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Impact of Wet Flue Gas Desulfurization (FGD) Design and Operations on Selenium Speciation: 2010 Update

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Technical Update, December 2010

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PRODUCT DESCRIPTION

This report discusses the results of a project to assemble and interpret selenium concentration and speciation data in water from wet flue gas desulfurization (FGD) systems on U.S. coal-fired power plants. The current project focused on sampling FGD absorber slurry to determine how absorber design and operating conditions impact the selenium species formed and present in the chloride purge water, and the partitioning of selenium between the solid and liquid phase.

Results and Findings

The report describes results from an ongoing Electric Power Research Institute (EPRI) project that is collecting selenium concentration and speciation results from full-scale limestone reagent, gypsum-producing (mostly forced oxidation) wet FGD systems. To date, EPRI has sampled nine FGD systems at seven sites. The authors have provided an interpretation of the effects of various FGD design and operating parameters on selenium chemistry based on this relatively limited data set. One finding of significance is a potential relationship between oxidation-reduction potential (ORP) in the FGD reaction tank slurry and selenate formation. Another finding of significance is that the presence of dibasic acid (DBA) in the absorber slurry may suppress selenate formation at a given ORP condition. The report also presents evidence of relationships between ORP and the phase partitioning of manganese and mercury in FGD absorber slurries. The manganese phase partitioning may directly or indirectly influence selenate formation rates. This report summarizes the data collected and the authors' findings from their analysis of the data, and makes recommendations for continued data collection efforts to improve understanding of selenium speciation and partitioning in FGD slurries.

Challenges and Objective(s)

This project compiles and integrates results and data from nine limestone reagent, gypsum-producing wet FGD systems in an attempt to understand the factors that control selenium speciation. The most significant challenges include sampling, preserving and analyzing the various selenium species in a highly complex matrix of varying FGD waters. The collection of additional data in the future, representing a wider range of FGD design and operating conditions, should provide greater insight into these factors.

Applications, Values, and Use

It is important to know what selenium species are or will be present when selecting wastewater treatment technology for a particular wet FGD system. If the factors controlling selenium speciation in wet FGD systems are understood, FGD design and operating conditions may be controlled to minimize the formation of selenate (oxidized from selenite in wet FGD systems), which is more difficult to remove than selenite in traditional physical/chemical processes. Also, the formation of "unknown" selenium species that may not be effectively removed by traditional physical/chemical processes may be avoided. Finally, conditions that favor selenium reporting to the solid phase in the FGD slurry may minimize the amount of selenium compounds that must be removed from the chloride purge water.

EPRI Perspective

This project is a follow-up to previous EPRI Research and Development (R&D) to better understand the selenium speciation in wet FGD systems. It has provided several additional insights into aqueous-phase selenium speciation in wet FGD systems using limestone and employing forced oxidation (or high natural oxidation). The limited data provide some initial theories that will require further sampling and analytical studies to confirm.

EPRI efforts to establish reliable and accurate selenium speciation sampling, preservation, and analytical procedures should be continued. At this time, EPRI believes the best approach is to filter the samples in the field, with no preservation of the samples except overnight shipment on ice to the analytical laboratory. In addition, site-specific information about other factors, including ORP, dithionate, manganese and iron concentrations, which may influence selenium chemistry, should be obtained when wet FGD samples are collected for selenium speciation. Coal, fly ash, FGD makeup water, and reagent samples should also be collected and analyzed to determine input and output quantities of contaminants found in FGD systems.

Approach

The project team collected full-scale wet FGD samples and other power plant process samples from four wet FGD systems at three different coal-fired stations during the first half of 2010. EPRI conducted additional sampling at five FGD systems during the summer of 2009. A single contractor collected all of the field samples, using consistent sampling and preservation techniques, and Trent University made measurements on selenium speciation. This approach eliminated differences in sampling, preservation, and analytical procedures that have complicated the evaluation of previous wet FGD selenium speciation data. The collection of other process samples from the host units and details of the FGD system operation provided the data necessary to begin to elucidate the factors that control selenium speciation in wet FGD waters.

Keywords

Selenium
Speciation
Selenite
Selenate
FGD
Wastewater treatment

ABSTRACT

Selenium is present as a trace element in all coal, and selenium species are removed from the flue gas in wet flue gas desulfurization (FGD) systems. Some of the selenium removed by FGD systems is incorporated into the solid phase of the FGD slurry, but a portion remains in the FGD liquor. Many wet FGD systems purge water to control chloride levels, and some are required to remove selenium before discharge of the purge water. The selenium in the FGD liquor can be in many forms or species. The speciation is known to vary significantly from site to site, and even to vary with time at a given FGD system. The various species of selenium present in FGD liquors respond differently to wastewater treatment processes, so the effectiveness of selenium removal from FGD wastewater can be highly dependent on the selenium species present.

This Technical Update presents and discusses new results from an ongoing project to collect and interpret selenium concentration and speciation data in water from wet FGD systems on U.S. coal-fired power plants. All of the FGD systems sampled use limestone reagent and produce gypsum byproduct; all but one system employs forced oxidation. The objective of the project is to collect detailed data from representative wet FGD systems, then review those data to determine what factors affect selenium concentrations and speciation in FGD waters. It is important to know what selenium species are or will be present when selecting wastewater treatment technology for a wet FGD system. Also, it may prove possible to alter FGD conditions to minimize the selenium in FGD wastewater by controlling its form and phase partitioning.

As part of several ongoing projects, the Electric Power Research Institute (EPRI) has collected full-scale wet FGD results over the past two years. URS Corporation engineers and scientists conducted the field sampling, and Trent University made the selenium concentration and speciation measurements. It is important to note that the data in this report reflect consistent sampling, preservation, and analytical procedures. These parameters have varied in previous full-scale wet FGD selenium speciation measurement data, which has complicated the overall evaluation of those data.

It has previously been observed that forced oxidation (gypsum producing) wet FGD systems tend to have higher percentages of selenate, a more oxidized form of selenium (Se (VI)) that is not removed at high efficiency in traditional physical/chemical wastewater treatment processes, than low oxidation systems. The range of oxidation to selenate in forced oxidation samples was previously measured to vary from very low percentages (<5%) of the total dissolved selenium to 100%. Previously there was not enough supporting information about the available samples to conclusively determine what factors affect the percent oxidation of selenium to selenate in forced oxidation wet FGD systems. However, results from samples collected over the past year in the current project continue to support the theory that higher oxidation-reduction potential (ORP) in the FGD slurry liquor correlate with higher conversion of selenite to selenate, and that the presence of dibasic acid (DBA) can limit selenate formation at a given ORP value.

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INTRODUCTION

Selenium is present in coals at average concentrations ranging from 1 to 10 ppm, depending on the coal source and rank. Coal combustion produces relatively volatile selenium compounds in the flue gas, believed to be predominantly in the form of selenium dioxide. Some selenium is captured with the fly ash in the particulate control device, but a portion of the remaining selenium species is captured in wet flue gas desulfurization (FGD) absorbers.[1]

Regulatory drivers such as the proposed and now vacated Clean Air Interstate Rule, Clean Air Visibility Rule, and state regulations have led to the retrofit of new wet FGD systems on a number of coal-fired power generation units. Most of these new FGD systems produce gypsum as a byproduct and must purge some of the FGD liquor to control the chloride concentrations in the FGD system. In some cases, wastewater treatment may be necessary to remove some trace metals prior to discharge.

Much of the selenium removed by FGD systems is incorporated into the solid phase of the FGD slurry, but a portion remains in the FGD liquor. As wet FGD systems purge FGD liquor to control chloride levels, some are required to remove selenium before the purge water can be discharged. The selenium in the FGD liquor can be in many forms or species. The speciation is known to vary significantly from site to site, and even to vary over time at a given FGD system. The various species of selenium present in FGD liquors respond differently to wastewater treatment processes, so the effectiveness of selenium removal from FGD wastewater can be highly dependent on the selenium species present.

Over the past several years, EPRI has funded research to measure the concentrations and speciation of selenium compounds in the aqueous phase of slurries and liquors at various locations in wet FGD systems. Also associated with these efforts has been development of improved analytical methods for determining the selenium species present. As mentioned above, the form of selenium is important because different selenium species are removed at differing efficiencies in FGD wastewater treatment plants. For example, selenite (SeO_3^{2-}, which represents selenium in the +4 valence state [Se(IV)]), is believed to be the predominant form of selenium as it is absorbed from the flue gas as selenium dioxide; selenite and biselenite ($HSeO_3^-$) represent the ionic forms of selenium dioxide after it is absorbed in FGD liquors. Selenite can be removed effectively by traditional physical/chemical treatment methods. Selenate (SeO_4^{2-}, a form of selenium in the +6 valence state [Se(VI)]), most likely represents selenite that is oxidized in the wet FGD system, and is removed less efficiently by traditional physical/chemical processes. Other selenium forms have been identified in FGD liquors, but less is known about how effectively they can be removed from FGD wastewaters by traditional water treatment processes. Appendix A lists the various forms of selenium that have been identified in FGD waters, including their chemical formulas.

Although data have been collected for selenium concentrations and speciation in wet FGD systems over the past several years, little has been known about what controls selenium oxidation from the +4 to the +6 valence state, or the formation of other selenium compounds. In early 2009 an EPRI-funded project was initiated to compile and interpret previously collected selenium concentration and speciation data from a wide range of U.S. wet FGD systems. The initial objective of the project was to elucidate factors that affect selenium reactions in wet FGD systems. A Technical Update report was published in March 2009 with results from this data analysis.[2] Some text from that report is repeated in this Technical Update for the benefit of readers who have not read the previous report.

That report noted several issues with the available data that limited its usefulness. One was that the data did not always reflect consistent sampling, preservation, and analytical procedures. Several approaches were used for collecting samples, and at least two laboratories with their own proprietary procedures conducted the selenium speciation analyses. Thus, it was not certain that the available data were directly comparable.

That report also included recommendations for future EPRI research efforts. One key recommendation was that EPRI efforts to establish reliable and accurate selenium speciation sampling, preservation and analytical procedures should continue. Another was that additional data be obtained when wet FGD samples are collected for selenium speciation, to provide site-specific information about factors that may influence selenium oxidation to the selenate form and/or the formation of other selenium species.

Subsequently EPRI funded the current project to collect detailed process data from full-scale wet FGD systems. At the end of 2009 a Technical Update report was published, presenting data collected from five FGD systems treating flue gas from eight individual coal-fired units[3].

This report provides an update of results for sampling conducted during calendar year 2010. Selenium speciation sampling and analyses were conducted at four FGD systems treating flue gas from four units at three electric generating stations. All of the FGD systems use limestone reagent and produce gypsum as a solid byproduct; three of the four FGD systems are forced oxidized, while one operates with high natural oxidation. The samples were collected over the time period April through June 2010. It is anticipated that additional samples and process data will be collected from other full-scale wet FGD systems over the coming year, and that as those additional data become available the understanding of what controls selenium speciation in wet FGD systems will continually be enhanced.

Report Organization

This report is organized in four sections and two appendices. Following this introduction, Section 2 provides background on what was generally understood about selenium chemistry in wet FGD systems at the outset of the project, and a description of the sampling and analytical effort conducted. This includes a description of the host stations and FGD systems (although they are not named) and a description of the sampling and analytical plan. Section 3 presents selenium concentration and speciation results from these efforts, and provides the authors' interpretation of the effects of various FGD design and operating parameters on selenium chemistry as indicated by this limited data set. Section 4 summarizes the tentative conclusions the authors have drawn from this analysis of the data, and makes recommendations about future collection efforts to support better understanding of these issues. Each section contains a separate subsection for references where appropriate. Appendix A presents a glossary of selenium compounds that have been identified or tentatively identified in wet FGD liquors, including their names and chemical formulas, and defines a number of acronyms used in this report. Appendix B provides additional analytical results that are not detailed in Section 3.

References

1. *Multimedia Fate of Selenium and Boron at Coal-fired Power Plants Equipped with Particulate and Wet FGD Controls*, EPRI, Palo Alto, CA: 2008. 1015615.
2. *Impact of Wet FGD Design and Operating Conditions on Selenium Speciation: Technical Update*. EPRI, Palo Alto, CA: 2009. 1017952.
3. *Impact of Wet FGD Design and Operations on Selenium Speciation: 2009 Update.* EPRI, Palo Alto, CA: 2009. 1017951.

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BACKGROUND AND TECHNICAL APPROACH

Background

Selenium can be found in many forms in liquors from wet FGD systems. Selenium has an atomic number of 34 and a molecular weight of 78.96. It is found in Periodic Table Group 6a, and is a Period 4 (4th row) element. It is a metalloid, which lies just below sulfur (atomic number 16, in Group 6a but Period 3) in the periodic chart. Like sulfur, selenium has six electrons in its outer shell, and can be found in valence states of 0 (elemental selenium), -2 (selenide), +4 (selenite), and +6 (selenate). Correspondingly, the chemistry of selenium in wet FGD systems is believed to be analogous to that of sulfur: it is present in the flue gas as selenium dioxide, is removed as selenite in the ionic form, can be oxidized to the selenate form, and/or can form other species. Much of the absorbed selenium can report to the solid phase by mechanisms such as adsorption or co-precipitation with iron hydroxide fines. This report focuses on selenium that remains in the aqueous phase of the FGD slurry, although selenium partitioning between phases is also discussed.

While selenite is believed to be a predominant form of aqueous-phase selenium in low-sulfite-oxidation FGD systems, selenate is often found in forced oxidation FGD systems. However, selenium is known to be more difficult to oxidize to the +6 state than sulfur, and correspondingly a mixture of selenite and selenate is often found in forced oxidation systems.

In several EPRI projects, other selenium species have been identified in wet FGD liquors, including selenosulfate ($SeSO_3^{2-}$) and selenocyanate ($SeCN^-$). As described in the previous Technical Update, selenosulfate is believed to form by reaction between selenite and sulfite in wet FGD environments, perhaps due to partial reduction of selenite to the elemental form[1]. The analogous all-sulfur ion is thiosulfate ($S_2O_3^{2-}$), which is formed in inhibited oxidation wet FGD systems by reaction between elemental sulfur and sulfite ion. The mechanism for the formation of selenocyanate is unknown, although it is possible that selenium reacts with cyanide or hydrogen cyanide if trace amounts are present in the furnace or flue gas.

Other selenium species have been determined in FGD liquors by ion chromatography-based analytical methods. Two such compounds have been tentatively identified as methylated species by one EPRI contractor, Applied Speciation, while a number of other species have been identified only by their elution times – no compound identification has been made. Analytical techniques for selenium species identification are not discussed in any detail in this report; readers are referred to other EPRI reports that discuss these procedures[2,3,4].

The objective of the current project is to collect and analyze data from full-scale wet FGD investigations to advance the understanding of selenium chemistry in those systems. A specific objective is to determine what factors affect the conversion of selenite to other selenium species in wet FGD systems. This knowledge is important because the form of aqueous selenium present in wet FGD purge liquor can impact the selection of wastewater treatment processes for new FGD systems, and can affect the performance of existing treatment processes. Furthermore, with better understanding of the factors that control selenium speciation it may be possible to optimize FGD design and operating conditions to produce selenium forms that are readily treated by traditional wastewater treating technology. With better understanding of what controls selenium partitioning between the absorber liquor and solid phases, it may also be possible to minimize the amount of selenium present in the FGD liquor versus in the absorber slurry solids.

