SELENIUM SPECIATION AND MANAGEMENT IN WET FGD SYSTEMS

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EXECUTIVE SUMMARY

This report discusses results from bench- and pilot-scale simulation tests conducted to determine the factors that impact selenium speciation and phase partitioning in wet FGD systems. The selenium chemistry in wet FGD systems is highly complex and not completely understood, thus extrapolation and scale-up of these results may be uncertain. Control of operating parameters and application of scrubber additives have successfully demonstrated the avoidance or decrease of selenite oxidation at the bench and pilot scale. Ongoing efforts to improve sample handling methods for selenium speciation measurements are also discussed.

Bench-scale scrubber tests explored the impacts of oxidation air rate, trace metals, scrubber additives, and natural limestone on selenium speciation in synthetic and field-generated full-scale FGD liquors. The presence and concentration of redox-active chemical species as well as the oxidation air rate contribute to the oxidation-reduction potential (ORP) conditions in FGD scrubbers. Selenite oxidation to the undesirable selenate form increases with increasing ORP conditions, and decreases with decreasing ORP conditions. Solid-phase manganese [Mn(IV)] appeared to be the significant metal impacting the oxidation of selenite to selenate. Scrubber additives were tested for their ability to inhibit selenite oxidation. Although dibasic acid and other scrubber additives showed promise in early clear liquor (sodium based and without calcium solids) bench-scale tests, these additives did not show strong inhibition of selenite oxidation in tests with higher manganese concentrations and with slurries from full-scale wet FGD systems. In bench-tests with field liquors, addition of ferric chloride at a 250:1 iron-to-selenium mass ratio sorbed all incoming selenite to the solid phase, although addition of ferric salts had no impact on native selenate that already existed in the field slurry liquor sample. As ORP increases, selenite may oxidize to selenate more rapidly than it sorbs to ferric solids.

Though it was not possible to demonstrate a decrease in selenium concentrations to levels below the project’s target of 50 µg/L during pilot testing, some trends observed in bench-scale testing were evident at the pilot scale. Specifically, reducing oxidation air rate and ORP tends to either retain selenium as selenite in the liquor or shift selenium phase partitioning to the solid phase. Oxidation air flow rate control may be one option for managing selenium behavior in FGD scrubbers. Units that cycle load widely may find it more difficult to impact ORP conditions with oxidation air flow rate control alone. Because decreasing oxidation air rates to the reaction tank showed that all “new” selenium reported to the solids, the addition of ferric chloride to the pilot scrubber could not show further improvements in selenium behavior. Ferric chloride addition did shift mercury to the slurry solids, specifically to the fine particles. Several competing pathways may govern the reporting of selenium to the slurry solids: co-precipitation with gypsum into the bulk solids and sorption or co-precipitation with iron into the fine particles. Simultaneous measurement of selenium and mercury behavior suggests a holistic management strategy is best to optimize the fate of both of these elements in FGD waters.

Work conducted under this project evaluated sample handling and analytical methods for selenium speciation in FGD waters. Three analytical techniques and several preservation methods were employed. Measurements of selenium speciation over time indicated that for accurate selenium speciation, it is best to conduct measurements on unpreserved, filtered samples as soon after sampling as possible.

The capital and operating costs for two selenium management strategies were considered: ferric chloride addition and oxidation air flow rate control. For ferric chloride addition, as might be expected the reagent makeup costs dominate the overall costs, and range from 0.22 to 0.29 mills/kWh. For oxidation air flow rate control, a cursory comparison of capital costs and turndown capabilities for multi-stage and single-stage centrifugal blowers and several flow control methods was completed. For greenfield systems, changing the selection of blower type and flow control method may have payback periods of 4 to 5 years or more if based on energy savings alone. However, the benefits to managing redox chemistry in the scrubber could far outweigh the savings in electricity costs under some circumstances.

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PROJECT NARRATIVE

Introduction

Many existing and planned coal-fired power plants use flue gas desulfurization (FGD) systems to control sulfur dioxide (SO_2) and to realize co-benefit mercury (Hg) control. Most wet FGD systems produce gypsum as a solid byproduct and must blow down some liquor to control dissolved chloride concentrations in the recirculating liquor. In many cases, this blowdown liquor must be treated to remove trace elements. Control of mercury emissions has been a high priority research and development area for over a decade. However, concern over other elements has increased, and attention to selenium wastewater discharges has recently accelerated as many new FGDs are being installed in response to the Cross-State Air Pollution Rule (CSAPR), the proposed and recently vacated Clean Air Mercury Rule (CAMR), and the Clean Air Visibility Rule (CAVR). Vapor-phase selenium (Se) not captured by the particulate control device, e.g., the electrostatic precipitator (ESP) or the baghouse, may be captured in the wet FGD. Selenium removal across FGD scrubbers has been measured from 53% to 95% (Senior, 2011). Scrubber design is a possible factor in this variation; formation of selenous acid mist, similar to the formation of sulfuric acid mist, may also impact the capture of flue gas selenium by FGD scrubbers. The selenium captured by the scrubber is eventually discharged in the FGD solids and/or the FGD water blowdown. Available data suggest that the fraction of selenium in the wastewater varies widely from site to site, and factors that affect the fate of selenium are currently under evaluation by the Electric Power Research Institute (EPRI) and others. By itself, selenium is known to cause toxicity to aquatic life, and selenium exhibits complex interactions with mercury, which could affect the design of mercury control strategies. Thus, understanding selenium chemistry in FGD systems and developing selenium management strategies and control technologies have become a pressing need.

Development of selenium management strategies has faced numerous challenges. Characterization of selenium chemistry in FGD scrubbers began only recently as attention to selenium discharges increased; field measurements have shown that selenium speciation in FGD slurry liquors can vary widely from plant to plant. Additionally, analysis of selenium speciation is complex and difficult, and sample handling methods were not well established before the current project. Finally, the selenium species present in FGD waters impact treatability in downstream wastewater treatment (WWT) facilities.

Untreated FGD waters may contain dissolved selenium concentrations ranging from less than 100 µg/L [i.e., parts per billions (ppb) levels] to several thousand µg/L [i.e., parts per million (ppm) levels], and may require some wastewater treatment. Selenium may be present in several forms and oxidation states, including selenite (SeO_3^{2-}), which represents selenium in the +4 oxidation state; selenate (SeO_4^{2-}, selenium in the +6 oxidation state); selenosulfate ($SeSO_3^{=}$); selenocyanate ($SeCN^-$); and possibly several unknown forms of selenium. Full-scale field data reveal that both total selenium concentrations and selenium speciation vary greatly from plant to plant. For limestone, forced oxidation (LSFO) FGD systems operating at highly oxidizing conditions without organic acids, the selenite is generally oxidized to selenate. However, selenite does not always fully oxidize to selenate in forced oxidation FGD systems, and unknown compounds may comprise a significant portion of the selenium discharges for some plants, especially for plants using organic acid additives (EPRI, 2009). Effective selenium water management strategies must address this variability in selenium speciation by developing a better understanding of selenium chemistry in the FGD systems.

Development of selenium control technologies is further complicated by difficulties in measuring and analyzing selenium speciation. Current analytical challenges with respect to understanding selenium behavior in FGD liquors are twofold: many common analytical methods yield inaccurate total selenium concentrations, and common selenium speciation procedures fail to account for the presence of any other selenium species besides Se(IV) and Se(VI) in FGD waters. While a small number of expert analytical laboratories use more advanced analytical methods that can compensate for these problems, many analytical results generated by routine compliance sample laboratories following established standard methods often produce incorrect results for FGD samples. For total selenium determinations, systematic errors can be both positive and negative and are often large. For selenium speciation, only hyphenated techniques coupling liquid ion chromatography (IC) separations to element-specific detectors (e.g., inductively coupled plasma-mass spectrometry, (ICP-MS) are capable of distinguishing between Se(IV) and Se(VI) and any other selenium species that might occur. Development of effective selenium control technologies should take into consideration these analytical challenges. In some cases, the tradeoffs between obtaining full speciation using an advanced technique versus obtaining a limited speciation with simpler approaches must be considered. The project team employed several different analytical techniques during the project; an evaluation of these techniques and tradeoffs is included in Section 3.

Analytical difficulties include challenges in preserving samples. Sample preservation refers to how a sample is handled and stored between the time when the sample is collected from the FGD system and the time when the sample is analyzed. At the beginning of the project, the best way to preserve FGD liquor samples for selenium speciation analysis was not well established. Under some conditions, analysis of parallel samples preserved by different methods yielded conflicting selenium speciation results. Exploration of the preservation method was needed to explain these differences. EPRI has sponsored research on the preservation of field samples for subsequent selenium speciation. As described in Section 3, work conducted under this program evaluated sample handling and preservation of laboratory samples.

Selenium is surprisingly difficult to remove from wastewaters, particularly those containing high levels of dissolved solids such as FGD blowdown streams. As noted, selenium can form a complex array of chemical species when it absorbs from the flue gas into FGD slurries. Many of these species are very soluble in most natural and process waters. High levels of sulfur present in wastewaters, such as the sulfates found in FGD liquors, tend to interfere with most selenium removal technologies. Other common anions, such as bicarbonate and nitrate, also interfere with many selenium removal technologies (Rowley, 1991). Because of its toxicity, discharge limits for selenium are typically quite low. The Environmental Protection Agency (EPA) is currently revising the effluent guidelines for the steam generating industry. Draft guidelines are expected in July 2012, and the final rule will go into effect in January 2014. The FGD wastewater stream is a high priority stream, and guidelines will likely stipulate internal concentrations (i.e., no benefit from dilution after leaving the FGD WWT system). A draft National Pollution Discharge

Elimination System (NPDES) permit issued in mid-2011 for a Region 1 facility has signaled the EPA's consideration of selenium average monthly discharge limits as low as 10 µg/L (approximately 10 ppbw) total selenium. Achieving these selenium discharge levels would be difficult even without the interference of common FGD constituents.

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Original Hypotheses and Technical Approach

Original Hypotheses

Much of the Phase I SBIR project comprised bench-scale FGD scrubber tests that collected data on the rates of selenite conversion to other selenium forms. Results from the Phase I project, as reported in the Phase II proposal, indicated that transition metals, particularly manganese and iron, may play a key role in the speciation of selenium in FGD systems. Specifically, the form of the metals (e.g., oxidation state, solid versus dissolved species) appeared to impact selenium chemistry significantly. Operating conditions, such as pH and oxidation reduction potential (ORP), and scrubber additives, such as dibasic acid (DBA), might be used to manage the impact of metals on selenium chemistry.

Impacts of Oxidation Reduction Potential and pH

Examination of the Pourbaix diagrams for key FGD trace element constituents provides context for understanding the Phase I results and also for the Phase II strategy. A Pourbaix diagram, also known as a redox potential vs. pH diagram, plots possible equilibrium phases of an aqueous electrochemical system. Predominant ion boundaries are represented by lines. Reference Pourbaix diagrams are created for pure species in water at 25°C. Although the reference diagrams are not quantitatively accurate in complex matrices, such as FGD waters, at elevated temperatures, the diagrams do provide qualitative trends for transitions between the various species for a given element. Figures 1-1, 1-2, and 1-3 show the Pourbaix diagrams for selenium, manganese, and iron, respectively. The vertical axis represents the redox potential or oxidation reduction potential (ORP). Positive values represent oxidating environments; a larger positive value is more strongly oxidizing. Lower values indicate more reducing environments. Forced oxidation FGD systems operate with positive ORP values. The ORP measured in FGD systems varies greatly but is usually below 1.0 V. FGD system reaction tanks typically operate between pH values of 5 and 6, though values outside of this range are occasionally used (pH 4.5 to pH 6.5). The slurry pH is generally lower within the absorber vessel because of the capture of SO_2 from the flue gas. At a given pH, the oxidation state of an element increases as the ORP increases.

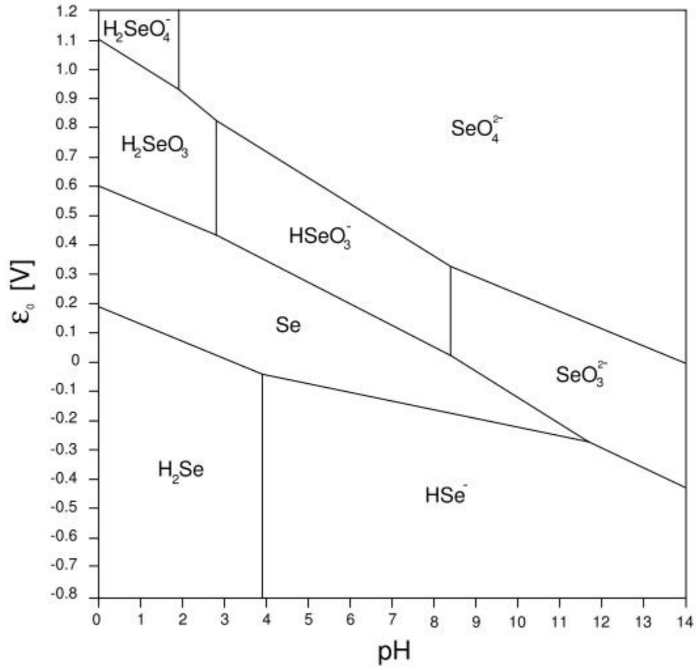

Figure 1-1
Selenium Pourbaix Diagram

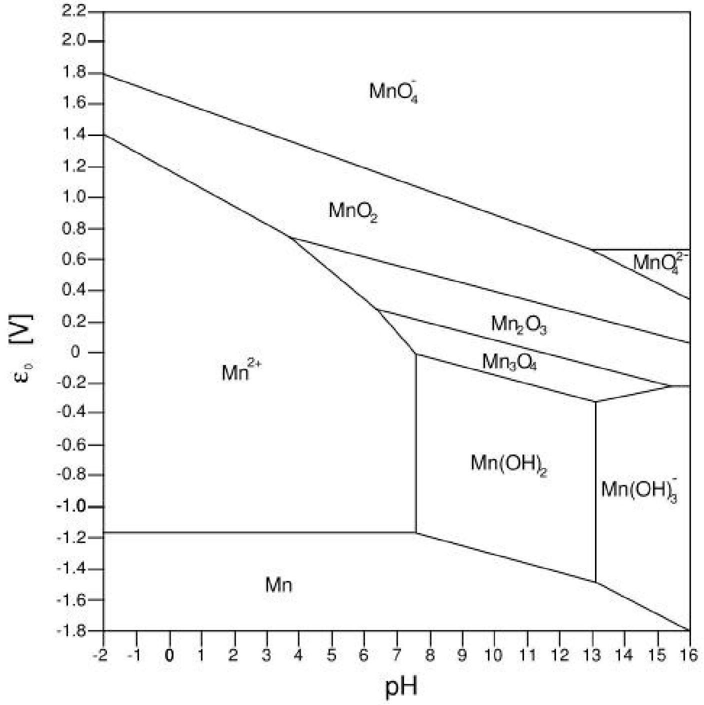

Figure 1-2
Manganese Pourbaix Diagram

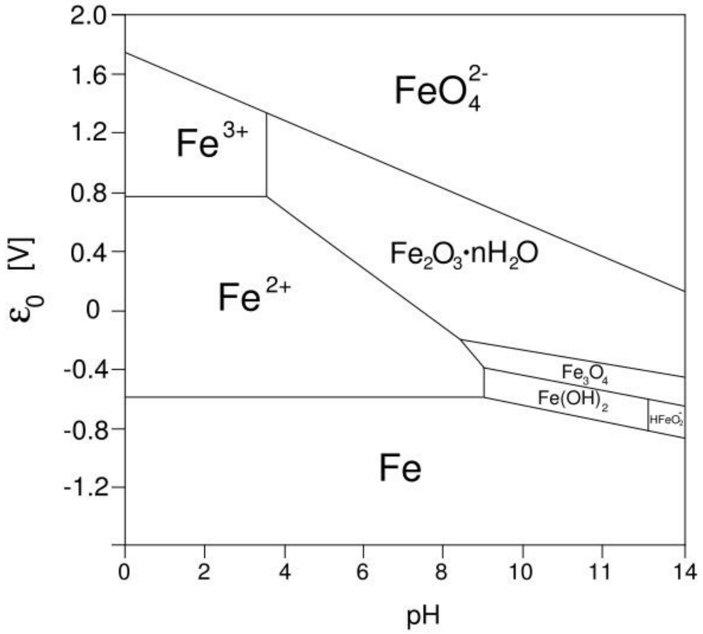

Figure 1-3
Iron Pourbaix Diagram

In Figure 1-1, elemental selenium is shown as Se in the solid phase. Se(IV) is shown as H_2SeO_3, $HSeO_3^-$, and SeO_3^{2-}. Se(VI) is shown as SeO_4^{2-}. The diagram shows that lower pH and lower ORP values favor reduced selenium species. Figure 1-2 shows the manganese Pourbaix diagram. Mn(II) is shown as dissolved Mn^{2+}, $Mn(OH)_2$, and $Mn(OH)_3^-$. Mn(IV) is shown as MnO_2, a solid. Figure 1-3 shows the Pourbaix diagram for iron. Fe(II) is shown as dissolved ferrous (Fe^{2+}) ion. Fe(III) is shown as dissolved ferric (Fe^{3+}) ion and various ferric oxides. Under typical operating conditions of FGD systems (<1.0 V, pH 4.5 to 6.5), multiple species of selenium, manganese, and iron can exist. In some cases (i.e., at certain ORP values), the slight pH change that occurs between the FGD absorber (pH ~4.5) and the FGD reaction tank (pH ~5.5) may cause a change of redox state and/or the transitions between solid and liquid phase species for iron, manganese, and selenium. Additionally, pH directly influences the strength of most oxidants and reductants that may cause conversion between different oxidation states of selenium in FGD systems. Thus, minor adjustments of pH and ORP in the FGD operating environment may have significant results on the form and oxidation state of metals and, therefore, the form and oxidation state of selenium.

Phase I results suggested that conditions that produce *solid* phase manganese also promote selenite oxidation to selenate, but conditions that favor *dissolved* manganese (excluding Mn species in high oxidation states such as permanganate, MnO_4^-) do not favor selenate formation. Additionally, when *solid* phase iron was present, selenium tended to precipitate from solution, and when *dissolved* iron was present, selenite oxidation to selenate was promoted. To minimize selenate formation, the Phase I results suggested that it is desirable to find a pH-ORP operating range at which iron is in the solid phase and manganese is in the liquid phase. The standard Pourbaix diagrams (in “clean” water at 25°C) indicate that it may be possible to find such conditions. Phase II testing investigated a range of ORP conditions with various concentrations of iron and manganese to search for conditions that would maintain near-complete sulfite oxidation, yet avoid selenite oxidation.

Technical Approach and Objectives

Two primary selenium control pathways in FGD scrubbers were considered. First, as noted in the previous paragraphs, scrubber operating conditions and additive usage may be optimized to prevent selenate formation and maintain selenium species that are more easily treated in downstream wastewater treatment facilities. In addition to this first strategy, scrubber conditions and additives may also be used to promote selenium precipitation in the scrubber such that selenium exits with the FGD solid byproduct. The Phase II program sought to develop these two control pathways in the FGD scrubber through extensive bench-scale FGD scrubber testing and subsequent pilot-scale scrubber testing. The primary technical objectives, achieved through the scrubber test campaigns, were the following:

1. Determine what factors control selenium species formed in wet FGD systems and how selenium partitions between FGD slurry solids and liquor.
2. Develop and validate recommendations for FGD operating ranges and scrubber additive use to reduce selenium discharges in FGD wastewaters via two possible methods:

    - Promote the formation of selenium liquid species that can be removed with conventional physical/chemical wastewater treatment (i.e., avoid selenate formation), and/or
    - Reduce FGD selenium water discharges by directing selenium to the slurry solids.

In conjunction with these primary objectives, the project also sought to evaluate and improve sample handling and analysis and to test WWT additives and other WWT strategies in the laboratory.

The originally proposed specific technical objectives for Phase II of this SBIR project included the following:

- At bench scale, optimize FGD operating conditions and scrubber additive usage to minimize selenate formation,
- At bench scale, demonstrate reporting of selenium to solid phase in FGD scrubber,
- At bench scale, conduct extended FGD scrubber runs with liquid residence times typical of full-scale wet FGD systems,
- At laboratory scale, demonstrate a reduction in selenium discharge concentration down to 10-50 µg/L,
- At pilot scale, demonstrate scrubber and wastewater control strategies, and
- Estimate the capital and operating cost impacts of the proposed control strategies.

The Phase II project was divided into the following tasks:

- **Task 1:** Bench-Scale Scrubber Testing and Lab-Scale Wastewater Treatment Tests,
- **Task 2:** Field Testing,
- **Task 3:** Engineering and Economics Analysis, and
- **Task 4:** Management and Reporting.

Under Task 1, bench-scale scrubber tests focused on optimal use of scrubber operating conditions and scrubber additives to control the solubility and behavior of selenium and other constituents that are key to selenium behavior. The Phase II scrubber test campaign included a larger number of standard-length 6-hour runs as well as several intermediate-length tests lasting 10 to 12 hours. The lab-scale wastewater treatment study tested a wider range of wastewater treatment (WWT) additives and operating conditions and tested a novel WWT approach presented in the Phase II proposal, which was intended to remove mixtures of selenium species from FGD wastewater.

Under Task 2, selenium management approaches in the scrubber were tested at the pilot scale with actual flue gas and FGD liquors using an existing skid-mounted FGD scrubber system. Under Task 3, the capital and operating costs for the selenium control strategies were estimated. Task 4 included ongoing project management and reporting for the project.

Problems Encountered and Departure from Planned Methodologies

Challenges Encountered During Bench-scale Scrubber Testing

Sample handling and analysis of selenium speciation in samples taken from FGD scrubbers is an ongoing challenge. Though they may be operating at steady state conditions, scrubber slurries are not at chemical equilibrium. Samples removed from the scrubbers are reactive, and some species present in sampled liquors may continue to react after removal from the scrubber. This phenomenon applies at the bench, pilot, and full scale.

Because the samples are reactive, the project team hypothesized that the selenium speciation might be changing between the time at which a sample is taken and the time at which a sample is analyzed. Therefore, additional analytical techniques were attempted that could be carried out on-site shortly after sampling.

The analytical method used to measure liquid-phase selenium speciation during earlier phases of this research was IC/ICP-DRC-MS, where “DRC” indicates a dynamic reaction cell. Trent University has conducted the IC/ICP-DRC-MS selenium speciation measurements throughout the program. As the bench-scale scrubber test campaign proceeded, the project team tried two additional selenium analytical methods to supplement the measurements by IC/ICP-DRC-MS. The other methods, cathodic stripping voltammetry (CSV) and hydride generation-cold vapor atomic absorption (HG-CVAA or “AA”), are carried out by URS in the same facility where bench-scale tests occur, and analysis of the samples occurs shortly after sampling. Both CSV and AA provide limited selenium speciation data (selenite and total selenium concentrations) on the same day as the test; samples sent to Trent University for full speciation are typically analyzed via IC/ICP-DRC-MS approximately 48 hours after sampling. Results obtained from the “day of test” measurements using CSV and/or AA revealed that, under some circumstances, the selenium speciation may change significantly within the first 48 hours of storage. Therefore, on-site day-of-test sample analysis was continued for remainder of the bench-scale scrubber test campaign. During the pilot tests, selenium speciation was measured on site by a method very similar to the AA method.

In addition to challenges with analyzing selenium speciation in FGD liquors, sample preservation methods and sample stability were not well established at the commencement of the project. Sample preservation refers to how a sample is handled and stored between the time when the sample is collected from the FGD system and the time when the sample is analyzed. A number of approaches have been previously employed to collect and analyze FGD liquor samples from full-scale wet FGD systems for selenium concentration and speciation. At the beginning of the Phase I project, three methods of sample collection and preservation were employed in parallel: unpreserved, acidified, and cryo-frozen in a liquid nitrogen bath. Samples were typically analyzed within two days of sampling.

During the Phase I effort it was decided through evidence in test results and from the results of sample spiking tests that the cryo-freezing technique best preserved the selenium speciation in the bench-scale FGD samples. However, subsequent results from field sample preservation studies indicated that filtered, unpreserved samples provided the best results. Therefore, a sample preservation study was conducted in Spring 2010. Ultimately, parallel unpreserved and cryo-preserved samples were analyzed by IC/ICP-DRC-MS during Phase II bench-scale scrubber testing. Section 3 provides additional details on the sample preservation study and the rational for the selection of two parallel preservation methods.

Challenges Encountered During Pilot-scale Scrubber Testing

Several challenges were encountered during pilot-scale scrubber testing.

Extensive on-site repairs were necessary to allow operation of the pilot scrubber system under the positive pressure conditions of the flue gas at the pilot host site. The costs of the pilot unit repairs decreased the budget remaining for scrubber testing. However, by consolidating the pilot testing with the selenium program, a longer pilot-scale test campaign was completed than would have been possible had each program conducted pilot testing separately.

Detailed material balance calculations around the pilot FGD scrubber revealed that the liquid turnover and sulfur input into the reaction tank were less than anticipated for all tests, for a variety of reasons that are discussed in the pilot test results section. Budget constraints dictated that the test duration could not be extended. The end result is that the changes in liquid-phase concentrations were less rapid than originally anticipated. Despite these challenges, some trends from the bench-scale testing were evident in pilot-scale results.

Accomplishments

Sample Preservation

Work conducted under this project evaluated sample handling and analytical methods for selenium speciation in FGD waters and resulted in recommended procedures for sample handling. Several analytical techniques were employed. Measurements made by different methods were generally consistent for samples measured at the same storage time and containing predominantly selenite and selenate. Measurements of selenium speciation over time indicated that for accurate selenium speciation, it is best to conduct measurements on unpreserved, filtered samples as soon after sampling as possible (<12 hours). For field locations, it is desirable to have on-site measurement capabilities. After the initial 48 to 72 hours, selenium speciation remains stable for two to three weeks. The impact of sample storage time on speciation depends on the sample matrix and the conditions at the time of testing.

conditions without organic acids, the selenite is generally oxidized to selenate. However, selenite does not always fully oxidize to selenate in forced oxidation FGD systems, and unknown compounds may comprise a significant portion of the selenium discharges for some plants, especially for plants using organic acid additives (EPRI, 2009). Effective selenium water management strategies must address this variability in selenium speciation by developing a better understanding of selenium chemistry in the FGD systems.

