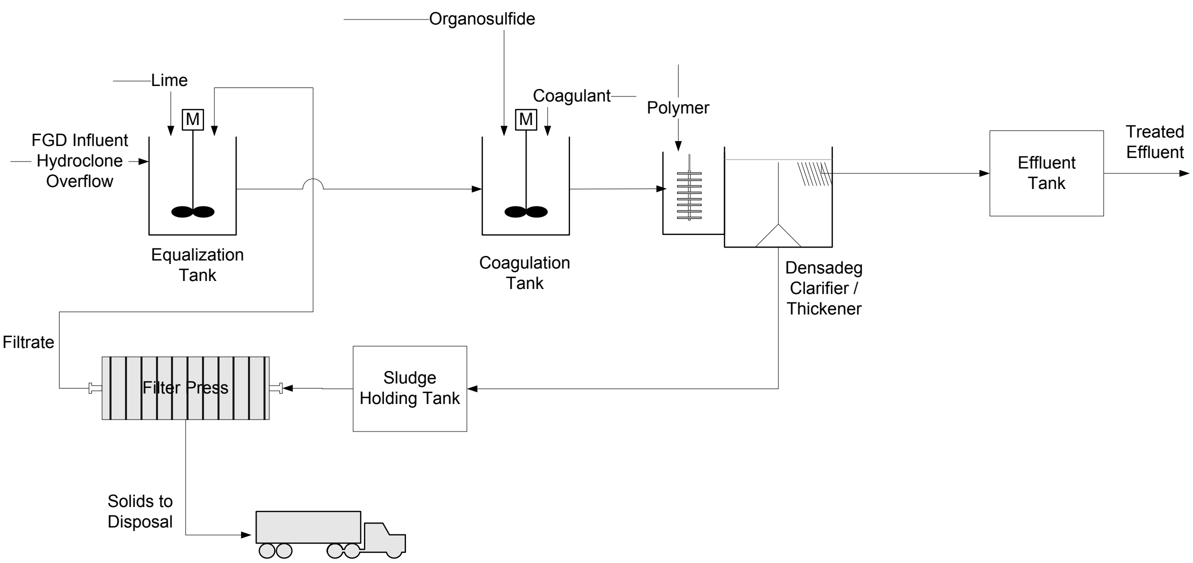

Figure 2-17
Site PC7 FGD Wastewater Treatment System Process Flow Diagram

The overflow is combined with the dewatering press filtrate and additional small flows in an equalization tank where lime is added to pH 8.8 to 9.2. The equalized FGD wastewater then flows to the coagulation mix tank where approximately 20 ppm of organosulfide (Nalmet-1689) is added for the removal of mercury and other metals. The FGD wastewater then flows to a high-rate clarifier (Densadeg). Polymer is added in the reaction tank of the Densadeg in order to increase flocculation of the precipitates and particulates.

The settled solids from the Densadeg are pumped to a solids holding tank and then dewatered using filter presses. The Densadeg supernatant is stored in an effluent tank and then discharged to ponds where it combines with other site flows.

Treatment Achieved

The focus of Site PC7's treatment is on the removal of TSS, not metals. However, trace metals are also removed. In the past operation, ferric chloride was added to aid in metals removal but testing performed on the wastewater indicated that the organosulfide alone was reaching the same levels of removal so feed of ferric chloride was stopped.

Lessons Learned

During the interview, Site PC7 representatives discussed several challenges that they have dealt with while operating their system.

- Site PC7 has difficulty supplying hydrated lime quickly enough to maintain the target pH during high wastewater flows. This indicates that chemical pumping systems should be sized carefully to provide a range of chemical feed rates for a variety of system flows. Turn up and turn down ratios of the chemical feed system should be carefully assessed before selection to maintain maximum flexibility in the treatment system.
- Site PC7 has explored several options to improve the performance of solids removal in the clarifier. The lamella plates in the Densadeg were prone to fouling due to accumulation of solids. Site PC7 operators focused on the location of polymer addition to improve polymer mixing and contact time. PC7 also used heated water for polymer dilution in order to promote polymer incorporation into solution. This has helped reduce the required polymer dosages needed.