Technical Approach for the Current Project

Sampling and Analytical Approach

A number of approaches have been previously employed to collect and analyze wet FGD liquor samples for selenium concentration and speciation. In some cases EPRI Project Managers have contacted operators of wet FGD systems and requested that plant personnel collect and ship samples to EPRI-contracted analytical laboratories. In other cases EPRI contractors have collected and sent samples to a third-party contractor for analyses as part of wastewater characterization or treatability studies. The previous data were collected over a period of several years (mostly 2006 through 2008), and analytical techniques were refined and improved over this time period. Thus, analytical results from 2006 may not be directly comparable to results from 2008.

In the current project, the FGD and other process samples for each site have been collected by FGD Process Engineers and Chemists. The selenium speciation measurements have been conducted by Trent University's Environmental & Resource Sciences Program and Department of Chemistry (Trent). Trent uses a form of ion chromatography combined with inductively-coupled-plasma mass spectrometry (ICP-MS) to speciate the selenium compounds. The results presented in this report were collected and analyzed over a relatively short period of time, from June through October 2009 for the samples collected last year and April through July 2010 for the most recent samples. Thus, the analytical techniques have been relatively static and data should be comparable from site to site.

Also, for previous data collection efforts, sample preservation techniques varied for the selenium speciation samples. Preservation techniques included cryo-freezing (rapidly freezing with liquid nitrogen), acidification, and shipping unpreserved. In the latter two cases the samples were generally shipped on regular ice. Most previous samples were shipped unfiltered and unpreserved (other than shipping on ice), and the solid and liquid phases were separated after the samples were received at the analytical laboratory.

In the 2009 efforts on the current project, all three preservation techniques were conducted to some extent, and both field and laboratory filtering was conducted. Trent analyzed aliquots of process samples filtered and preserved by each technique. Also during the 2009 efforts, some samples were spiked with known quantities of selenite and selenate ions, to determine how well the spiked amounts were recovered by the analytical techniques for each preservation type and filtration approach. The results of these efforts led to the conclusion that the best approach for preserving selenium speciation in full-scale wet FGD liquor samples was to filter these samples in the field through a 0.45-µm filter media, then ship the filtered liquor to the laboratory overnight, on ice but with no other preservation. For the current data, from samples collected in 2010, only this filtering and preservation technique was used. Results for this filtering and preservation technique were presented in the previous Technical Update for this project[1], so those results are directly comparable to the current results presented in this report.

Samples were shipped to Trent University via overnight delivery services and stored in refrigerators or nitrogen-filled glove boxes until analyzed. Whenever possible, the results presented in this report are for samples that were analyzed within two days after collection.

As for the 2009 data set, information was collected about the plant and FGD process conditions, such as slurry pH and oxidation-reduction potential (ORP), slurry solid-phase selenium concentration, etc. A relatively comprehensive set of plant process data and samples was collected for each selenium speciation data set. Table 2-1 summarizes the typical FGD process stream samples collected and analyses completed, although there was some site-to-site variation. Table 2-2 summarizes the other plant process samples collected and analyzed, while Table 2-3 details the FGD absorber sample analyses completed.

Table 2-1
Typical FGD Process Stream Samples and Analyses

	FGD Liquor Phase Analysis				**FGD Solid Phase Analysis**	
FGD Sample Stream	**Trace Elements***	**Se Speciation**	**Slurry pH, Temp., ORP**	**FGD Analytes****	**Trace Elements***	**FGD Analytes****
Absorber Slurry	X	X	X	X	X	X
Limestone Slurry	X				X	
Makeup Water(s)	X					
Equalization Tank Effluent (Wastewater treatment system inlet)***	X	X	X		X	
Wastewater Treatment System Discharge***		X				

*List of trace elements varies by site and sample location; for some streams selenium was the only trace element analyzed
**See Table 2-3 for typical FGD analytes
***As appropriate depending on FGD system design

Table 2-2
Other Process Stream Samples and Analyses

Other Process Sample Streams	Trace Elements*	Short Proximate	Chloride
Coal	X	X	X
Fly Ash	X		
Gypsum	X		
Limestone Un-ground Rock (in lieu of limestone slurry sample for some sites)	X		

*List of trace elements varies by site; for some sites selenium was the only trace element analyzed

Table 2-3
Typical FGD Absorber Liquor, Solid, and Slurry Analytes

Analyte	FGD Solid Phase	FGD liquor phase	Slurry
Wt% Solids			X
Wt% Inerts	X		
Calcium	X	X	
Sodium		X	
Magnesium	X	X	
Chloride		X	
Sulfite	X	X	
Sulfate	X	X	
Carbonate	X	X	
Total Hydrolyzable Sulfur (THS)		X	
Unaccounted Sulfur Species/Potential Sulfur-Nitrogen Species		X	
Dithionate		X	
Peroxydisulfate		X	

Host Sites

As described in the Introduction, this project has involved collecting data from full-scale wet FGD systems to try to elucidate the factors that control selenium speciation. It is possible that if these factors are well understood, FGD design and operating conditions may be controlled to minimize the formation of selenate, which is more difficult to remove than selenite in traditional physical/chemical wastewater treatment processes. The sampling has concentrated on limestone reagent, forced oxidation FGD systems that produce gypsum as a solid byproduct.

The full-scale sampling efforts were all conducted anonymously, so individual plant names are not being published. Two of the three sites had site code names used in previous reports, so these same plant codes are used here. A new code name was assigned for the third site.

In the 2009 sample and data collection effort, two sites used DBA as a performance additive (three FGD systems) and two did not. In the current effort none of the four FGD systems sampled used DBA. Additional features of each site are summarized in Table 2-4 for the sites sampled in 2009 and in Table 2-5 for the sites sampled in 2010.

Table 2-4
Salient Features of Limestone Forced Oxidation FGD Systems Sampled in 2009

Plant Code	**Plant B**	**LMA007L**	**Plant E1**		**Plant C**
No. of FGD Systems Sampled at Site	1	1	2		1
No. of Units per FGD System	1	2	2 (Units 1 and 2)	2 (Units 3 and 4)	1
No. of Absorbers per FGD System	2	2	1	4	1
Absorber Type	Spray Tower	Spray/Tray Tower	Spray/Tray Tower	Dual Loop Spray/Tray	Jet Bubbling Reactor
Selective Catalytic Reduction for NO_x Control	No	Yes, both units	1 of 2 units	Yes, both units	No
Coal Type	Eastern bituminous	Eastern bituminous	Eastern bituminous	Eastern bituminous	Eastern bituminous
Coal Sulfur, wt%	1.9 – 2.5	2.2 – 2.9	3.4	3.3	1.5
Particulate Control Upstream of FGD	Cold-side ESP	Cold-side ESP	Cold-side ESP		Cold-side ESP
FGD Wastewater Treatment	Physical/ chemical (ferric chloride) plus biological	Physical/ chemical (ferric chloride + TMT-15 + polymer); de-sat. pH 8.2	Physical/chemical (ferric chloride + polymer); Reaction Tank 1 pH 9.05		None

Table 2-5
Salient Features of Limestone Forced Oxidation FGD Systems Sampled in 2010

Plant Code	Plant D-3*	Plant D-4*	Site U	Plant D-5
No. of FGD Systems Sampled at Site	2		1	1
No. of Units per FGD System	1 (Unit 1)	1 (Unit 2)	1 (Unit 1)	1 (Unit 4)
No. of Absorbers per FGD System	1	1	2 + 1 spare	1
Absorber Type	Spray/Tray Tower	Spray/Tray Tower	Spray/Tray Tower	Spray/Tray Tower
Selective Catalytic Reduction for NO_x Control	Yes	Yes	No	Yes
Coal Type	Eastern bituminous	Eastern bituminous	Powder River Basin	Eastern bituminous
Coal Sulfur, wt% (as received)	1.56 – 2.52	0.98 – 1.22	0.30	3.29 – 3.39
Particulate Control Upstream of FGD	Cold-side ESP	Cold-side ESP	Reverse-gas fabric filter	Pulse-jet fabric filter; wet ESP downstream of FGD absorber
FGD Wastewater Treatment	Physical/ chemical (pH adjustment, proprietary WWT additive, polymer; clarifier, filter press)		pH adjustment and settling of total suspended solids	Physical/chemical (head tank/ reaction tank, polymer addition, clarifier)

*Two FGD systems sampled at a single generating station

The five FGD systems sampled in 2009 treat flue gas from eight units. All eight units fire bituminous coal. Coal short proximate analysis data are shown in Table 2-6. The bituminous coal fired ranged from low to high sulfur content, and represented a range of chloride content. The four FGD systems sampled in 2010 treat flue gas from four units. One unit fires Powder River Basin coal, two fire low- to medium-sulfur bituminous coal, and one fires high-sulfur, high-chloride bituminous coal. Coal short proximate analysis data for the 2010 sites are shown in Table 2-7.

Table 2-6
Coal Short Proximate Analysis Data for 2009 Host Sites

Site	**Plant B**				**Site LMA007L**		**Plant C**	**Site E1**	
Units	1	1	1	1	1	2	1	Units 1 & 2	Units 3 & 4
Date	6/21/09	6/21/09	6/23/09	6/23/09	6/23/09	6/23/09	8/10/09	9/21/09	9/21/09
Time	9:30	21:00	9:30	21:30	9:00	9:17	11:30	-	-
% Total Moisture	7.20	6.20	7.53	6.99	7.57	7.44	5.89	9.84	10.13
Dry Basis Values:									
Heating Value, Btu/lb	13,523	13,333	13,166	13,878	13,163	12,837	13,205	12,974	13,151
% Sulfur	2.47	1.92	2.34	2.26	2.22	2.87	1.52	3.4	3.34
% Ash	9.21	11.26	11.79	6.01	9.53	12.19	11.99	9.57	9.35
Cl (ppm)	114	88.6	104.1	105.7	1,834	2,006	471	1,676	1,915

Table 2-7
Coal Short Proximate Analysis Data for 2010 Host Sites

Site	**Plant D-3**		**Plant D-4**		**Site U**	**Plant D-5**	
Units	1	1	2	2	1	4	4
Date	4/13/10	4/14/10	4/14/10	4/15/10	5/6/10	6/29/10	6/30/10
Time	13:00	09:00	14:00	10:00	16:30	09:00	09:00
% Total Moisture	5.62	5.40	4.70	4.06	30.27	16.29	17.61
Dry Basis Values:							
Heating Value, Btu/lb	11,284	12,910	12,867	13,368	11,912	12,558	12,459
% Sulfur	2.67	1.65	1.03	1.27	0.43	3.93	4.11
% Ash	12.2	14.5	14.4	12.8	7.93	11.8	12.5
Cl (ppm)	1,052	534	688	538	25	2,260	2,450

At each site, samples were collected of absorber slurry. For the 2009 sites this included two absorbers on the host FGD system at Plant B, the absorbers on each of two units at Site LMA007L, the single JBR absorber at Site C, and the single Units 1 and 2 absorber for Site E1. For Units 3 and 4 at Site E1, all four absorbers blow down from their lower loop to a common blow down tank, and the absorber sample for this FGD system was collected from this tank rather than from any one particular absorber. At Sites LMA007L and E1, samples were also collected of the feed to the FGD wastewater treating system (Equalization Tank effluent) and wastewater treatment discharge.

For the 2010 sites the absorber samples include the individual absorbers for Plant D-3 (Unit 1) and Plant D-4 (Unit 2), both operating absorbers (A and C) at Site U, and the single absorber at Plant D-5 (Unit 4). For Plants D-3/D-4 (two units at a single station) and Plant D-5, samples were also taken of the inlet and outlet water streams from the on-site FGD wastewater treatment (WWT) systems. At Plant D-5 the FGD WWT system also treats the chloride purge stream from another unit that was not sampled. Figure 2-1 illustrates typical sampling locations at the host sites in a generic fashion.

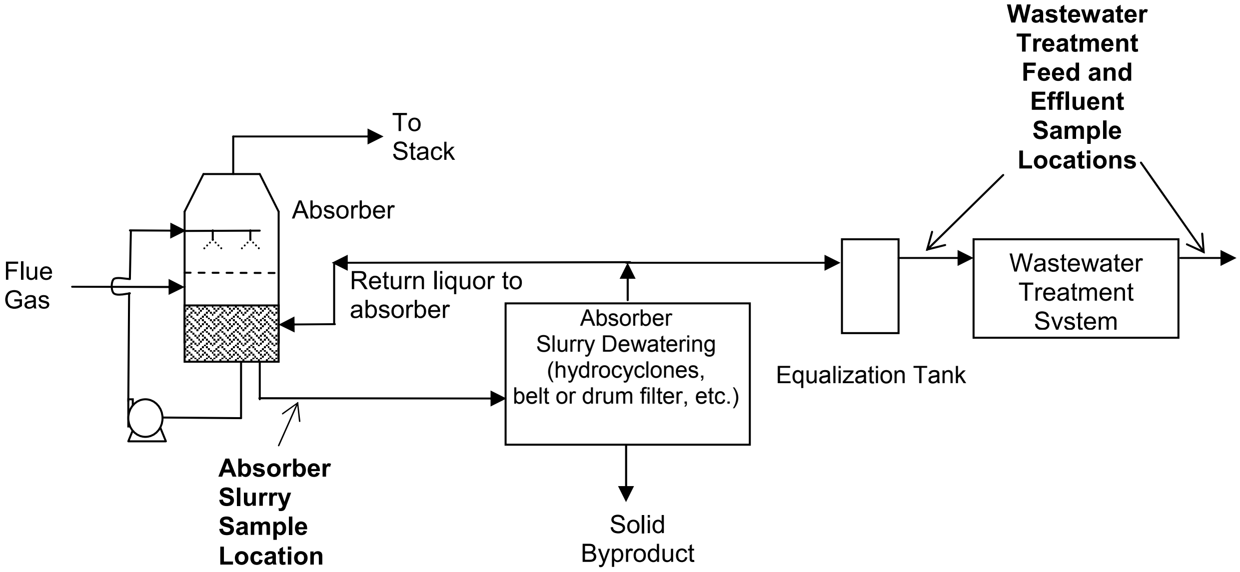

Figure 2-1
Simplified Diagram of a Wet FGD System Showing Typical Selenium Speciation Sample Locations

The results from this sampling and analysis effort are presented in Section 3 of this report. Where appropriate, illustrative tables and graphs are presented to support the conclusions and recommendations made in Section 4.

References

1. Impact of Wet FGD Design and Operations on Selenium Speciation: 2009 Update. EPRI, Palo Alto, CA: 2009. 1017951
2. Identification of Unknown Selenium Species in Flue Gas Desulfurization Water. EPRI, Palo Alto, CA: 2008. 1014944.
3. Speciation of Selenium in Flue Gas Desulfurization Waters. EPRI, Palo Alto, CA: 2009. 1015586.
4. Flue Gas Desulfurization (FGD) Wastewater Characterization and Management: 2007 Update. EPRI, Palo Alto, CA: 2008. 1014073.