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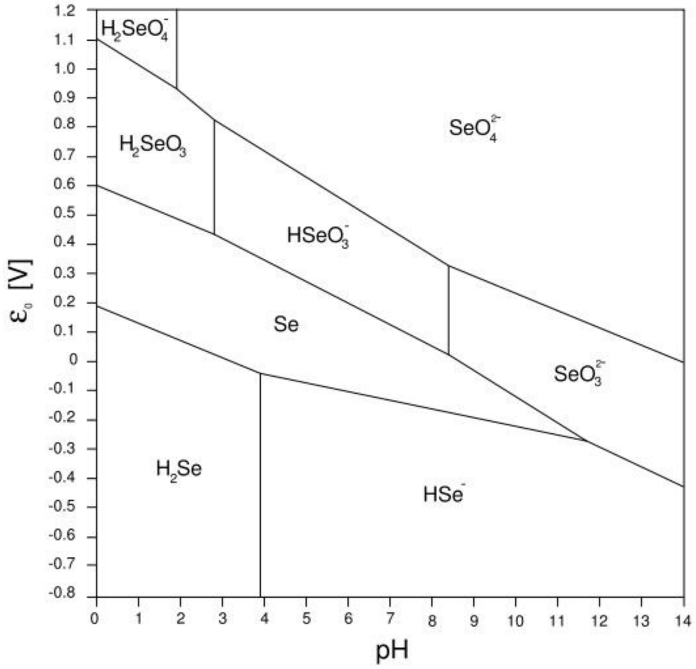


Figure 1-1
Selenium Pourbaix Diagram

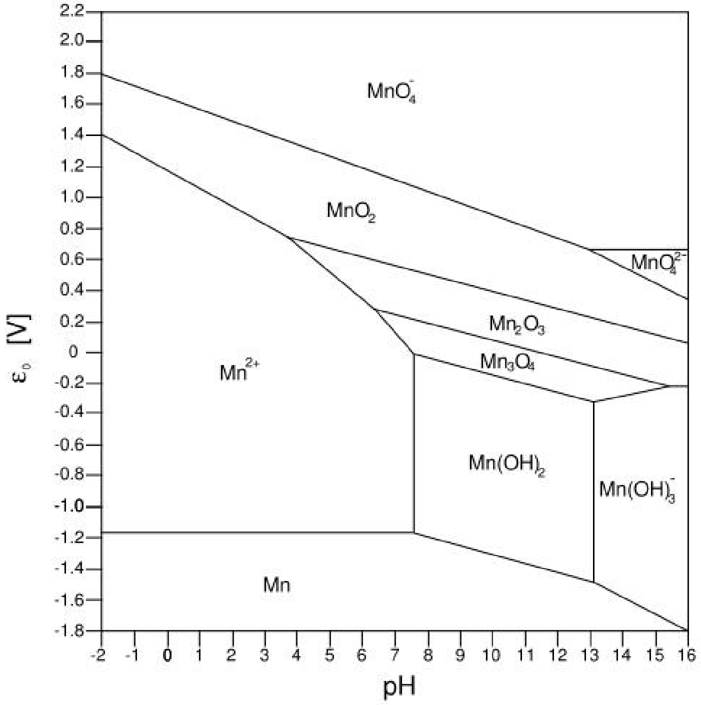


Figure 1-2
Manganese Pourbaix Diagram

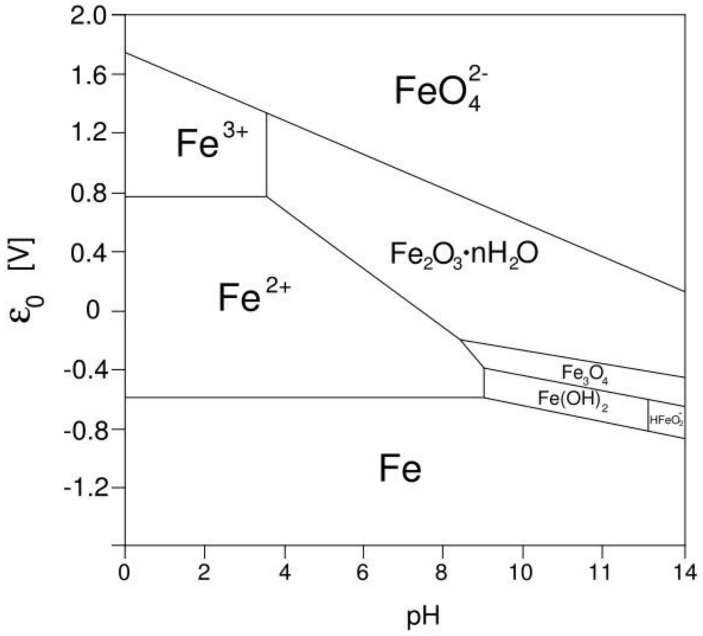


Figure 1-3
Iron Pourbaix Diagram

In Figure 1-1, elemental selenium is shown as Se in the solid phase. Se(IV) is shown as H_2SeO_3, $HSeO_3^-$, and SeO_3^{2-}. Se(VI) is shown as SeO_4^{2-}. The diagram shows that lower pH and lower ORP values favor reduced selenium species. Figure 1-2 shows the manganese Pourbaix diagram. Mn(II) is shown as dissolved Mn^{2+}, $Mn(OH)_2$, and $Mn(OH)_3^-$. Mn(IV) is shown as MnO_2, a solid. Figure 1-3 shows the Pourbaix diagram for iron. Fe(II) is shown as dissolved ferrous (Fe^{2+}) ion. Fe(III) is shown as dissolved ferric (Fe^{3+}) ion and various ferric oxides. Under typical operating conditions of FGD systems (<1.0 V, pH 4.5 to 6.5), multiple species of selenium, manganese, and iron can exist. In some cases (i.e., at certain ORP values), the slight pH change that occurs between the FGD absorber (pH ~4.5) and the FGD reaction tank (pH ~5.5) may cause a change of redox state and/or the transitions between solid and liquid phase species for iron, manganese, and selenium. Additionally, pH directly influences the strength of most oxidants and reductants that may cause conversion between different oxidation states of selenium in FGD systems. Thus, minor adjustments of pH and ORP in the FGD operating environment may have significant results on the form and oxidation state of metals and, therefore, the form and oxidation state of selenium.

Phase I results suggested that conditions that produce *solid* phase manganese also promote selenite oxidation to selenate, but conditions that favor *dissolved* manganese (excluding Mn species in high oxidation states such as permanganate, MnO_4^-) do not favor selenate formation. Additionally, when *solid* phase iron was present, selenium tended to precipitate from solution, and when *dissolved* iron was present, selenite oxidation to selenate was promoted. To minimize selenate formation, the Phase I results suggested that it is desirable to find a pH-ORP operating range at which iron is in the solid phase and manganese is in the liquid phase. The standard Pourbaix diagrams (in "clean" water at 25°C) indicate that it may be possible to find such conditions. Phase II testing investigated a range of ORP conditions with various concentrations of iron and manganese to search for conditions that would maintain near-complete sulfite oxidation, yet avoid selenite oxidation.

Technical Approach and Objectives

Two primary selenium control pathways in FGD scrubbers were considered. First, as noted in the previous paragraphs, scrubber operating conditions and additive usage may be optimized to prevent selenate formation and maintain selenium species that are more easily treated in downstream wastewater treatment facilities. In addition to this first strategy, scrubber conditions and additives may also be used to promote selenium precipitation in the scrubber such that selenium exits with the FGD solid byproduct. The Phase II program sought to develop these two control pathways in the FGD scrubber through extensive bench-scale FGD scrubber testing and subsequent pilot-scale scrubber testing. The primary technical objectives, achieved through the scrubber test campaigns, were the following:

1. Determine what factors control selenium species formed in wet FGD systems and how selenium partitions between FGD slurry solids and liquor.
2. Develop and validate recommendations for FGD operating ranges and scrubber additive use to reduce selenium discharges in FGD wastewaters via two possible methods:

    - Promote the formation of selenium liquid species that can be removed with conventional physical/chemical wastewater treatment (i.e., avoid selenate formation), and/or
    - Reduce FGD selenium water discharges by directing selenium to the slurry solids.

In conjunction with these primary objectives, the project also sought to evaluate and improve sample handling and analysis and to test WWT additives and other WWT strategies in the laboratory.

The originally proposed specific technical objectives for Phase II of this SBIR project included the following:

- At bench scale, optimize FGD operating conditions and scrubber additive usage to minimize selenate formation,
- At bench scale, demonstrate reporting of selenium to solid phase in FGD scrubber,
- At bench scale, conduct extended FGD scrubber runs with liquid residence times typical of full-scale wet FGD systems,
- At laboratory scale, demonstrate a reduction in selenium discharge concentration down to 10-50 µg/L,
- At pilot scale, demonstrate scrubber and wastewater control strategies, and
- Estimate the capital and operating cost impacts of the proposed control strategies.

The Phase II project was divided into the following tasks:

- **Task 1:** Bench-Scale Scrubber Testing and Lab-Scale Wastewater Treatment Tests,
- **Task 2:** Field Testing,
- **Task 3:** Engineering and Economics Analysis, and
- **Task 4:** Management and Reporting.

Under Task 1, bench-scale scrubber tests focused on optimal use of scrubber operating conditions and scrubber additives to control the solubility and behavior of selenium and other constituents that are key to selenium behavior. The Phase II scrubber test campaign included a larger number of standard-length 6-hour runs as well as several intermediate-length tests lasting 10 to 12 hours. The lab-scale wastewater treatment study tested a wider range of wastewater treatment (WWT) additives and operating conditions and tested a novel WWT approach presented in the Phase II proposal, which was intended to remove mixtures of selenium species from FGD wastewater.

Under Task 2, selenium management approaches in the scrubber were tested at the pilot scale with actual flue gas and FGD liquors using an existing skid-mounted FGD scrubber system. Under Task 3, the capital and operating costs for the selenium control strategies were estimated. Task 4 included ongoing project management and reporting for the project.

Problems Encountered and Departure from Planned Methodologies

Challenges Encountered During Bench-scale Scrubber Testing

Sample handling and analysis of selenium speciation in samples taken from FGD scrubbers is an ongoing challenge. Though they may be operating at steady state conditions, scrubber slurries are not at chemical equilibrium. Samples removed from the scrubbers are reactive, and some species present in sampled liquors may continue to react after removal from the scrubber. This phenomenon applies at the bench, pilot, and full scale.

Because the samples are reactive, the project team hypothesized that the selenium speciation might be changing between the time at which a sample is taken and the time at which a sample is analyzed. Therefore, additional analytical techniques were attempted that could be carried out on-site shortly after sampling.

The analytical method used to measure liquid-phase selenium speciation during earlier phases of this research was IC/ICP-DRC-MS, where "DRC" indicates a dynamic reaction cell. Trent University has conducted the IC/ICP-DRC-MS selenium speciation measurements throughout the program. As the bench-scale scrubber test campaign proceeded, the project team tried two additional selenium analytical methods to supplement the measurements by IC/ICP-DRC-MS. The other methods, cathodic stripping voltammetry (CSV) and hydride generation-cold vapor atomic absorption (HG-CVAA or "AA"), are carried out by URS in the same facility where bench-scale tests occur, and analysis of the samples occurs shortly after sampling. Both CSV and AA provide limited selenium speciation data (selenite and total selenium concentrations) on the same day as the test; samples sent to Trent University for full speciation are typically analyzed via IC/ICP-DRC-MS approximately 48 hours after sampling. Results obtained from the "day of test" measurements using CSV and/or AA revealed that, under some circumstances, the selenium speciation may change significantly within the first 48 hours of storage. Therefore, on-site day-of-test sample analysis was continued for remainder of the bench-scale scrubber test campaign. During the pilot tests, selenium speciation was measured on site by a method very similar to the AA method.

In addition to challenges with analyzing selenium speciation in FGD liquors, sample preservation methods and sample stability were not well established at the commencement of the project. Sample preservation refers to how a sample is handled and stored between the time when the sample is collected from the FGD system and the time when the sample is analyzed. A number of approaches have been previously employed to collect and analyze FGD liquor samples from full-scale wet FGD systems for selenium concentration and speciation. At the beginning of the Phase I project, three methods of sample collection and preservation were employed in parallel: unpreserved, acidified, and cryo-frozen in a liquid nitrogen bath. Samples were typically analyzed within two days of sampling.

During the Phase I effort it was decided through evidence in test results and from the results of sample spiking tests that the cryo-freezing technique best preserved the selenium speciation in the bench-scale FGD samples. However, subsequent results from field sample preservation studies indicated that filtered, unpreserved samples provided the best results. Therefore, a sample preservation study was conducted in Spring 2010. Ultimately, parallel unpreserved and cryo-preserved samples were analyzed by IC/ICP-DRC-MS during Phase II bench-scale scrubber testing. Section 3 provides additional details on the sample preservation study and the rational for the selection of two parallel preservation methods.

Challenges Encountered During Pilot-scale Scrubber Testing

Several challenges were encountered during pilot-scale scrubber testing.

Extensive on-site repairs were necessary to allow operation of the pilot scrubber system under the positive pressure conditions of the flue gas at the pilot host site. The costs of the pilot unit repairs decreased the budget remaining for scrubber testing. However, by consolidating the pilot testing with the selenium program, a longer pilot-scale test campaign was completed than would have been possible had each program conducted pilot testing separately.

Detailed material balance calculations around the pilot FGD scrubber revealed that the liquid turnover and sulfur input into the reaction tank were less than anticipated for all tests, for a variety of reasons that are discussed in the pilot test results section. Budget constraints dictated that the test duration could not be extended. The end result is that the changes in liquid-phase concentrations were less rapid than originally anticipated. Despite these challenges, some trends from the bench-scale testing were evident in pilot-scale results.

Accomplishments

Sample Preservation

Work conducted under this project evaluated sample handling and analytical methods for selenium speciation in FGD waters and resulted in recommended procedures for sample handling. Several analytical techniques were employed. Measurements made by different methods were generally consistent for samples measured at the same storage time and containing predominantly selenite and selenate. Measurements of selenium speciation over time indicated that for accurate selenium speciation, it is best to conduct measurements on unpreserved, filtered samples as soon after sampling as possible (<12 hours). For field locations, it is desirable to have on-site measurement capabilities. After the initial 48 to 72 hours, selenium speciation remains stable for two to three weeks. The impact of sample storage time on speciation depends on the sample matrix and the conditions at the time of testing.

Bench-scale FGD Scrubber Tests

Bench-scale scrubber tests measured the impacts of oxidation air rate, trace metals, scrubber additives, and natural limestone in selenium speciation in synthetic FGD liquors. Several bench-scale scrubber tests were conducted in samples of field absorber slurries. Bench-scale tests demonstrated that the presence and concentration of redox-active chemical species as well as the oxidation air rate contribute to the ORP conditions in FGD scrubbers, and the ORP conditions correlate strongly with liquid-phase selenium speciation and, in some cases, with selenium phase partitioning. Selenite oxidation increases with increasing ORP conditions, and decreases with decreasing ORP conditions. Trace metals, such as manganese and iron, typically enter FGD systems as limestone impurities. These metals significantly impact the range of ORP under which the FGD scrubbers can operate.

Scrubber additives, such as DBA, were tested for their ability to inhibit selenite oxidation. Though DBA and other scrubber additives showed early promise in clear liquor tests, later tests with higher concentrations of metals, natural limestone, and field slurries showed less promise. These scrubber additives may be effective in managing selenium chemistry for systems employing limestone with lower metal impurities concentrations or higher chloride purge rates.

The influence of iron on selenium speciation and phase partitioning was measured over a range of iron concentrations and ORP conditions, and the ability of iron to direct selenite to the absorber slurry solid phase was demonstrated. In bench-scale tests conducted in synthetic liquors, increasing concentrations of ferric [Fe(III)] solids resulted in increasing selenite reporting to the solid phase. Under high ORP conditions, selenite may oxidize more rapidly before it sorbs to ferric solids. In bench tests with field liquors, addition of ferric chloride at a 250:1 Fe:Se mass ratio sorbed all added selenite to the solid phase, though addition of ferric salts had no impact on native selenate that already existed in the field slurry sample. If ferric chloride were used to manage scrubber selenium chemistry, process excursions would have to be avoided or rapidly corrected to avoid accumulation of selenate in the scrubber liquor. Any selenate that forms during process excursions would remain until the reaction tank liquor turned over due to blow down.

As might be expected, the oxidizing or reducing conditions in a scrubber, as reflected by the ORP, affect not only selenium, but also other trace elements such as mercury. The impacts of ORP management on the behavior of these other trace elements must also be considered when developing selenium management strategies. In the case of mercury, higher ORP conditions may be desired to limit mercury concentrations in the gypsum byproduct, whereas lower ORP conditions are desirable for limiting selenite oxidation. Research into mercury or selenium management may require a holistic approach that uses both ORP and scrubber additives to define an operating range that maintains SO_2 removal performance, avoids selenite oxidation to less desirable species, and prevents mercury from entering the FGD byproduct gypsum stream.

Bench-scale tests that simultaneously monitored mercury and selenium behavior suggested one possible holistic management strategy. As mentioned earlier in this subsection, addition of ferric chloride to the scrubber in bench-scale tests conducted with field liquors resulted in selenite sorbing to the slurry solids. Under these conditions, mercury re-emissions decreased and the fraction of mercury reporting to the solid phase increased. The mercury preferentially reported to the small solid particles (i.e., “fines”) in the slurry. These small particles may exit with the chloride purge stream for systems that employ hydrocyclones for primary dewatering and thus prevent mercury from entering the byproduct gypsum. Thus, addition of ferric chloride to the scrubber may be one approach that simultaneously addresses selenium and mercury management.

Pilot-scale FGD Scrubber Tests

Pilot testing demonstrated that decreasing oxidation air flow rates shifted selenium phase partitioning to the solid phase of the scrubber slurry. Oxidation air flow control may be one option for managing selenium behavior in FGD scrubbers. It was not possible to demonstrate a benefit to selenium behavior by adding ferric chloride to the scrubber because all "newly absorbed" selenium reported to the solid phase in the natural oxidation (reduced oxidation air rate) test, and no further improvement could be demonstrated. For tests with reduced oxidation air rate and with ferric chloride addition, selenium enrichment in the fine particles was either modest or negligible. Under these conditions, the selenium would exit both with the fines in the purge stream and in the gypsum byproduct. The stability of solid selenium species during the processing of byproduct gypsum into wallboard is unknown. In the absence of this data, capturing selenium in the slurry solids may be preferable to generating selenate, which would likely occur under the higher ORP conditions that retain mercury in the liquid phase.

Pilot testing demonstrated that selenite formed and remained in the slurry liquid phase under low ORP conditions. However, concentrations of sulfite remained in the absorber liquor that are undesirable for forced oxidation systems. Because the low ORP test was cut short, it was not possible to demonstrate appropriate sulfite oxidation levels while retaining selenium as selenite in the liquor. Mercury data were not available for this test; the test was ended early due to a host-site plant shutdown.

Pilot-scale testing also demonstrated that the addition of ferric chloride to the scrubber causes mercury to preferentially report to the slurry fine particles. As noted earlier, the "fines" can exit with the FGD chloride purge stream in systems that use hydrocyclones for primary dewatering. Thus, application of ferric chloride effectively achieves the goal of increasing the mercury content that exits with the liquid purge stream. No decrease in gypsum mercury concentration was measured by the end of the pilot-scale test of this technology; however, mercury concentrations were trending down over time and it is possible that with continued operation some benefit may have been observed.

Wastewater Treatment

Lab-scale WWT tests in synthetic liquors found many additives that could remove selenite. Only high dosages (100 g/L) of elemental iron were successful in removing high percentages of selenate. Low elemental iron dosages (1 g/L) were not very effective. The high elemental iron dosage required for effective selenate removal results in excessive sludge generation, which is undesirable. Lab-scale WWT tests in samples of field liquors generated during pilot scrubber testing showed only modest removal of selenate (<30%) at intermediate elemental iron dosages (10 mg/L and 50 mg/L). Though the kinetics of selenate removal may be improved by adjusting pH or temperature, removal of selenate by physical/chemical treatment with acceptable rates of byproduct generation remains a challenge.

Engineering and Economic Evaluation

The capital and operating costs for two selenium management strategies were considered: ferric chloride addition and oxidation air flow rate control. For ferric chloride addition, as might be expected the reagent makeup costs dominate the overall costs, and range from 0.22 to 0.29 mills/kWh. Impacts on gypsum formation and salability require further evaluation. As part of the evaluation of oxidation air control, blower types and flow control methods typically used for oxidation air blowers were identified. A cursory comparison of capital costs and turndown capabilities for multi-stage and single-stage centrifugal blowers and several flow control methods was completed. For greenfield systems, changing the selection of blower type and flow control method may have payback periods of 4 to 5 years or more if based on energy savings alone. However, the benefits to managing redox chemistry in the scrubber could far outweigh the savings in electricity costs under some circumstances.

Technology Transfer Activities

During the Phase II project, team members presented results from the project at four conferences; citations are listed below.

Searcy, K.; M. Richardson; G. Blythe; D. Wallschläger; P. Chu; and C. Dene. “Selenium Speciation and Partitioning in Wet FGD Systems.” Paper accepted and presented at Air Quality VIII Conference. October 24-27, 2011. Arlington, VA.

Searcy, K.; M. Richardson; G. Blythe; D. Wallschläger; P. Chu; and C. Dene. “Selenium Control in Wet FGD Systems.” Paper accepted and presented at the International Water Conference. November 14-17, 2011. Orlando, FL.

Blythe, G., M. Richardson, P. Chu, C. Dene, D. Wallschläger, K. Searcy, and K. Fisher, "Selenium Speciation and Partitioning in Wet FGD Systems." Paper accepted and presented at the 2010 International Water Conference, San Antonio, Texas, October 24-28, 2010.

Blythe, G., M. Richardson, P. Chu, C. Dene, D. Wallschläger, K. Searcy, and K. Fisher, "Selenium Speciation and Partitioning in Wet FGD Systems." Paper accepted and presented at the 2010 Power Plant Air Pollutant Control "MEGA" Symposium, Baltimore, MD August 30 - September 2, 2010.

Report Organization

Section 2 describes the bench-scale scrubber test apparatus and test method. Section 3 reviews the evaluation of sample handling and analysis techniques for selenium speciation measurements for both bench- and pilot-scale scrubber test campaigns. Then, the results of the bench-scale scrubber testing are summarized in Section 4. The equipment and test approach for pilot testing are outlined in Section 5, and Section 6 details the pilot test campaign results. Laboratory WWT tests were conducted to complement the bench- and pilot-scale scrubber tests; WWT results are discussed in Section 7. Section presents the economic evaluation of two selenium management approaches: ferric chloride addition to the scrubber and oxidation air control. Finally, Section 9 summarizes work conducted throughout the two-year Phase II project and highlights the resulting recommendations for selenium management in wet FGD systems.

2

BENCH-SCALE FGD SCRUBBER TESTS – EXPERIMENTAL APPROACH

Test Method and Apparatus

A schematic of the bench-scale FGD test apparatus used in this research is shown in Figure 2-1. The bench-scale wet FGD system has a bubbler-type flue gas contactor, with simulated flue gas (24 L/min) entering the contactor through a central dip tube into a pool of gypsum and limestone slurry at the base of the absorber vessel. After contact with the slurry, the flue gas exits through the annulus between the dip tube and the outer vessel wall. A stirred 5-L reaction tank is configured directly below and integrally mounted to the gas contactor. The slurry is circulated between the reaction tank and absorber vessel with a peristaltic pump, with gravity flow back to the reaction tank. The pump speed is varied to maintain a desired slurry level in the absorber, which in turn controls the mass transfer properties of the absorber. The bench-scale apparatus is heat traced, insulated and controlled to typical full-scale wet scrubber temperatures.

The reaction tank pH is controlled by makeup of either sodium hydroxide solution, reagent-grade calcium carbonate (limestone slurry), or natural limestone slurry based on feedback control from a pH meter. The pH of the reaction tank slurry liquor is continuously monitored and used to start and stop a reagent makeup pump. A second pH meter monitors, but does not control the slurry liquor pH in the absorber.

Bench-scale tests are run with or without solids added to the initial charge to the reaction tank. Tests without solids are called “clear liquor” tests, and were used in screening and proof-of-concept tests. Sodium hydroxide is generally used for clear liquor tests, and synthetic or natural limestone is generally used for “slurry” tests, where gypsum solids are added to the reaction tank at the beginning of the test and continue to form as the test progresses. Unless otherwise noted, most of the bench-scale tests discussed in this paper used sodium hydroxide as the SO_2 removal reagent and were conducted in the clear liquor mode.

The reaction tank can be operated in inhibited, natural or forced sulfite oxidation modes. All tests discussed in this paper involved operation in the forced oxidation mode. In limestone forced-oxidation wet FGD systems, the liquor sulfite concentration is controlled to low concentrations, typically less than 1.0 mM (80 mg/L), with the oxidation air rate. A UV/visible spectrum (UV/Vis) spectro-photometric method has been developed to measure sulfite concentrations on a continuous basis during clear-liquor tests. For tests with solids present, sulfite is determined by iodometric titration of filtered absorber samples.

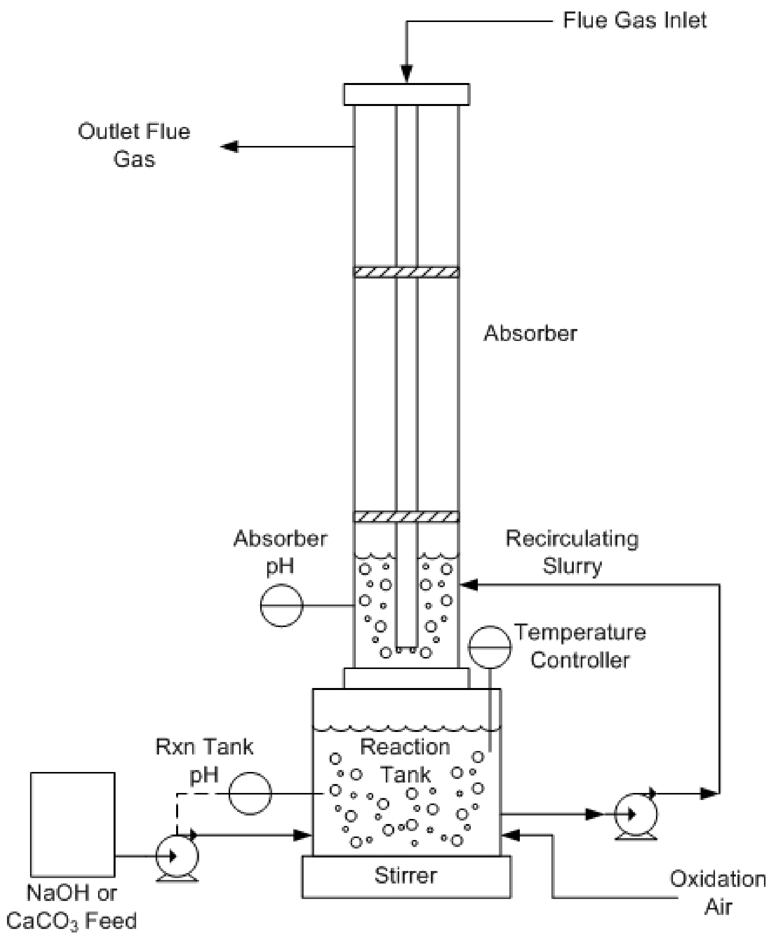


Figure 2-1
Schematic of Bench-scale Wet FGD Scrubber System

Oxidation air is sparged through the reaction tank; the air flow rate may be adjusted manually or controlled automatically up to approximately 6 L/min based on operating parameters. Phase I tests employed manual control of oxidation air flow rate to maintain an acceptable sulfite concentration. In Phase II tests, oxidation reduction potential (ORP), rather than sulfite concentration, was the parameter that was directly controlled by adjusting the oxidation air flow rate. ORP is a measure of whether the slurry liquor is under chemically oxidizing or reducing conditions, and the strength of those conditions. ORP is continuously measured in the liquor feed to the absorber. The readings are made in units of millivolts (mV); positive values correspond with oxidizing conditions and negative values correspond with reducing conditions. All ORP measurements shown or discussed in this report are relative to a silver/silver chloride reference electrode in 4-M potassium chloride. The reported values should have 200 mV added to put them relative to a standard hydrogen electrode, or 41 mV subtracted to put them relative to a saturated calomel electrode (SCE).