Case Study Summary

From the survey of the operational information and data provided by the seven plants, several important points are evident:

- All plants interviewed use some form of lime to raise the pH of the saturated FGD wastewater for desaturation. Although the target pH varied, it was typically 8.0 to 9.0.
- Six of the seven plants interviewed used organosulfide to improve metals removal.
- Most plants use ferric iron as a coagulant to improve solids and metals removal.
- Solids recycle is a common approach to improving solids settling and metals removal. However, solids recycle can cause equipment problems within the system. Pump type, pipe sizing, and materials of construction should be carefully selected.
- Only one (PC6) of the four plants with available arsenic data would be able to meet both the daily maximum and average monthly limits in the proposed ELGs. PC4 may be able to achieve the daily maximum limit, but not consistently. All four of the plants operated at pH between 8.0 and 8.9. Optimal arsenic removal has been shown to occur between pH 6.0 – 7.0. Therefore, plants are not generally optimized for arsenic removal. A physical/chemical treatment system may need additional stages of oxidation (to convert dissolved arsenic to arsenate form for removal with iron co-precipitation), pH adjustment, or other additional polishing systems to remove arsenic.
- None of the four plants with available mercury data would be able to meet the limits in proposed ELGs consistently. PC1 has a median concentration below the daily maximum limit, but maximum detected concentrations are considerably higher than the limit. Three of the four plants currently add organosulfide.

Following the interviews, EPRI reached out to three of the facilities, Sites PC1 through PC3, to conduct jar testing to investigate methods for further improving the physical/chemical treatment of FGD wastewater. Chapter 3 presents the findings of the jar test studies.

3
BENCH-SCALE TREATABILITY TESTING RESULTS

This section presents the results of bench-scale testing to evaluate removal of trace metals using physical/chemical treatment. It should be noted that the treatability testing was limited, and does not necessarily reflect the lowest levels of metals that physical/chemical treatment can achieve. It should also be noted that a limited number of samples were tested. In addition, the results do not ensure that such treatment could achieve the same metals levels across the range of FGD wastewaters in the industry, or even at a given plant over time.

Treatability Testing Overview

The most advanced physical/chemical treatment of FGD wastewater generally involves chemical precipitation with the use of iron (usually in the form of ferric chloride) and organosulfide as chemical additives. In addition, flocculants or acids/bases are used to improve settling or adjust pH of the system.

Treatability testing on existing systems to optimize system performance can be very beneficial. Facilities use jar testing to resolve performance issues by running jar tests of their FGD wastewater and then applying results to their full-scale FGD wastewater treatment system. Jar testing can be used to test new chemicals and adjust dosages of existing chemicals to obtain optimal removal performance.

A treatability testing case study is presented within this section. The treatability tests within this study simulate the state of the practice for physical/chemical treatment of FGD wastewater by simulating chemical precipitation with iron and organosulfide addition. The treatability tests were conducted to remove trace elements (including but not limited to mercury and selenium) that are present in FGD wastewater.

Treatability Testing Methods

In treatability testing of physical/chemical treatment it is important to collect samples at the appropriate point. It is best if a sample can be taken upstream of chemical addition to the wastewater, after bulk solids removal. If this is not possible, it is more important to collect the sample before chemical addition. A process flow diagram of the sampled treatment system should be evaluated to help verify understanding of where the sample should be collected. In the case study testing, plant staff collected samples of FGD wastewater prior to chemical addition at the equalization tank for Sites PC1 through PC3. Lime is added at the equalization tank for Sites PC1 through PC3. The purpose of sample collection before equalization was to collect samples that did not have any treatment through chemical addition in the field so that chemical precipitation could be simulated in the laboratory. Samples were not field filtered. Samples were shipped to CH2M HILL for analysis.

The following test methodology was used to conduct the jar tests for Sites PC1 through PC3.

1. Place 1 liter of FGD water into a clean beaker and settle for 1 hour.
2. Decant the supernatant into a clean container.
3. Adjust the pH of the samples to 8.5.
4. Add 20 ppm by volume of organosulfide (Nalmet-1689) and 50 ppm by volume of commercially available ferric chloride (35 percent solution) to the remaining sample and mix thoroughly. These doses were chosen as on the high end of what is typically used. No efforts were made to optimize the chemical dosage.
5. After 20 minutes, stop stirring and allow the sample to settle for 30 minutes. Decant the supernatant for analysis.