3
RESULTS

Selenium Species Concentration Results

This section presents and discusses recent full-scale wet FGD system selenium speciation results for samples collected in April through June of 2010, from FGD systems on four coal-fired units at three electric generating stations. Also reported for comparison are results from sampling in June through September of 2009, on five wet FGD systems sampled at four different utility stations. The 2009 results were reported in a previous Technical Update[1].

Table 3-1 summarizes the selenium speciation results for all nine wet FGD systems sampled in 2009 and 2010. Some details about each FGD system and sample location are shown along with the selenium speciation data. The sample locations primarily include absorber recycle slurry and dewatered FGD liquor sampled upstream and downstream of WWT processes. Not all sites were sampled at WWT locations; some of the wet FGD systems do not have WWT systems. Also, one of the FGD systems (Plant D-5) has a wet electrostatic precipitator (WESP) immediately downstream of the FGD absorber, to remove fine particulate and sulfuric acid mist from the scrubbed flue gas. Water purge from the two fields of the WESP were sampled for liquid-phase selenium concentration and speciation.

The selenium speciation data in Table 3-1 are separated into columns to show the concentrations of the various species identified. These include selenite (SeO_3^{2-}, Se(IV)), selenate (SeO_4^{2-}, Se(VI)), selenocyanate ($SeCN^-$), and selenosulfate ($SeSO_3^{2-}$). The speciation results shown in the table all represent analyses conducted by Trent University.

There are also columns for “unknown” selenium species in the table. These are compounds that elute at various times from the ion chromatography column, and that have been determined by ICP-MS to contain selenium, but for which the exact chemical composition has not been determined. The number of unknown species is also shown in the table, indicating how many peaks were seen at various unidentified-selenium-species elution times. Unknown selenium species were not reported for all samples.

Table 3-1
Summary of FGD System Selenium Speciation Data (all concentrations in µg/L [ppb] as selenium)

EPRI Sample/ Site ID	Coal	Reagent	Oxida-tion	Solids Sep.	Perf. Add.	Sample Location	Sample Date	Se (IV)	Se (VI)	SeCN	$SeSO_3$	Un-known	No. of Un-known	Unac-counted -for Se	Sum of Species	Total Dis-solved
2009 Site Data:																
Plant B	E Bit	LS	Forced	HC/belt	DBA	Absorber A	6/22/09	282	36	21	16	46	3	38	403	440
Plant B	E Bit	LS	Forced	HC/belt	DBA	Absorber B	6/22/09	246	27	21	71	34	3	33	400	432
LMA007L	E Bit	LS	Forced	HC/belt	None	Absorber 1	6/23/09	119	39	2	7	5	2	6	172	178
LMA007L	E Bit	LS	Forced	HC/belt	None	Absorber 2	6/23/09	239	52	9	18	6	1	24	323	347
LMA007L	E Bit	LS	Forced	HC/belt	None	EQ Tank*	6/23/09	155	45	5	26	13	3	-23	244	221
LMA007L	E Bit	LS	Forced	HC/belt	None	WWT effluent	6/23/09	87	44	5	4	5	1	72	145	217
Plant C	E Bit	LS	Forced	Stacking pond	None	Absorber	8/10/09	1	3,909	2	2	2	1	-	3,917	-
E-1	E Bit	LS	Forced	HC/drum	DBA	Abs. Units 1&2	9/22/09	941	15	49	148	988	5	-	2,141	-
E-1	E Bit	LS	Forced	HC/drum	DBA	Abs. Units 3&4	9/22/09	1,680	27	98	253	569	5	-	2,627	-
E-1	E Bit	LS	Forced	HC/drum	DBA	EQ Tank	9/22/09	611	<10	33	116	527	4	-	1,297	-
E-1	E Bit	LS	Forced	HC/drum	DBA	WWT effluent	9/22/09	444	11	54	57	669	4	-	1,235	-
2010 Site Data:																
D-3	E Bit	LS	Forced	HC/belt	None	U1 Absorber	4/14/10	<10	2,090	<10	<10	-	-	-40	<2,120	2,080
D-4	E Bit	LS	Forced	HC/belt	None	U2 Absorber	4/14/10	<10	1,710	<10	<10	-	-	-40	<1,740	1,700
D-3	E Bit	LS	Forced	HC/belt	None	FGD out 1	4/14/10	<10	2,110	<10	<10	-	-	-70	<2,140	2,070

EPRI Sample/ Site ID	Coal	Reagent	Oxida-tion	Solids Sep.	Perf. Add.	Sample Location	Sample Date	Se (IV)	Se (VI)	SeCN	SeSO$_3$	Un-known	No. of Un-known	Unac-counted -for Se	Sum of Species	Total Dis-solved
D-4	E Bit	LS	Forced	HC/belt	None	FGD out 2	4/14/10	<10	1,770	<10	<10	-	-	-110	<1,800	1,690
D-3/4	E Bit	LS	Forced	HC/belt	None	WWT inlet	4/14/10	<10	1,900	<10	<10	-	-	-80	<1,930	1,850
D-3/4	E Bit	LS	Forced	HC/belt	None	WWT effluent	4/14/10	<10	1,810	<10	<10	-	-	-120	<1,840	1,720
Site U	PRB	LS	Natural	Thickener /drum	None	Absorber A	5/7/10	16.5	5.9	-	4.0	-	-	1.5	26.4	27.9
Site U	PRB	LS	Natural	Thickener /drum	None	Absorber C	5/7/10	12.1	7.3	-	5.4	-	-	0.4	24.8	25.2
Site U	PRB	LS	Natural	Thickener /drum	None	Thickener Overflow	5/7/10	4.1	4.2	-	<0.4	-	-	0.0	8.7	8.7
D-5	E Bit	LS	Forced	HC/belt	None	U4 Absorber	6/30/10	39	108	6	1	10	5	17	164	181
D-5	E Bit	LS	Forced	HC/belt	None	WESP Field 1	6/30/10	34	2	0	0	16	2	-5	52	47
D-5	E Bit	LS	Forced	HC/belt	None	WESP Field 2	6/30/10	24	1	0	0	6	1	-5	31	26
D-5	E Bit	LS	Forced	HC/belt	None	FGD out	6/30/10	8	88	0	0	1	1	-1	97	96.5
D-5	E Bit	LS	Forced	HC/belt	None	WWT inlet	6/30/10	4	406	0	1	5	4	-11	416	405
D-5	E Bit	LS	Forced	HC/belt	None	WWT effluent	6/30/10	4	346	0	0	1	1	-16	351	335

*Abbreviations: E Bit – Eastern bituminous; PRB – Powder River Basin; LS – limestone, HC – hydrocyclone; WWT – wastewater treatment; EQ Tank – equalization tank effluent/WWT inlet

The last two columns in the table are for the sum of the species identified and the total dissolved selenium. The sum of the species represents the total selenium concentrations of all of the individual species described above, including unknown species. Ideally, this total should equal the total amount of selenium in the liquid phase (total dissolved selenium) as determined by a direct ICP-MS measurement (no ion chromatography involved). Total dissolved selenium concentrations were not measured by Trent for all of the 2009 samples; they are only available for the data from Plant B and Site LMA007L. For the 2010 samples, all were analyzed for total dissolved selenium concentration by Brooks Rand Laboratories, and these results are shown in the table.

For some samples, the sum of the species and the dissolved selenium values do not agree. If this difference is a large positive number, this suggests there is selenium missing from the speciated results. This difference is called “unaccounted-for” selenium, and is shown to the left of the Sum of Species column in the table. There could be several possible reasons for unaccounted-for selenium, such as colloids that contain selenium that do not pass through the ion chromatographic column, aqueous selenium compounds that do not elute from the columns for some reason, or uncertainties in quantifying peak areas in the ion chromatograms. In these samples the amount not accounted for in the sum of the species varies from positive to negative values, and may just represent analytical error or uncertainty.

The absorber sample selenium species concentration data are also plotted in Figure 3-1. In Table 3-1 and Figure 3-1 it can be seen that the absorber liquor-phase selenium concentrations vary over a wide range, totaling less than 100 µg/L at Site U to nearly 4,000 µg/L at Plant C.

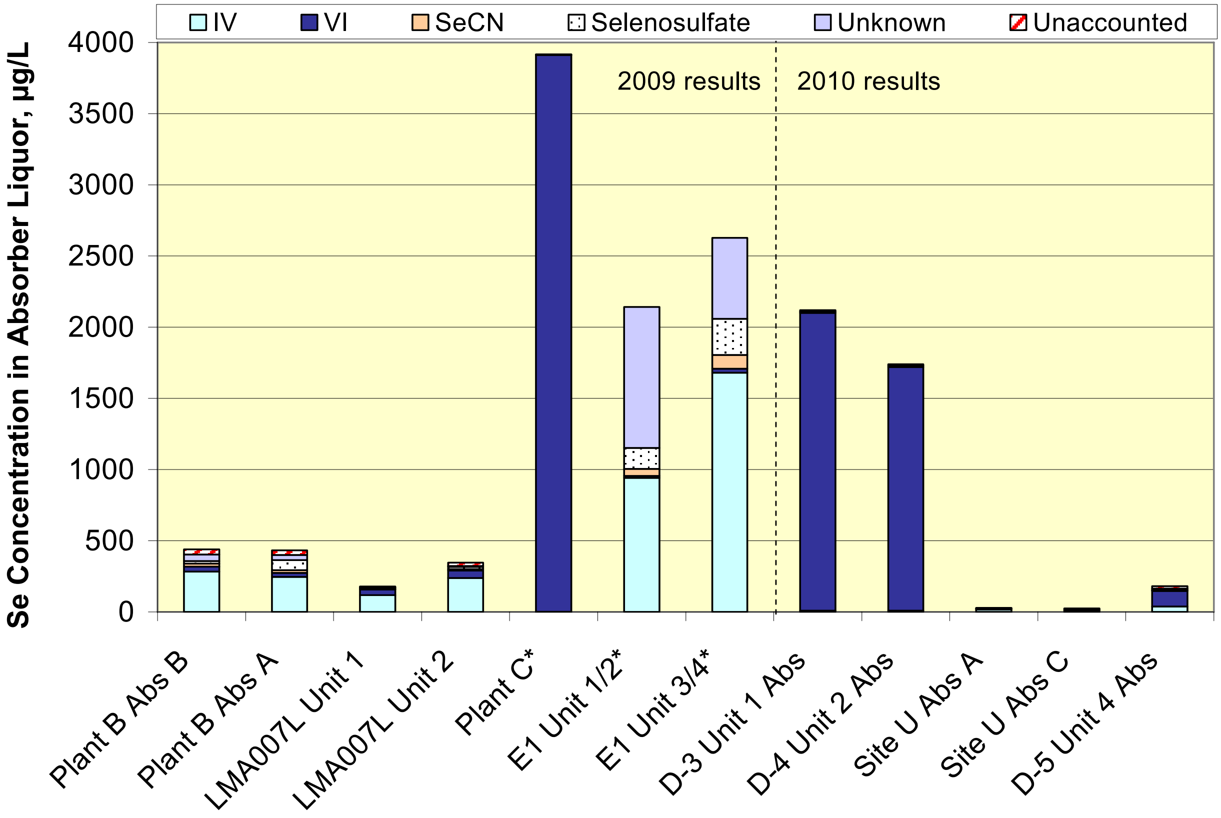

Figure 3-1
Absorber Sample Selenium Concentration Data by Species for the 2009 and 2010 Data Sets

*No unaccounted for selenium values could be calculated for these sites since no dissolved selenium analyses were conducted

For Plant D-5, selenium speciation and concentration data are shown for the water blow down from the plate wash of the two fields of the wet ESP installed downstream of the FGD absorber. The results show considerably lower concentrations of total selenium in the wet ESP blow down than in the absorber liquor, and considerably higher percentages of selenite versus selenate when compared to the absorber liquor selenium speciation. This suggests that the selenium present in the wet ESP blow down liquor represents selenium absorbed from the flue gas in the wet ESP rather than from carryover of selenium species in absorber slurry droplets that are collected. If the selenium was due to carryover, a much higher percentage of selenate would be expected. An unexpected result is the relatively high proportion of unknown selenium species in the wet ESP blowdown water. It is not apparent why unknown selenium species might be forming in these streams.

The selenium species concentration data in Table 3-1 can also be used to determine selenium removal by species across the WWT systems at Sites LMA007L, E1, D-3/D-4, and D-5. Results of these calculations are shown as percent removal by species in Table 3-2.

Table 3-2
Observed Selenium Removal by Species across Wastewater Treatment Systems Sampled

EPRI Sample/Site ID	Observed Selenium Removal Across Wastewater Treatment Plant, % of Dissolved Selenium Total						Observed Selenium Removal Based on Total Dissolved
	Se (IV)	Se (VI)	SeCN	$SeSO_3$	Unknown Species	Total Based on Sum of Species	
LMA007L	44	2	-2	84	63	40	2
E1	27	-10	-64	51	-27	5	Not measured
D-3/D-4	-	5	-	-	-	5	7
D-5	0	15	-	100	80	16	17

The results show that two systems remove selenite at significant percentages, with the system at Site LMA007L being somewhat more effective than that at E1 (44% removal versus 27%). For the other two WWT systems, at Plants D-3/D-4 and D-5, the selenite concentrations are so low that meaningful removal percentages cannot be calculated. None of the four systems is very effective at removing selenate, with apparent removal percentages ranging from -10 to +15%. Low removal percentages are an expected result, as selenate is not typically removed at high efficiency by traditional iron co-precipitation processes. Also, none of the systems remove selenocyanate, and the system at Site E1 may even form some. However, these results may be within sampling and analytical variability due to the low selenocyanate concentrations measured. Three of the systems appear to remove selenosulfate at significant percentages (51% to 100%), although at Plant D-5 the concentrations measured are low and the percentages may not be meaningful. The systems at Site LMA007L and Plant D-5 appear to remove a significant percentage of the unknown selenium species, while unknown species appear to form across the system at Site E1.

As mentioned above, for all of the species other than selenate and (for some sites) selenite, the concentrations measured at the WWT inlets were generally low, so the percentage removal values may not be meaningful. Also, in some cases there could be conversion to other species across the WWT systems due to pH and ORP changes, rather than removal per se. The best indicator of the WWT system effectiveness is to compare the inlet and effluent total dissolved selenium concentrations (or sum of the species for Plant E1, where the total dissolved selenium was not measured). Overall, the WWT systems removed only 2 to 17% of the total dissolved selenium (5% of the sum of the selenium species at Plant E1). These results suggest that none of the four WWT systems is very effective at removing selenium, even the two treating low-selenate-content waters, at Site LMA007L and Plant E1.