Table 2-1 lists the baseline conditions for bench-scale scrubber tests.

Table 2-1
Baseline Conditions for Bench-scale Scrubber Tests

Parameter	Units	Value
General:		
Reaction Tank pH	-	5.5
Temperature	°F	131
Liquid Composition:		
NaCl	mM	100
Ca^{2+}	mM	15
Na_2SO_4	mM	50
Liquor recirculation rate	gpm	~0.3
Gas Phase:		
CO_2	%	12
O_2	%	3
N_2	balanced	balance
SO_2	ppmv	1000
HCl	ppmv	15
NO_x	ppmv	0
Total Flow	actual L/min	24
Oxidation air rate	L/min @ 60 ºF, Patm	≤6

The liquid phase of the absorber slurry is generally spiked at the beginning of a test with reagent-grade chemicals to simulate the steady-state salt composition of a full-scale wet FGD system. Unless otherwise noted, the liquor in the reaction tank was spiked and/or controlled to the values reflected in Table 2-1.

The simulated flue gas composition and flow rate are shown in Table 2-1. The dry constituents are mixed from bottled compressed gases and house compressed air. A portion of the gas is sent through a water saturator prior to mixing in the acid gases to add the moisture.

Typically the simulated scrubber solution is made up with all ingredients added, including trace elements except selenium, which is later added as sodium selenite (Na_2SeO_3) to produce the desired scrubber liquor selenite concentration. The reaction tank solution is heated to the steady state temperature, then acid gas flow through the absorber is started. The pH and ORP control are stabilized and when the system is at steady operation, baseline (time = 0) samples are collected. Next, sodium selenite is injected into the reaction tank liquor to a desired concentration of approximately 1000 µg/L (nominally 1 ppm as Se) to start the test. Standard-length tests are conducted for a period of six hours from the time the sodium selenite is first injected. For these runs, liquor samples are taken at 15 min., 45 min., 90 min., 3 hr, and 6 hr after injection. In Phase II, eight tests were conducted that lasted 10 to 12 hours after selenite injection. For these longer tests, the 45-minute sample was eliminated, and a 10- or 12-hour sample was added.

During Phase I, the selenium speciation measurements were all conducted by Trent's Environmental & Resource Sciences Program and Department of Chemistry, using a form of ion chromatography (IC) combined with inductively-coupled-plasma mass spectrometry with dynamic reaction cell (ICP-DRC-MS) to speciate the selenium compounds. For some tests the samples were also analyzed for total selenium concentration by ICP-DRC-MS (no separation by IC). During Phase II, other selenium analysis methods were employed. Evaluation of the advantages and disadvantages of these other methods is discussed in Section 3.

Test Matrix

The original test matrix for the Phase II bench-scale scrubber campaign was designed to address the technical objectives of the project: to optimize FGD operating conditions and additive usage to prevent selenate formation, to demonstrate selenium precipitation as a means to avoid selenate formation, and to conduct extended-length scrubber tests in order to identify selenium species or behavior that may only occur at long residence times typical of some full-scale FGD systems.

Based on the Phase I findings, variables considered for the bench-scale tests include the following:

- pH,
- ORP,
- Concentration and phase (solid vs. liquid) of metals (e.g., iron, manganese),
- FGD scrubber additives (e.g., dibasic acid vs. pure adipic acid),
- Selenium species (e.g., selenite, selenate, selenosulfate, other),
- Presence of solids,
- Total selenium concentration,
- Alternate sulfur species concentrations (e.g., peroxydisulfate, dithionate),
- Temperature, and
- Actual FGD liquors (in lieu of synthetic liquors).

The first three variables (pH, ORP and metals concentration and phase) represent the primary matrix of conditions required to explore the Phase I hypotheses on how to limit selenite oxidation in wet FGD systems. .

The original bench-scale scope included thirty two (32) regular length (6-hour) tests and four (4) five-day tests. As the test program proceeded, the test matrix was adapted based on test results. During the project, 35 bench-scale scrubber tests were completed: 27 standard-length tests of 6 hours and 8 intermediate-length tests of 10- to 12–hour durations. The shift in scope covered the costs of sample preservation studies, the use of two sample preservation methods, more analyses per test (e.g., dithionate - $S_2O_6^{2-}$, peroxydisulfate - $S_2O_8^{2-}$), evaluation of a bench-top CSV instrument for selenium analysis, and same-day sample analysis using HG-CVAA or "AA" at URS. Two standard-length tests were conducted at the project commencement to monitor the behavior of common FGD constituents as a function of ORP. Then, testing of selenium behavior in synthetic liquors began.

Table 2-2 shows the test matrix for the bench-scale scrubber campaign. Tests in synthetic liquors comprised 15 tests of 6 hours and 8 tests of 10- to 12–hour durations. The test matrix extended the range of metal concentrations evaluated. Earlier research tested the impacts of manganese at 1 to 5 mg/L (approximately 1 to 5 ppm); this program tested up to 35 mg/L manganese in whole slurry, which more accurately reflects recent field measurements (Blythe and Richardson, 2009). The range of iron concentrations was extended up to 600 mg/L iron (Fe) in the whole slurry, which corresponds to using the iron as a scrubber additive. Intermediate concentrations of iron correspond to the "natural" levels found in full-scale absorber slurries as a result of limestone impurities. A number of bench-scale tests investigated competing oxidation and sorption pathways related to iron, and the impacts of four scrubber additives were tested. Four tests with synthetic limestone for pH control were conducted. The natural limestone tests were conducted in collaboration with a mercury research program; therefore, mercury and selenium behaviors were measured simultaneously. Finally, six tests were conducted with samples of field slurries from the host site. Results and additional details for each of these test categories are presented in Section 4.

Table 2-2
Test Matrix for Bench-scale Scrubber Tests

Test Category	**Test #**	**Test Target Conditions**	**Test Length (hours)**
ORP and Mn	29	5 mg/L Mn @ 150 mV (10 h)	10
ORP and Mn	33	5 mg/L Mn @ 150 mV (10 h) Repeat	10
ORP and Mn	34	35 mg/L Mn @ 100 mV	6
ORP and Mn	40	35 mg/L Mn @ 150 mV	6
ORP and Mn	42	5 mg/L Mn with variable ORP (Test 15 re-creation)	6
ORP and Mn	43	5/35 mg/L Mn with variable ORP (Complete Oxidation)	6
ORP and Mn	47	35 mg/L Mn @ 200 to 400 mV	11
ORP and Mn	49	35 mg/L Mn @ 400 mV, 100 mV	10
DBA	30	5 mg/L Mn @ 150 mV with DBA (10 h)	10
DBA	50	35 mg/L Mn @ 400 mV, 1000 mg/L DBA	6
Adipic Acid	32	1000 mg/L adipic acid @ 200 mV (5 mg/L Mn)	6
Acetic Acid	48	35 mg/L Mn @ 400 mV, 1000 mg/L Acetic Acid	10
8-HQS	51	35 mg/L Mn and 3100 mg/L 8-HQS @ 400 mV	6
Selenate	31	Selenate @ 100 mV (5 mg/L Mn)	6
Selenate	44	Mn with Variable ORP (50% Se4, 50% Se6, Complete Oxidation)	6
Fe	37	Low Fe @ 150 mV	6
Fe	35	Med Fe @ 100 mV	6
Fe	36	Med Fe @ 150 mV	6
Fe	41	100 mg/L Fe @ 150 mV	6
Fe	38	High Fe @ 100 mV	6
Fe + Mn	39	High Fe and High Mn @ 150 mV	6
Fe + Solids	45	24 mg/L Fe @ 150 mV with 8% gypsum (actual 115 to 130 mV ORP)	10
Fe + DBA	46	24 mg/L Fe @ 150 mV with 8% gypsum and 1000 mg/L DBA	10

"8-HQS" indicates 8-hydroxyquinoline sulfate.

3

SAMPLE PRESERVATION AND ANALYSIS

Analytical Methods

The analytical method used to measure liquid-phase selenium speciation during earlier phases of this research was IC/ICP-DRC-MS. Trent University conducted the IC/ICP-DRC-MS selenium speciation measurements throughout the program. As the bench-scale scrubber test campaign proceeded, the project team tried two additional selenium analytical methods to supplement the measurements by IC/ICP-DRC-MS. The other methods, CSV and HG-CVAA or “AA”, are carried out by URS in the same facility where bench-scale tests occur. Both CSV and AA provide limited selenium speciation data (selenite and total selenium concentrations) on the same day as the test; samples sent to Trent University for full speciation are typically analyzed via IC/ICP-DRC-MS approximately 48 hours after sampling. Results obtained from the “day of test” measurements using CSV and/or AA revealed that, under some circumstances, the selenium speciation may change significantly within the first 48 hours of storage. During pilot testing, on-site selenium measurements were made using an atomic fluorescence (HG-CVAF or “AF”) instrument in lieu of an atomic absorption instrument; the methods of sample pretreatment for the HG-CVAA and HG-CVAF are nearly identical. Table 3-1 highlights salient attributes for each of the three analytical methods. A brief description along with the pros and cons of each method is provided next.

Inductively Coupled Mass Spectrometry (ICP-MS)

ICP-MS is a highly sensitive and element-specific detector. In this instrument, samples are nebulized into an aerosol, which is introduced into the plasma, where all elements are ionized. Subsequently, the generated ions are separated in a mass spectrometer based on their mass/charge ratio. In the present study, an ICP-MS using dynamic reaction cell (DRC) technology was employed. In the DRC, interferences that would create false positive results are removed by reactions with a reactive gas, while the element of interest, selenium, passes without being affected. Therefore, ICP-DRC-MS yields more accurate results for the determination of elements with many spectroscopic interferences (like selenium) in complex matrices such as FGD waters.

ICP-DRC-MS was used in this project to determine total dissolved selenium concentrations. Additionally, it was coupled to anion-exchange chromatography, a form of ion chromatography (IC) to measure individual dissolved selenium species. Here, the role of IC is to separate different selenium species from each other prior to detection, and the role of ICP-DRC-MS is to quantify both known and unknown selenium species accurately. The independent measurement of total dissolved selenium then helps to assess how complete the selenium speciation mass balance is, i.e. if any major fractions of dissolved selenium remained undetected during the speciation analysis.

Through the remainder of this report, the acronym “ICP-DRC-MS” is often shortened to “ICP-MS.” However, it is implicit that all of the ICP-MS measurements were made using a dynamic reaction cell. ICP-MS measurements of unpreserved and cryo-preserved samples were conducted for all successfully-completed bench-scale scrubber tests; all analyses were conducted approximately 48 hours after sampling.

Atomic Absorption Spectroscopy

The HG-CVAA technique measures selenium by reacting a strong reductant (e.g., sodium borohydride) with an acidified solution containing selenite to form volatile selenium hydride. The volatile hydride is carried to a quartz cell where the hydride is converted to gas-phase selenium atoms, which are measured by atomic absorption spectroscopy (AAS) (Perkin Elmer). In AAS, the concentrations of analytes of interest, such as selenium, are directly proportional to the amount of light absorbed at a specific wavelength. In atomic fluorescence spectrometry (AFS), the concentration of the element of interest is measured by first absorbing radiation of an element-specific wavelength (as in AAS), and then re-emitting it in a different spatial direction. This typically makes AFS about a factor of ten more sensitive than AAS under otherwise identical conditions (sample pretreatment, hydride generation). Selenite is the only selenium species converted to the volatile selenium hydride. Thus, to measure selenium species other than selenite, samples must be digested using techniques designed to convert various selenium species to selenite.

In Phase II, “Day-of-Test” measurements of selenite and total selenium in unpreserved synthetic FGD liquor samples were conducted for 25 tests using the HG-CVAA technique; of these 25 tests, subsequent analysis after 48 hours of storage was conducted for 12 tests.

Cathodic Stripping Voltammetry

The CSV technique utilizes electrochemistry to identify and measure analytes of interest in solution. To measure selenium by CSV, the sample is mixed with a copper solution to form a selenium copper compound, and this compound is adsorbed to the surface of an electrode via a cathodic voltage. Next, the compound is stripped from the electrode surface by sweeping the voltage from approximately -400 mV to approximately -800 mV. During the stripping process, the selenium changes oxidation state by gaining electrons, which creates a current that is measured by a potentiostat and is directly proportional to the selenium concentration in the sample. Analogous to HG-CVAA, this technique is able to measure selenium in the selenite form only, thus various selenium species are measured using digestion methods similar to those used in HG-CVAA.

In Phase II, “Day-of-Test” measurements of selenite and total selenium in unpreserved samples were conducted for 11 tests using CSV. This method was not used to analyze any samples after storage periods beyond the day of test.

Each of the selenium analytical approaches has advantages and disadvantages. Table 3-1 compares the three approaches. IC/ICP-MS has low detection limits and uses chromatography to separate selenium species, which allows for a “full” speciation characterization of all selenium species. Analysis time is rapid, and a high degree of QA/QC is possible. However, the instrument is quite expensive and requires a high degree of training to operate and to interpret the data. Additionally, the project team did not have one of these instruments at the same location as the bench-scale tests during the program, and the instruments are not mobile.

The HG-CVAA technique has moderate detection limits, and its rapid measurement time allows for a high level of QA/QC, making this technique well-suited for research programs that need frequent readings and fast turnaround time. The speciation capabilities provided by this technique are somewhat limited, as speciation is determined by the chemistry of the digestion technique employed rather than separation in a chromatography column as in the IC/ICP-MS technique. The reporting of species other than selenite or selenate, such as selenosulfate and other unknown selenium species, by HG-CVAA is not well documented or understood at this time. Furthermore, preliminary results obtained in this program indicate that selenosulfate is detected by this method as selenite. Although this instrument may not provide full speciation results, its rapid measurements and availability to the project team at the site of the bench-scale tests have proven useful for this research program. The HG-CVAA is moderately expensive, is not mobile, and requires moderately to highly trained staff to operate and interpret the data.

The CSV instrument is mobile (bench-top, but not hand-held), moderately priced, and provides selenite and total selenium measurements. It has the same limitations for determining selenium species as the HG-CVAA technique, and it may have interferences from organic components. Due to its relatively long analysis time and the need to conduct multiple measurements to improve it relative accuracy, the instrument is not well-suited for research programs that need frequent measurements and fast turnaround times. The long analysis time also limits the extent of QA/QC that can be conducted on samples that are changing over time. However, the instrument may be well suited for full-scale plant laboratories, where conditions may not change rapidly and daily monitoring is sufficient.

Table 3-1
Comparison of Selenium Analytical Methods

Technology	**IC/ICP-DRC-MS**	**HG-CVAA**	**CSV**
Sample digestion	None	Yes (TSe* only)	Yes (TSe only)
Selenium species	"Full" speciation	Se(IV), TSe	Se(IV), TSe
Detection limit	1 µg/L or less	30 µg/L	80-100 µg/L
Available for day of test measurements?	No	Yes	Yes
Time per measurement	Minutes	Minutes (excluding digestion time for TSe)	~2.5 hours (excluding digestion time for TSe)
Mobile?	No	No	Yes
Required level of staff training	High	Moderate	Low
Cost	High	Moderate	Moderate

**"TSe" indicates total dissolved selenium.*

Sample Preservation and Stability

Sample Preservation

In addition to challenges with analyzing selenium speciation in FGD liquors, sample preservation methods and sample stability were not well established at the commencement of the project. Sample preservation refers to how a sample is handled and stored between the time when the sample is collected from the FGD system and the time when the sample is analyzed. A number of approaches have been previously employed to collect and analyze FGD liquor samples from full-scale wet FGD systems for selenium concentration and speciation. At the beginning of the Phase I project, three methods of sample collection and preservation were employed in parallel. In each case the sample was taken from the bench-scale FGD reaction tank and immediately filtered through a 0.45-µM pore size filter. The filtered samples were then either 1) Left unpreserved, 2) Acidified to 1% hydrochloric acid (HCl), or 3) Cryo-frozen in the sample bottle in a bath of liquid nitrogen. The first two types of samples were shipped on water-based ice and the third type on dry ice overnight to the Trent analytical laboratory and stored in refrigerators or nitrogen-filled glove boxes until analyzed. Whenever possible, the samples were analyzed within two days after collection.

During the Phase I effort it was decided through evidence in test results and from the results of sample spiking tests that the cryo-freezing technique best preserved the selenium speciation in the bench-scale FGD samples. Thus, for a portion of bench-scale tests sponsored by EPRI, only the cryo-freezing technique was employed, as reported previously (Blythe, 2010). Results from field sample preservation studies indicated that filtered, unpreserved samples provided the best results for those sample types; field sample results suggested a loss of selenium from samples that had been cryo-frozen. Therefore, a sample preservation study for bench-scale scrubber samples was conducted in Spring 2010, which is described next. Ultimately, parallel unpreserved and cryo-preserved samples were analyzed by IC/ICP-MS during Phase II bench-scale scrubber testing.

In the sample preservation study, the stability of selenite, selenate, and selenosulfate were tested using the three preservation methods. The first two were described previously: unpreserved, and cryo preservation, while the third was a novel borate buffer with formaldehyde (“FBB”) preservation. FBB was selected because it is commonly used to preserve samples for wet FGD analyses and “masks” sulfite. It was thought that this masking might prevent trace levels of sulfite in FGD samples from reacting with selenium species during transport or storage. For selenite and selenate, measurement results from unpreserved samples were comparable to results using the cryo and FBB methods. However, for selenosulfate, cryo preservation was favored over no preservation and the FBB method; analysis of unpreserved samples by IC/ICP-MS did not measure appreciable selenosulfate concentrations for parallel samples in which cryo preservation did measure selenosulfate. The project team elected to continue collecting both unpreserved and cryo-preserved samples for selenium speciation in bench-scale scrubber samples to have the greatest probability of accurately measuring the three most common soluble selenium species in FGD systems: selenite, selenate, and selenosulfate.

Short-term Sample Stability

The use of additional selenium analytical methods later in the Phase II bench-scale scrubber test campaign enabled onsite measurement of selenium speciation shortly after sampling, rather than after 48 hours required for shipment for offsite analysis, and greatly improved the ability to quantify and understand sample handling and preservation issues. Comparison of results before and after storage revealed that the selenium speciation for some samples was changing during the first 48 hours after sampling, and the magnitude and nature of the change could depend on the operating conditions at the sampling time. Though the new information presented challenges for sample handling and required re-evaluation of data collected earlier in the program, the data were also encouraging in that the IC/ICP-MS, AA, and CSV measurements were generally consistent with each other for samples measured at the same elapsed time after collection.

Figures 3-1, 3-2, and 3-3 show the selenite oxidation for tests conducted with 35 mg/L manganese only, 35 mg/L manganese with 1000 mg/L acetic acid, and 35 mg/L manganese with 1000 mg/L DBA, respectively. All tests were conducted at an ORP value of ~400 mV (relative to a silver/silver chloride reference in 4-M KCl). In Figures 3-1 through 3-3, the test run time in minutes is shown along the x-axis. At a minimum, liquor samples were typically collected from the bench reaction tank 15, 45, 90, 180, and 360 minutes after injection of selenium for six-hour tests. For ten-hour tests, samples were typically collected at 15, 90, 180, 360, and 600 minutes after selenium injection. Additional samples were occasionally taken for day-of-test AA selenium speciation measurements. The percent selenium oxidation, shown on the y-axis in Figures 3-1 through 3-3, is based on AA results on unpreserved samples at the time of sampling and for unpreserved samples stored for 48 hours. With manganese only, the selenite oxidation ranged from roughly 20 to 40%. After 48 hours of storage, speciation measurements showed complete oxidation for samples originally sampled at high ORP conditions. Thus, storage time may cause a high bias in the conversion of selenite to selenate for high-ORP tests with manganese alone.

In Test 49 (Figure 3-1), the ORP set point was decreased to 100 mV after 360 minutes of run time. The purpose of this change was to observe whether the selenate formed at higher ORP values would then convert back to selenite at the lower ORP conditions. Measurements on the day of the test indicate that the selenate formed did initially convert back to selenite, but the final sample at 600 minutes of run time confounds this observation by showing partial conversion back to selenate. The cause for the increase in oxidation for the final sample is not conclusively known. The final, 600-minute sample taken at nominally 100 mV ORP did not show oxidation of selenite during storage. Review of sulfite, dissolved oxygen, dissolved manganese, dithionate, and peroxydisulfate concentrations from day-of-test measurements and measurements after storage did not reveal an explanation for why the Test 49 samples taken at high ORP apparently oxidized selenite during storage but the final sample at low ORP did not exhibit selenite oxidation after 48-h of storage, though. Dissolved manganese concentrations (not shown in the figure) reached steady-state concentrations within 15 minutes after test commencement and did not change significantly during storage. Therefore, it is not believed that manganese is oxidizing from Mn(II) (aq) to Mn(IV) (s) during storage and subsequently oxidizing the selenite. The Test 49 results provide an example demonstrating the complexity of selenium chemical interactions in FGD samples and the importance of expedient sample analysis.

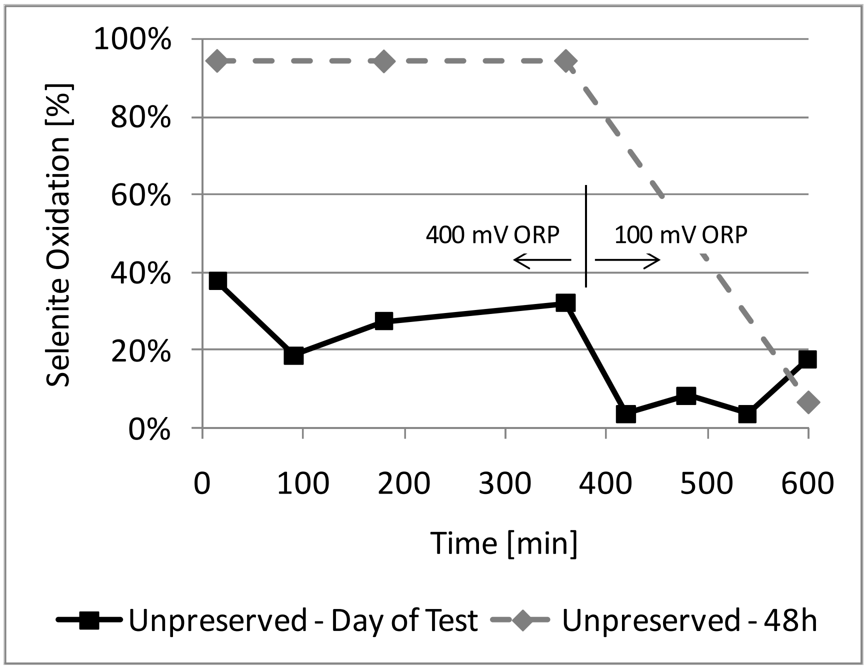


Figure 3-1
Selenite oxidation for 35 mg/L Mn only at 400 to 100 mV ORP (Test 49) before and after storage

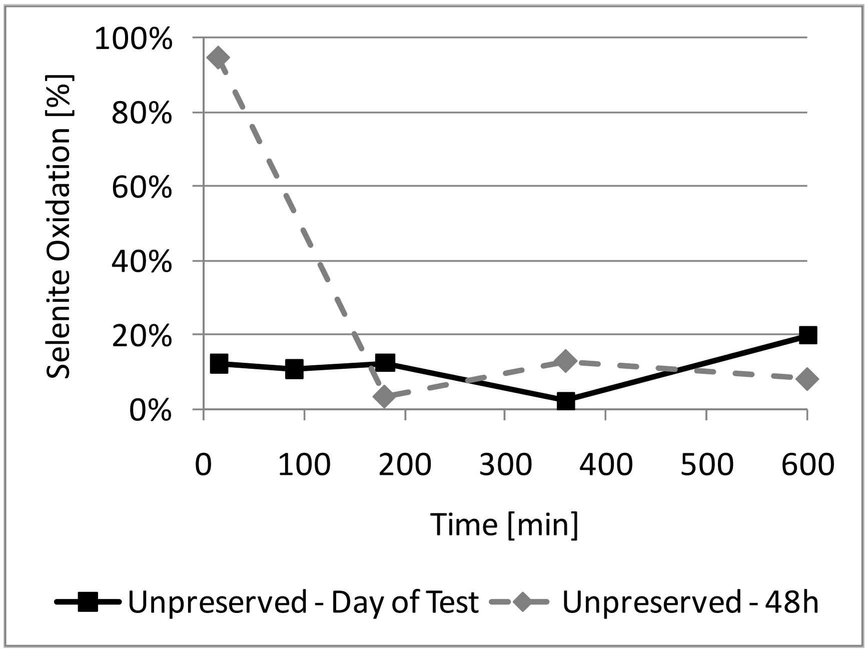


Figure 3-2
Selenite oxidation for 35 mg/L Mn and 1000 mg/L acetic acid at ~400 mV ORP (Test 48) before and after storage

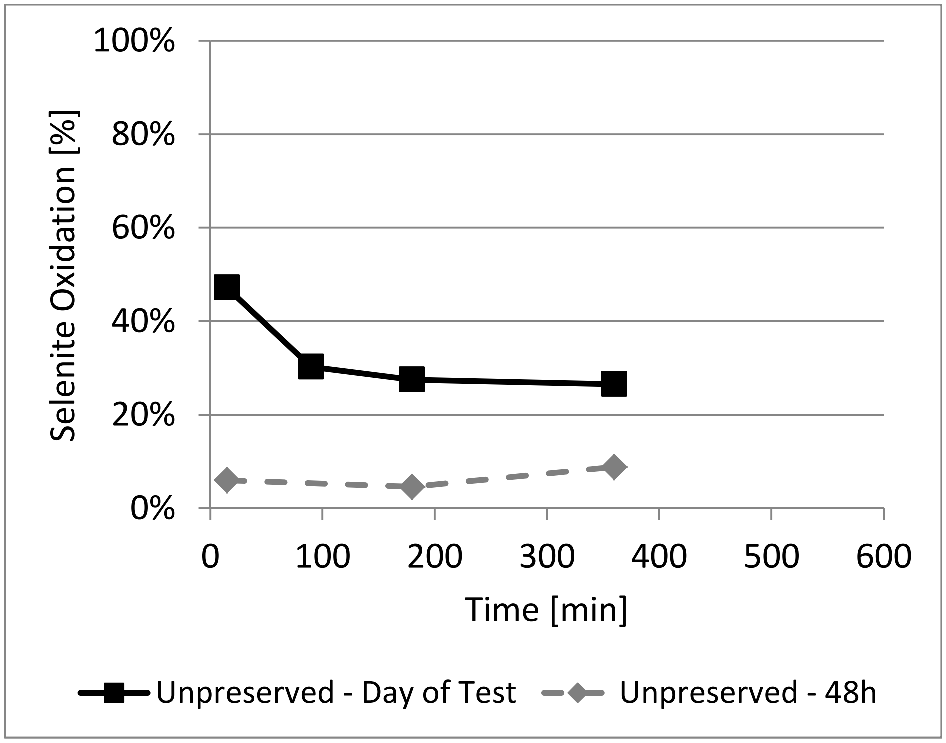


Figure 3-3
Selenite oxidation for 35 mg/L Mn and 1000 mg/L DBA at ~400 mV ORP (Test 50) before and after storage

Data for the acetic acid test (Figure 3-2) show that speciation in the latter samples remains stable at a low oxidation during storage. This result may indicate that acetic acid effectively decreases selenite oxidation and may stabilize the selenium speciation during dewatering and wastewater treatment in a full-scale wet FGD system. Data from the test with DBA (Figure 3-3) are intriguing. Day-of-test results for the test with DBA show similar or even somewhat higher selenite oxidation than the test with manganese alone. However, after storage, measurements show little to no oxidation. These results may indicate that selenate was converted back to selenite during storage.