The testing methodology was determined and tests were conducted prior to the proposed ELGs being published. The optimal pH for arsenic removal, which is typically in the range of pH 6 to 7, was not tested. Since the proposed ELGs include an arsenic limitation, future testing should incorporate the optimal pH for arsenic removal.

Summary and Representativeness of the Untreated Data Set

Appendix A contains a complete set of the analytical results from Sites PC1, PC2, and PC3. Table 3-1 includes a summary of the results of removal of soluble metals at each of the sites.

Table 3-1
Summary of Treatability Testing for Soluble Metals

		Plant PC1		Plant PC2		Plant PC3	
		Untreated	Jar Test effluent*	Untreated	Jar Test effluent*	Untreated	Jar Test effluent*
Aluminum	µg/L	319	399	673	746	303	273
Antimony	µg/L	<34.5	<34.5	<34.5	<34.5	<34.5	<34.5
Arsenic	µg/L	117	94	265	276	52	50
Barium	µg/L	108	105	643	597		
Beryllium	µg/L	<1.06	<1.06	<1.1	<1.1	<1.1	<1.1
Boron	µg/L	340,000	325,000	617,000	614,000	491,000	464,000
Cadmium	µg/L	75	<2.44	66	<2.4	227	6
Chromium	µg/L	25	23	43	39	<7.3	<7.3
Cobalt	µg/L	12	<3.51	207	57	200	74
Copper	µg/L	35	36	107	66	37	22
Iron	µg/L	<80	<80	<80	<80	<80	<80
Lead	µg/L	15	20	19	19	<14.6	<14.6
Magnesium	µg/L	4,560,000	4,350,000	7,350,000	7,360,000	3,970,000	3,730,000
Manganese	µg/L	26,000	24,400	80,000	64,400	54,600	47,100

Table 3-1 (continued)
Summary of Treatability Testing for Soluble Metals

Mercury	µg/L	0.055	0.017	79	0.33	0.14	<0.0028
Molybdenum	µg/L	310	297	22	18	189	176
Nickel	µg/L	56	<38.0	3,300	2,000	1,910	1,200
Selenium	µg/L	914	851	92	118	398	360
Silver	µg/L	8	<7.64	28	17	10	<7.6
Thallium	µg/L	<33.9	<33.9	<33.9	<33.9	<33.9	<33.9
Tin	µg/L	<20	<20	<20	<20	<20	<20
Titanium	µg/L	<6.39	<6.39	<6.4	<6.4	<6.4	<6.4
Vanadium	µg/L	<8.88	<8.88	<8.9	<8.9		
Zinc	µg/L	55	43	1,670	115	2,290	115

*pH adjustment, ferric chloride, organosulfide

In 2009, EPA's contractor, Eastern Research Group, Inc. (ERG) published a memorandum entitled "Technology Option Loads Calculation Analysis for Steam Electric Detailed Study" that included a data set used by the EPA to calculate loading associated with various forms of treatment including physical/chemical treatment [14]. Analytical data from Sites PC1, PC2, and PC3 are generally comparable to the ERG data for most parameters. These results are representative of the industry, although FGD influent wastewater chemistry is known to vary.

Dissolved arsenic results for the three sites, which ranged from 52 to 265 µg/L in untreated samples, were generally higher than the dissolved arsenic results used by EPA in ELG limits setting[13]. As stated in the previous section, samples collected were not field filtered. Instead, the samples collected at the facilities were filtered by the laboratory within 24 hours.

In treatability testing of physical/chemical treatment it is important to understand the speciation of selenium and arsenic, as some species (selenite (Se[IV]) and arsenate (As[V])) can be removed by physical/chemical treatment under the right conditions, while other species (selenate (Se[VI]) and arsenite (As[III])) have much less removal by physical/chemical treatment. In the case study testing, selenium and arsenic species were analyzed in the untreated samples. Table 3-2 presents a summary of the speciation results. The results presented in Table 3-2 do not include all species that may be present within the sample. Arsenic was mainly present in the arsenate form (As[V]), which is generally more easily removed by physical/chemical treatment than the arsenite form (As[III]).