Selenium Speciation by Percentage of Total Dissolved Selenium

Table 3-3 shows the results in Table 3-1 expressed as a percentage of the total dissolved selenium concentrations in the liquor samples. For the samples from Plant C and Site E1 there are no separate total dissolved selenium analytical results, so for these samples the percentages in

Table 3-3 are based on the sum of the individual species concentrations from the selenium speciation results in Table 3-1. The absorber sample selenium speciation results are also plotted as percentages in Figure 3-2.

The data show a relatively consistent range of selenite concentration percentages in the absorber samples from five of the nine FGD systems sampled: Plant B, Site LMA007L, Site U and both FGD systems at Site E1. Selenite percentages range from 44% to 69% in these samples. However, the absorber samples from Plant C and Plants D-3 and D-4 show essentially no selenite. Instead, 100% of the selenium species in these samples were identified as selenate. The Plant D-5 absorber sample results lie between these extremes, showing a low percentage of selenite (22%) and a relatively high percentage of selenate (60%) but not 100% selenate. A potential explanation for the wide range in selenate percentage seen in these results is discussed later in this section.

These data show low percentages of selenocyanate in all of the samples (0 to 5%) and relatively low percentages of selenosulfate in the absorber samples (0% to 21%). A much wider range is seen for the percentage of unknown selenium species in the absorber samples (0% to 46%).

In a previous report, some discussion was included about an apparent relationship between the use of DBA to enhance SO_2 removal performance in the FGD system and the formation of unidentified selenium compounds[2]. This effect is relatively consistent in the 2009 data, where three of the FGD systems used DBA as a performance additive. The previous Technical Update for this project included a data plot that illustrated this effect[1].

Table 3-3
Selenium Speciation Results for Samples from Limestone Forced Oxidation FGD Systems with and without DBA Additive

							Percent of Dissolved Selenium Total					
EPRI Sample/Site ID	**Coal**	**Reagent**	**Oxidation**	**Solids Sep.**	**Perf Add.**	**Sample Location**	**Se (IV)**	**Se (VI)**	**SeCN**	**SeSO$_3$**	**Unknown Species**	**Unaccounted-for Selenium**
2009 Site Data:												
Plant B	E Bit	LS	Forced	HC/belt	DBA	Absorber A	64%	8%	5%	4%	10%	9%
Plant B	E Bit	LS	Forced	HC/belt	DBA	Absorber B	57%	6%	5%	16%	8%	8%
LMA007L	E Bit	LS	Forced	HC/belt	None	Absorber 1	67%	22%	1%	4%	3%	3%
LMA007L	E Bit	LS	Forced	HC/belt	None	Absorber 2	69%	15%	2%	5%	2%	7%
LMA007L	E Bit	LS	Forced	HC/belt	None	EQ Tank	70%	20%	2%	12%	6%	-10%
LMA007L	E Bit	LS	Forced	HC/belt	None	WWT Effluent	40%	20%	2%	2%	2%	33%
Plant C*	E Bit	LS	Forced	Stacking pond	None	Absorber	0%	100%	0%	0%	0%	-*
E-1*	E Bit	LS	Forced	HC/drum	DBA	Absorber 1/2	44%	1%	2%	7%	46%	-*
E-1*	E Bit	LS	Forced	HC/drum	DBA	Absorber 3/4	64%	1%	4%	10%	22%	-*
E-1*	E Bit	LS	Forced	HC/drum	DBA	EQ Tank	47%	<1%	3%	9%	41%	-*
E-1*	E Bit	LS	Forced	HC/drum	DBA	WWT Effluent	36%	1%	4%	5%	54%	-*
2010 Site Data:												
D-3	E Bit	LS	Forced	HC/belt	None	U1 Absorber	<0.5%	100%	<0.5%	<0.5%	-	-2%
D-4	E Bit	LS	Forced	HC/belt	None	U2 Absorber	<0.6%	100%	<0.6%	<0.6%	-	-2%
D-3	E Bit	LS	Forced	HC/belt	None	FGD out 1	0.5%	100%	0.5%	0.5%	-	-3%
D-4	E Bit	LS	Forced	HC/belt	None	FGD out 2	<0.6%	100%	<0.6%	<0.6%	-	-7%
D-3/4	E Bit	LS	Forced	HC/belt	None	WWT inlet	<0.5%	100%	<0.5%	<0.5%	-	-4%

EPRI Sample/Site ID	Coal	Reagent	Oxidation	Solids Sep.	Perf Add.	Sample Location	Percent of Dissolved Selenium Total					
							Se (IV)	**Se (VI)**	**SeCN**	**$SeSO_3$**	**Unknown Species**	**Unaccounted-for Selenium**
D-3/4	E Bit	LS	Forced	HC/belt	None	WWT outlet	<0.6%	100%	<0.6%	<0.6%	-	-7%
Site U	PRB	LS	Natural	Thickener/drum	None	Absorber A	59%	21%	-	14%	-	5%
Site U	PRB	LS	Natural	Thickener/drum	None	Absorber C	48%	29%	-	21%	-	2%
Site U	PRB	LS	Natural	Thickener/drum	None	Thick. OF	47%	48%	-	5%	-	0%
D-5	E Bit	LS	Forced	HC/belt	None	U4 Absorber	22%	60%	3%	1%	6%	9%
D-5	E Bit	LS	Forced	HC/belt	None	WESP-1	72%	4%	0%	0%	34%	-11%
D-5	E Bit	LS	Forced	HC/belt	None	WESP-2	92%	4%	0%	0%	23%	-19%
D-5	E Bit	LS	Forced	HC/belt	None	FGD out	8%	91%	0%	0%	1%	-1%
D-5	E Bit	LS	Forced	HC/belt	None	WWT inlet	1%	100%	0%	0%	1%	-3%
D-5	E Bit	LS	Forced	HC/belt	None	WWT outlet	1%	100%	0%	0%	0%	-5%

*No total dissolved selenium analyses for these samples, percentages are based on the sum of the species; by definition there are no unaccounted-for species

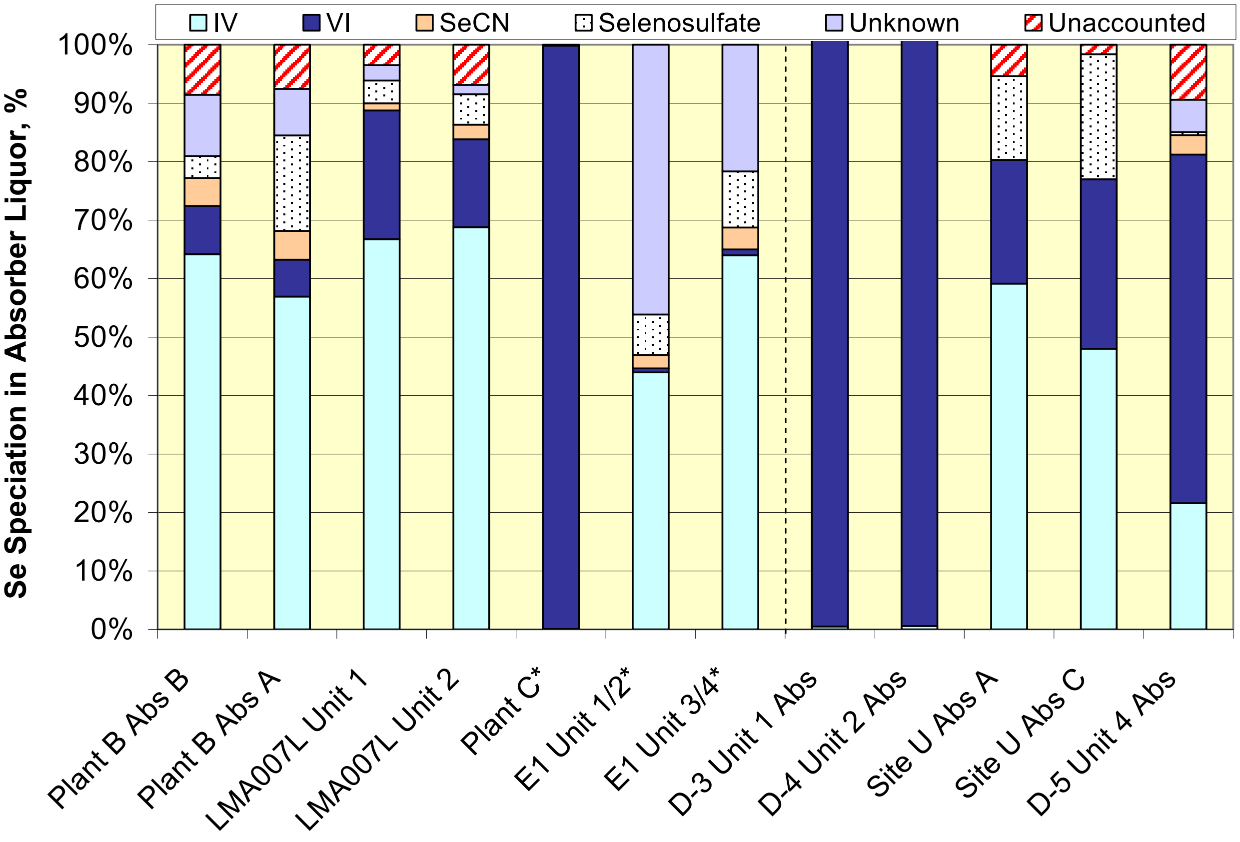

Figure 3-2
Absorber Sample Selenium Speciation Percentages for the Current Data Set

*No unaccounted for selenium values could be calculated for these sites since no total dissolved selenium analyses were conducted

The percentage of "unaccounted-for" selenium can be calculated for the samples from Plant B and Site LMA007L of the 2009 sites, which have total dissolved selenium analysis results available, and all of the 2010 site results. Of the available absorber samples for which unaccounted-for selenium could be calculated, the results show -2% to +9% unaccounted for, which is likely within analytical tolerances. Because most of the calculated percentages were low, no trends were apparent in these data for effects of FGD conditions on percentage of unaccounted-for selenium.

FGD Major Analyte Results

Table 3-4 summarizes the results of major FGD analyte analyses in samples collected during the 2009 and 2010 sampling efforts. The absorber slurry solid results show essentially complete sulfite oxidation in these gypsum-producing FGD systems, including Site U that was operating in a high, natural sulfite oxidation mode. Only the Site E1 Unit 3/4 results show less than 100% oxidation. The absorber pH values measured were all in the range of 5.24 to 5.95, again with the exception of the Site E1 Unit 3/4 sample, which reflects lower pH operation in the lower loop of this dual-loop absorber. Correspondingly, the absorber samples show good limestone utilization, in the range of 92% to 98%, this time with the exception of the sample from the JBR at Plant C.

Table 3-4
Summary of FGD Absorber Analyte Results

	Plant B				**Site LMA007L**		**Plant C**	**Site E1**		**Plant D-3**	**Plant D-4**	**Site U**		**Plant D-5**
Description	Abs A	Abs B	Abs A	Abs B	Unit 1	Unit 2	JBR	Units 1&2	Units 3&4	Unit 1	Unit 2	Abs A	Abs B	Unit 4
Date	6/21/09		6/23/09		6/23/09		8/10/09	9/22/09		4/14/10		5/7/10		6/30/10
Time	8:01	8:18	12:20	12:30	11:02	11:15	7:20	14:02	14:25	8:15	8:53	10:05	11:03	11:50
pH	5.50	5.65	5.61	5.57	5.43	5.50	5.68	5.52	4.62	5.24	5.68	5.29	5.48	5.95
Temperature	51.1	50.9	52.3	52.1	52.3	53.5	48.7	57.5	54.0	51.9	52.1	57.8	58.2	56.7
ORP	201	208	-*	-*	-*	-*	632	155	134	622	595	114	107	216
Solid Results:														
Ca, mg/g	226	232	231	231	228	234	251	234	227	252	243	241	248	257
Mg, mg/g	0.30	0.30	0.56	0.64	0.3	0.1	0.7	0.13	0.06	0.1	0.2	0.07	0.10	0.5
SO_3, mg/g	-	-	-	-	<7	<7	<0.7	<0.7	8	<0.6	<0.6	<0.6	<0.6	<0.7
SO_4, mg/g	497	503	499	491	514	516	445	521	519	548	538	553	554	550
CO_3, mg/g	7.2	9.5	14	23	0	0	84	17.3	6.9	0.1	2.9	0.2	0.4	10
Inerts, wt%	3.92	3.39	2.85	2.91	2.71	2.29	1.72	0.64	0.48	2.78	2.19	1.66	1.51	1.30
Solids, wt%	10.8	10.8	12.6	12.8	17.3	25.2	19.3	25.4	26.1	17.9	16.0	10.7	11.3	20.0
Sulfite Oxidation, %	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	98.2	100.0	100.0	100.0	100.0	100.0
Limestone Utilization, %	95.6	94.9	93.9	91.5	98.0	97.3	76.1	94.2	97.6	96.8	96.9	98.4	97.6	94.4
Solid Phase Analysis Closures:														
Weight, %	-4.3	-3.3	-4.0	-4.1	-3.8	-3.3	-3.5	-2.6	-3.9	3.3	0.8	1.9	2.6	3.7
Molar, %	3.4	3.6	3.2	2.7	3.1	4.3	2.1	1.3	0.5	4.9	3.6	2.3	3.5	6.4

	Plant B				**Site LMA007L**		**Plant C**	**Site E1**		**Plant D-3**	**Plant D-4**	**Site U**		**Plant D-5**
Liquor Results:														
Ca^{++}, mg/L	5,135	4,055	5,668	4,905	4,409	5,305	2,016	8,144	8,057	2,755	4,579	780	733	4,927
Mg^{++}, mg/L	4,793	3,600	5,319	4,488	4,230	4,912	1,853	6,208	5,848	1,333	1,366	1,594	1,767	2,251
Na^+, mg/L	1,375	1,095	1,580	1,341	399	436	383	2,641	2,547	111	119	4,043	4,440	410
Br^-, mg/L	386	297	441	385	285	330	-	0	0	22	28	144	146	38
Cl^-, mg/L	22,200	16,700	24,600	21,400	19,000	21,900	7,027	34,100	28,700	8,149	8,740	6,333	6,688	12,270
$CO_3^=$, mg/L	87	114	140	142	112	112	83	98	20	170	184	24	20	71
$SO_3^=$, mg/L	2	<3	<5	<3	<3	<4	<1	52	665	<2	<2	51	71	<2
$SO_4^=$, mg/L	2,095	2,186	2,111	2,367	2,156	2,075	2,408	2,264	2,535	3,617	1,843	7,212	7,401	1,558
$S_2O_6^=$, mg/L	861	774	861	789	130	146	-	2,150	2,089	935	2,002	194	180	4,525
$S_2O_8^=$, mg/L	<30	<30	<30	<30	<30	<40	-	<30	<40	<6	2,487	<5	<4	2
NO_3^-, mg/L	-	-	-	-	-	-	1,235	-	-	-	-	-	-	-
Succinic, mg/L	<10	<20	<10	<20	-	-	-	403	372	-	-	-	-	-
Glutaric, mg/L	18	24	<5	<9	-	-	-	1,485	1,409	-	-	-	-	-
Adipic, mg/L	<3	<3	<3	<4	-	-	-	197	208	-	-	-	-	-
THS, mm/L as $SO_4^=$	57.3	49.1	65.3	61.4	27.2	28.1	24.8	49.9	61.7	45.8	56.6	86.2	91.5	62.8
Potential S/N Species, mm/L as $SO_4^=$ (see text)	35.5	26.3	43.3	36.7	3.1	4.7	-0.3	-1.1	1.0	-3.5	-13.5	8.1	11.4	-9.9
Liquor Charge Imbalance Calculated %**	0.0	-0.2	0.1	-1.7	-0.4	1.2	0.3	-0.2	5.1	-10.4	5.5	0.9	2.5	9.7

*ORP values not available – field-recorded ORP values misplaced for Plant B on 6/23/09; ORP meter mistakenly not packed for day trip to Site LMA007L

**Charge imbalance % calculated as total cation meq/L minus total anion meq/L divided by average of total cations and total anions, times 100

It is not known why this sample exhibited such low utilization at this pH. It is known that a JBR is, by design, not completely well mixed like in a conventional FGD reaction tank, so it is possible that this sample represents effects of excess limestone settled to the bottom of the reaction tank.