Longer-term Sample Stability

In April 2011, the stability of selenium speciation was measured over two to three weeks. The purpose of this study was to measure whether samples continue to change after the initial one- to three-day period. Results would help establish a "shelf life" for the samples and could help to minimize sample shipping and analysis costs during the subsequent sampling efforts.

Table 3-2 shows the IC/ICP-MS results for measured selenite (Se^{4+}) and selenate (Se^{6+}) at two to three days and after two to three weeks for unpreserved samples. These filtered samples were obtained from bench-scale scrubber tests that used host site (full-scale FGD) liquor. These results indicate that the measured species concentrations change by less than 10%, and often by much less, between nominally two days and several weeks of elapsed time after sample collection. Measurements by AA, as shown in Table 3-3, showed more variation, typically showing a slight decrease in selenite concentration over time.

Table 3-2
Stability of Selenium Speciation by IC/ICP-MS

	Se$^{(4+)}$ (µg/L)		Se$^{(6+)}$ (µg/L)		Sum of Species (µg/L)	
	2 to 3 days	2 to 3 weeks	2 to 3 days	2 to 3 weeks	2 to 3 days	2 to 3 weeks
54-1U	14.4	16.2	2478	2502	2493	2518
54-3U	857	848	2647	2548	3504	3396
54-5U	534	582	2327	2400	2861	2982
55-1U	2.5	<0.5	2755	2748	2757	2748
55-3U	914	845	2866	2776	3780	3621
55-5U	622	624	2786	2793	3408	3417

Table 3-3
Stability of Selenium Speciation by AA

	Se^{4+} (µg/L)		
ID	Day of test	2 to 3 days	2 to 3 weeks
54-1	<50	<50	<50
54-3	910	978	842
54-5	740	705	626
55-1	<50	<50	<50
55-3	1002	949	783
55-5	728	686	685

Summary

The ability to measure selenium speciation on the day of a test has improved the ability to quantify and understand sample handling and preservation issues. Comparison of results before and after storage revealed that the selenium speciation for many samples was changing during the first 48 hours of storage, and the change could depend on the operating conditions when the sample was collected. Though the new information presented challenges for sample handling and required re-evaluation of data collected earlier in the program, the data were also encouraging in that the IC/ICP-DRC-MS, AA, and CSV measurements were generally consistent with each other for samples measured at the same elapsed time after sample collection.

As these discoveries were made, the sampling and analytical plan was expanded to explore why the speciation was changing. In addition to improving accuracy of measurements, the reasons for the change might also lead to new selenium management strategies. The concentrations of other FGD constituents as well as pH and ORP were measured before and after storage. However, the data did not reveal any definitive explanations.

The key findings from the selenium speciation measurements from the day of the test versus measurements after some time had elapsed are the following:

- For accurate selenium speciation for these synthetic FGD water samples, it was best to conduct measurements on unpreserved, filtered samples as soon after sampling as possible (<12 hours). For field locations, it is desirable to have on-site measurement capabilities. In the absence of on-site measurement capabilities, samples should be filtered immediately through a 0.45-µm pore size filter, diluted 10% with deionized water, placed in a HDPE bottle with no headspace, and stored on ice or in a refrigerator. Dilution of the filtered samples reduces the potential for precipitation of solids in the saturated liquor samples. Analysis should be conducted as rapidly as possible after sampling. After the initial 48 to 72 hours, selenium speciation appears to remain stable for two to three weeks. It is not well established whether the selenium speciation of field liquors changes to the same extent as laboratory-generated synthetic liquors. As the majority of the available "full-scale" selenium speciation data from various field sites were not analyzed within the initial 48 to 72 hours, there is some uncertainty about these data.
- The trend of increasing selenite oxidation with increasing values of ORP remains valid, though the specific values of ORP that correspond to a particular selenite oxidation level may depend on the sample age at the time of analysis.
- In light of the day-of-test speciation results, the benefits of DBA are less conclusive, but the results indicate some reasonable probability that DBA inhibits selenite oxidation. The apparent benefits of other scrubber additives were not affected by the preservation study.
- The impact of sample storage time on speciation depends on the sample matrix and the conditions at the time of testing.

4

BENCH-SCALE FGD SCRUBBER TEST RESULTS

The bench-scale tests can be divided into five groups of tests that focused on the impacts of: 1) manganese and ORP, 2) scrubber additives, 3) iron, 4) natural limestone, and 5) actual FGD liquors. Results from each of these groups are discussed in separate subsections. Detailed analytical data for each bench-scale test are included in Appendix A.

ORP and Manganese

All else being equal, increasing the scrubber ORP by increasing the oxidation air rate increases selenite oxidation and vice versa; however, the mechanism by which oxidation air brings about the change in selenite oxidation is not yet clear. In general, low ORP conditions that favor manganese being present in the dissolved Mn(II) form tend to show little selenite oxidation, whereas moderate to high ORP conditions that favor manganese being oxidized to the Mn(IV) form and predominantly found in the solid phase tend to favor selenite oxidation. Several examples exhibiting this behavior are presented.

Figure 4-1 shows the selenite oxidation, as a percentage of the initial selenite spike of 1000 µg/L, for a test with 35 mg/L manganese at 100 mV ORP (Test 34). Little selenite oxidation was observed and the manganese remained in the liquid phase.

Figure 4-2 shows the selenite oxidation with 35 mg/L manganese for a variable ORP test in which the ORP set point began at 200 mV and was increased to 400 mV after six hours (Test 47). The selenite oxidation was ~20% at 200 mV, which is an increase from no oxidation observed at 100 mV ORP. As the ORP increased further to 400 mV, the selenite oxidation also increased to 40% and finally 80%. At 200 mV, the manganese remained predominantly in the liquid phase. The dissolved manganese concentrations equaled the target manganese concentration within a few percent. Review of the test logs indicates that small amounts of manganese were precipitating on the system walls at moderate ORP, though the bulk liquor remained clear. Thus, conditions favoring only very small quantities of solid-phase Mn(IV) may be sufficient to maintain low selenite oxidation percentages.

Scrubber Additives

Three scrubber additives showed promise for managing selenium chemistry in clear-liquor tests: dibasic acid (DBA), adipic acid, and acetic acid. Results with each of these additives are presented.

DBA shows promise as a scrubber additive to control selenite oxidation, but this promise now comes with some caveats revealed late in the Phase II bench-scale test campaign. Dibasic acid is a byproduct of adipic acid production, a mixture of adipic, succinic, and glutaric acids, and is used as a performance additive in some wet FGD systems. Phase I results and early Phase II results indicated that DBA effectively decreased selenite oxidation that would otherwise occur in the presence of transition metals at moderate to high ORP conditions. The ability to measure selenium speciation on the day of the test has given a more complex view of DBA's impact on selenium chemistry.

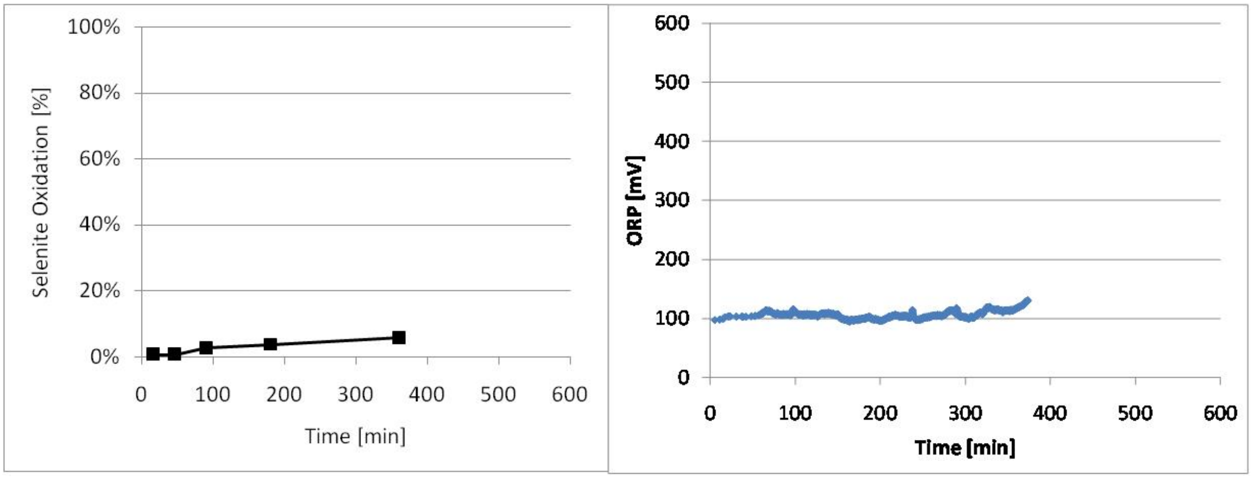


Figure 4-1
Selenite oxidation and ORP for 35 mg/L Mn at 100 mV ORP (Test 34)
(Unpreserved samples measured via IC/ICP-MS after 48h of storage)

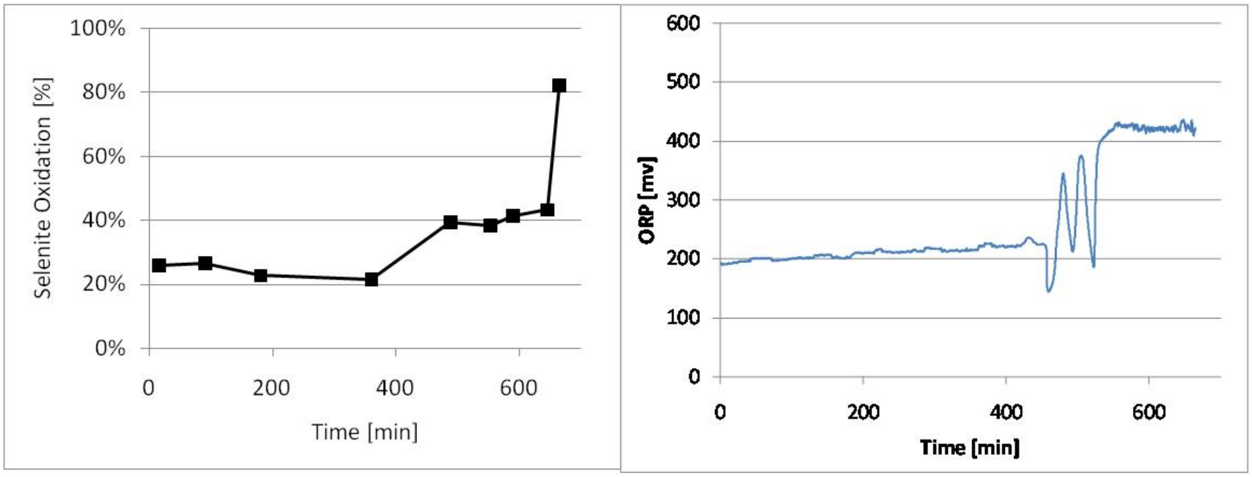


Figure 4-2
Selenite oxidation and ORP for 35 mg/L Mn at Variable ORP (Test 47)

Figure 4-3 shows the effects of DBA and storage time on selenite oxidation for tests with 35 mg/L manganese at 400 mV ORP; these results were also shown in Figures 3-1 and 3-2 as part of the discussion on sample stability. Comparison of the day-of-test oxidation measurements show that selenite oxidation in the presence of manganese is the same or slightly higher (within 10%) when DBA is present than when DBA is absent. However, after storage for 48 hours, the Mn-only samples are completely oxidized, and the Mn-DBA samples show very low oxidation. For the DBA test, the selenate has apparently converted back to selenite during sample storage. These are the only samples for which measurements indicate that selenate was reduced to selenite during storage. The DBA results after 48 hours of storage are consistent with previous measurements (also conducted on 48-hr-old samples) for analogous tests showing that DBA eliminates selenite oxidation. Although the speciation change during storage is promising, it is unknown whether DBA will decrease selenite oxidation in full-scale FGD liquors with time after blow down from the absorber (e.g., in a WWT equalization tank).

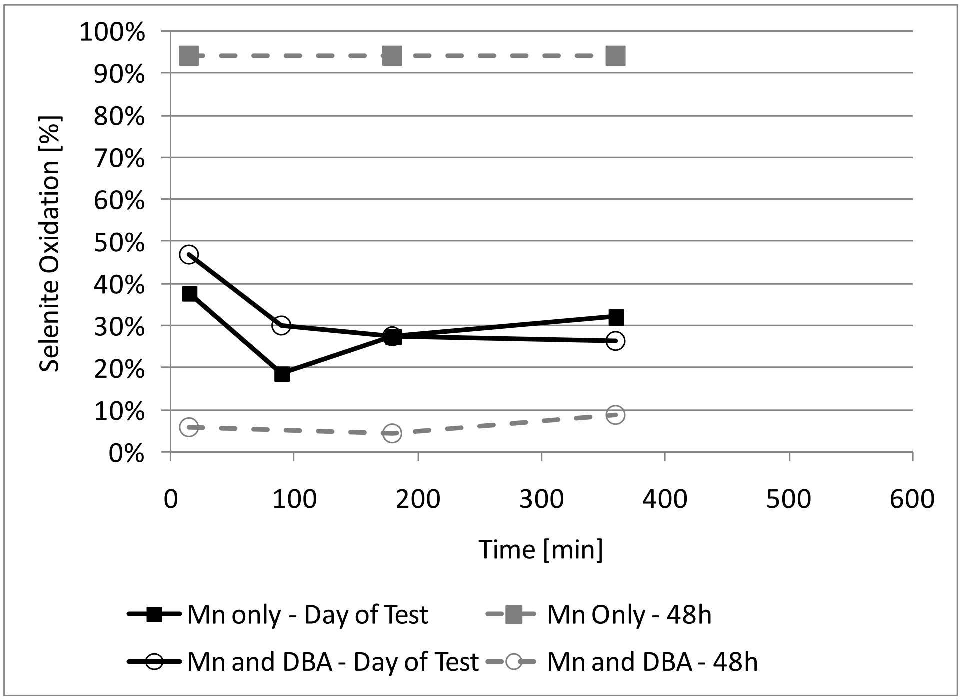


Figure 4-3
Effects of DBA and storage time on selenite oxidation for tests with 35 mg/L Mn at 400 mV ORP

Adipic acid shows promise as a scrubber additive to minimize selenite oxidation, with caveats similar to DBA. A clear-liquor test early in the Phase II program with 5 mg/L manganese and adipic acid, conducted at 200 mV ORP, showed little to no selenite oxidation in samples analyzed by IC/ICP-MS 48 hours after sampling. Similar tests with manganese only (no adipic acid) showed 27-47% oxidation.

Acetic acid also shows promise for decreasing selenite oxidation in FGD systems based on clear liquor bench-scale tests. Figure 4-4 shows selenite oxidation for tests with 35 mg/L manganese at 400 mV ORP both with and without acetic acid. With manganese only, selenite oxidation ranges from 18 to 38%. When acetic acid is present, selenite oxidation was 13% or less. With the exception of the first sample taken 15 minutes into the bench-scale test, all other samples showed no further oxidation of selenite during the 48 hours required to ship the samples off site for IC/ICP-MS analyses for the test with acetic acid. These results indicate that acetic acid may help decrease selenite oxidation and perhaps stabilize that speciation once the FGD liquor exits the scrubber. However, results from subsequent bench-scale tests conducted in this program indicate that higher concentrations of manganese or the impurities in natural limestone may diminish the benefits of acetic acid or require higher dosage levels.

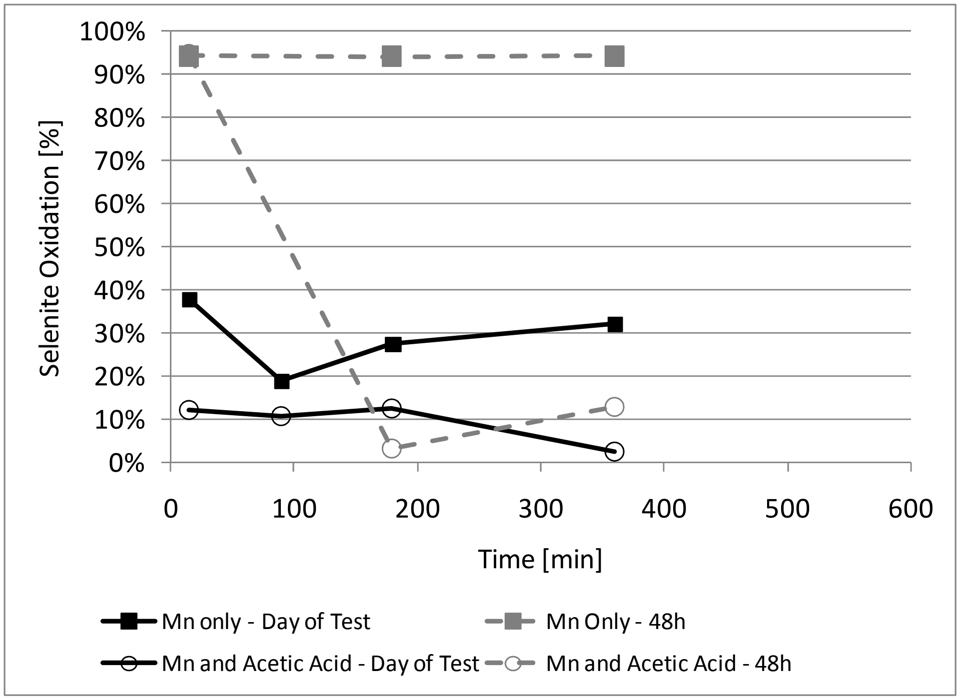


Figure 4-4
Effect of acetic acid and storage on selenite oxidation for tests with 35 mg/L Mn at 400 mV ORP

Iron

Bench-scale testing has demonstrated that various forms of iron can effectively adsorb and/or co-precipitate selenite, and that the amount of selenium adsorbed increases with increasing iron concentration. Figure 4-5 shows the distribution of selenium from the final samples of several tests conducted at a variety of iron dosages; unless otherwise noted, samples were taken after six hours of run time. The amount of selenium adsorbed was estimated by difference between the amount of selenium injected and the total amount of soluble selenium species measured. Reagent ferrous sulfate was added at the beginning of each test with the assumption that all ferrous iron would be oxidized to an insoluble, ferric form. Liquid- and solid-phase measurements for iron confirmed the validity of this assumption; dissolved iron was at or below detection limits within 15 minutes after starting each test. The percent of sorbed selenium, shown by gray-shaded sections in Figure 4-5, increases with increasing iron dosages, though the relationship may not be linear.

Figure 4-6 shows the selenium distribution for tests with 24 mg/L iron at several low and moderate ORP values. As shown by Figure 4-6, selenite sorption decreases as ORP increases, which likely occurs under these conditions because the selenite oxidizes more rapidly than it sorbs to the ferric solids. Addition of synthetic gypsum solids did not cause an appreciable increase in the amount of sorbed selenium.

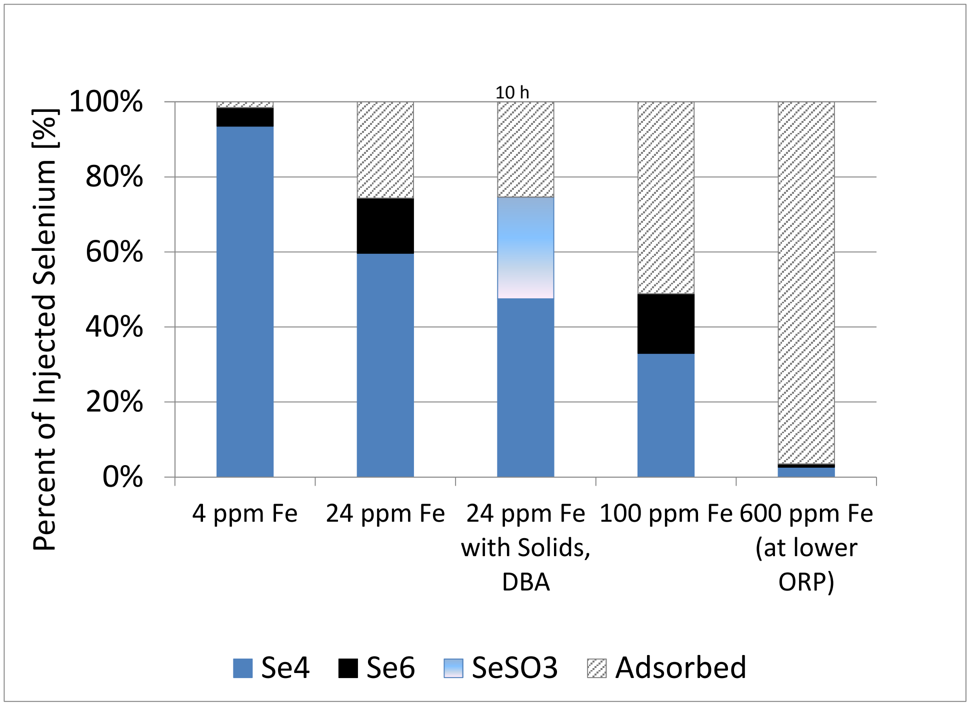


Figure 4-5
Selenium distribution for tests with iron at moderate ORP conditions

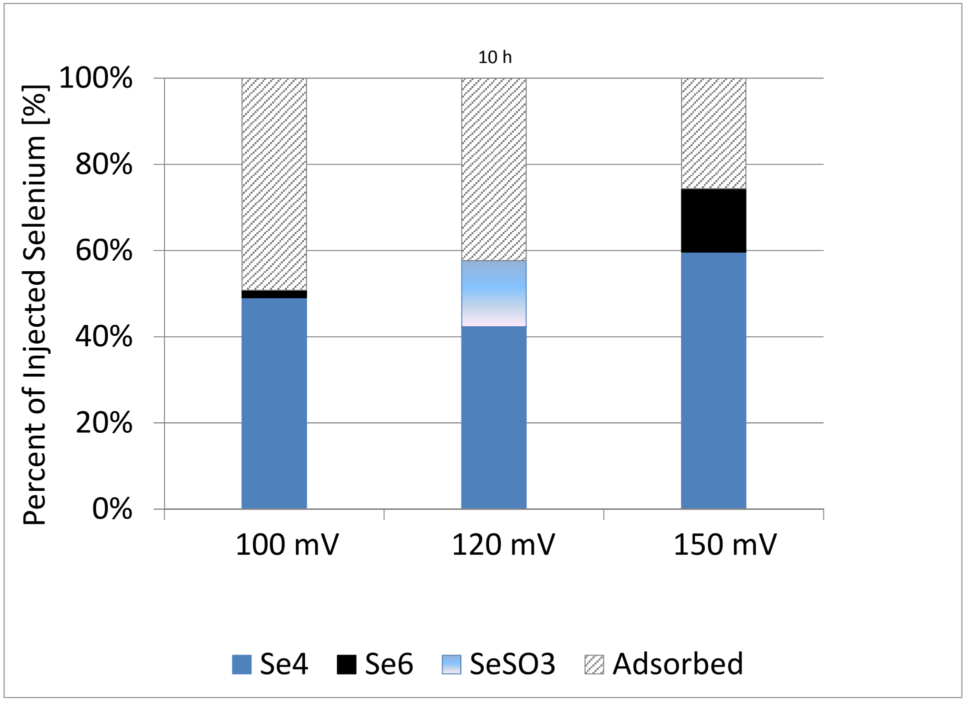


Figure 4-6
Impact of ORP on Selenium distribution for tests with 24 mg/L Iron

As with tests containing manganese, DBA may inhibit the oxidation of selenite in the presence of iron. The stability of sorbed selenium on the iron is unknown. Some researchers have suggested that selenium adsorbed to amorphous iron oxides may re-adsorb to other minerals and subsequently be oxidized to selenate and desorbed if the mineral contacts liquor in an oxidative environment (Al-Abed, 2008). Pilot testing with iron was subsequently conducted as part of this program to observe the stability of sorbed selenium. These results are discussed in Section 6 of this report.

CH2MHill has a recent patent application (#20090130013) for the use of various iron salts in limestone forced-oxidation FGD scrubbers to adsorb selenium and several heavy metals such that the selenium reports to the solid phase of FGD slurries. The SBIR research reported here complements the CH2MHill work by exploring whether selenium management techniques developed under this SBIR project, such as changes to operating conditions or the use of scrubber additives, could enhance or interfere with selenium sorption to iron. The testing conducted under this program also serves to independently verify some of the claims made in the patent application.