Table 3-2
Summary of Arsenic and Selenium Species in Untreated FGD Wastewater

Parameter	Units	Site PC1	Site PC2	Site PC3
As(V)	µg/L	33.8	<50	<25
As(III)	µg/L	<5	<50	<25
Se(IV)	µg/L	582	59.2	240
Se(VI)	µg/L	90	<50	77
SeCN	µg/L	<50	<50	<50
SeCN = Selenocyanate				

Similarly selenium is mainly present in both oxidized species (Se[IV] and Se[VI]), with the majority of selenium in the selenite form (Se[IV]), which is more easily treated with physical/chemical treatment than the selenate form. Selenite is most efficiently removed with physical/chemical treatment when the pH of the solution is acidic (pH about 5 to 6).

Effect of Chemical Precipitation and Settling on Trace Metals Removal

Treatability test results for trace metals from Sites PC1, PC2, and PC3 showed some physical/chemical treatment removal, however not sufficient to meet the draft limits in the proposed ELGs. It should be noted that the jar tests were a rudimentary test, not optimizing pH or chemical feed for specific target pollutants. Jar tests should be optimized through multiple rounds of testing to fully understand the effectiveness of the treatment. For example, arsenic and manganese are known to be precipitated by iron addition, but in a narrow pH window. It is suspected that the limited removal in jar testing was due to not optimizing conditions for their removal.

Treatment was not optimized for individual metals. Removal may expect to be improved if target pH ranges and chemicals are used. The hydroxide solubility of individual metals is commonly presented as in the solubility curves shown in Figure 3-6. With metals being regulated to µg/L or nanograms per liter (ng/L) levels, it may be difficult to have an optimum pH for precipitation of all metals of concern.

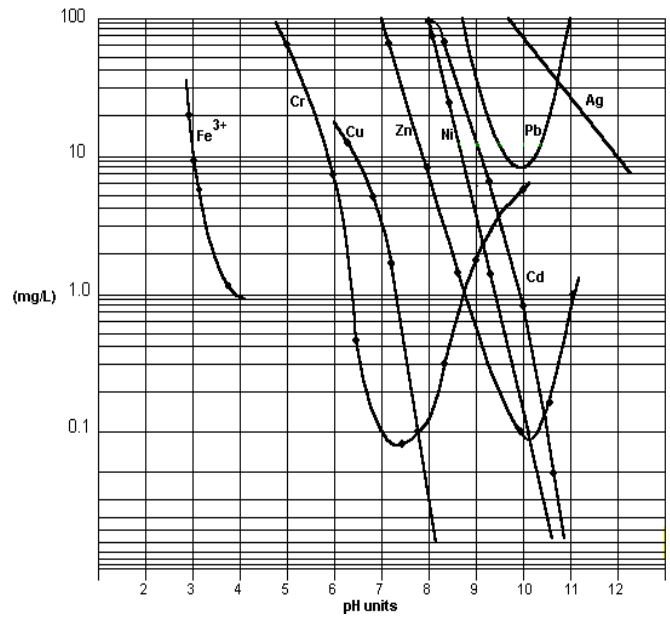

Figure 3-1
Solubility of Trace Metals as Hydroxides[10]

Theoretical solubility for various metal sulfides is shown in Figure 3-2. The most insoluble metal sulfide is mercury sulfide. The theoretical solubility of mercury sulfide is so low that it would take over 300 liters of water to dissolve one molecule. Direct use is not practical because it precipitates so fast that it forms a colloid that is difficult to remove from water. Therefore, much work has been done to develop organic molecules with sulfide or thiofunctional groups that can form larger particles that are easier to remove [3].