The table includes oxidation-reduction potential (ORP) values for most of the samples. All of the ORP values shown are relative to a silver/silver chloride (Ag/AgCl) reference electrode. The intent was to collect ORP for all measurements, but during the 2009 sampling effort the ORP meter was inadvertently not packed for the trip to Site LMA007L (these samples were collected in a day trip while sampling at a station several hours away). Also, the recorded ORP values for one day of measurements at Plant B were misplaced.

The ORP values for the FGD systems that do not use DBA as a performance additive appear to correlate well with the selenate percentages in the corresponding absorber samples. This relationship is illustrated in Figure 3-3.

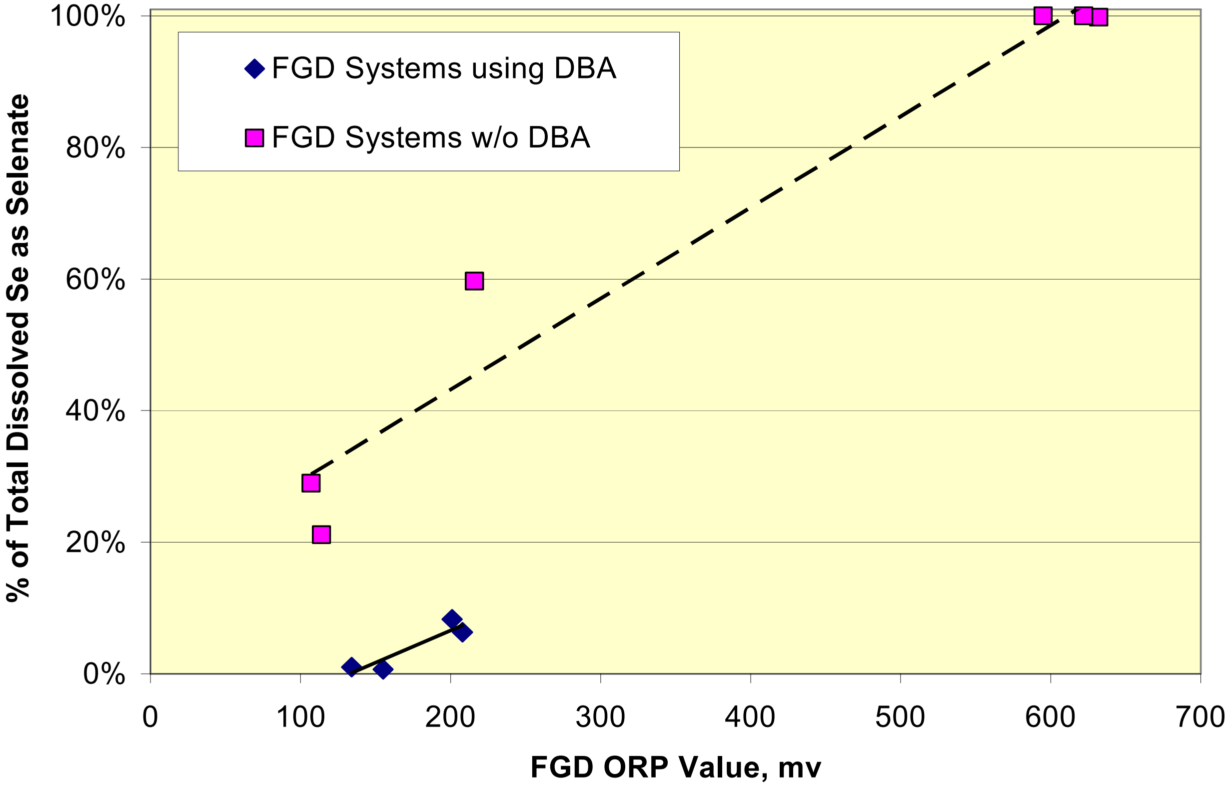

Figure 3-3
Absorber Liquor ORP versus Selenate Percentage in the Liquor

Higher ORP values correspond with more oxidizing conditions in the absorber liquor. At Plants C, D-3 and D-4 the measured ORP values of 595 mV or higher correspond with complete oxidation of selenite to selenate. In contrast, at Site U the ORP values of 107 to 114 mV correspond with low conversion to selenate (21 to 29%). The selenate conversion percentage for Plant D-5, with an intermediate ORP value of 216 mV, falls between these two extremes. While the figure includes relatively few data points, these data suggest that ORP conditions in the absorber reaction tank liquor may strongly influence the conversion of selenite to selenate. In fact, Mitsubishi Heavy Industries reportedly has a patented process where the ORP in the reaction tank of their limestone forced oxidation wet FGD systems is controlled to an optimum value to ensure complete sulfite oxidation while minimizing selenate formation[3].

Four of the ten data points for which ORP values are available are from FGD systems that use DBA as a performance additive. These data points are plotted separately in Figure 3-3. At a given ORP value the selenite-to-selenate oxidation percentages for the systems that use DBA fall well below the percentages for the systems that do not use DBA. An apparent beneficial effect of DBA addition in lowering selenite to selenate oxidation at FGD conditions has been noted in previous EPRI funded bench-scale testing[4], and this effect is supported by this limited number of full-scale FGD data points.

Of the four DBA user data points, the two lower ORP data are from Site E1 with relatively high DBA concentrations, while the ~200 mV ORP data are from Plant B with low DBA concentrations. If there is a DBA effect on selenite oxidation and the effect is concentration dependent, it may be greater at Site E1 than at Plant B. Thus, although these data appear to show a DBA effect (e.g., the presence of DBA lowers conversion to selenate), the slope of the “with DBA” line may be impacted by the relative DBA concentrations in the FGD systems at these two stations.

The authors of this report have collected ORP data on reaction tank slurry from approximately 20 limestone forced oxidation FGD systems over the past four years, and can state that the values measured as part of this effort reasonably represent that range. A review of unpublished data showed values ranging from 75 mV to over 600 mV ORP values measured at previously sampled FGD systems. Corresponding selenium speciation results are not available for these previous ORP measurements.

The FGD liquor analytical results in Table 3-4 show that four of the nine FGD systems sampled operate in relatively closed-loop fashion with respect to wastewater blow down. Plant B operates with 17,000 to 25,000 ppm chloride levels, Site LMA007L operates with about 19,000 to 21,000 ppm chloride levels, and the two FGD systems at Site E1 operate with upwards of 30,000 ppm chloride levels. The other five FGD systems operate more open loop, with chloride levels of 6,000 to 12,000 ppm (the latter representing relatively open-loop operation for the Plant D-5 FGD system treating flue gas from a high-chloride coal).

Several of the absorber samples were analyzed for sulfur species other than the traditional sulfite and sulfate ions, including dithionate ($S_2O_6^{2-}$), peroxydisulfate ($S_2O_8^{2-}$), and total hydrolyzable sulfur (THS). Dithionate is thought to be formed by competing reactions among the metal-catalyzed chain reactions that lead to sulfite oxidation, while peroxydisulfate, also called peroxodisulfate or persulfate, is formed similarly but under more highly oxidizing conditions. Research conducted in Japan has shown that the presence of peroxydisulfate in oxidizing FGD environments correlates with high selenite oxidation.[5]

Only one of the samples analyzed contained measurable concentrations of peroxydisulfate, from Plant D-4 (ORP ~600 mV). Peroxydisulfate was not found in measurable concentrations in the liquors from the other two highly oxidized FGD systems at Plant C and Plant D-3. However, the sample preservation techniques may not have been optimized for stabilizing peroxydisulfate, so it is possible that these results are influenced by loss of peroxydisulfate from some samples. All of the samples were pressure filtered at the sample tap into preserving solutions. The samples from Site E1 and all of the 2010 site samples were diluted and adjusted to pH 8 with sodium hydroxide according to the method of Gutberlet, et al.[6], while for the 2009 sites other than Site E1 the peroxydisulfate samples were diluted and preserved in a borate buffer/formaldehyde solution at pH 7.5 according to EPRI Method A-1.[7]

One theory discussed in a previous Technical Update from this project is that dithionates could serve as a precursor to reactions that form seleno-sulfur species, and that these seleno-sulfur species represent a portion of the unknown selenium species found during selenium speciation measurements[1]. If so, the presence of dithionates should correlate with the presence of unknown selenium species in FGD liquors. This potential relationship is explored in Figure 3-4. Although the earlier data from the 2009 sites showed a possible correlation, the data from Site D-5, with a high dithionate concentration but a low measured percentage of unknown selenium species, does not support such a correlation.

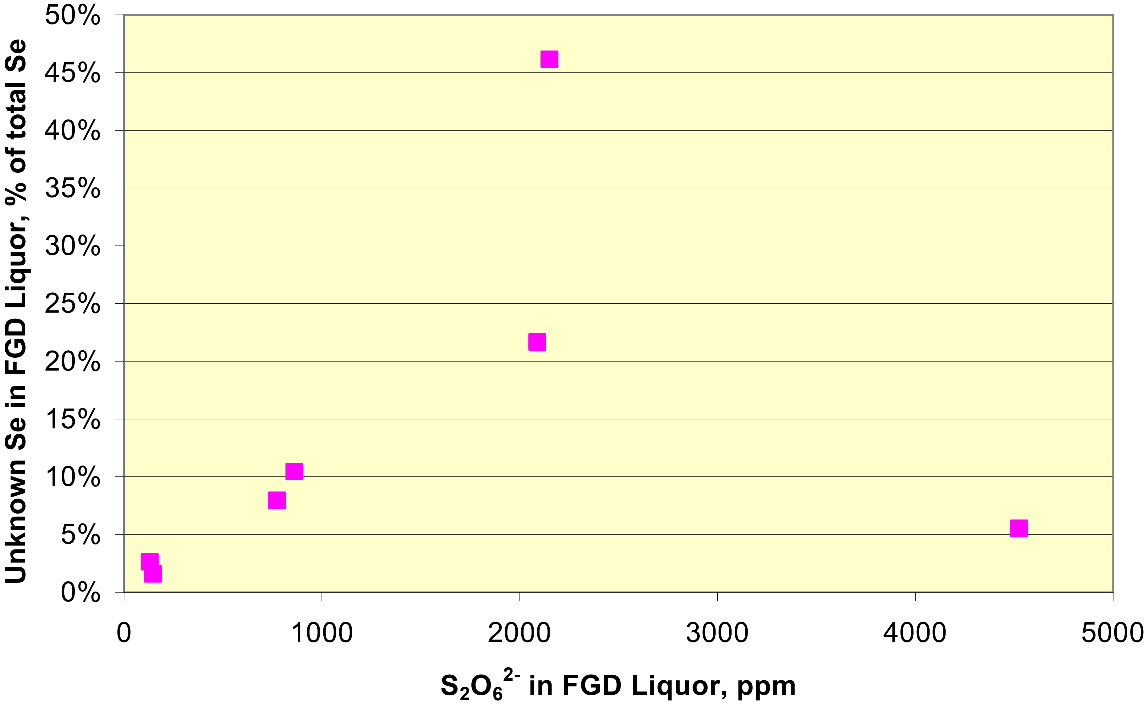

Figure 3-4
Observed Percentage of Unknown Selenium Compounds in FGD Absorber Liquor versus Dithionate Concentrations

The third additional sulfur analysis conducted was for total hydrolyzable sulfur (THS). In this analysis the FGD liquor is digested under strong hydrolysis conditions to convert all sulfur forms to sulfate. The digested sample is analyzed for liquid-phase sulfate and this number is compared to the concentrations of all previously analyzed sulfur species (sulfite, sulfate, and for these samples, dithionate and peroxydisulfate). This difference is called the potential sulfur-nitrogen (S/N) species in the FGD liquor. Sulfur-nitrogen species are formed in some FGD systems by reaction of sulfite with nitrite formed by absorption of NO_X species from the flue gas. Only the FGD liquor from Plant B and possibly Site U showed measurable concentrations of potential sulfur-nitrogen species; Plant B and Site U do not have any NO_X controls other than low NO_X burners, so nitrites may be absorbed in these FGD liquors. Also, the Plant B FGD system operates relatively closed loop with respect to water balance, so there is opportunity for the highly soluble sulfur-nitrogen species to concentrate. Thus, the presence of sulfur-nitrogen species in significant quantities is quite plausible for this FGD system. The other samples that did not show measurable quantities of potential sulfur-nitrogen species appear to have no sulfur species present other than the sulfite, sulfate, dithionate and peroxydisulfate concentrations indicated.

Trace Element Concentration Results for FGD Samples

Samples of absorber liquor and solids were analyzed for trace metals as part of the current project. The results of these analyses are summarized in Tables 3-5 and 3-6, respectively. The tables include data quality flags in parentheses immediately following each flagged datum in the tables. The key to the data quality flags is included in Table 3-7.

The results in Table 3-5 show that the liquors from the FGD systems at Site E1 contain elevated concentrations of chromium, copper and vanadium compared to the liquors from the other FGD systems sampled. This may be a result of the DBA used at Site E1, which is added to maintain relatively high DBA concentrations (>2000 ppm). It is not known if any of these trace metals influence the formation of unknown selenium species.

Other notable concentration results in Table 3-5 are that the liquor manganese concentrations were relatively high at Plant B (283,000 µg/L or higher), and that the liquor mercury concentrations were relatively high at Plant D-4 (>500 µg/L). These results are discussed further below.

The results in Tables 3-5 and 3-6 were combined with wt% solids data from Table 3-4 to calculate the partitioning of selenium, manganese, iron and mercury between the liquors and solids in these FGD systems. The results of these calculations are summarized in Table 3-8.