Tests with Natural Limestone and Mercury

Research conducted under this program has shown that reducing the ORP favors formation of a selenium species (selenite) that is more easily removed in conventional FGD WWT systems. Research conducted under a separate, concurrent Phase II SBIR project on mercury control (DOE Grant DE-FG02-07ER84682) has indicated that increasing scrubber ORP conditions tends to maintain mercury in soluble, oxidized forms (e.g., Hg^{2+}) such that mercury reports to the liquid phase of the FGD slurry. In some cases, it may be desirable to retain mercury in the liquid phase of the scrubber slurry to avoid impurities in solid byproducts (e.g., gypsum) and then subsequently remove the mercury from the FGD chloride purge stream. Thus, for selenium management lower ORP is desirable, while for mercury management, higher ORP may be desirable. Research into the control of mercury or selenium management may require a holistic approach that uses both ORP and scrubber additives to define an operating range that maintains SO_2 removal performance, avoids selenite oxidation to less desirable species, and prevents mercury from entering the FGD byproduct gypsum stream. If the mercury cannot be retained in the liquid phase under conditions that prevent selenite oxidation, it may be possible to direct the mercury to the slurry fine particles ("fines") and reduce mercury content in the bulk gypsum solids.

Results from both the mercury and the selenium programs indicated that DBA may promote the targeted behavior of both mercury and selenium. Phase I results and early Phase II results, based on measurement by IC/ICP-MS 48 hours after testing, indicated that DBA effectively decreased selenite oxidation that would otherwise occur in the presence of transition metals at moderate to high ORP conditions. Day-of-test measurements by AA gave a more complex view of DBA's impact on selenium chemistry. Results indicated that selenite oxidation in the scrubber was similar with or without DBA and that DBA may convert selenate back to selenite during storage. Those results were confounding because it is unknown whether the DBA will decrease selenite oxidation in the FGD scrubbers or downstream dewatering equipment in full-scale FGD systems. The tests with DBA in the selenium program have used synthetic FGD liquors; tests either contained no solids or used reagent solids. For mercury, DBA caused a marked increase in mercury partitioning to the liquid phase under conditions that would otherwise result in mercury reporting nearly completely to the solid phase.

Given the early promise shown by DBA, several tests were conducted with DBA in which the behavior of mercury and selenium were monitored simultaneously at the bench scale. One test with another scrubber additive, acetic acid, was conducted at high ORP (Test 52). In the selenium program, acetic acid had inhibited selenite oxidation under high ORP condition in synthetic liquors, so the purpose of Test 52 was to determine if acetic acid could inhibit selenite oxidation in the presence of solids reacted from natural limestone under the high ORP conditions that might retain mercury in the liquid phase. Table 4-1 presents the related test matrix, and Table 4-2 shows the test conditions that are common to the four runs.

Table 4-1
Test Matrix and Mercury Partitioning Results for Bench-Scale Scrubber Tests with Natural Limestone, Mercury and Selenium

Test #	Additive	Actual ORP (mV)	Purpose	% Hg in Liquor	% Hg in Solids
49	DBA	175 - 200	Effect of DBA at new manganese baseline and 200 mV ORP	0%	100%
50	DBA	250-275	Effect of DBA at 300 mV ORP	12%	88%
51	DBA	150	Effect of DBA at 150 mV ORP	0%	100%
52	Acetic acid	300	Effect of acetic acid at 300 mV ORP	18%	82%

Table 4-2
Test Conditions for Bench-Scale Tests with Simultaneous Mercury and Selenium Measurement

Description	Units	Value
Reaction tank pH	-	5.5
pH control		10 wt% natural limestone slurry
Solids initial charge		8 wt% Synthetic Gypsum
Manganese - $MnSO_4$	mg/L as Mn	35
Chloride - NaCl	M (mg/L as Cl)	0.1 (3500)
Selenite - Na_2SeO_3 (Se IV)	µg/L as Se	1000
Inlet Flue Gas		
$HgCl_2$	µg/Nm3	30 (note 1)
CO_2	%	12
O_2	%	3
N_2	balanced	Balance
SO_2	ppmv	1000
HCl (g)	ppmv	15
Total Flow	actual L/min	24
Oxidation air rate	L/min @ 60 F, 1 atm	Controlled by ORP set point

Note 1: The inlet mercury concentration is intentionally high so that mercury partitioning behavior may be measured within the test length while also accumulating mercury gradually in the system.

Figure 4-7 shows the final selenium results from the four tests. At the beginning of each test, 1000 µg/L (as Se) of selenite was injected into the reaction tank. The liquid-phase selenite and total selenium concentrations were measured; selenate was estimated by difference. These were the first tests conducted with selenium in the presence of natural limestone solids. In all tests, the total dissolved selenium concentration declined throughout the test, which likely indicates sorption of selenite to the scrubber solids. The amount of selenium sorption after six hours was similar for the four tests. In addition, most tests showed modest to high selenite oxidation for the selenium that remained in solution. At 150 to 200 mV ORP, the measured selenate concentration in the liquor did not increase after the initial 15-minute sample; at 300 mV ORP, selenate concentrations did increase throughout the tests for DBA and acetic acid. The final concentration of selenate in solution was similar for tests with DBA at 300 mV both with and without natural limestone. The oxidation rates in the natural limestone tests were higher than the rates observed for DBA tests in clear liquor tests or tests with reagent solids. These results call into question the benefits of DBA for selenium management and may indicate a shift in the recommended ORP operating ranges. As shown in the results for Test 52, acetic acid did not significantly inhibit selenite oxidation in the natural limestone tests; nearly all dissolved selenium was oxidized to selenate during the six-hour test.

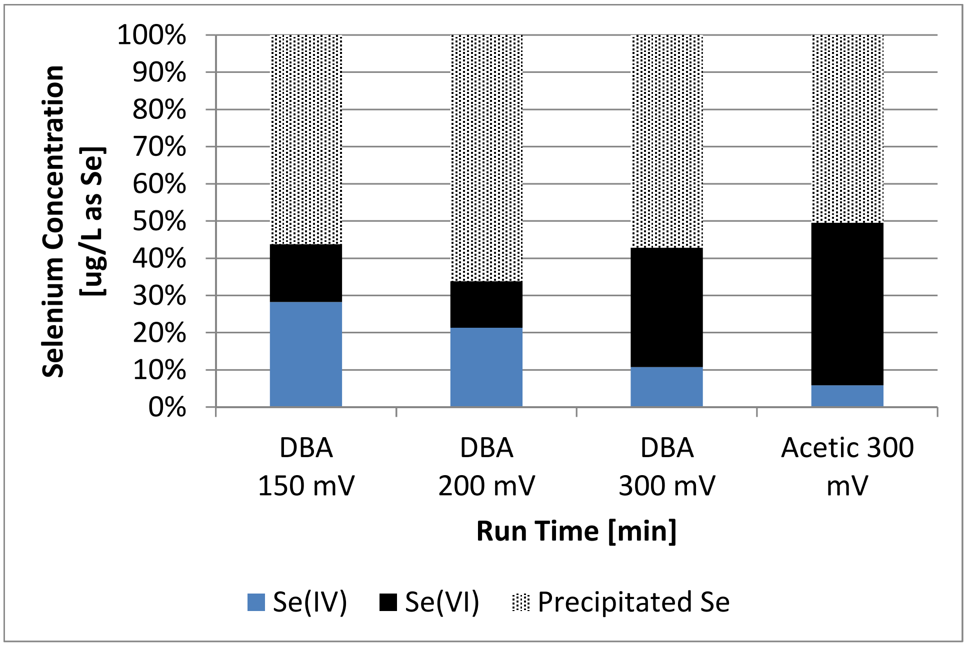


Figure 4-7
Selenium Speciation and Partitioning for Tests with Natural Limestone

At ORP conditions ranging from 150 mV to 300 mV, the percentage of mercury reporting to the liquid phase was low (<18%). The primary difference between an earlier test in the mercury program, which contained DBA and had 87% of the mercury in the liquor, and Tests 49 to 51 is that the latter tests contained higher concentrations of manganese as well as containing selenite. Different dosages of DBA may be warranted at the higher metals concentration, given that DBA can serve as a mild metal complexant. Test 52 with acetic acid showed 18% mercury in the liquid phase despite the elevated ORP conditions.

Given the positive results shown by the earlier mercury test and other tests conducted for the selenium program, further evaluation of DBA was warranted to try and understand why DBA shows benefits to mercury partitioning and selenium speciation under some circumstances but not others.

Tests with Field Liquors

Six bench-scale scrubber tests were conducted with samples of pilot-host-site slurries during April 2011. The purpose of these screening tests was to run test conditions at the bench scale that were under consideration for pilot testing. During these tests, the behavior of both selenium and mercury were monitored. Results from these tests confirmed that selenite oxidation was inhibited by decreasing the ORP conditions. Mercury reporting to the liquid phase increased with increasing ORP and vice versa. Addition of ferric chloride to the scrubber reduced mercury re-emissions and increased the percentage of mercury reporting to the solid phase. A low dosage of ferric chloride sorbed all incoming selenite to the solid phase, although addition of ferric salts had no impact on native selenate that already existed in the field slurry sample. Results from tests with DBA cast some doubt on the benefits of using DBA for selenium or mercury management in FGD scrubbers. Additional details on the test method, test matrix, and results are presented below.

The test method used with the pilot-host-site materials was similar to the method used for synthetic liquors, with a few exceptions. The initial charge added to the bench-scale reaction tank comprised filtered host site absorber liquor recombined with the filtered solids to achieve 8 wt% solids. The pH was controlled using host site limestone slurry, which was filtered and re-combined to achieve 10 wt% solids in the limestone slurry make-up. The maximum reaction tank solids loading is dictated by the degree of agitation that is achievable in the current bench system, and the limestone slurry solids loading was selected to maintain water balance. Mercury addition and measurement techniques were the same as all previous bench-scale scrubber tests. The selenium addition for these tests differed from tests in synthetic liquors. The pilot host site liquor sample provided contained nominally 3000 µg/L as Se of "native" selenate; therefore, the selenite "spike" amount was increased to 2000 µg/L as Se so that changes of selenite could be more easily measured with the higher background amount of selenate. For tests with iron, the selenite and ferric chloride were added gradually throughout the test rather than spiking at the beginning of the test. For these tests, if all selenium remained in the liquor phase, the final total dissolved selenium concentration would be approximately 5000 µg/L as Se.

Table 4-3 shows the test matrix for the screening tests as well as the final selenium speciation as measured on the day of test. The first test was conducted with plant materials at the plant ORP conditions to establish a baseline at the bench scale and to determine how bench-scale results would compare to full-scale results. The remaining tests explored the impacts of ORP and scrubber additives on selenium behavior. The target ferric chloride addition rate was selected for both mercury and selenium management; in this case, selenium was the controlling species, so the "Low" and "High" target addition rates were 250:1 and 500:1 g Fe:g Se, respectively. The ferric chloride addition rate was based on estimates for the amount of selenite added into the bench-scale scrubber.

In the final selenium speciation data as measured on the day of test for these six tests, at least some of the selenite spiked into solution left the liquid phase for all tests, presumably reporting to the solid phase. However, total selenium measurements showed variability and scatter, making it difficult to quantify selenium phase partitioning and selenite oxidation. Under baseline conditions, the selenium speciation generally agreed with the full-scale measurements: all selenite was oxidized to selenate, which is reflected by the final total dissolved selenium concentration of over 4500 µg/L and no detected selenite.

Table 4-3
Final Selenium Speciation for 6-hour Bench-scale Tests with Pilot Host-site Feedstocks

Run #	Test	ORP (mV)	Se^{4+} (µg/L as Se)	Se^{6+} (µg/L as Se)	Total Se (µg/L as Se)
53	Plant ORP (Baseline)	450	<50	4526	4526 (Note 1)
54	Low ORP	200	740	3336	4076
55	High DBA at Low ORP	200	728	3227	3955
56	Ferric Chloride (Concentration 1)	100 - 200	<50	3018	3018 (Note 1)
57	Ferric Chloride (Concentration 2)	100 - 200	<50	2022	2022 (Note 1)
58	DBA at Low ORP and variable pH	200	Note 2	Note 2	Note 2

Note 1: A zero value was assumed in calculating the total dissolved selenium concentration when concentrations of individual species were not above the detection limit.
Note 2: Not reported

Decreasing the ORP decreased the rate of selenite oxidation: 740 µg/L of selenium remained as selenite at the end of Test 54. DBA (Test 55) did not show a clear benefit to inhibiting selenite oxidation when compared with decreasing the ORP alone. Addition of ferric chloride (Test 56) reduced the total liquid phase selenium concentration, and presumably adsorbed or precipitated the selenium. Increasing the ferric chloride dosage rate (Test 57) increased the amount of selenium leaving the liquid phase, presumably by adsorption or co-precipitation with the iron.

Mercury was added to the bench-scale system in a manner similar to the tests with natural limestone, and mercury behavior was monitored during the tests with pilot host-site feedstocks. Figure 4-8 shows the mercury phase partitioning behavior, and Table 4-4 lists both the phase partitioning and the overall mercury re-emissions results.

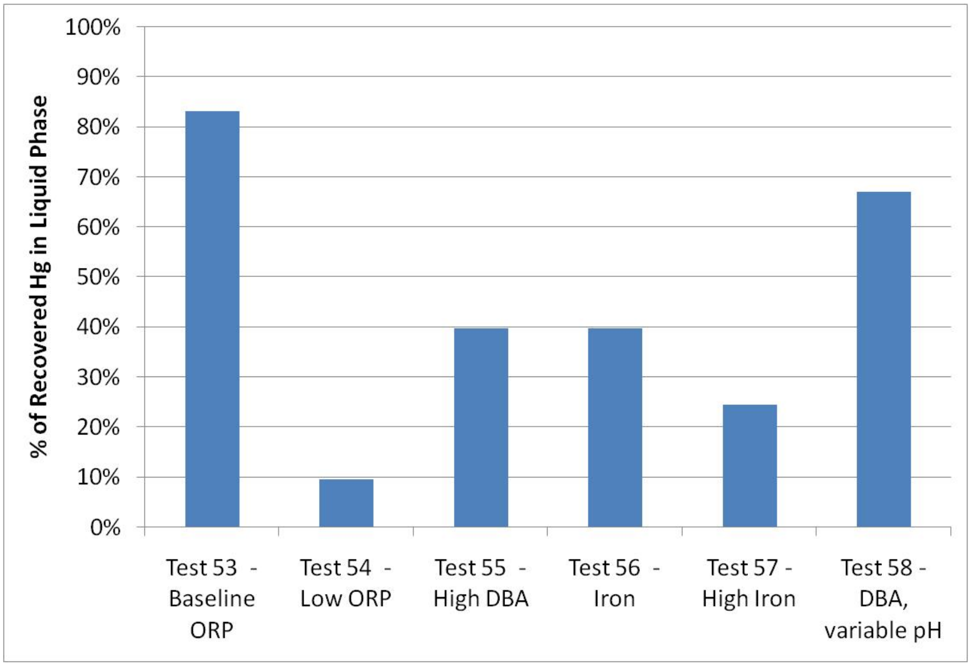


Figure 4-8
Mercury Phase Partitioning for Tests with Pilot Host-Site Feedstocks

Table 4-4
Final Mercury Phase Partitioning and Re-emissions for Tests with Pilot Host-Site Feedstocks

Test Description	% recovered Hg in liquid phase	% recovered Hg in solid phase	% of Hg Re-emitted (as function of Hg Recovered)	% of Hg Re-emitted (as function of initial/native Hg)
Test 53 - Baseline ORP	83%	17%	2%	1%
Test 54 - Low ORP	10%	90%	5%	2%
Test 55 - High DBA	40%	60%	13%	7%
Test 56 - Iron	40%	60%	1%	1%
Test 57 - High Iron	24%	76%	2%	1%
Test 58 - DBA, variable pH	67%	33%	11%	5%

Under baseline conditions (Test 53), the mercury phase partitioning generally agrees with the full-scale measurements: approximately 80% of the mercury reported to the liquor. Decreasing the ORP (Test 54) shifted mercury partitioning to the solid phase of the slurry, as would be expected based on earlier bench-scale scrubber tests. Due to operational problems, little mercury was added to the system during the low ORP test. Therefore, the impacts of ORP on mercury re-emissions cannot be established conclusively from this data set. The conditions with high DBA and moderate ORP (Test 55) resulted in mercury re-emissions and a percentage of mercury reporting to the liquid phase that fell between the baseline, high-ORP test and the low-ORP test percentages. It should be noted that the oxidation air rates during the DBA test were comparable to the air rates during the high ORP test. The DBA acted as a mild reductant, in that the ORP was lowered at the high-ORP air rate and the percentage of mercury partitioning to the liquid phase was reduced. Further testing with DBA (Test 58) indicated that the re-emissions observed with DBA may be a brief transient effect as the system re-equilibrates. Therefore, the impact of DBA on mercury re-emissions is inconclusive. Lower pH conditions may promote mercury partitioning to the solid phase. Addition of ferric chloride to the scrubber (Test 56) reduced mercury re-emissions, and promoted conditions under which mercury shifts to the solid phase. Increasing the ferric chloride rate (Test 57) increased the percentage of mercury reporting to the solid phase; however, even at the higher iron addition rate, 24% of the mercury remained in the liquid phase. Subsequent sample analyses from the pilot-scale testing determined the extent to which the mercury and iron concentrated in the fines.

Summary

The key results from the bench-scale scrubber campaign are the following:

- Selenite oxidation increases with increasing ORP conditions and decreases with decreasing ORP conditions. ORP may be affected by the presence of catalytically-active metals, the rate of oxidation air added to the scrubber reaction tank, the blowdown rate of liquid and fine solids from the FGD system and the corresponding accumulation of oxidizing species, and the use of scrubber additives.
- Solid-phase Mn(IV) catalytically oxidizes selenite to selenate.
- Solid-phase Fe(III) tends to sorb selenite.
- Under higher ORP conditions, the rate of selenite oxidation increases such that selenite may oxidize before it sorbs to ferric solids.
- Though DBA and other scrubber additives showed early promise in clear liquor tests, later tests with higher concentrations of metals, natural limestone, and field slurries showed less promise. These scrubber additives may be effective in managing selenium chemistry for systems employing limestone with lower metal impurities concentrations and/or higher FGD chloride purge rates. Further testing of scrubber additives as a means to manage scrubber ORP and selenium chemistry may be warranted.
- The addition of ferric chloride to the scrubber increased selenite reporting to the slurry solids, though existing selenate was not affected. If ferric chloride were used to manage scrubber selenium chemistry, process excursions would have to be avoided or rapidly corrected to avoid accumulation of selenate in the scrubber liquor. Any selenate that forms during process excursions would remain until the reaction tank liquor turned over due to blow down.
- As would be expected, the oxidizing or reducing conditions in a scrubber, as reflected by the ORP, affect not only selenium, but also other trace elements such as mercury. The impacts of ORP management on the behavior of these other trace elements must also be considered when developing selenium management strategies.
- In the case of mercury, higher ORP condition are often desired from the perspective of minimizing mercury content in the byproduct gypsum, whereas lower ORP conditions are desirable for limiting selenium oxidation. Research into mercury and selenium management may require a holistic approach that uses both ORP and scrubber additives to define an operating range that maintains SO_2 removal performance, avoids selenite oxidation to less

desirable species, and prevents mercury from entering the FGD byproduct gypsum stream. If the mercury cannot be retained in the liquid phase under conditions that prevent selenite oxidation, strategies to direct the mercury to the slurry fine particles (“fines”) and reduce mercury content in the bulk gypsum solids are desirable.

5

PILOT-SCALE FGD SCRUBBER TEST APPROACH

Pilot System Equipment

The wet FGD pilot unit is designed to treat flue gas at a flow rate ranging from 1200 to 2000 acfm, which corresponds to approximately 0.33 to 0.50 MW capacity. It can be operated with lime or limestone reagent (often provided by the host site full-scale wet FGD system reagent preparation system) and with inhibited, natural or forced oxidation. The flue gas contactor includes a single spray nozzle and a perforated plate tray. There is a single mist eliminator stage after the gas absorption section. Figure 5-1 is a simplified schematic for the system.

A pilot-scale hydrocyclone is used periodically (nominally once or twice per day) to blow down reaction tank slurry to control its solids loading. The hydrocyclone is used to separate most of the water and fine particles in the feed slurry, which exit in the overflow, from the bulk of the particles (mostly larger particles) and the remaining water in the feed slurry, which exit in the underflow. A schematic of the pilot hydrocyclone is shown in Figure 5-2.

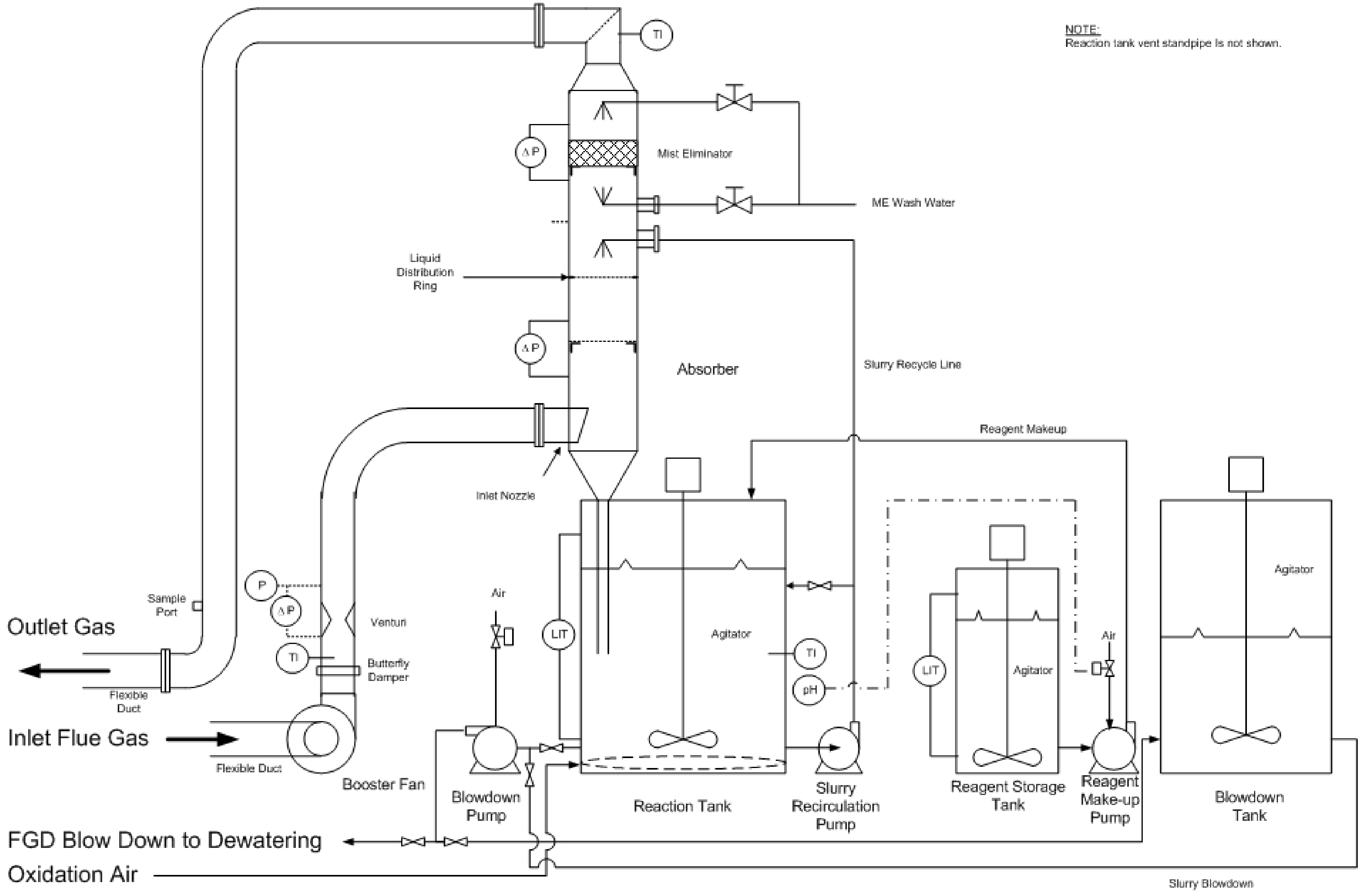
Test Method

For this program, the pilot wet FGD system was operated to treat a slipstream from the full-scale wet FGD inlet flue gas at a target flow rate of 1700 acfm and temperature of 300 °F. Treated flue gas at 125 °F was returned to the wet FGD inlet duct approximately 30-ft downstream of the original draw-off. The flue gas flow rate through the wet FGD pilot is automatically controlled with a butterfly control valve. Sulfur dioxide (SO_2) and other species are removed from the flue gas by contact with an alkaline slurry introduced to the FGD absorber vessel through a spray nozzle. Gas-liquid contact in the absorber is enhanced with a perforated plate tray located below the nozzle.

The pilot wet FGD tests were conducted around the clock for five days each, which allowed for up to one turnover of the liquor in the system. Each test began with a slurry of approximately one-third full-scale wet FGD reaction tank slurry and two-thirds service (makeup) water with an initial spike of chloride salts to achieve expected steady-state concentrations for that anion. Over the five days of test duration the pilot wet FGD approached steady-state values for dissolved species in the liquor, such as chloride and selenium.

Limestone slurry from the full-scale wet FGD system was used for the SO_2 removal reagent in the pilot wet FGD. Limestone is added to the pilot reaction tank as needed based on automatic pH control.

With time in operation, a portion of the reaction tank slurry must be blown down to control the suspended solids concentration in the pilot FGD recycle slurry. This blowdown is directed to the pilot hydrocyclone, with its underflow slurry representing the byproduct gypsum solids from the pilot system, and the dilute overflow slurry containing fine solids returning to the pilot absorber reaction tank.



NOTE:
Reaction tank vent standpipe is not shown.

Figure 5-1
Schematic of Pilot FGD Scrubber System

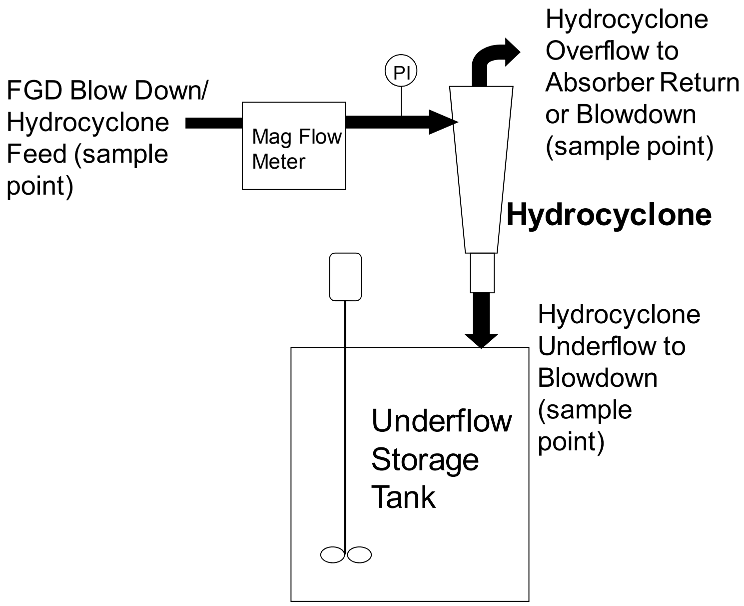


Figure 5-2
Schematic of Pilot Hydrocyclone

In full-scale systems, the hydrocyclone overflow would primarily be returned to the absorber, as it was for these tests, but the underflow would typically flow to secondary dewatering, such as a rotary drum or belt filter, to achieve the final target moisture level in the byproduct gypsum solid cake. In full-scale systems configured as such, the filtrate from the secondary dewatering step and/or a portion of the overflow from the primary hydrocyclones would constitute the chloride purge stream from the FGD system, which is purged through a pond or a wastewater treatment system to prevent excessive buildup of chlorides in the FGD system. In the operation of this pilot unit, the purging of the hydrocyclone underflow slurry took care of limiting the buildup of both solid byproducts resulting from SO_2 removal and dissolved chlorides resulting from HCl removal from the inlet flue gas. Thus, the relative amounts of solids purging and chloride purging was set by the wt% suspended solids in the hydrocyclone underflow stream.