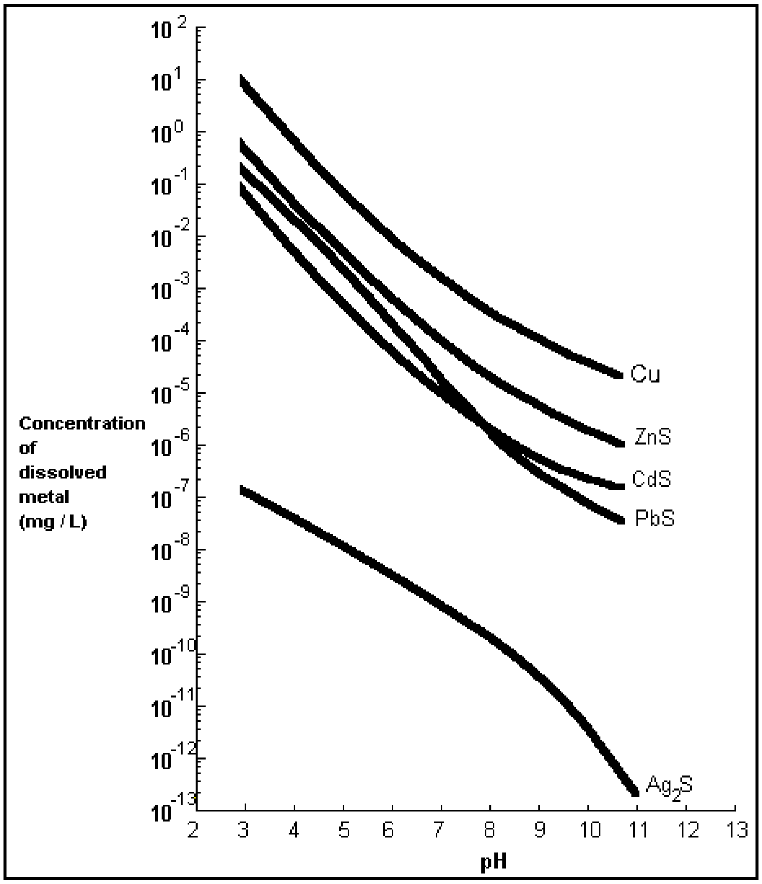

Figure 3-2
Solubility of Trace Metals as Sulfides[3]

Plant PC2 had very different mercury in its FGD water – both the amount of mercury and its treatability when compared to PC1 and PC3. Past EPRI research has shown that mercury treated with organosulfides forms solids that include very small, sub-micron particles. These can remain in water after settling and filtration with a standard lab 0.45 micron filter. [3,5,6,9,10,11] Therefore, additional testing with solids recirculation (to grow particles to the point that they can be removed), polymer addition, and /or microfiltration or ultrafiltration to remove small particles could be done to further evaluate physical/chemical treatment. It should be noted that solids recirculation is problematic to simulate in a jar study, and typically has to be tested in flow-through systems.

4 EVALUATION OF PHYSICAL/CHEMICAL TREATMENT

EPRI published a study in 2010 entitled "Evaluation of Technologies for Treatment of Mercury from FGD Wastewater." [11] This study provided a review of mercury removal from FGD wastewater through case studies of facilities with active FGD wastewater treatment plants. The treatment of mercury in the physical / chemical portions of the case study treatment plants is shown in Figure 4-1. The plants with filters (Sites M1 and M2, with physical/chemical treatment systems upstream of their bioreactors, and Sites M4 and M7) had mercury levels at least an order of magnitude lower than the other sites, which accomplished solids removal only by settling (M3, M5, M6, M9). However, it should be noted that the lower mercury concentrations in treated FGD wastewater at plants with filters did not indicate that media filtration was necessarily the reason for the lower mercury concentrations. Media filtration was used at several plants without improving mercury removal. The full-scale system at M5 operated with and without a sand filter, and saw no mercury-removal benefit from the filter. Pilot studies of treatment alternatives at M6 showed no improvement in mercury removal from sand filtration. It is likely that the lower mercury concentrations at plants with filters is due to these plants taking extra care to remove solids through mercury precipitation due either to regulatory pressures or the need to minimize solids in bioreactor influent.