Table 3-5
Absorber Liquor Trace Metals Summary (all concentrations in µg/L [ppb])*

Site	**Plant B**				**LMA007L**		**Plant C**	**E1**		**Plant D-3**	**Plant D-4**	**Site U**		**Plant D-5**
Date	6/21/09	6/23/09	6/21/09	6/23/09	6/23/09		8/10/09	9/22/09		4/14/10	4/14/10	5/7/10		6/30/10
Loc.	Abs A	Abs A	Abs B	Abs B	Abs 1	Abs 2	JBR	Abs 1&2	Abs 3&4	Unit 1 Abs.	Unit 2 Abs.	Abs. A	Abs. C	Unit 4 Abs.
Ag	<2.0 (ML)	<2.0 (ML)	<2.0 (ML)	<2.0 (ML)	<2.0	<2.0	-	3.87 (ML)	5.44	-	-	-	-	-
Al	1,040	980	621	698	1,150	803	-	176	1,777	358	84.5	-	-	51.2 (MRL)
As	222 (LCSL)	269	144 (LCSL)	212	154	199	70.6	1,120	938	1.66	2.22	-	-	5.02
Ba	691	883	537	696	1120	1430	-	3,780 (MH)	2,680	315	453	-	-	734
Be	5.21	4.39 (CH)	3.87	2.66 (CH)	2.29	3.21	1.17	<1.0	<1.0	2.70	1.62 (M)	-	-	0.428 (MRL)
Cd	53.2	59.2	42	48.1	28.4	29.1	195	331 (ML)	259	8.33	7.69	-	-	16.3
Co	676	709	500	589	253	269	-	379	317	13.2	6.28	-	-	51.8
Cr	22.2 (MH)	24.7 (MH)	16.6 (MH)	21.8 (MH)	37.1	46.9	32.1	81.6 (MH)	165	26.3	51.9	-	-	≤1.05
Cu	51.5	49.1 (CL)	33	28.9 (CL)	15.9	39.6	54.9	146 (ML)	154	60.8	9.90	-	-	16.4
Fe	642	921 (CH)	572	764 (CL)	1,460	1,230	166	656	2,860	64.2 (MRL)	121 (MRL)	RP**	RP	169 (MRL)
Hg	<0.71	0.36	0.426	0.52 (D)	2.38	11.1	84.0	1.76	5.01	146	521	5.29	5.74	0.38

Site	**Plant B**				**LMA007L**		**Plant C**	**E1**		**Plant D-3**	**Plant D-4**	**Site U**		**Plant D-5**
Date	6/21/09	6/23/09	6/21/09	6/23/09	6/23/09		8/10/09	9/22/09		4/14/10	4/14/10	5/7/10		6/30/10
Loc.	Abs A	Abs A	Abs B	Abs B	Abs 1	Abs 2	JBR	Abs 1&2	Abs 3&4	Unit 1 Abs.	Unit 2 Abs.	Abs. A	Abs. C	Unit 4 Abs.
Mn	410,000	346,000	380,000	283,000	28,900	28,400	-	39,800	35,600	11,300	1,380	RP	RP	60,400
Mo	12.4	8.61	23.2	17.4	65.6	45.7	-	329 (MH)	259	0.627	0.942	-	-	40.2
Ni	2,650	2,830	1,980	2,310	2,100	2,530	710	1,660	1,610	270	207	-	-	1,070
Pb	<7.0	<7.0	<7.0	<7.0	<7.00	<7.00	<0.51	19.2	<10.00	≤0.158	≤0.158	-	-	≤0.158
Sb	2.53 (B)	4.5 (B)	<2.00	2.29 (B)	4.8	2.76	-	16	15	0.398	0.725	-	-	3.39
Se	<20.0 (ML)	<20.0 (ML)	<20.0 (ML)	<20.0 (ML)	<20.0	<20.0	4,180	1,820	3,930	2080	1700	27.9	25.2	181
Sr	63,600 (MH)	59,900 (MH)	47,900 (MH)	50,400 (MH)	35,100	38,800	-	42,900	36,400	10,200	14,600	-	-	13,000
Tl	48.3	55.2	33.1	40.3	14.9	16.4	33.4	29.9	21.8	0.427	1.75	-	-	3.46
Ti	603 (MH)	698 (MH)	510 (MH)	638 (MH)	484	519	-	806 (MH)	812	-	-	-	-	-
V	187 (MH)	201 (MH)	136 (MH)	179 (MH)	190	223	-	656 (MH)	1,120	≤0.158	0.197 (MRL)	-	-	≤0.158
Zn	342 (ML)	373 (ML)	237 (ML)	261 (ML)	2,200	2,720	8,170	2,390	1,940	371	137	-	-	119

*See Table B-6 in Appendix B for key to data flags.
**RP – results pending

Table 3-6
Absorber Slurry Solids Trace Metals Summary (all concentrations in µg/g [ppm])*

Site	**Plant B**				**LMA007L**		**Plant C**	**E1**		**Plant D-3**	**Plant D-4**	**Site U**		**Plant D-5**
Date	6/21/09	6/23/09	6/21/09	6/23/09	6/23/09		8/10/09	9/22/09		4/14/10	4/14/10	5/7/10		6/30/10
Loc.	Abs A	Abs A	Abs B	Abs B	Abs 1	Abs 2	JBR	Abs 1&2	Abs 3&4	Unit 1 Abs.	Unit 2 Abs.	Abs. A	Abs. C	Unit 4 Abs.
Ag	<0.40 (LCSH)	<0.40 (LCSH)	<0.40 (LCSH)	<0.40 (LCSH)	<0.40	<0.40	-	<0.40	<0.40	-	-	-	-	-
Al	3,615	2,620	3,150	2,620	3,820	3,160	-	1,020	408	2,800	3,630	928	909	667
As	7.9 (LCSH)	5.88 (LCSH)	6.78 (LCSH)	5.87 (LCSH)	1.96 (LCSH)	1.89 (LCSH)	7.19	3.40	2.50	5.22	4.38	3.31	0.75	1.62
Ba	133	92	124	101	27.0 (CH)	24.2 (CH)	-	7.07	3.40	22.1 (J-M, J-N)	29.9 (J-M, J-N)	6.89 (J-M, J-N)	7.08 (J-M, J-N)	5.63 (D, M)
Be	<0.20	<0.20	<0.20	<0.20	<0.20 (CL)	<0.20 (CL)	0.307	0.333 (CH)	0.244 (CH)	0.82 (MRL)	≤0.30	≤0.29	0.31 (MRL)	0.29 (D)
Cd	0.153	<0.10	<0.10	<0.10	<0.10	<0.10	0.144	0.183	0.252	≤0.035	≤0.036	≤0.035	≤0.036	≤0.034
Co	2.65	2.1	2.49	2.37	1.75	1.62	-	2.43	1.76	0.98	1.22	≤0.39	≤0.40	0.39 (MRL)
Cr	8.29	6.34	7.24	6.48	7.82	7.49	16.7	59.0	48.3	5.28	4.77	4.09	2.57 (MRL)	10.5
Cu	5.08	3.62	4.5	3.92	2.97	2.59	6.06	5.5	3.65	4.67	4.33	7.81	2.33	3.04
Fe	5,170	3,840	4,830	3,980	2,320	1,955	1,370	841	479	2,040	1,810	1,070	681	1,350
Hg	0.782	0.736	0.811	0.810	5.84	5.66	0.061	0.480	0.414	0.07	0.19	3.38	2.8	0.27
Mn	46.9	44.7	50.2	64.4	6.74 (CH)	5.35 (CH)	29.6	9.24 (CH)	10.8 (CH)	134	166	8.12	3.73 (MRL)	70.6
Mo	1.58	1.13	1.41	1.24	1.67	1.61	-	0.689	0.469	≤0.68	≤0.70	0.77 (MRL)	≤0.71	1.02 (MRL)

Site	**Plant B**				**LMA007L**		**Plant C**	**E1**		**Plant D-3**	**Plant D-4**	**Site U**		**Plant D-5**
Date	6/21/09	6/23/09	6/21/09	6/23/09	6/23/09		8/10/09	9/22/09		4/14/10	4/14/10	5/7/10		6/30/10
Loc.	Abs A	Abs A	Abs B	Abs B	Abs 1	Abs 2	JBR	Abs 1&2	Abs 3&4	Unit 1 Abs.	Unit 2 Abs.	Abs. A	Abs. C	Unit 4 Abs.
Ni	30.8	28.4	30.8	32.8	22.4	23	28.6	5.26	2.88	3.17	4.17	1.64 (MRL)	1.79 (MRL)	1.94 (MRL)
Pb	4.04	2.84	3.35	3.5	1.89 (LCSH)	1.79 (LCSH)	3.97	2.8	1.91	1.18 (J-N)	1.60 (J-N)	0.42 (J-N)	0.46 (J-N)	1.82 (M)
Sb	0.854	0.327	0.44	0.279	<0.20	<0.20	-	<0.20	<0.20	0.09 (MRL)	0.12 (MRL)	0.17 (MRL)	0.09 (MRL)	0.24
Se	7.48	6.73	6.43	6.67	19.9	21.7	10.2	5.24 (CH)	<4.0 (CH)	10.1	11.4	≤0.59	≤0.61	1.27 (MRL)
Sr	370	347	386	359	285	285	-	256	256	112	115	88.8	86.7	83.3
Tl	0.159	0.135	0.137	0.121	0.047	0.044	0.18	0.054	<0.03	≤0.066	≤0.068	≤0.066	≤0.069	≤0.065
Ti	182	134	155	132	187	159	-	83.9	49.9	-	-	-	-	-
V	12.2	9.21	10.3	9.2	5.09	4.59	-	14.8 (CL)	9.89 (CL)	3.59 (MRL)	4.14	4.80	4.09	1.61 (MRL)
Zn	22.1	17	18.4	20.6	20.5 (LCSH)	17.5 (LCSH)	21.9	16.7	13.1	5.28 (MRL)	6.47	≤2.22	≤2.12	3.85 (MRL)

*See Table B-6 in Appendix B for key to data flags

Table 3-7
Key to Data Flags Used in Trace Element Analysis Data Tables

Qualifier	Reason
B	Analyte is detected in blank and is within 5x sample concentration
M	Matrix spike is outside acceptance criteria (varies depending on method-includes digestion and post digestion spikes)
C	Continuing calibration verification (CCV) result outside of acceptance, CH (100% + 10%) or CL (100% - 10%)
D	Relative percent difference (RPD) for duplicate analyses above acceptance (varies depending on method)
LCS	Laboratory control sample result was high (LCSH) or low (LCSL), therefore sample result is expected to be biased accordingly
L	Sample result is biased low (this will be attached to the end of a specific flag, e.g. "ML")
H	Sample result is biased high (this will be attached to the end of a specific flag, e.g. "CH")
MRL	Result is greater than the method detection limit but less than the method reporting limit
J-M	Result is estimated; RPD for associated QC sample was above acceptance (varies depending on method)
J-N	Result is estimated; spike recovery for associated QC sample was not within acceptance (varies depending on method)

Table 3-8
Summary of Absorber Slurry Phase Partitioning of Selenium, Manganese, Iron and Mercury

		Se Concentration		Se Partitioning	Mn Concentration		Mn Partitioning	Fe Concentration		Fe Partitioning	Hg Concentration		Hg Partitioning
Site	**Location**	**Liquor* (µg/L)**	**Solids (µg/g)**	**% Se in Liquor**	**Liquor (µg/L)**	**Solids (µg/g)**	**% Mn in Liquor**	**Liquor (µg/L)**	**Solids (µg/g)**	**% Fe in Liquor**	**Liquor (µg/L)**	**Solids (µg/g)**	**% Hg in Liquor**
Plant B	A Abs.	440	7.48	32.7%	410,000	46.9	98.6%	642	5,170	0.1%	<0.71	0.78	<0.7%
	B Abs.	432	6.43	35.6%	380,000	50.2	98.4%	572	4,830	0.1%	0.43	0.81	0.4%
	A Abs.	440	6.73	31.3%	346,000	44.7	98.2%	921	3,840	0.2%	0.36	0.74	0.3%
	B Abs.	432	6.67	30.6%	283,000	64.4	96.8%	764	3,980	0.1%	0.52	0.81	0.4%
LMA-007L	U1 Abs.	178	19.9	4.1%	28,900	6.74	95.3%	1,460	2,320	0.3%	2.38	5.84	0.2%
	U2 Abs.	347	21.7	4.5%	28,400	5.35	94.0%	1,230	1,955	0.2%	11.1	5.66	0.6%
Plant C	JBR	3,971	10.2	61.7%	No data	No data	No data	166	1,370	0.1%	84.0	0.06	85.2%
Site E1	Abs 1&2	2,141	5.24	54.6%	39,800	9.24	92.7%	656	841	0.2%	1.76	0.48	1.1%
	Abs 3&4	2,627	<4	>65.0%	35,600	10.8	90.3%	2,860	479	1.7%	5.01	0.41	3.3%
Plant D-3	U1 Abs.	2,080	10.1	48.5%	11,300	134	27.8%	64	2,040	0.01%	146	0.07	90.3%
Plant D-4	U2 Abs.	1,700	11.4	43.9%	1,380	166	4.2%	121	1,810	0.04%	521	0.19	93.4%
Site U	Abs. A	27.9	0.59	28.3%	No data	8.12	No data	No data	1,070	No data	5.29	3.38	1.3%
	Abs. C	25.2	0.61	24.4%	No data	3.73	No data	No data	681	No data	5.74	2.80	1.6%
Plant D-5	U4 Abs.	181	1.27	36.4%	60,400	70.6	77.4%	169	13.5	4.8%	0.38	0.27	0.6%

Selenium partitioning is of interest because it shows the extent to which selenium absorbed in the FGD system is retained in the liquor and potentially becomes a wastewater treatment issue. Manganese partitioning is an indicator of the extent of oxidizing conditions in the FGD absorber (Mn^{2+} is relatively soluble at FGD conditions while the more oxidized Mn^{4+} is relatively insoluble). Also, lab-scale testing conducted by EPRI suggests that manganese in FGD liquors promotes selenium oxidation, perhaps through some form of catalysis[4]. Iron partitioning is of interest because ferric iron (Fe^{3+}) can precipitate as ferric hydroxides which can adsorb or co-precipitate selenite, removing it from the liquid phase before it is oxidized to selenate or converted to other forms. Finally, mercury partitioning is of interest because, like manganese, it can be an indicator of the extent of oxidizing conditions in the FGD absorber. However, opposite the effect seen for manganese, mercury is more likely to be found in the liquor than adsorbed to the solids at highly oxidizing conditions.

The results in Table 3-8 show a wide range of selenium partitioning in these nine FGD systems, from 4% of the selenium in the absorber slurry in the liquor at Site LMA007L Unit 1 to >65% in the liquor at Site E1 Units 3&4 (Note: the latter percentage was incorrectly reported as >99% in the previous Technical Update[1]. The manganese data show an even wider range, from only 4% in the liquor at Plant D-4 to 97% to 99% in the liquor at Plant B. The iron concentration data show a very narrow range, with most sites showing very little iron in the liquor (0.01 to 0.3% in the liquor). The exceptions are at Site E1, which shows 1.7% of the iron in the liquor in the Unit 3/4 FGD system, and Plant D-5, which shows 4.8% of the iron in the liquor; both are still relatively low percentages in the liquor.