Test Plan

During operation, the pilot FGD inlet and outlet flue gas were monitored for mercury concentration and SO_2 concentration. Gas-phase mercury concentrations were measured using semi-continuous emission monitors (SCEMs) with some modifications to allow for long-term operation in the field. SO_2 concentration was originally slated to be measured using a continuous emissions monitor (CEM), but repeated problems with the instrument precluded its use. Therefore, SO_2 was measured periodically using gas detection stain tubes. A data logger continuously recorded numerous operating parameters such as flue gas temperatures, pressures, and flow rate; reaction tank slurry pH, ORP, and tank level; and others.

At each blowdown episode, a suite of whole slurry, filtered liquor and retained solid samples was collected and preserved from the hydrocyclone feed, underflow and overflow slurries, for on-site and off-site analyses. On-site analyses included wt% solids, sulfite concentrations in the liquor, and selenite and total selenium concentrations in the liquor. Off-site analyses included major FGD analytes, liquid- and solid-phase mercury concentrations, total selenium concentrations in the slurry solids and liquor, concentrations of other trace elements, and selenium speciation in the liquor phase.

At the end of each test, pilot hydrocyclone overflow liquor samples were collected, and beaker-scale WWT simulation tests were subsequently conducted on those samples in the laboratory.

During each test, host unit coal and ash samples were collected, as were full-scale wet FGD recycle slurry and host unit WWT inlet and outlet samples. These samples were analyzed for a suite of analytes, including mercury, total selenium, and selenium speciation in selected liquid-phase samples.

Host Site Description

The confidential pilot host site facility fires low- to-medium-sulfur bituminous coal and is located in the Southeastern United States. The full-scale FGD system operates in forced oxidation mode and does not currently use scrubber additives other than limestone reagent. The host site was selected for a variety of reasons. The primary reason was their willingness to host testing for both of our concurrent SBIR programs and to support installation, operations, and decommissioning. However, the site was also desirable for this testing because of high observed concentrations of mercury and selenium species in their FGD absorber slurry. The absorber operates at elevated ORP conditions (approximately 450 to 625 mV relative to a silver/silver chloride reference electrode in 4-M KCl). As might be expected from the bench-scale results, operation at high ORP conditions results in high concentrations of liquid-phase selenate in the absorber liquor. Analysis of samples from the host unit scrubber confirmed expectations; the liquid-phase selenate concentrations were high at ~1600 to 2100 µg/L as selenium. Earlier samples, used in bench-scale tests with field liquors, from the same full-scale absorber contained selenate concentrations of ~3000 µg/L as selenium. The elevated ORP conditions in the scrubber also result in approximately 90% of the total mercury in the absorber slurry partitioning to the liquid phase. The absorber slurry mercury concentrations are nominally 200 µg/L in the liquor but only 0.1 µg/g in the *bulk* solids.

Targeted Pilot Test Operating Conditions

The targeted test conditions for pilot testing are shown in Table 5-1. The high ORP condition was a baseline condition intended to mimic the behavior of the full-scale absorber at the host site. The high ORP case is actually a desired condition for mercury management when the goal is to retain mercury in the liquid phase. For the host site, decreasing the ORP might benefit selenium management but could create a problem for mercury management by shifting mercury to the gypsum byproduct. The low ORP pilot-scale test, which was expected to result in mercury partitioning to the pilot slurry solids but a reduction in selenate production, was intended to serve as a baseline to be improved upon for the mercury program and the desired condition for the selenium program. The goal of the test with ferric chloride addition to the scrubber was to measure whether ferric chloride could simultaneously adsorb or co-precipitate selenite that was absorbed from the flue gas before it became oxidized to selenate, and direct mercury preferentially to the fine particles, rather than to the product gypsum solids.

Table 5-1
Targeted Pilot Test Conditions

Test	ORP (mV)	pH	Target SO_2 Removal (%)	Wt % Suspended Solids	Mass Ratio of Fe Added to Se in Absorber Liquor
High ORP	450	5.4	>90	6-12	-
Low ORP	200	5.4	>90	7-11	-
Ferric Chloride	200	5.4	>90	9-15	250:1 - 500:1

It should be noted that, as discussed in Section 6, the targeted ORP conditions for the low ORP and ferric chloride addition tests could not be attained. The low ORP test became a natural oxidation test, but the measured slurry ORP remained above 400 mV, while the ferric chloride addition was also conducted at ORP values higher than intended.

The pH set point for all tests was pH 5.4, and the SO_2 removal target was >90% removal. The target ferric chloride addition rate was selected for both mercury and selenium management; in this case, selenium was the controlling species, so the target addition rate was between 250:1 and 500:1 g Fe:g Se. The ferric chloride addition rate was based on estimates for the amount of selenium absorbing into the pilot FGD slurry.

6
PILOT-SCALE TEST RESULTS

Pilot-scale scrubber tests occurred during June and July 2011. Figure 6-1 shows the pilot FGD skid during installation at the host facility. During the pilot test campaign, three five-day tests were conducted: high ORP, low ORP, and ferric chloride addition. The first attempt to operate at low ORP conditions ended after one day of operation due to an unplanned outage at the host site facility; that test was repeated later and conducted for the entire five-day duration.

Figure 6-1
Pilot Wet FGD System

The following subsections describe operations of the full-scale host facility during pilot testing, results for each of the tests, and operational challenges encountered. Discussion of pilot-scale results includes selenium speciation and phase partitioning in the scrubber slurries; mercury capture, re-emissions, and phase partitioning in the scrubber slurries; and results for the behavior of other trace metals (e.g., iron, manganese). The trace metal behavior may correlate with or cause selenium oxidation and sorption, and impact mercury behavior across and within the pilot scrubber. Particular attention is devoted to the distribution of trace metals among different solid particle size fractions because this distribution may provide insight into the mechanisms impacting trace element phase partitioning. Management of the trace element distribution between different solid size fractions might also offer a means to manage the fate of these elements upon exiting FGD systems.

Host Site Data and Operations

During the pilot test campaign, samples and operating data were obtained from the host facility to monitor the pilot system feed streams and to observe full-scale trends in mercury behavior. Coal and fly ash samples were obtained on approximately a daily basis. Scrubber slurry samples were obtained at the beginning of each pilot-scale test and correspond with the initial charge of host site slurry used to partially fill the pilot reaction tank. Limestone slurry samples were obtained each time the pilot reagent tank was filled with a charge of limestone slurry from the host site.

Table 6-1 presents analytical results for samples taken from the full-scale scrubber at the beginning of each five-day test. Operation of the full-scale scrubber was relatively consistent at the beginning of the three tests. In all cases, the dissolved selenium consisted completely of selenate, and 40-45% of the total selenium in the absorber slurry remained in the liquid phase. Liquid-phase mercury concentrations in the full-scale absorber slurry remained high at around 200 µg/L. Mercury was found predominantly in the liquor (>90%) for the samples collected at the beginning of the low ORP (natural oxidation) and ferric chloride addition tests. The solid-phase mercury measurement for the initial, high ORP test suffered from poor precision and may be suspect, calling into question the lower fraction of mercury calculated to have remained in the liquid phase for that sample. As would be expected based on a typical Pourbaix diagram (see Figure 1-2), manganese remained predominantly in the solid phase under the consistently high ORP conditions; iron reported completely to the solid phase as well. Dissolved total organic carbon (TOC) was low in all samples.

Table 6-1
Host Site Full-Scale Absorber Samples from the Beginnings of the Three Pilot FGD Tests

Description	Units	Baseline High ORP	Natural Oxidation	Ferric Chloride Addition
Sample Date		6/15/2011	7/13/2011	7/19/2011
Temperature	ºF	125	125	121
pH (reaction tank)	-	5.34	5.14	5.23
ORP	mV	605	621	n/a
Selenium:				
Dissolved Selenium (HG-CVAA)				
Total Selenium	µg/L as Se	1610	2120	na
Selenite	µg/L as Se	nd	nd	na
Selenate (by difference)	µg/L as Se	1610	2120	na

Table 6-1 (continued)
Host Site Full-Scale Absorber Samples from the Beginnings of the Three Pilot FGD Tests

Description	Units	Baseline High ORP	Natural Oxidation	Ferric Chloride Addition
Dissolved Selenium (IC-ICP-DRC-MS)				
Total Selenium	µg/L as Se	1530	1800	1620
Selenite	µg/L as Se	<0.5	<0.5	<0.5
Selenate	µg/L as Se	1530	1800	1610
Solid Selenium	µg/g	10.9	10.0	11.1
% Se in liquor	%	41	45	40
Mercury:				
Liquor Hg	µg/L	196	211	232
Solid Hg	µg/g	0.45	0.093	0.108
% Hg in Liquor		68%	90%	91%
Iron:				
Liquor Fe	µg/L	<548	<541	n/a
Solid Fe	µg/g	1870	1600	1830
Manganese:				
Liquor Mn	mg/L	0.32	3.93	0.14
Solid Mn	µg/g	159	116	167
% Mn in Liquor		1%	12%	0%
Sulfur Species:				
Sulfite (SO_3)	mg/L	<2	<2	<2
Sulfate (SO_4)	mg/L	1300	1310	1510
Dithionate (S_2O_6)	mg/L	1040	684	259
Peroxydisulfate (S_2O_8)	mg/L	1070	946	805
Halogens:				
Bromide	mg/L	33	80	80
Chloride	mg/L	5260	5430	4780
Suspended Solids content	wt% solids	17.1	19.4	17.9
Liquor TOC (total organic carbon)	mg/L	7	8	8

The host site WWT system comprises a conventional physical/chemical system followed by constructed wetlands. Samples were collected at the WWT inlet and upstream of the constructed wetlands from an equalization basin. The samples were collected prior to beginning each pilot-scale test at approximately the same time samples were collected from the full-scale absorber. Table 6-2 shows the total liquid-phase selenium concentrations at the two sample points. At the WWT inlet, the liquid selenium was almost completely selenate. The wastewater is diluted 4:1 to control the chloride concentration entering the wetlands. After accounting for dilution, the selenate concentrations measured upstream of the wetlands indicated that, as might be expected, selenate was not removed in the conventional physical/chemical portion of the WWT system.

Table 6-2
Liquid-phase Selenium at Host Site WWT Inlet and Outlet

Pilot Test Condition	**Full-Scale Sample Point**	**Se(IV) (µg/L)**	**Se(VI) (µg/L)**	**Sum of Se Species (µg/L)**
Baseline	WWT Inlet	15	1493	1513
	Equalization Basin	<0.5	333	333
Low ORP - 1st Attempt	WWT Inlet	1.0	1853	1857
	Equalization Basin	2.0	376	379
Natural Oxidation	WWT Inlet	1	2347	2348
	Equalization Basin	<0.5	323	323
$FeCl_3$	WWT Inlet	<0.5	1974	1977
	Equalization Basin	<0.5	542	542

Note: Wastewater is diluted 4:1 prior to entering the equalization tank.

Analytical data for coal and ash samples taken from the full-scale host site are presented in Appendix B. Appendix C contains analytical results for trace metal concentrations in samples taken from the full-scale and pilot-scale systems.

Pilot Scrubber Results

The behavior of selenium and numerous other species was measured throughout the pilot test campaign to test the impacts of ORP and ferric chloride addition on selenium behavior. The selenium speciation in the absorber liquor was measured onsite by HG-CVAF, when possible, and offsite by IC/ICP-DRC-MS. The selenium concentrations in the bulk solids, in the hydrocyclone overflow (HCOF) solids, and hydrocyclone underflow (HCUF) solids were also measured during several blowdown events for each test. A limited number of absorber slurry solids samples were separated into particle size fractions by wet sieving; these “wet sieve” data complement the HCOF and HCUF results in observing whether selenium and mercury preferentially reported to smaller particles or dispersed through the bulk slurry solids.

Process operating conditions, flows and system performance indicators were also monitored in order to completely characterize the test conditions. Data on other species may serve to correlate with or explain selenium behavior. Operating data can reveal whether or not the pilot scrubber was operating as desired and may provide some explanation for selenium behavior.

Operational Challenges

Detailed material balance calculations revealed that the sulfur input to and the liquid turnover from the reaction tank were less than anticipated for all tests, for a variety of reasons. First, the host site cycled load during the test campaign. At night, the unit effectively idled such that SO_2 concentrations were roughly half of the daytime concentrations and the flue gas oxygen content was high (up to 10 vol%). The inlet gas flow meter readings also had a suspected high bias. Therefore, blowdown from the system was not as frequent as expected. Additionally, hydrocyclone performance model calculations provided by the vendor underestimated the liquid content of the hydrocyclone underflow, which further decreased liquid turnover. Budget constraints dictated that the test durations could not be extended. The end result was that the changes in liquid-phase concentrations were less rapid than originally anticipated, and it was not possible to demonstrate a reduction of dissolved selenium levels to below 50 µg/L due to the relatively high concentrations of selenate present in the initial charge of host site slurry to the reaction tank. Despite these challenges, some trends from the bench-scale testing were evident in pilot-scale results.

Summary of Test Operations

During the initial, high ORP test, pH and SO_2 removal targets were maintained; ORP ran slightly higher than in the full-scale unit. Pilot FGD ORP values for the baseline test are shown in Figure 6-2. The second test condition was intended to be a low ORP test. However, low ORP conditions were not attainable; therefore, the second test became a natural oxidation test; ORP conditions for this run are shown in Figure 6-3. Oxidation air was turned off within a few hours of beginning the test, yet ORP remained above 400 mV throughout the test. Sulfur removal and sulfite oxidation performance were maintained. These conditions may result from lower than anticipated average inlet SO_2 concentrations, higher than expected flue gas oxygen concentrations, and low flue gas flow rates, which could enhance the relative O_2 to SO_2 pickup rates across the pilot scrubber. In the third test, ferric chloride salts were added continuously to the scrubber via the recirculating slurry stream. Figure 6-4 shows the ORP conditions during this test; the ORP during this test also remained above 400 mV.

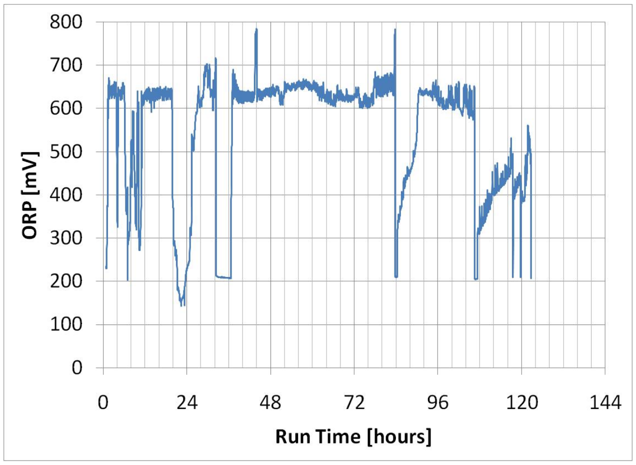


Figure 6-2
ORP – Baseline High ORP Test

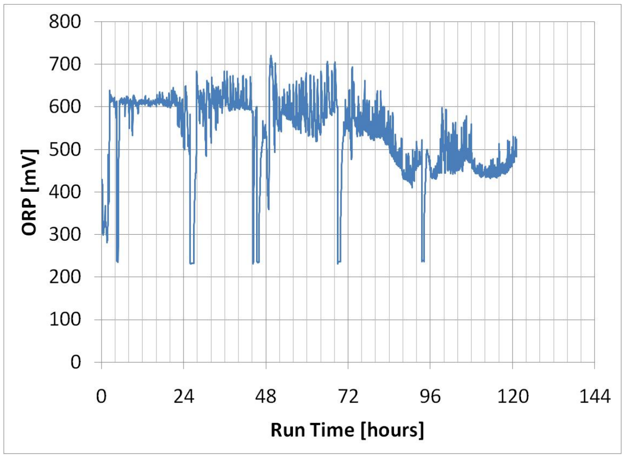


Figure 6-3
ORP – Natural Oxidation Test

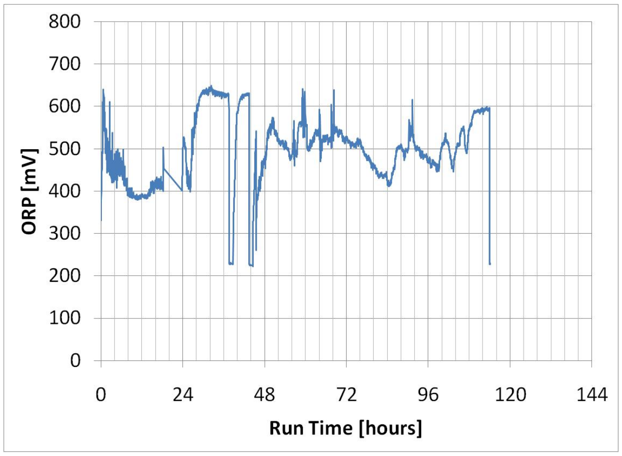


Figure 6-4
ORP – Ferric Chloride Addition Test

Selenium Results

Baseline High ORP Test

Selenium behavior observed during the baseline test in the pilot scrubber was relatively consistent with behavior observed in the full-scale scrubber. Table 6-3 shows the measured total selenium in the liquid and solid phases of the slurry for the initial charge of full-scale scrubber slurry and for the pilot-scale scrubber slurry over the course of the High ORP test. “BD” indicates a blowdown event. All dissolved selenium was measured as selenate throughout the test. Due to the fluctuations in slurry suspended solids loading and level in the pilot FGD reaction tank, a material balance is required to present a complete picture of the selenium phase partitioning. Material balances indicate that most (~75-80%) selenium that was added to the pilot system from the flue gas reported to the slurry solids, although a modest fraction (~20-25%) accumulated in the liquor as selenate. The estimated fraction reporting to the solids is somewhat higher than in the full-scale system, in which slightly less than 60% of the slurry selenium reports to the solid phase.

Table 6-3
Baseline High ORP Test - Scrubber Selenium Measurements

Event	Run Time (h)	Suspended Solids Loading (wt%)	Total Se in Liquor (µg/L)	Total Se in Bulk Solids (µg/g)
Full-Scale				
	0	17.1	1570	10.9
Pilot-Scale				
Initial	0	6.1	487	11.4
BD 1	32	11.3	752	8.1
BD 2	84	11.3	1132	7.6
BD 3	107	12.1	1090	7.4
Final	123	11.3	1112	7.2

Natural Oxidation Test

The second target test condition was a low ORP test. However, as described above low ORP conditions were not attainable; therefore, this became a natural oxidation test. Oxidation air was turned off within a few hours of beginning the test, yet ORP remained above 400 mV throughout the test. Sulfur removal and oxidation performance were maintained. As described above, these conditions may result from lower than anticipated average inlet SO_2 concentrations, higher than expected oxygen concentrations, and low flue gas flow rates, which could enhance the relative O_2 to SO_2 pickup rates across the pilot scrubber.

Table 6-4 shows the measured total selenium in the slurry liquor and solids for the natural oxidation test. As with the baseline test, all dissolved selenium was found in the selenate form. A material balance indicates that nearly all “new” selenium that accumulated in the slurry from the flue gas reported to the solid phase of the slurry. Thus, lowering the oxidation air rate may cause a shift of selenium partitioning from the slurry liquor to the slurry solids.

Table 6-4
Natural Oxidation - Scrubber Selenium Measurements

Event	Run Time (h)	Suspended Solids Loading (wt%)	Total Se in Liquor (µg/L)	Total Se in Bulk Solids (µg/g)
Full-Scale				
	0	19.4	1960	10.0
Pilot-Scale				
Initial	0	7.0	611	9.23
BD 1	26	11.0	767	8.42
BD 2	45	10.8	589	7.74
BD 3	69	10.3	701	7.06
BD 4	94	11.2	779	6.58
Final	121	11.3	720	6.09

Ferric Chloride Addition Test

In the third test, ferric chloride salt solution was added continuously to the scrubber via the recirculating slurry stream. The ORP remained above 400 mV. A material balance indicates that selenium absorbed from the flue gas into the slurry reported almost entirely to the solid phase, as with the natural oxidation test. Measurements of liquid- and solid-phase iron concentrations confirmed that all iron reported to the solid phase of the pilot slurry, and the mass ratio of added iron to accumulating selenium was nominally 500:1. Due to the low liquid turnover during the test, it was not possible to demonstrate reduction of dissolved selenium concentrations to low levels (e.g., <50 µg/L as Se). Given that the natural oxidation test showed nearly all "newly absorbed" selenium entering the system reporting to the solid phase, it was not possible to demonstrate the benefits of ferric chloride addition to the scrubber for selenium management in these tests. Slurry liquor and solid selenium concentrations during this test are summarized in Table 6-5.

Table 6-5
Ferric Chloride Addition Test - Scrubber Selenium Measurements

Event	Run Time (h)	Suspended Solids Loading (wt%)	Total Se in Liquor (µg/L)	Total Se in Bulk Solids (µg/g)
Full-Scale				
	0	17.9	1616	11.1
Pilot-Scale				
Initial	0	9.0	665	9.26
BD 1	38	15.0	746	8.54
BD 2	59	14.5	737	7.86
BD 3	68	12.7	623	-
BD 4	91	11.5	684	-
Final	114	12.7	650	6.75

Low ORP Test, First Attempt

In addition to the three five-day tests that were completed, the first attempt at operating under low ORP conditions ran for one day before shutting down due to an unplanned outage of the host unit. Oxidation air was stopped after two hours of operation due to high observed ORP conditions. During this test, low ORP conditions were achieved during the last five hours of the test. Selenite (68 µg/L as Se) was measured in the final pilot absorber samples from this short test period. Examination of operating data explains how the low ORP conditions were achieved during this test: liquid-to-gas (L/G) ratios were close to typical full-scale values, and flue gas oxygen concentrations were relatively low. It is possible that lower ORP operation might have been realized in the other tests had similar conditions been possible. However, for those tests the host unit load was cycling to very low load, which prevented such conditions from being realized.

The results also indicate that oxidation air flow control may represent one part of a scrubber selenium management approach, though this approach might not be effective for plants that cycle load over a wide range. Figure 6-5 shows the ORP conditions for this test, Figure 6-6 shows the absorber tray pressure drop, and Figure 6-7 shows the flue gas oxygen concentration. During this test, problems with the pilot FGD flue gas control valve were encountered, and the valve opened fully just after six hours of operation. The valve opening is reflected by the sharp increase in absorber tray pressure drop at that time; due to flow meter problems during this time, the higher actual flow rate was not accurately reflected by recorded flow rates. As more SO_2 was absorbed into the system as sulfite, the ORP began dropping rapidly. Then, just after eight hours of operation, the plant began decreasing load, the flue gas oxygen content increased, and the ORP increased simultaneously. After 18 hours of operation, the unit began cycling up in load, the flue gas oxygen decreased, and ORP dropped to nominally 200 mV, where the ORP remained for the last five hours of the test.

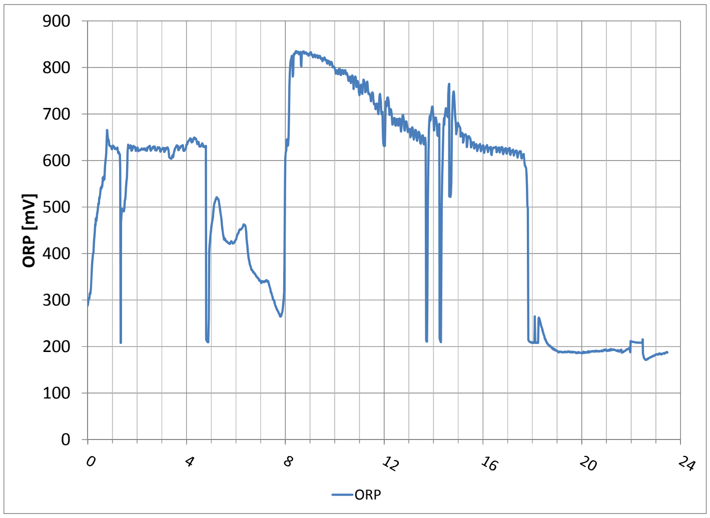


Figure 6-5
ORP – First Attempt at Low ORP

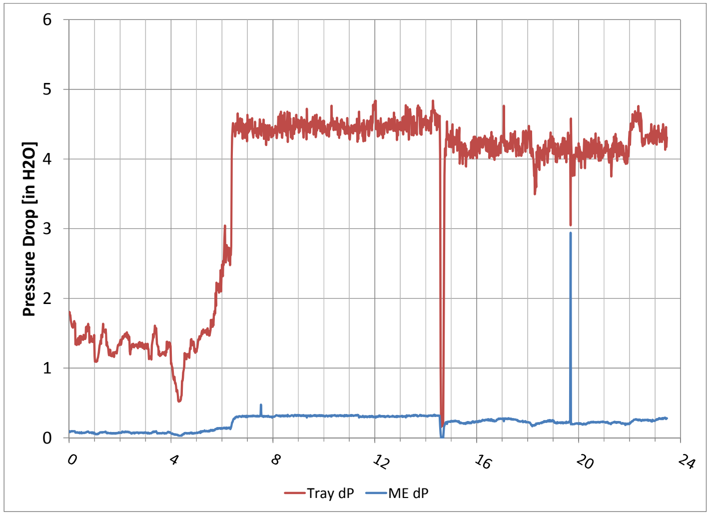


Figure 6-6
Absorber Tray Pressure Drop – First Attempt at Low ORP

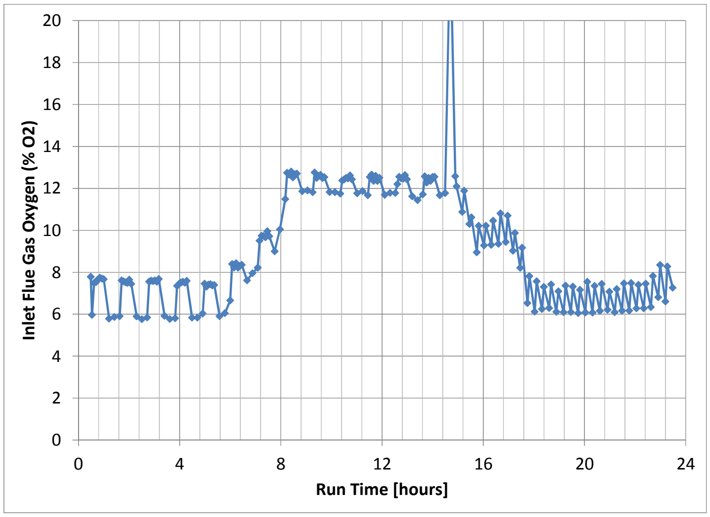


Figure 6-7
Flue Gas Oxygen Concentration – First Attempt at Low ORP

As noted earlier, the final pilot absorber sample for this one-day test contained 68 µg/L selenium of selenite, and this was the only absorber sample measured with selenite during the entire pilot test campaign. High levels of sulfite (376 mg/L) were measured in this sample, which indicates that insufficient oxidation was occurring, though SO_2 removal across the scrubber remained at 97% during this time. It is possible that some low level of oxidation air could have served to oxidize the sulfite yet avoid selenite oxidation, and thus more closely represent acceptable forced oxidation conditions. This would strengthen the results showing less selenate formation and increased reporting of selenium to the solid phase with decreasing oxidation air and ORP, as measured during the second attempt to operate at low ORP (the natural oxidation test).