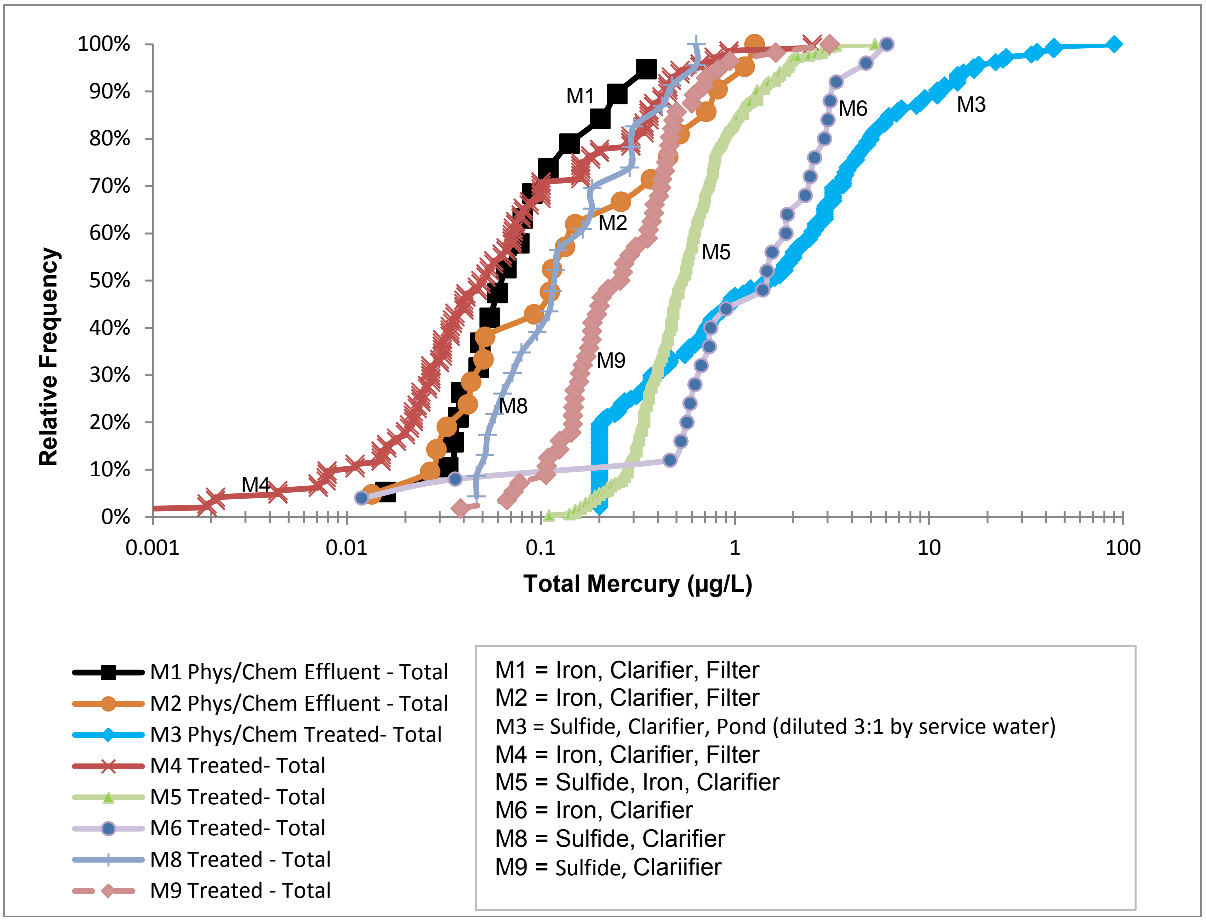

Figure 4-1
FGD Wastewater Total Mercury Removal by Physical/Chemical Treatment[11]

Overall findings from the 2010 EPRI study are similar to the findings of the current study, and included:

- Treatment achieved by a given technology varies significantly between different plants.
- Treatment achieved by a technology at a given plant varies significantly over time.
- Removal of both particulate and dissolved mercury is needed in order to reach low ng/L levels.
- Some of the sites using physical / chemical treatment reported improved mercury removal over time through treatment plant optimization.

5
RECOMMENDED FUTURE RESEARCH

Overall, the results of this study helped provide information on how optimized physical/chemical treatment can remove trace metals from FGD wastewater. This study showed FGD wastewater treatment systems are likely operating well in terms of chemical addition. A limitation of this study was that samples were not field filtered prior to shipment to the laboratory and were filtered and tested within the laboratory several days after collection. Physical/chemical treatment removes very large percentages of most pollutants of concern. It is a robust treatment system. Due to the variability of results over time seen from the various case studies, further research could be performed to characterize how upstream variability affects the FGD wastewater treatment plant influent and treatment performance. There is a growing experience in optimizing these systems for FGD wastewater treatment. Further research is needed to determine how much removal can be achieved with polishing technologies, such as adsorptive technologies and/or advanced membrane filtration, and if these technologies can be reliably used with FGD wastewater. Additional polishing technologies, however, may not be cost effective or feasible for the large majority of plants.