The mercury partitioning results vary over a wide range. Many of the FGD systems were found to have very low percentages of mercury in the liquor, with less than 1% of the mercury found in the liquor at Plants B, LMA007L, and D-5. However, at Plants C, D-3 and D-4, 85 to 93% of the mercury in the FGD slurry was found in the liquor. Factors that appear to affect manganese and mercury partitioning in FGD liquors are discussed further below.

The data in Table 3-8 show that Plant B had the highest iron and manganese concentrations in the absorber slurries of any of the systems sampled. These two metals often enter an FGD system predominantly from the limestone reagent. Limestone reagent trace metal analyses were summarized in Appendix B of the previous Technical Update[1], and show that the limestone used at Plant B has a considerably higher iron and manganese content than the limestones used at the other sites sampled in 2009. The limestone samples from the 2010 sites were analyzed only for selenium content.

ORP and pH values each are known to impact trace element partitioning in FGD slurries. With the exception of the lower loop of the Site E1 Unit 3/4 system, all of the FGD systems sampled were operating in a relatively narrow pH range of 5.29 to 5.95. Thus, ORP may be the predominant factor that controls the partitioning of trace elements in these FGD systems.

Figure 3-5 plots the percentage of each element in the FGD slurry liquor versus the measured ORP for each FGD system for which data are available. This plot shows no apparent trend for selenium with ORP. The percentage found in the liquor varies from 24% to greater than 65% over a narrow range of ORP, and the high ORP (600 mV) partitioning data do not look much different than the low ORP (100-200 mV) data with respect to selenium partitioning. The iron data also show no trend with ORP in this range. Most of the samples show a low percentage of iron in the slurry liquor regardless of ORP over the range of 100 to 600 mV.

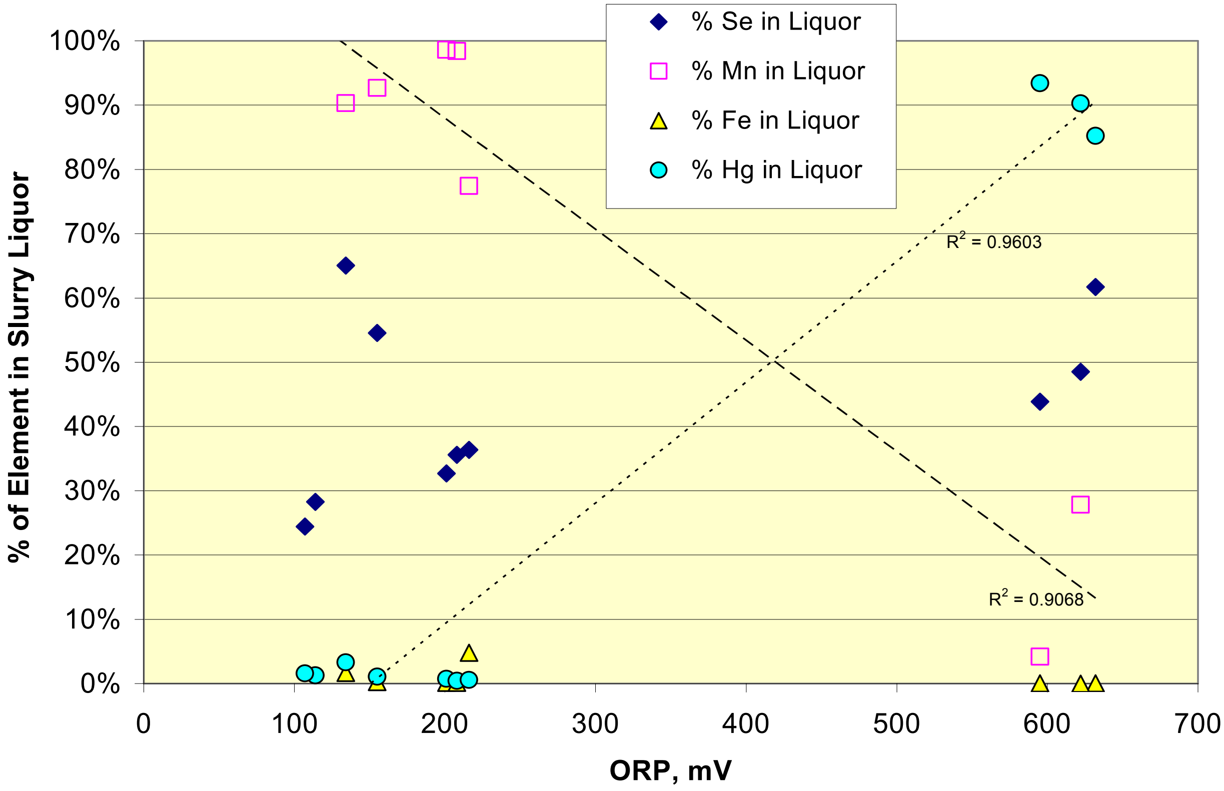

Figure 3-5
Selenium, Manganese and Iron Partitioning to the FGD Liquor versus ORP in the Absorber Slurry

Manganese and mercury both show significant trends with ORP, although in opposite directions. In the 2009 data set no manganese data were available for the one high ORP FGD system at Plant C. With the addition of the data for Plants D-3 and D-4, manganese partitioning data are now available over a wide range of limestone forced oxidation FGD ORP values. The results show an expected trend: below an ORP value of approximately 200 mV, 90% or higher percentages of the manganese was found in the liquor, while at an ORP value around 600 mV, 30% or less was found in the liquor. This trend was expected based on a review of a Pourbaix diagram for manganese. At typical FGD pH values, the diagram shows that the highly soluble Mn^{2+} form is prevalent a lower ORP, but at higher ORP the relatively insoluble MnO_2 (Mn^{4+}) is favored. Bench-scale testing funded by EPRI has shown that ORP conditions that favor manganese partitioning to the solid phase also favors selenite oxidation to the selenate form.

The mercury data also follow an expected trend. At lower ORP nearly all of the mercury is found adsorbed to solids in the FGD slurry, while at high ORP (~600 mV or greater) most of the mercury remains in the liquor. This trend has not often been seen in data from U.S. limestone forced oxidation FGD systems, but Gutberlet, et al., noted this phenomenon on a German limestone forced oxidation FGD system in 1992[8].

One theory on a factor that controls selenium partitioning to the solid phase in FGD systems is the amount of iron hydroxide fines present relative to the mass of selenium. Selenium apparently co-precipitates and/or adsorbs on these fines. A previous EPRI report used field data from a number of full-scale limestone forced oxidation wet FGD systems to show that the mass ratio of iron to selenium in absorber solids was relatively constant.[9] This leads to a theory that in systems with a greater mass ratio of iron precipitates to selenium in the absorber slurry, more selenium should partition to the solid phase.

The selenium and iron concentration data and slurry wt% solids from these samples were used to calculate the ratio of total selenium to solid-phase iron, and the ratio of solid-phase selenium to solid-phase iron. Based on the theory proposed in the previous EPRI report, the latter was expected to show a relatively constant ratio. Instead, this ratio varied over a wide range, from 90:1 to approximately 1,800:1. The percentage of total selenium in the absorber slurry found in the liquor was plotted versus these values in Figure 3-6. With a higher ratio of solid-phase iron to total selenium in the absorber slurry, it might be expected that less selenium would remain dissolved in the liquor. With the exception of the data from Site LMA007L, the data for a low mass ratio of iron to selenium (approximately 500:1 or less) show this expected trend. At higher ratios, the percentage of selenium remaining in the liquor remains relatively flat, in the range of 24% to 36%. It is not obvious why this relationship should “flatten” at this level rather than continuing a downward trend for percentage of selenium remaining in the liquor at higher iron-to-selenium ratios.

It is not known why the data for Site LMA007L (in the lower left corner of Figure 3-6) do not appear to follow the trend seen in the other data at similar iron-to-selenium mass ratios. ORP was not measured at this site, so there is possibly an ORP effect that cannot be quantified with the available data. It is also possible that an unidentified analytical error has lead to an erroneous ratio calculation for the data from this site.

Additional selenium concentration data were collected for the coal, fly ash, limestone, and makeup water at each of the sites sampled in 2010. These results are included in this report in Appendix B, Table B-1. More detailed trace element data were collected for the sites sampled in 2009, and were reported in an appendix to the previous Technical Update[1].

Selenium Mass Balances Around 2010 Sampling Host Units

The process samples collected and analyzed for the host units provide input that can be used to calculate selenium mass balances around these units. However, for the 2009 sites there were no flue gas measurements to indicate the extent to which selenium was emitted with the flue gas, and meaningful selenium mass balances could not be calculated. The 2010 sampling events all corresponded with times where the host utilities were sampling for stack flue gas multi-metals concentrations, including selenium. Results of these measurements were provided to the project team. Thus, for the 2010 sampling sites it was possible to calculate unit-wide selenium balances with data for all significant input and output streams. The input streams include the coal, FGD limestone, and FGD makeup water, and the output streams include fly ash, FGD gypsum, FGD chloride purge stream, and stack flue gas. For a rigorous balance the bottom ash should also be included, but since selenium is relatively volatile, the percentage of selenium reporting to the bottom ash is likely minor.

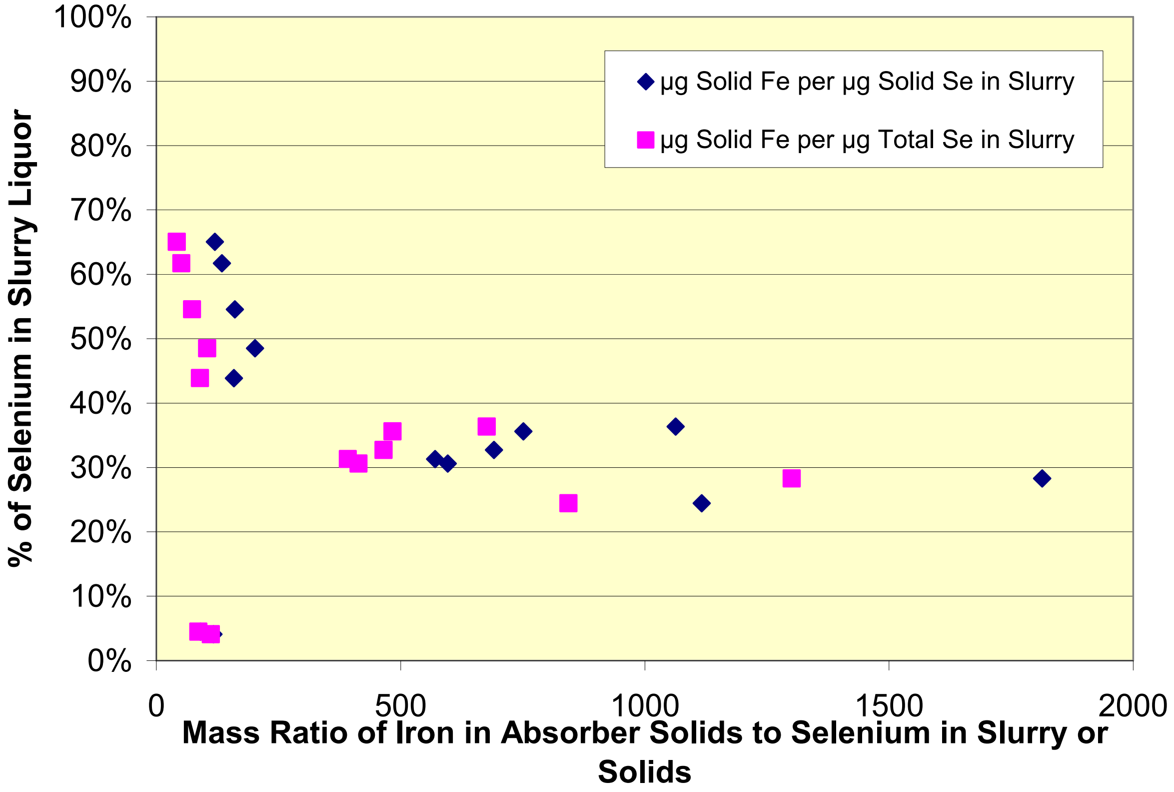

Figure 3-6
Selenium Partitioning in Absorber Slurry versus Ratio of Iron in Solids to Selenium in Slurry or Solids

Many process streams in a coal-fired power plant are not continuously measured for flow rate. Therefore, to calculate a selenium balance around the host units, relative stream rates had to be estimated from other parameters, such as coal proximate analyses from Table 2-7 and FGD absorber analyses from Table 3-4. Some simplifying assumptions had to be made, such as that the fly ash stream represents 80% of the coal ash, and that the FGD system was operating at steady state with respect to chloride (i.e., the chloride purge rate was equal to the chloride in coal rate). Once relative stream rates were estimated, on a lb/MMBtu basis, the selenium rates in these streams were calculated using selenium concentration data from Tables 3-1, 3-5, 3-6, and B-1. The results are summarized on a percentage basis in Table 3-9.

Table 3-9
Summary of Selenium Balances for 2010 Sampling Sites

	Inputs - % of Total Input			Outputs - % of Input				
Host Unit	**Coal**	**Limestone**	**FGD Make-up Water**	**Fly Ash**	**Gypsum**	**Cl^- Purge Water (solid and liquid phases)**	**Stack Gas**	**Total % Recovery of Input Se**
Plant D-3	≥ 98.6%	<1.4%	0.0%	66.3%	40.8%	8.0%	9.8%	125%
Plant D-4	≥ 99.1%	<0.9%	0.0%	120.2%	28.8%	7.0%	10.5%	166%
Site U	<99.3%	<0.7%	0.0%	109.1%	1.2%	0.0%	<1.1%	111%
Plant D-5	≥ 93.4%	<6.4%	0.2%	23.7%	21.4%	3.1%	<1.5%	50%

The results show that nearly all of the selenium input to the units is with the coal. All of the limestone samples showed “less than” results for selenium below analytical detection limits, and all of the FGD makeup water streams showed insignificant quantities of selenium. For one site, Site U, the selenium concentration for even the coal was at or below the analytical detection limit. Thus, for Site U the coal percentage is shown as a “less than” value. In these balances, a number at or below the detection limit was quantified at the detection limit. For the other three coal numbers in the table, the input selenium percentages from the coal are shown as “greater than or equal” values since the limestone contribution is uncertain.

Results of the output stream calculations show that most of the selenium was recovered in the fly ash and to a lesser extent in the gypsum. The units with hydrocyclones for primary dewatering in their wet FGD systems (Plants D-3, D-4 and D-5) showed a significant percentage of selenium leaving with the chloride purge stream, primarily in the fine solids in that stream that are enriched in selenium. Site U, with a thickener for primary dewatering, showed virtually no selenium in the chloride purge, primarily because thickeners remove almost 100% of the solids contained in the slurry being dewatered and because the liquor concentrations were also quite low. At Plants D-3 and D-4 about 10% of the input selenium was found in the stack gas, whereas at Site U and Plant D-5 the selenium in the stack gas was very low, below analytical detection limits for the measurement method.

Both Site U and Plant D-5 have fabric filters for particulate control. These results suggest that fabric filters may enhance selenium capture with the fly ash relative to plants with ESPs for particulate control, and hence may lead to lower selenium emissions in the scrubbed flue gas. However, it would take more data to support such a conclusion.