Solid-phase Selenium Results

The distribution of solid-phase selenium within different particle size fractions of the pilot scrubber slurry solids was measured during pilot testing. Two measurement approaches were used: (1) distribution between pilot HCOF and HCUF streams during blowdown events and (2) distribution between different size fractions in the absorber slurry based on wet-sieved slurry solid samples. Table 6-6 presents the solid selenium measured in pilot HCOF and HCUF streams.

Table 6-6
Solid Selenium in Pilot Hydrocyclone Underflow and Overflow

Test Condition	Run Time (h)	HC Underflow		HC Overflow		% of Solid Se in HCOF solids
		Se in Solids (µg/g)	Wt % Solids	Se in Solids (µg/g)	Wt % Solids	
Baseline High ORP	84	8.0	61.0	9.0	2.7	16%
Baseline High ORP	123	7.1	59.7	11.3	3.4	17%
Natural Oxidation	26	8.1	63.0	10.9	3.1	17%
Natural Oxidation	69	7.2	62.0	9.0	2.6	20%
Natural Oxidation	121	5.7	60.9	8.1	3.4	30%
Ferric Chloride Addition	38	9.6	61.9	10.9	5.9	25%
Ferric Chloride Addition	68	8.1	60.6	14.3	2.5	14%
Ferric Chloride Addition	114	5.6	61.1	11.2	4.0	39%

In all cases, the selenium concentrations measured in the fine particles, as reflected by the HCOF results, were higher than the selenium concentrations measured in the bulk solids. However, the ratio of selenium concentrations in the finer overflow solids to concentration in the underflow solids was less than 2.0 in all but the final blowdown samples from the ferric chloride addition test. The percentages of selenium reporting to the fine particles show slight variations between tests. The natural oxidation test showed a slightly higher fraction of selenium reporting to the fines, and the ferric chloride tests showed slightly more selenium in the fines relative to the natural oxidation test. The distribution of selenium between the solid size fractions for the ferric chloride test showed more variation between samples and did not exhibit a monotonic trend, so the results are not conclusive.

Wet sieving of solid samples separated fractions comprised of particles >20 µm (bulk solids) and particles <20 µm (fines). Solid samples from the initial charge of full-scale absorber slurry and from the final pilot-scale absorber slurry were wet-sieved; the results are presented in Figure 6-8 and Table 6-7.

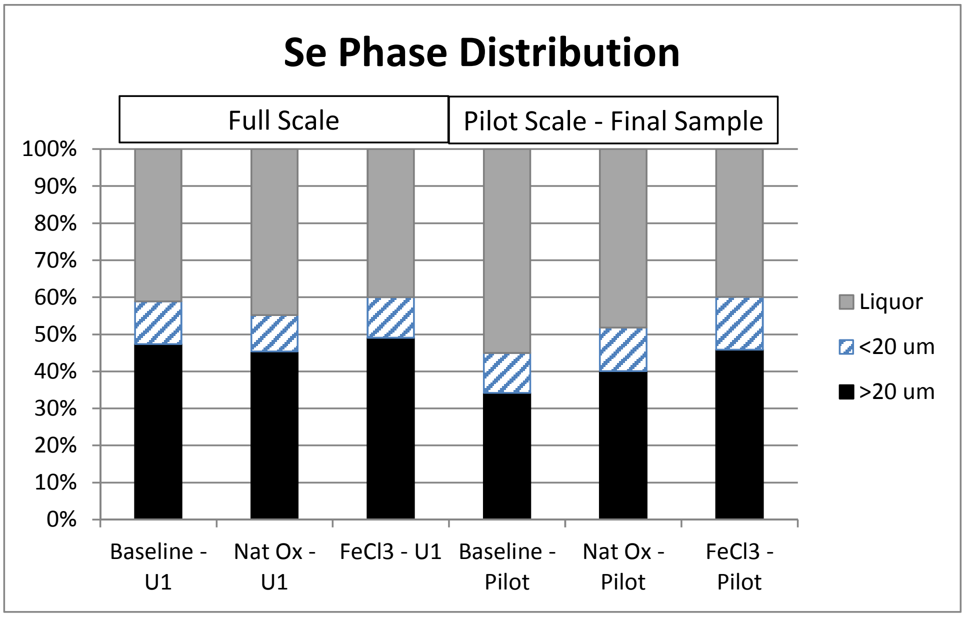


Figure 6-8
Selenium Phase Partitioning in Full-scale and Pilot-scale Absorber Samples

Table 6-7
Solid-phase Selenium Results in Wet-Sieved Samples

Master Sample	Se Conc. (>20 µm) (µg/g)	Se Conc. (<20 µm) (µg/g)	<20 µm (wt% of solids in size range)	<20 µm (% of solid Se)	% Se in Solids (% total Se)	% Se in >20 µm (% total Se)	% Se in <20 µm (% total Se)	% Se in Liquor (% total Se)
Full-scale (for samples collected at the beginning of the pilot-scale test shown):								
Baseline High ORP	9.69	10.2	19%	20%	59%	47%	12%	41%
Natural Oxidation	9.18	10.1	16%	18%	55%	45%	10%	45%
Ferric Chloride Addition	10.2	9.02	20%	18%	60%	49%	11%	40%
Pilot-scale (end-of-test samples):								
Baseline High ORP	6.34	7.40	21%	24%	45%	34%	11%	55%
Natural Oxidation	5.20	6.72	18%	23%	52%	40%	12%	48%
Ferric Chloride Addition	4.80	14.0	10%	24%	60%	46%	14%	40%

The wet-sieving results exhibited little variation in the mass fraction of solid selenium that reported to each of the size fractions, both in full-scale and pilot-scale scrubber samples. The ratio of the selenium concentrations in the fines to selenium concentrations in the bulk solids was less than 1.5 except for the final ferric chloride pilot scrubber sample. The mass fraction of selenium that reported to the fines during the ferric chloride test is similar to that in the other tests despite a much higher selenium *concentration* in the fines, because the fines in the ferric chloride test represented a smaller portion of the total solids content of the slurry. Enrichment of other trace metals (e.g., iron and mercury) in the slurry fines is typically much higher than the enrichment observed for selenium and may be employed to manage the fate of those species upon exiting the FGD system. Thus, the relatively low enrichment of selenium in the fines during the baseline and natural oxidation tests may indicate that under those conditions some selenium co-precipitates with the gypsum rather than associating with iron impurities in the limestone. In light of the bench-scale results in which ferric chloride addition caused a clear shift of selenium phase partitioning to the solid phase, several competing pathways may govern the reporting of selenium to the slurry solids: co-precipitation with gypsum into the bulk solids and sorption or co-precipitation with iron into the fine particles. The dominance of these pathways in controlling selenium behavior may depend on scrubber operating conditions.

Mercury

Several metrics were used to monitor the behavior of mercury in the pilot scrubber during these tests: gas-phase mercury capture and re-emissions across the scrubber, phase partitioning of mercury in the absorber slurry, and distribution of mercury between solid size fractions of the absorber slurry.

The data for capture and re-emissions of mercury across the scrubber for each of the four tests (including the initial low ORP test that was stopped after one day by a unit outage) are summarized as test averages and standard deviations in Table 6-8. Detailed mercury concentration data are presented graphically in Appendix D. The mercury removal across the scrubber is calculated as a percentage of total inlet mercury, and the mercury re-emission is the percentage of inlet oxidized gas-phase mercury that is chemically reduced in the scrubber and re-emitted as elemental gas-phase mercury. For all tests, the inlet flue gas mercury oxidation averaged above 90%, with concentrations of total mercury typically at or below 5 $\mu g/Nm^3$ (corrected to 3% O_2 and reported on a dry basis); the concentrations were considerably lower on a wet and actual air dilution basis, particularly when the flue gas O_2 concentration was in the range of 10%. As reflected in Table 6-8, the three five-day tests showed similar mercury capture across the scrubber. The low ORP test showed slightly lower mercury capture and slightly higher re-emissions. However, the variability in capture and re-emissions for all tests, as reflected by the standard deviations of mercury removal and re-emissions, prevents reaching strong conclusions regarding the impact of ORP and ferric chloride use on mercury capture and re-emissions.

Table 6-8
Mercury Removal and Re-emissions across Pilot Scrubber

Test	% Hg Removal		% Hg Re-emissions	
	Average	**Std Dev**	**Average**	**Std Dev**
Baseline	74%	25%	8%	11%
Low ORP – 1	62%	17%	19%	21%
Natural Oxidation	75%	17%	11%	12%
Ferric Chloride	77%	14%	5%	8%

Table 6-9 shows the mercury concentrations and the phase partitioning for mercury in the pilot absorber slurry as well as in the hydrocyclone overflow and underflow streams during blowdown events. In the baseline, high ORP test and in the natural oxidation test, about 70 to 80% of the mercury remained in the liquor, while 20 to 30% reported to the solids. In contrast, in the full-scale absorber, approximately 90% of the mercury reports to the slurry liquor, so the pilot high ORP test, which was intended to mimic the full-scale operation, shows a lower fraction of mercury reporting to the liquor. A lower fraction reporting to the liquor was expected during the natural oxidation test but was not achieved, likely because the measured pilot absorber slurry ORP never dropped below 400 mV.

Table 6-9
Mercury Phase Partitioning in Bulk Pilot Absorber Slurry, HCOF, and HCUF Streams

		Absorber Slurry Phase Partitioning				Hydrocyclone Underflow		Hydrocyclone Overflow		% of Solid Hg in Feed Reporting to Hydrocyclone Overflow solids
Test	Run Time (h)	Hg Conc. in Liquor (µg/L)	Hg Conc. in Solids (µg/g)	Wt % Solids	% Hg Reporting to Solids	Hg Conc. in Solids (µg/g)	Wt % Solids	Hg Conc. in Solids (µg/g)	Wt % Solids	
Baseline High ORP										
	0	21	0.11	6.1	24%	-	-	-	-	-
	32	67	0.17	12.3	26%					
	84	90	0.24	11.3	25%	0.08	61.0	0.79	2.7	72%
	123	76	0.22	11.3	27%	0.09	59.7	0.68	3.4	71%
Natural Oxidation										
	0	52	0.29	7.0	29%	-	-	-	-	-
	26	79	0.16	11.0	20%	0.08	63.0	0.41	3.1	61%
	69	97	0.18	10.2	17%	0.05	62.0	0.65	2.6	79%
	121	89	0.19	11.3	21%	0.05	60.9	0.60	3.4	82%
Ferric Chloride Addition										
	0	83	0.13	9.0	13%	-	-	-	-	-
	38	113	0.19	15.0	22%	0.05	61.9	0.29	5.9	82%
	68	96	0.19	12.7	23%	0.08	60.6	0.99	2.5	64%
	114	67	0.51	12.7	52%	0.12	61.1	2.33	4.0	82%

During the ferric chloride test, the percentage of mercury in the slurry found in the solids rather than the liquor was observed to increase over time, from 13% at the beginning of the test to over 50% at the end. This likely reflects an increased inventory of iron in the slurry solids available to adsorb/co-precipitate mercury as time progressed and the iron addition continued. This effect is substantiated by the iron concentration data presented later in this section. It is possible that with continued operation, and if steady state were achieved, an even higher percentage of mercury in the slurry would have reported to the solids. While higher partitioning of mercury to the solids goes counter to the initial premise of the mercury SBIR research program (keeping the mercury in the liquor and not in the gypsum byproduct), the data also show that the mercury was preferentially accumulating in the fine particles over the course of the ferric chloride test. The slurry blowdown at 38 hours was marked by an abnormally high suspended solids content in the hydrocyclone overflow, which skews this comparison, but the remaining results show that the percentage of mercury found in the fine overflow solids was increasing over time. This would mean the percentage of the mercury reporting to the underflow (product gypsum) was decreasing, and may have continued to decrease as steady state was achieved. This observation supports a hypothesis that mercury associates with the enriched iron fractions in the fines during ferric chloride addition, and may have the effect of lowering the product gypsum mercury concentration. However, because of the reduced turnover of solids and liquor in the pilot wet FGD system, for the reasons described above, this effect was not clearly demonstrated; the end-of-test partitioning of solid-phase mercury between the hydrocyclone overflow and underflow was similar for all three tests.

Mercury concentrations were measured in solid absorber slurry samples that were wet sieved to produce fractions comprising particles >20 µm (primarily product gypsum) and particles <20 µm (fines), as described above for the selenium results. Solid samples from the initial charge of full-scale absorber slurry and from the final pilot-scale absorber slurry were wet sieved; the results for mercury distribution are presented in Figure 6-9 and Table 6-10. The mercury wet-sieve results are consistent with the mercury measurements in the hydrocyclone overflow and underflow streams during blowdown events. Mercury behavior under baseline and natural oxidation tests showed only minor differences, and the use of ferric chloride appears to promote mercury reporting to the solid phase, specifically to the fine particles.

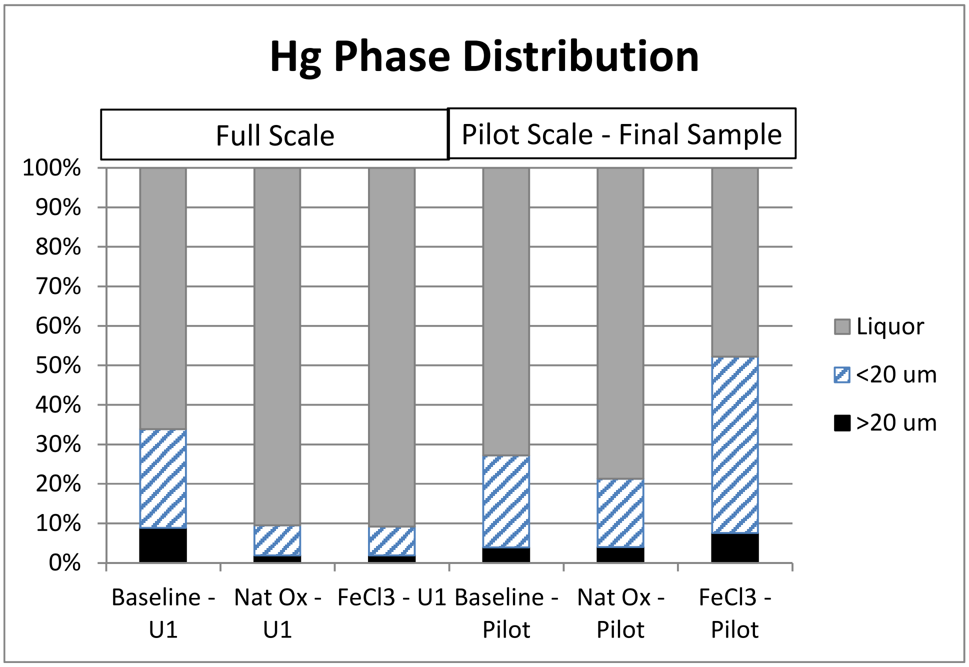


Figure 6-9
Mercury Phase Partitioning in Full-scale and Pilot-scale Absorber Samples

Table 6-10
Solid-phase Mercury Results in Wet-Sieved Samples

Master Sample	Hg Conc. >20 µm (µg/g)	Hg Conc. <20 µm (µg/g)	% of solids >20 µm (%)	% of solids <20 µm (%)	Hg Reporting to Solids (% of total Hg)	% Hg Reporting to >20 µm (% of total Hg)	% Hg Reporting to <20 µm (% of total Hg)	% Hg Reporting to Liquor (% of total Hg)
Full-scale (for samples collected at the beginning of the pilot-scale test shown):								
Baseline High ORP	<0.052	0.63	81%	19%	34%	9%	25%	66%
Natural Oxidation	0.053	1.08	84%	16%	10%	2%	8%	90%
Ferric Chloride Addition	<0.041	0.61	80%	20%	9%	2%	7%	91%
Pilot-scale (end-of-test samples):								
Baseline High ORP	0.056	1.22	79%	21%	27%	4%	23%	73%
Natural Oxidation	0.067	1.26	82%	18%	21%	4%	17%	79%
Ferric Chloride Addition	0.100	5.48	90%	10%	52%	8%	45%	48%

Part of the reason for conducting these wet-sieving experiments was to determine mercury concentrations as a function of particle size. While particle size impacts are indicated by comparing HCOF and HCUF solids, hydrocyclones typically do not make sharp size cuts at a particular diameter; instead, they produce broad particle size distributions that are skewed towards either smaller or larger particles. If sharp size cut points could be made when dewatering absorber slurry (e.g., with advanced hydrocyclone designs), it is possible that conditions favoring the formation of mercury-rich fine particles could result in a lower-mercury-content gypsum product. Ferric chloride addition was considered a candidate for this approach. However, the results do not clearly support this hypothesis. The percent of the slurry mercury reporting to the >20 µm solids (the product gypsum) ranged from 2% to 9% in the full-scale FGD results, and from 4% to 8% in the pilot-scale tests, with the ferric chloride addition test solids actually showing the highest percentage of total mercury in the product gypsum size fraction. However, since the pilot-scale results for this size range are bracketed by the range of normal variation in the full-scale results, there is no clear indication whether ferric chloride addition impacted the amount of mercury found in the >20 µm solids.

Iron and Manganese

Iron remained almost completely in the solid phase throughout pilot testing, as would be expected. Iron is typically found with greater than 99% in the slurry solid phase at typical wet

FGD pH and ORP conditions. Table 6-11 shows the iron concentrations and the phase partitioning for iron in the absorber slurry as well as in the hydrocyclone overflow and underflow streams during blowdown events. The percentages of iron found in the solid phase of the absorber slurry are not shown, but with the liquid-phase concentrations all below the reported detection limits, the percentages in the solids were all calculated to be greater than 99.8% or higher. Iron enrichment in the fines was also high with 72 to 92% of the absorber slurry iron reporting to the hydrocyclone overflow solids.

Table 6-11
Iron Phase Partitioning in Bulk Pilot Absorber Slurry, HCOF, and HCUF Streams

		Bulk Absorber Slurry			**Hydrocyclone Underflow**		**Hydrocyclone Overflow**		**% of Solid Fe in Hydro-cyclone Overflow solids**
Test	**Run Time (h)**	**Fe in Liquor (µg/L)**	**Fe in Solids (µg/g)**	**Wt % Solids**	**Fe in Solids (µg/g)**	**Wt % Solids**	**Fe in Solids (µg/g)**	**Wt % Solids**	
Baseline High ORP									
	0		1890	6.1	-	-	-	-	-
	84		2220	11.3	599	61.0	9230	2.7	79%
	123	<538	2850	11.3	674	59.7	8380	3.4	82%
Natural Oxidation									
	0		1580	7.0	-	-	-	-	-
	26		1530	11.0	568	63.0	4500	3.1	72%
	69		1860	10.2	568	62.0	6820	2.6	76%
	121	<543	2210	11.3	652	60.9	6140	3.4	78%
Ferric Chloride Addition									
	0	<278	1860	9.0	-	-	-	-	-
	38	<275	2590	15.0	833	61.9	4650	5.9	79%
	68	<273	2800	12.7	503	60.6	16,000	2.5	85%
	114	<275	5990	12.7	640	61.1	21,500	4.0	92%

During all tests, the manganese remained predominantly in the oxidized Mn(IV) solid state. Table 6-12 shows the manganese concentrations and the phase partitioning for manganese in the absorber slurry as well as in the hydrocyclone overflow and underflow streams during blowdown events. These results show that manganese tends to concentrate in the smaller particles found in the overflow. Manganese enrichment in the fines is greater than was seen for selenium, but generally less than was seen for iron.

Table 6-12
Manganese Phase Partitioning in Bulk Pilot Absorber Slurry, HCOF, and HCUF Streams

		Bulk Absorber Phase Partitioning				Hydrocyclone Underflow		Hydrocyclone Overflow		
Test	Run Time (h)	Mn in Liquor (µg/L)	Mn in Solids (µg/g)	Wt % Solids	% Mn in Solids	Mn in Solids (µg/g)	Wt % Solids	Mn in Solids (µg/g)	Wt % Solids	% of Solid Mn in Hydro-cyclone Overflow solids
Baseline High ORP										
	0	671	127	6.1	92%					
	84	86	127	11.3	99%	59	61.0	450	2.7	63%
	123	105	137	11.3	99%	52	59.7	362	3.4	72%
Natural Oxidation										
	0	63	145	7.0	99%	0		0		
	26	1510	121	11.0	91%	71	63.0	289	3.1	56%
	69	80	124	10.2	99%	<23	62.0	308	2.6	86%
	121	91	128	11.3	99%	58	60.9	283	3.4	66%
Ferric Chloride Addition										
	0	362	136	9.0	97%					
	38	118	125	15.0	99%	63	61.9	166	5.9	66%
	68	112	111	12.7	99%	55	60.6	368	2.5	58%
	114	122	159	12.7	99%	n/a	61.1	513	4.0	

Other FGD Analytes

Numerous other species were measured in the absorber liquid and solid phases to monitor performance of the pilot scrubber. Sulfur removal, sulfite oxidation, limestone utilization, halogen concentrations, and secondary sulfur species (e.g., dithionate and peroxydisulfate) were monitored; detailed data tables are presented in Appendix E. Throughout the pilot test campaign, sulfur removal remained at roughly 90% or higher and met the SO_2 removal target. Sulfite oxidation remained consistently high with the exception of the last few hours during the one-day initial low ORP attempt. Limestone utilization remained above 96% in all tests. Dithionate and peroxydisulfate were monitored because they correspond with the sulfur oxidation mechanisms present in the scrubber; one researcher proposes that peroxydisulfate is formed primarily under highly oxidizing conditions that the authors of this report believe may also favor selenate formation (Gutberlet, 2000). Little accumulation or decay of the inventory of these species was observed except for moderate accumulation of dithionate during the baseline test. No strong correlations may be drawn between the presence of the secondary sulfur species and selenium behavior based on the pilot testing data set.

Summary

The key findings of the pilot-scale scrubber tests are the following:

- Decreasing oxidation air shifted selenium phase partitioning to the solid phase of the scrubber slurry. Oxidation air control may be one option for managing selenium behavior in FGD scrubbers.
- It was not possible to demonstrate a benefit to selenium behavior by adding ferric chloride to the scrubber because all “newly absorbed” selenium reported to the solid phase in the natural oxidation (reduced oxidation air) test, and no further improvement could be demonstrated. However, addition of ferric chloride to the pilot scrubber did shift mercury to the slurry solids, specifically to the slurry fine particles.
- Selenium enrichment in the fine particles was modest or negligible. The relatively low enrichment of selenium in the fines during the baseline and natural oxidation tests may indicate that under those conditions selenium co-precipitates with the gypsum rather than associating with iron impurities from the limestone. In light of the bench-scale results in which ferric chloride addition caused a clear shift of selenium phase partitioning to the solid phase, several competing pathways may govern the reporting of selenium to the slurry solids: co-precipitation with gypsum into the bulk solids and sorption or co-precipitation with iron into the fine particles. The dominance of each pathway in controlling selenium behavior may depend on scrubber operating conditions as well as the concentration and form of iron in the scrubber.
- Under low ORP conditions, selenite formed and remained in the slurry liquid phase. However, under these conditions at the pilot scale, concentrations of sulfite remained in the absorber liquor that are undesirable for forced oxidation systems. Because the test was cut short, it was not possible to demonstrate appropriate sulfite oxidation levels while retaining selenium as selenite in the liquor.
- Mercury phase partitioning between the solid and liquid phases of the slurry were similar under baseline (high ORP) and natural oxidation conditions. Both tests showed more mercury in the solid phase and less in the liquor than in the full-scale wet FGD system.
- Addition of ferric chloride to the scrubber increased the percentage of slurry mercury reporting to the solid phase. Mercury displaced from the liquor preferentially reported to the fine particles. No decrease in gypsum mercury concentration was measured by the end of this test; however, mercury concentrations were trending down over time and it is possible that with continued operation some benefit may have been observed.
- The three five-day tests showed similar mercury capture across the scrubber, although the natural oxidation test showed slightly lower mercury capture and slightly higher re-emissions. However, the variability in capture and re-emissions for all tests prevents reaching strong conclusions regarding the impact of ORP and ferric chloride use on mercury capture and re-emissions.

- Units that cycle load over a wide range may find it more difficult to control ORP conditions with oxidation air control.

Due to the low liquid turnover during pilot testing, reducing the liquid selenium concentration below 50 µg/L selenium was not possible. However, despite numerous operational challenges, some trends from bench-scale scrubber testing were evident during pilot testing. Specifically, reducing oxidation air and ORP tends to either retain selenium as selenite in the liquor or shift selenium phase partitioning to the solid phase. Additionally, the use of ferric chloride as a scrubber additive may prove useful in controlling mercury behavior within FGD scrubbers. A holistic strategy for simultaneous selenium and mercury management might comprise operating at the lowest ORP that maintains sulfite oxidation (via management of oxidation air flow) and the use of ferric chloride in the scrubber to direct mercury to the fine particulate solids. This approach might reduce selenite oxidation and promote selenite reporting to the solid phase. The selenium would then exit with the bulk byproduct gypsum, and the mercury would predominantly exit with the fine particles in the FGD chloride purge stream; subsequent precipitation of remaining liquid-phase mercury and separation of the mercury-rich solids could be effected in the FGD WWT system.

7

LABORATORY WASTEWATER TREATMENT TESTS

Tests in Synthetic Liquors

The Phase II WWT tests measured the efficacy of several precipitation agents to remove various selenium species from synthetic FGD liquors. The goals of Phase II WWT tests were the following:

- Confirm the selenium removal efficiencies observed in Phase I,
- Test a wider range of precipitation agents,
- Test removal efficiencies in liquor matrices with metals and organic acids, and
- Test the multi-stage control strategy presented in the Phase II proposal.