6
REFERENCES

1. Electric Power Research Institute. 2006. *Flue Gas Desulfurization (FGD) Wastewater Characterization: Screening Study.* Product 1010162.
2. Electric Power Research Institute. 2006. *EPRI Technical Manual: Guidance for Assessing Wastewater Impacts of FGD Scrubbers.* Product 1013313.
3. Electric Power Research Institute. 2008. *Flue Gas Desulfurization (FGD) Water Blowdown Characterization and Management: 2007 Update*. Product 1014073.
4. Electric Power Research Institute. 2008. *Multi-Media Fate of Selenium and Boron at Coal-Fired Power Plants Equipped with SCR and Wet FGD Controls*. Product 1015615.
5. Electric Power Research Institute. 2008. *Multimedia Mercury Fate at Coal-Fired Power Plants Equipped with SCR and Wet FGD Controls*. Product 1014095.
6. Electric Power Research Institute. 2009. *Flue Gas Desulfurization (FGD) Water Characterization: 2008 Update*. Product 1015588.
7. Electric Power Research Institute. 2009. *Impact of Wet FGD Design and Operating Conditions on Selenium Speciation.* Product 1017952.
8. Electric Power Research Institute. 2009. *Review of Water Treatment Technologies for Selenium Removal Implemented at Power Plants.* EPRI, Palo Alto, CA. Product ID: 1020813.
9. Electric Power Research Institute. 2010. *Evaluation of Mercury Speciation and Its Treatment Implication in Flue Gas Desulphurization (FGD) Waters.* EPRI, Palo Alto, CA. Product ID: 1019867.
10. Electric Power Research Institute. 2010. *Pilot-Scale and Full-Scale Evaluation of Treatment Technologies for the Removal of Mercury and Selenium in FGD Water*. Palo Alto, CA. Product ID: 1017955.
11. Electric Power Research Institute. 2010. *Evaluation of Technologies Implemented for Treatment of Mercury from FGD Wastewater.* EPRI, Palo Alto, CA. Product ID: 1019867.
12. EPA, 2013. U.S. Environmental Protection Agency. “Effluent Limitations Guidelines and Standards for the Steam Electric Power Generating Point Source Category,” Proposed Rule. *Federal Register*, Volume 78, Number 110, Friday, June 7.

13. EPA, 2013. U.S. Environmental Protection Agency. *Technical Development Document for the Proposed Effluent Limitations Guidelines and Standards for the Steam Electric Power Generating Point Source Category*. EPA-HQ-OW-2009-0819-2257, DCN SE01964.

14. Eastern Research Group, Inc. 2009. *Technology Option Loads Calculation Analysis for Steam Electric Detailed Study.* October 9.

A

RESULTS OF TREATABILITY TESTING

		Plant PC1		Plant PC2		Plant PC3	
		Untreated	Jar Test effluent*	Untreated	Jar Test effluent*	Untreated	Jar Test effluent*
General Chemistry Analysis							
TSS	mg/L	19	46.0	20	118.0	21	102
Ammonia	mg/L as N	5	5.82	6	6	3	3
Nitrate/Nitrite	mg/L as N	94	92.90	118	116	34	34
Sulfate	mg/L	5470	5250	2550	2570	8290	7650
Metals Speciation							
As(V)	µg/L	34		<50		<25	
As(III)	µg/L	<5		<50		<25	
Se(IV)	µg/L	582		59		240	
Se(VI)	µg/L	90		<50		77	
SeCN	µg/L	<50		<50		<50	
Total Metals							
Aluminum	µg/L	1,080		779		1,330	
Antimony	µg/L	<34.5		<34.5		<34.5	
Arsenic	µg/L	125		256		52	
Barium	µg/L	118		643			
Beryllium	µg/L	<1.06		<1.1		<1.1	
Boron	µg/L	362,000		605,000		506,000	
Cadmium	µg/L	82		68		231	
Chromium	µg/L	31		39		11	
Cobalt	µg/L	13		208		209	
Copper	µg/L	55		129		47	
Iron	µg/L	<80		<80		1,110	
Lead	µg/L	<31.7		30		<14.6	
Magnesium	µg/L	4,840,000		7,270,000		4,120,000	