Total recoveries of input selenium in the output streams ranged from only 50% for Plant D-5 to 166% for Plant D-4, whereas 100% recovery would be ideal. The balance for Site U came nearest to closing, and even this result is questionable because the coal, limestone, and stack gas selenium concentrations were at or below analytical detection limits.

It is likely that difficulty collecting representative fly ash samples led to most of the error in these balances. Since selenium is relatively volatile, it tends to condense on fly ash particles after leaving the furnace. Smaller particles have a higher surface-area-to-mass ratio than larger particles, so selenium can become enriched on smaller fly ash particles compared to larger fly ash particles. A grab sample of fly ash may not represent the same particle size distribution as the overall fly ash stream, and thus the selenium concentration measured on that sample may not be representative. As an example, at Site D-5, which has a fabric filter for particulate control, fly ash samples were taken from two compartments, one on each side of the unit. One sample was measured to contain less than 1 mg/kg of selenium content, while the other was measured to contain greater than 5 mg/kg. This represents a wide variation in two samples that would each be assumed to be representative of the overall stream. In this case the average of these two results was used in the mass balance calculation. Since the majority of the output selenium was measured in the fly ash streams, errors in quantifying that stream could have a large impact on the overall selenium mass balance.

Similarly, grab samples of coal may not represent the average selenium concentration in the overall coal fired in the unit over the residence time of the FGD system, and could contribute to mass balance closure problems.

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4

SUMMARY AND RECOMMENDATIONS

In the current phase of this project, four FGD systems at three sites were sampled and analyzed for selenium speciation in the FGD liquor, including absorber slurry and other FGD process stream samples. All four FGD systems operate with limestone reagent and produce gypsum as a solid byproduct. Three of the four operate in a forced-oxidized mode. The sample preservation and analysis techniques employed in these measurements represent the "state of the art" for selenium speciation as of 2009/2010. These results should be comparable to FGD sample results from five FGD systems sampled in 2009 in an earlier phase of this project, and reported in an earlier Technical Update[1].

The data from the 2009 and 2010 sampling and analysis efforts were reviewed and support the observations discussed below. While the 2010 sample results almost double the number of available results compared to the 2009 Technical Update, this still represents a small data set compared to the overall population of FGD systems in the U.S. Therefore it is premature to call the following observations conclusions.

Also, there is a significant caveat to all of these data. The project team members used what is currently considered best practice for sampling, preserving, and analyzing FGD samples for selenium speciation. However, it remains uncertain how accurately the results of selenium speciation analyses conducted 48 hours or more after the samples were collected reflect the actual speciation within the FGD systems.

Observations from the Current Data Set

The predominant process chemistry for new FGD systems is limestone reagent with in situ (within the reaction tank) forced oxidation to produce gypsum as a solid byproduct, although some very low-sulfur systems can produce gypsum without adding oxidation air. The gypsum is typically dewatered to a low moisture content (nominally 10 wt% free moisture), and is often washed with fresh water to reduce the chloride content. Such systems typically have to purge a portion of the FGD liquor to control chloride levels in the system, and this purge stream often must be treated before discharge. These high-oxidization conditions can produce variable percentages of selenate in absorber liquors and wastewater. The selenate form is typically not removed at high efficiency in conventional physical/chemical WWT processes.

The range of conversion to the selenate form observed in the limestone, gypsum-producing/forced oxidation samples reviewed in this project varied widely, from less than 1% conversion to 100% conversion to selenate. In the relatively small data set available, an FGD variable that appears to correlate well with percentage selenate formation is the oxidation-reduction potential

(ORP) in the FGD absorber slurry. Higher ORP was observed to correlate with increased conversion to selenate. Although only six data points are available for systems that do not use dibasic acid (DBA) as a performance additive, these data points form a linear correlation between selenite oxidation to the selenate form and ORP with a convincing R^2 value of 0.95. This correlation is not surprising, given that higher ORP values correspond with greater electrochemical oxidizing potential in the slurry liquor, and selenate is a fully oxidized form of selenium.

Research conducted in Japan also suggests that the presence of peroxydisulfate ($S_2O_8^{2-}$) in highly oxidizing FGD environments may promote selenite oxidation. Peroxydisulfate would also be expected to form in wet FGD environments at high ORP. Samples collected during the current project did not always identify the presence of peroxydisulfate under the highly oxidizing conditions that produced 100% conversion to the selenate form. However, the FGD liquor sample preservation techniques employed may not have been optimum for preserving this species until analyses were conducted.

Some limestone wet FGD systems use weak organic acid buffers to enhance SO_2 removal performance and/or to improve limestone utilization. A commonly used additive has been DBA, a combination of adipic, succinic and glutaric acid. The use of DBA in three wet FGD systems sampled at two sites during 2009 appeared to lower the percentage of selenium oxidation to the selenate form compared to the systems that do not use additives. For example, at an ORP value of 200 mV, the current data from FGD systems that do not use DBA suggest that the percent conversion to selenate would be in the range of 50% to 60%, while data from a system that uses DBA shows only 8% conversion. This effect of DBA has also been observed in EPRI-funded bench-scale wet FGD research[2].

However, as suggested by previous data, it appears from the 2009 data that the use of DBA promotes the formation of other selenium compounds in FGD liquors, characterized as "unknown" selenium compounds. There was an apparent relationship between DBA species concentrations in the FGD liquor and the percentage formation of unknown selenium compounds.

In the 2009 data there was an apparent relationship between DBA concentration and the formation of a sulfur species called dithionate in FGD liquors. It is not known whether the formation of dithionate and unknown selenium species are related. The data were also investigated to determine if there was an apparent relationship between dithionate concentrations and the formation of unknown selenium species. Such a relationship was apparent in the 2009 data, but additional data added from the 2010 sampling make this relationship seem unlikely.

Data from four sites with FGD wastewater treatment systems showed limited effectiveness of conventional physical/chemical processes on the removal of selenium species. Selenium speciation results showed that some systems were effective at removing selenite and selenosulfate from the FGD purge water. However, dissolved selenium totals from the four wastewater treatment systems indicate that none is effective at significantly lowering the total selenium concentration in the treated water. Total dissolved selenium concentration reductions across the wastewater treatment plants were 17% or less.

No firm conclusions can be drawn from this limited data set. However, the 2010 data set further supports the initial indication that the ORP at which the absorber reaction tank operates influences the percentage conversion of selenite to selenate. The data also provide evidence that DBA addition can lower the percentage conversion of selenite to selenate, but may correlate with the formation of other selenium species in some FGD systems.

There are two corollary observations from these data related to trace element behavior in wet FGD systems. One is that manganese partitioning between the FGD slurry liquor and solids is strongly influenced by ORP. At low ORP manganese appears to remain primarily in the liquid phase, while at high ORP (e.g., 600 mV) it is found mainly in the solid phase, presumably as MnO_2. Bench-scale results funded by EPRI suggest that the form of manganese in FGD slurry can impact selenium oxidation[2]. The other observation is that mercury partitioning appears to vary with ORP in the opposite direction. At low ORP mercury appears to be found primarily associated with the solids, whereas at high ORP it appears to be found remaining in the liquor. Thus, conditions that favor mercury remaining in the FGD liquor also appear to favor selenite conversion to selenate.

Recommendations

The first recommendation is that EPRI should continue its efforts to develop reliable and accurate sampling, preservation and analytical procedures for selenium speciation in FGD liquors. This should provide more confidence that selenium speciation data produced by off-site laboratories accurately reflect conditions within the FGD system. It remains uncertain whether the speciation results presented in this Technical Update accurately represent the selenium speciation within the FGD systems sampled. Also, the development of standard procedures should allow selenium speciation data to be more confidently compared from study to study. EPRI research is currently focusing in this area, as well as attempting to identify the remaining unknown selenium peaks in FGD liquor samples.

Another recommendation is that current EPRI programs to acquire and analyze FGD aqueous samples should continue. Any time an FGD system is being characterized through on-site process sampling and subsequent analyses, selenium speciation analyses should be considered as an “add on” to the project.

After reviewing these most recent data, it is clear that comprehensive information should be collected about the FGD systems from which selenium speciation data are collected. In particular, the FGD absorber pH, ORP and slurry temperature should be recorded at the time of sampling. The FGD samples collected should be characterized for concentrations of chloride, dissolved metals, and slurry solids trace elements (including solid-phase selenium concentrations). Coal, fly ash, FGD makeup water and reagent samples should be collected and analyzed as needed to determine input and output quantities of chloride, selenium, other trace elements, etc. If the system uses performance additives such as DBA or formate, a sample of the additive should also be collected, and the source of the additive should be recorded. Where possible, a flow diagram should be acquired or developed for the FGD system, including dewatering, FGD liquor return, and wastewater treatment processes. Size information for key process tanks and vessels would also be useful for estimating residence times in the FGD system.

Information about other processes operating upstream of the FGD system would also be useful, such as SCR, particulate control device type, and whether there are SO_3 control systems.

Future investigations should continue to focus on limestone forced oxidation, or at least gypsum-producing systems. This is the predominant chemistry expected for new wet FGD systems that will require wastewater treatment. Furthermore, for this chemistry a wide range of formation of selenate and unknown selenium species has been observed.

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A

GLOSSARY OF SELENIUM COMPOUNDS IDENTIFIED IN WET FGD LIQUORS AND LIST OF ACRONYMS

Glossary of Selenium Compounds

Biselenite – $HSeO_3^-$; represents the ionic form of selenium dioxide after it is absorbed in FGD liquors, at lower pH values.

Selenate – SeO_4^{2-}, a form of selenium in the +6 valence state [Se(VI)], most likely represents selenite that is oxidized in the wet FGD system.

Selenite – SeO_3^{2-}, which represents an ionic form of selenium in the +4 valence state [Se(IV)], believed to be the predominant form of selenium as it is absorbed from the flue gas, at higher pH values.

Selenium – Se(0); the elemental form of selenium.

Selenocyanate – $SeCN^-$; the mechanism for formation is unknown. Possibly represents the reaction of selenium with trace amounts of cyanide or hydrogen cyanide in furnace or flue gas.

Selenosulfate – $SeSO_3^{2-}$, believed to form by reaction between selenite and sulfite in wet FGD environments, perhaps due to partial reduction of selenite to the elemental form. The analogous all-sulfur ion is thiosulfate ($S_2O_3^{2-}$), which is formed in inhibited oxidation wet FGD systems by reaction between elemental sulfur and sulfite ion.

Acronyms

DBA – Dibasic acid, a mixture of adipic, glutaric and succinic acids used as a performance additive in some wet FGD systems.

EQ Tank – Equalization tank; a large tank used to accumulate chloride purge liquor from wet FGD systems so as to provide for a relatively constant feed rate to a wastewater treatment plant.

FGD – Flue gas desulfurization.

LS – Limestone reagent.

ORP – Oxidation-reduction potential; usually measured in units of millivolts.

S/N – Sulfur/nitrogen species, which form in some wet FGD systems due to reactions between sulfite and nitrite (formed by removal of a small percentage of flue gas NO_X in the FGD system).

THS – Total hydrolyzable sulfur; the result of analyzing a wet FGD liquor sample for sulfate content after digesting it under strong hydrolyzing conditions to convert other sulfur-containing species (e.g., S/N compounds) to the sulfate form.

WWT – Wastewater treatment.

B

SELENIUM CONCENTRATION DATA FOR ADDITIONAL PROCESS SAMPLES

Table B-1
Additional Process Sample Selenium Analysis Results

Site	Sample Location	Date	Phase	Value	Units	Data Flags
D-3	Unit 1 - FGD Cl Purge	4/14/2010	Liquor	2,070	µg/L	
D-4	Unit 2 - FGD Cl Purge	4/14/2010	Liquor	1,690	µg/L	
D-3/D-4	WWT Outlet	4/14/2010	Liquor	1,720	µg/L	
D-3/D-4	Makeup Water	4/14/2010	Liquor	0.448	µg/L	MRL
D-3/D-4	WWT Inlet	4/14/2010	Liquor	1,850	µg/L	
Site U	Thickener Overflow	5/7/2010	Liquor	8.75	µg/L	
Site U	Makeup Water	5/7/2010	Liquor	<0.450	µg/L	
D-5	WESP - Field 1	6/30/2010	Liquor	47.0	µg/L	
D-5	WESP - Field 2	6/30/2010	Liquor	26.0	µg/L	
D-5	FGD Cl Purge	6/30/2010	Liquor	96.5	µg/L	
D-5	WWT Inlet	6/30/2010	Liquor	405	µg/L	
D-5	WWT Outlet	6/30/2010	Liquor	335	µg/L	
D-5	Makeup Water Tank	6/30/2010	Liquor	2.22	µg/L	
D-5	Makeup Water – CTBD	6/30/2010	Liquor	4.27	µg/L	
D-3/D-4	LS Rock	4/14/2010	Solids	<0.57	mg/kg AR	
D-3/D-4	U1 & U2 Gypsum	4/14/2010	Solids	9.93	mg/kg AR	
D-3	Unit 1 - FGD Cl Purge	4/14/2010	Solids	45.4	mg/kg AR	
D-3	Unit 1 Fly Ash	4/13/2010	Solids	13.4	mg/kg AR	
D-4	Unit 1 Coal	4/14/2010	Solids	2.1	mg/kg AR	
D-4	Unit 2 - FGD Cl Purge	4/14/2010	Solids	23.9	mg/kg AR	
D-4	Unit 2 Fly Ash	4/15/2010	Solids	27.0	mg/kg AR	
D-4	Unit 2 Coal	4/14/2010	Solids	2.4	mg/kg AR	

Site	**Sample Location**	**Date**	**Phase**	**Value**	**Units**	**Data Flags**
Site U	Limestone Rock	5/7/2010	Solids	<0.57	mg/kg AR	
Site U	Thickener Overflow	5/7/2010	Solids	4.79	mg/kg AR	MRL
Site U	Makeup Water	5/7/2010	Solids	<30.0	mg/kg AR	
Site U	Unit 1 Fly Ash	5/7/2010	Solids	21.9	mg/kg AR	D, M
Site U	Unit 1 Coal	5/7/2010	Solids	<1.0	mg/kg AR	
D-5	Gypsum	6/30/2010	Solids	1.30	mg/kg AR	MRL
D-5	Limestone Rock	6/30/2010	Solids	<0.62	mg/kg AR	
D-5	WESP - Field 1	6/30/2010	Solids	<5.36	mg/kg AR	
D-5	WESP - Field 2	6/30/2010	Solids	<5.77	mg/kg AR	
D-5	FGD Cl Purge	6/30/2010	Solids	8.64	mg/kg AR	
D-5	Unit 4 Fly Ash – Hopper 1	6/30/2010	Solids	0.90	mg/kg AR	MRL
D-5	Unit 4 Fly Ash – Hopper 5	6/30/2010	Solids	5.38	mg/kg AR	
D-5	Unit 4 Coal	6/30/2010	Solids	1.2	mg/kg AR	

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