		Plant PC1		Plant PC2		Plant PC3	
		Untreated	Jar Test effluent*	Untreated	Jar Test effluent*	Untreated	Jar Test effluent*
Manganese	µg/L	29,000		80,900		57,000	
Mercury	µg/L	0.055		87		0.86	
Molybdenum	µg/L	335		22		199	
Nickel	µg/L	63		3,290		2,000	
Selenium	µg/L	956		156		415	
Silver	µg/L	16		34		14	
Thallium	µg/L	<33.9		<33.9		<33.9	
Tin	µg/L	<20		35		<20	
Titanium	µg/L	<6.39		<6.4		<6.4	
Vanadium	µg/L	14		<8.9			
Zinc	µg/L	64		1730		2,330	
Soluble Metals							
Aluminum	µg/L	319	399	673	746	303	273
Antimony	µg/L	<34.5	<34.5	<34.5	<34.5	<34.5	<34.5
Arsenic	µg/L	117	94	265	276	52	50
Barium	µg/L	108	105	643	597		
Beryllium	µg/L	<1.06	<1.06	<1.1	<1.1	<1.1	<1.1
Boron	µg/L	340,000	325,000	617,000	614,000	491,000	464,000
Cadmium	µg/L	75	<2.44	66	<2.4	227	6
Chromium	µg/L	25	23	43	39	<7.3	<7.3
Cobalt	µg/L	12	<3.51	207	57	200	74
Copper	µg/L	35	36	107	66	37	22
Iron	µg/L	<80	<80	<80	<80	<80	<80
Lead	µg/L	15	20	19	19	<14.6	<14.6
Magnesium	µg/L	4,560,000	4,350,000	7,350,000	7,360,000	3,970,000	3,730,000
Manganese	µg/L	26,000	24,400	80,000	64,400	54,600	47,100
Mercury	µg/L	0.055	0.017	79	0.33	0.14	<0.0028
Molybdenum	µg/L	310	297	22	18	189	176
Nickel	µg/L	56	<38.0	3,300	2,000	1,910	1,200
Selenium	µg/L	914	851	92	118	398	360
Silver	µg/L	8	<7.64	28	17	10	<7.6
Thallium	µg/L	<33.9	<33.9	<33.9	<33.9	<33.9	<33.9
Tin	µg/L	<20	<20	<20	<20	<20	<20

		Plant PC1		Plant PC2		Plant PC3	
		Untreated	**Jar Test effluent***	**Untreated**	**Jar Test effluent***	**Untreated**	**Jar Test effluent***
Titanium	µg/L	<6.39	<6.39	<6.4	<6.4	<6.4	<6.4
Vanadium	µg/L	<8.88	<8.88	<8.9	<8.9		
Zinc	µg/L	55	43	1,670	115	2,290	115

*pH adjustment, ferric chloride, organosulfide

Export Control Restrictions

Access to and use of EPRI Intellectual Property is granted with the specific understanding and requirement that responsibility for ensuring full compliance with all applicable U.S. and foreign export laws and regulations is being undertaken by you and your company. This includes an obligation to ensure that any individual receiving access hereunder who is not a U.S. citizen or permanent U.S. resident is permitted access under applicable U.S. and foreign export laws and regulations. In the event you are uncertain whether you or your company may lawfully obtain access to this EPRI Intellectual Property, you acknowledge that it is your obligation to consult with your company's legal counsel to determine whether this access is lawful. Although EPRI may make available on a case-by-case basis an informal assessment of the applicable U.S. export classification for specific EPRI Intellectual Property, you and your company acknowledge that this assessment is solely for informational purposes and not for reliance purposes. You and your company acknowledge that it is still the obligation of you and your company to make your own assessment of the applicable U.S. export classification and ensure compliance accordingly. You and your company understand and acknowledge your obligations to make a prompt report to EPRI and the appropriate authorities regarding any access to or use of EPRI Intellectual Property hereunder that may be in violation of applicable U.S. or foreign export laws or regulations.

The Electric Power Research Institute, Inc. (EPRI, www.epri.com) conducts research and development relating to the generation, delivery and use of electricity for the benefit of the public. An independent, nonprofit organization, EPRI brings together its scientists and engineers as well as experts from academia and industry to help address challenges in electricity, including reliability, efficiency, affordability, health, safety and the environment. EPRI also provides technology, policy and economic analyses to drive long-range research and development planning, and supports research in emerging technologies. EPRI's members represent approximately 90 percent of the electricity generated and delivered in the United States, and international participation extends to more than 30 countries. EPRI's principal offices and laboratories are located in Palo Alto, Calif.; Charlotte, N.C.; Knoxville, Tenn.; and Lenox, Mass.

Together…Shaping the Future of Electricity

3002001202