The third objective of the WWT tests was added after commencement of the Phase II project.

Table 2-1, presented earlier, lists the baseline liquor composition used in the bench-scale wet FGD tests. Table 7-1 shows the compositions of other liquors used in the WWT tests. Table 7-2 presents the WWT test matrix. The variables tested via this matrix include selenium species (e.g., selenite, selenate), WWT additive, the presence of manganese, and the presence of scrubber additives (e.g., DBA, acetic acid). The pH conditions were selected specifically for each additive based on the literature or vendor recommendations. Two dosages of elemental iron were selected; the higher dosage was selected for proof-of-concept testing; it is understood that lower, intermediate dosages would be required for larger-scale applications. Intermediate dosages were tested during subsequent beaker-scale WWT tests with field liquors.

Table 7-1
Liquor Compositions

Liquor Abbreviation	Composition
Mn	35 mg/L Mn + baseline
Mn + DBA	35 mg/L Mn + 1000 mg/L DBA + baseline
Mn + Acetic Acid	35 mg/L Mn + 1000 mg/L Acetic Acid + baseline

Table 7-2
Phase II Precipitation Test Matrix

Selenium Species	Additive	Target Dosage (g/L)	Target pH	Baseline	Mn1	Mn + DBA	Mn + Acetic Acid
Se(IV)	Fe(0)	Low = 1 High = 100	5.5 *	X	X	X	X
	$FeCl_3$	0.05	5.5	X	X	X	X
	Additive “X”	0.5	5	X	X	X	X
	$FeCl_3 + CuSO_4$	0.0025 Cu/ 0.05 Fe	8	X	X		
	Calmet	0.03	9	X	X		
	8-HQS	0.16	9		X		
	NTA	1.4	7		X		
Se(VI) anhydrous	Fe(0)	Low = 1 High = 100	5.5 *	X	X	X	X
	Additive “X”	0.5	5	X	X	X	X
	$FeCl_3 + CuSO_4$	0.0025 Cu/ 0.05 Fe	8	X	X		
	Calmet	0.03	9	X	X		
Se(VI) decahydrate	Fe(0)	Low = 1 High = 100	5.5 *	X			
	$FeCl_3 + CuSO_4$	0.0025 Cu/ 0.05 Fe	8	X			
	Calmet	0.03	9		X		

Note: Tests with elemental iron employed a stepwise increase in pH with sampling at each pH value.

Results from the WWT tests in synthetic liquors were generally consistent with earlier laboratory studies. Selenite was easily removed by numerous additives in synthetic liquors, and elemental iron at very high dosages removed significant fractions of selenate under some conditions, which are elaborated below. Four commercially available additives (ferric chloride, ferric chloride with copper sulfate, Additive “X”, and Calmet) consistently showed high removal (85%-100%) of selenite from synthetic liquors. For these successful additives, the presence of manganese, acetic acid, and DBA did not affect selenite removal substantially. The addition of copper sulfate did not affect removal as proposed in some patent literature. Two additives, 8-HQS and NTA, were unsuccessful in precipitating significant amounts of selenite from any liquor. None of these six additives removed selenate.

The selenite removal efficiency of elemental iron in synthetic liquors is shown in Figure 7-1. At the high iron dosage, elemental iron removed all selenite within the first 30 minutes at pH 5.5 for the baseline liquor, which initially contained no catalytically-active transition metals. Low iron dosages in liquors with manganese removed 95% of the selenite under moderate pH conditions within 30 minutes. Acetic acid did not inhibit the elemental iron's selenite removal efficiency.

Liquor-phase manganese concentrations increased with in time in the pH 5.5 cementation step, including tests in baseline liquors, which contain no initial manganese. Other researchers have observed this behavior. It is possible that manganese is an impurity in the elemental iron. All manganese precipitated out of solution at pH 8.8 and above, as would be expected.

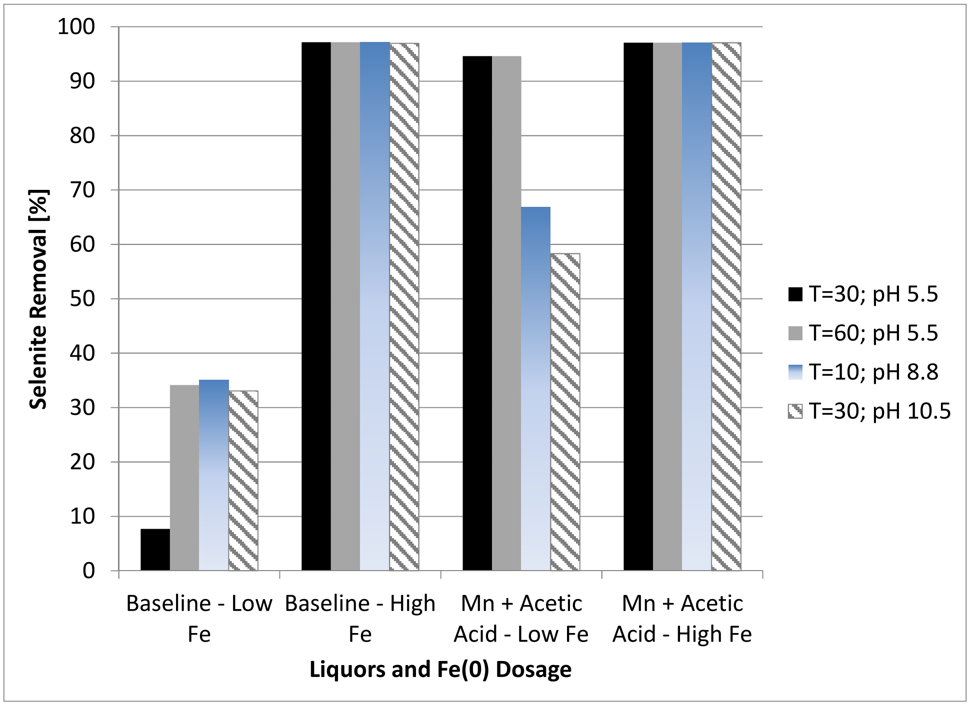


Figure 7-1
Selenite Removal in Synthetic Liquors with Elemental Iron

The *selenate* removal efficiency of elemental iron was also tested in several synthetic liquors and under various pH conditions; results are shown in Figure 7-2. High dosages of elemental iron removed over 85% of the selenate from baseline liquors under some conditions. Manganese increased the removal of selenate at the higher iron dosage. DBA and acetic acid did not affect the selenate removal efficiency. Selenate removal with low iron dosages was roughly 30% or less. Though elemental iron is effective in removing selenate, high dosages can generate unacceptably large quantities of iron sludge. Some articles in the literature have reported that pH and temperature can impact the kinetics of the reaction, so a decrease in required dosages may be feasible such that sludge generation is within an acceptable range.

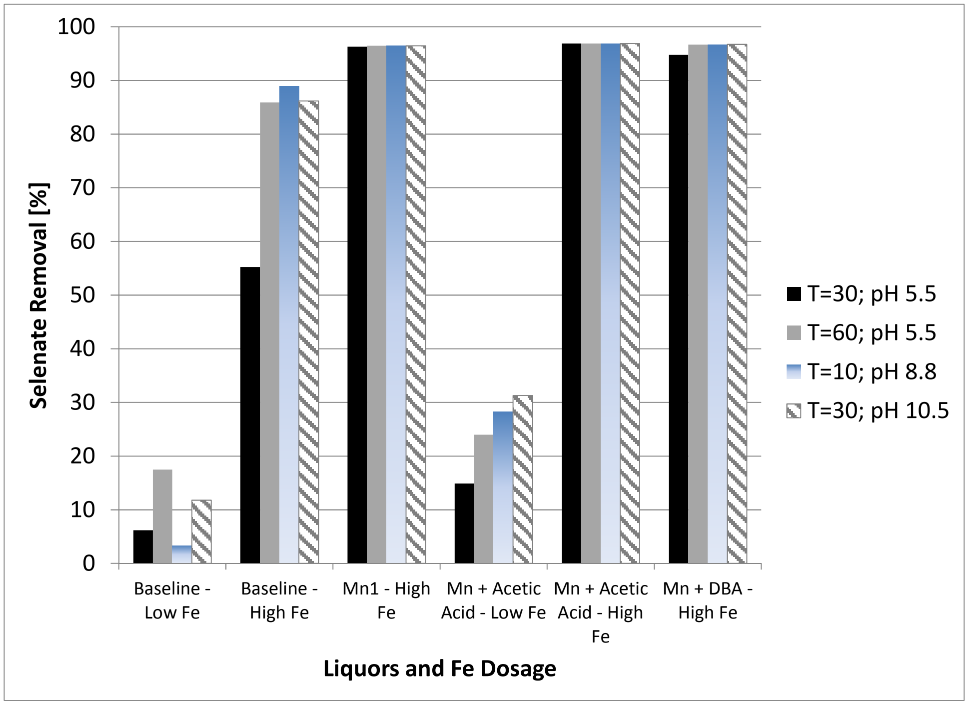


Figure 7-2
Selenate Removal in Synthetic Liquors with Elemental Iron

Tests in Field Liquors

At the end of the field pilot-scale tests, a portion of the final (HCOF was reserved for later WWT testing. The following table shows the WWT test matrix conducted on the pilot HCOF samples. Two intermediate dosages were selected for the elemental iron tests (10 g/L and 50 g/L). Each additive was mixed with a filtered sample for 30 minutes. After collecting the 30-minute sample, elemental iron tests were continued for an additional 30 minutes. Table 7-3 shows the test matrix. The baseline liquor samples contained 1215 µg/L of selenate and no selenite, so selenite removal efficiency could not be evaluated in these tests.

Table 7-3
Test Conditions for Beaker-Scale Precipitation Tests in Field Liquors

Matrix	Additive	Target pH	High pH	Low pH	Target Dosage (g/l)	Actual Dosage (g/L)
Baseline	$FeCl_3$	5.5	6.53	5.85	0.05	0.050
Baseline	Additive “X”	5	6.95	6.54	0.5	0.510
Baseline	Calmet	9			0.03	0.033
Baseline	Fe(0)	5.5 *	6.00	6.76	10	10.0
Baseline	Fe(0)	5.5 *	5.87	7.96	50	49.8

Figure 7-3 shows the results for beaker-scale WWT tests run on the sample taken from the final pilot scrubber HCOF of the baseline test. As expected for a solution containing only selenate, only the elemental iron successfully removed any selenium, and a longer duration of 60 minutes was required. It was noted that the sample became rust-colored at the lower iron dosage of 10 g/L, and that the sample became dark green at the higher dosage of 50 g/L. The green color may indicate green rust, a layered double hydroxide predominantly comprising ferrous hydroxide.

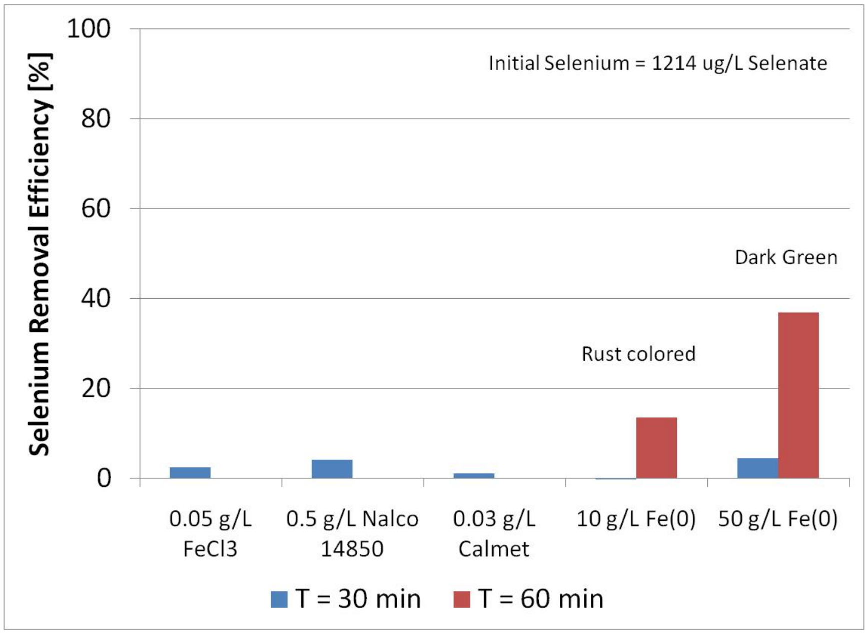


Figure 7-3
Beaker-scale WWT Test Results using Final HCOF sample from Baseline Pilot-Scale Test

Summary

Lab-scale WWT tests in synthetic liquors found many additives that could remove selenite. Only high dosages (100 g/L) of elemental iron were successful in removing high percentages of selenate. Low elemental iron dosages (1 g/L) were not very effective. The high elemental iron dosage required for effective selenate removal results in excessive sludge generation, which is undesirable. Lab-scale WWT tests in samples of field liquors generated during pilot scrubber testing showed only modest removal of selenate (<30%) at intermediate elemental iron dosages (10 mg/L and 50 mg/L). Though the kinetics of selenate removal may be improved by adjusting pH or temperature, removal of selenate by physical/chemical treatment with acceptable rates of byproduct generation remains a challenge.

8

ENGINEERING AND ECONOMIC EVALUATION

The capital and operating costs for two selenium management strategies were considered: ferric chloride addition and oxidation air flow rate control. The evaluations of ferric chloride addition and oxidation air flow rate control have not been presented in prior reports; therefore, the results are presented here in some detail.

Ferric Chloride Addition

Addition of ferric chloride to FGD scrubbers may provide one option for managing selenium and mercury in wet FGD scrubbers, given several caveats presented earlier in this report. Therefore, the capital and operating costs for ferric chloride addition were estimated. As might be expected, the reagent makeup costs dominate the economic evaluation. The basis for estimating the ferric chloride addition rate and the equipment costs are described next.

In the original ferric chloride addition patent application (Higgins, 2009), the effectiveness of iron addition to wet FGD systems is based on field data which show the iron-to-selenium and iron-to-mercury mass ratios in samples collected of fine particles from full-scale wet FGD system slurries. This analysis shows consistent ratios of iron to each of these two trace species, suggesting an intrinsic limit to the amount of each of these species that can be adsorbed or co-precipitated by a given mass of iron hydroxides. The data also suggest that more of each trace species could be adsorbed/co-precipitated if more ferric iron were added.

To conduct an economic analysis of ferric chloride addition, two cases were considered: a model plant similar to the host site for the pilot testing, and a DOE standard example case for Illinois #6 bituminous coal (“FOA 403” coal). For each coal, the coal characteristics were first assembled. For the host unit coal, the actual coal data from samples collected of the host unit’s feedstock were averaged for parameters including heat and ash content, and concentrations of sulfur, chloride, selenium, and mercury. These values were specified by DOE for the FOA 403 coal, other than the selenium concentration. The selenium concentration for that coal was assumed to be the average of data for a subset of sites selected for the 2009/2010 Information Collection Request (ICR) for non-mercury metals analyses. A 2010 EPRI project conducted selenium balances across the same subset of power plants that were chosen for the ICR (Senior, 2011).

To estimate the ferric chloride addition rates for each case, it was necessary to estimate the amount of selenium and mercury entering the liquid phase of the FGD slurry, and then to determine which species, mercury or selenium, required the higher addition rate of ferric chloride. To do this, approximate mass balances for mercury and selenium were generated throughout the flue gas path for each case. For the host site case, the mass balance was estimated using a mixture of data collected as part of the current project and, since the host site had participated in the EPRI project mentioned above, data from that project. Concentrations of mercury and selenium in the coal and in the ash were averaged for all host unit samples collected in the current project. Coal samples for the current project were also analyzed for ash content. By assuming that 80% of the coal ash was fly ash, the percentages of the coal mercury and selenium captured with the fly ash were estimated; the balance of mercury and selenium equaled the estimated amounts of each species at the FGD inlet.

Based on the amount of mercury and selenium at the FGD inlet for each case, estimates were made for the percentage of each species captured across the scrubber and for the percentage retained in the slurry liquid phase. For mercury, in both cases it was assumed that the FGD system removes oxidized mercury at high efficiency (90% of the FGD inlet total mercury), and that 90% of the captured mercury then reported to the slurry liquid phase. Thus, the percentage of the coal mercury ending up in the FGD liquor was different for each of the cases only because the two coals had different ash content, and thus a different percentage of the coal mercury remaining in the FGD inlet flue gas. For selenium, a different approach was used for each case. For the host site case, selenium capture across the scrubber was estimated using data from the EPRI project mentioned above, and selenium partitioning between the slurry liquid and solid phases was the average for the full-scale absorber data collected during the current project. For the FOA 403 case, the percentage of coal selenium reporting to the FGD liquor was based on the average of data from the EPRI project mentioned above. The resulting percentage of 5.1% was considerably lower than the value estimated for the host site case (24.1%), as the host site data indicated more selenium going to the FGD liquor than in most of the ICR sites that participated in the EPRI project.

Table 8-1 shows the coal data and other inputs used to estimate the ferric chloride addition rates, which are also shown in Table 8-1. The makeup costs assume a 78% capacity factor for the generating units, as presented later in the generic unit load profile (Table 8-4).

Table 8-1
Inputs and Results for Estimating Ferric Chloride Addition Rates

Description	Units	Pilot Host Site	DOE Illinois #6 Coal
Coal heating value	Btu/lb	12,500	12,500
Coal composition (dry basis)			
Hg	ppm	0.0489	0.15
Se	ppm	2.14	4.05
Cl	ppm	700	3000
S	wt%	1.42	2.5
Ash	wt%	15.76	9.7
Gross generating capacity	MW	500	500
F-factor	dscf/MMBtu	9780	9780
Heat rate	Btu/kWh	10,000	10,000
% of coal Hg to FGD inlet flue gas	%	80%	80%
% of Hg to FGD liquor	%	81%	81%
% of Coal Se to FGD liquor	%	24.1%	5.1%
Coal Hg	lb/Tbtu	3.92	12.0
Coal Se	lb/Tbtu	171	324
Hg to FGD liquor	lb/Tbtu	2.54	7.78
Se to FGD liquor	lb/Tbtu	41.3	16.5
Fe:Hg mass ratio		2000	2000
Fe:Se mass ratio		500	500
$FeCl_3$ rate based on Hg	lb Fe/TBtu	14,700	45,200
$FeCl_3$ rate based on Se	lb Fe/TBtu	60,000	24,000
Concentrated “42 Be” $FeCl_3$ solution makeup rate	gpm	1.12	0.93
	gal/week	11,300	9,330
Reagent unit cost	$/gal	2.2	2.2
$FeCl_3$ Makeup Costs	$/year	1,010,000	760,000
$FeCl_3$ Makeup Costs	mills/kWh	0.29	0.22

Table 8-1 (continued)
Inputs and Results for Estimating Ferric Chloride Addition Rates

Purchased Equipment Costs	$	100,000	84,000
Total Capital Cost (4x purchased equipment costs)	$	400,000	336,000
Total Capital Cost	$/kW	0.80	0.67

For 500 MW gross generating capacity, the estimated addition rates of concentrated (42 Baumé, "42 Be" or 38.4 wt%) ferric chloride solution are ~11,300 gal/week for the host site case and ~9,300 gal/week for the DOE FOA 403 case. These rates correspond to $1.01 MM/year and $0.76 MM/year in reagent makeup costs at an average annual capacity of 78.1%, or approximately 0.29 mills/kWh and 0.22 mills/kWh, respectively. The ratios of iron to mercury and iron to selenium used in this evaluation are at the upper end of the recommended range; therefore, it is possible that the addition rates could be optimized for each site and decrease the ferric chloride costs.

The capital costs associated with ferric chloride addition consist primarily of a large storage tank with up to two weeks' liquid storage capacity, chemical addition pumps, and associated piping and instrumentation. The approximate purchased cost of a fiberglass tank and the pump were $100,000 and $84,000. A factor of four was applied to the purchased equipment costs to estimate total capital cost. Though simple in the number of unit operations (e.g., a tank and some pumps), the ferric chloride system may require additional safety precautions and infrastructure (i.e., secondary containment). Therefore, the total capital cost was estimated at $0.67 to $0.80 /kW. With an annual capital recovery charge of 17%, the capital costs affect the total annual costs by less than 2%.

Concentrated ferric chloride is very acidic, and its safe handling requires extra precaution. Due to these inherent hazards, the liquid storage capacity of the tank and the associated capital costs might be adjusted on a case-by-case basis.

The estimated iron concentration in the byproduct gypsum is 1.0% for the Host Site case and 0.4% for the DOE FOA 403 case. Although these elevated concentrations of iron may not exceed total impurity specifications for byproduct gypsum, they may impact the ability to sell the gypsum for wallboard due to color. It is unknown how the ferric chloride may impact gypsum quality. These safety and byproduct impact issues should be evaluated in greater detail before implementing this management approach at full scale.

Oxidation Air Control

Control of the oxidation air flow rate into the FGD absorber reaction tank is one option for managing the redox chemistry in FGD scrubbers, though air control alone may be insufficient for some systems. The oxidation air system is sized to handle the air requirement at the design coal sulfur content and at an established ratio of air to sulfur input to the FGD scrubbers. Often, plants operate firing coal below the design coal sulfur level, and many plants may operate below design load at night and in the Spring and Fall. Many oxidation air systems currently in place do not control the flow rate and simply operate the blowers at maximum flow rate on a continuous basis, particularly in older FGD systems. For systems that operate at maximum air output, the air rate is often much higher than what is required to maintain sulfite oxidation, thus wasting power. Beyond the benefits attributed to ORP control, control of oxidation air flow also reduces energy costs for the blowers.

The turndown capacity and flow control of oxidation air blowers may become a higher priority if future research confirms that oxidation air control can benefit trace metals management in FGD systems. Therefore, a cursory comparison of capital costs and turndown capabilities for several scenarios was completed as part of the engineering and economic evaluation. For a new system, the benefits of increased turndown capacity for the oxidation air rate may influence the blower configuration selected for installation. For retrofit cases, the benefits of air flow rate control could warrant installation of flow rate control if it is not already in place, or in the extreme case, replacement of oxidation air blowers. Retrofit applications will have very site-specific considerations and are not evaluated in this report. This preliminary evaluation has not investigated the impacts of oxidation air rate on slurry mixing in the FGD reaction tank, which in turn impacts sulfite oxidation kinetics and slurry solids suspension. These issues should be considered as part of more detailed evaluations in future work. The remainder of this section presents background information on blower types, flow control methods, and typical blower configurations; the cases selected for evaluation; and the results of the evaluation.

Two types of blowers are typically installed for FGD oxidation air service: single-stage centrifugal blowers and multi-stage centrifugal blowers. Multi-stage blowers tend to have lower capital costs and lower efficiencies than single-stage blowers, so a cost-benefit analysis between operating costs, in the form of energy, and capital costs may influence the selection of blower type. Additionally, multi-stage blower capacities tend toward the lower flow range, and single-stage blowers tend to be available in larger capacities, though the application spaces for the two blower types do overlap.

The turndown capacity of blowers is a function not only of the type of blower used, but also the controls installed with the blower. The control of a multistage unit is normally achieved via throttling of a butterfly valve or guide vanes at the blower inlet, which is recommended, or by throttling on the fan discharge side. Variable frequency drives (VFDs) can be used on multistage blowers, though the practice currently is not common for oxidation air blowers. Application of VFDs for flow control must consider the specific design curve of the fan. It should be noted that the required discharge pressure depends on scrubber slurry density and liquid height, which are usually relatively constant.

The control of a single-stage unit is typically achieved via the use of inlet vanes, an outlet diffuser with vanes, or a combination of both. Single-stage blowers are usually equipped with a VFD that operates in conjunction with the inlet and outlet vanes. An advantage of a single-stage unit is that the efficiency remains more consistent over the turndown range when both inlet vanes and an outlet diffuser are used, and single-stage units typically have a wider turndown range. For example, one supplier documented that over a turn down from 100% to 50% of the design flow rate, the efficiency of a single stage unit would remain constant at 78%. When turning down a corresponding multi-stage unit, the efficiency would drop from 78% to approximately 60%. Figure 8-1 shows the efficiencies and turndown capabilities of the two blower types, each with two flow control options. The turndown is expressed as percentage decrease from maximum flow. It should be noted that the figure was supplied in the promotional materials of a single-stage blower supplier (Turblex, 2008). Table 8-2 shows the turndown and efficiency values selected from Figure 8-1 for use in the economic analysis.

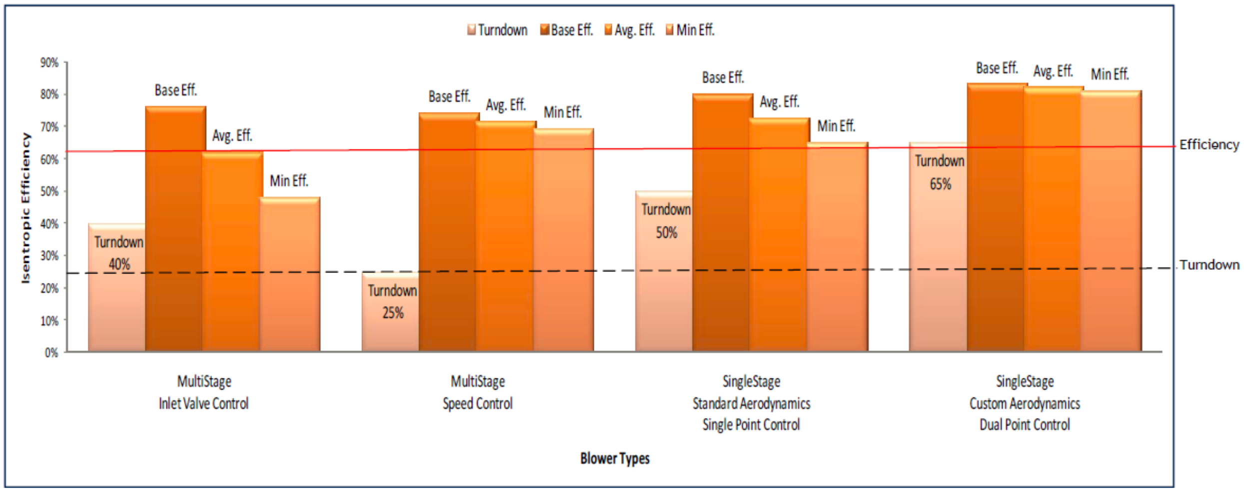


Figure 8-1
Efficiency and Turndown for Multi-stage and Single-stage Blowers

Table 8-2
Turndown and Efficiencies for Centrifugal Blowers using Several Flow Control Methods

Blower Type	Flow Control Type	Maximum Turndown (% decrease from design flow)	Average Efficiency (%)	Efficiency at Maximum Turndown (%)
Multi-stage centrifugal	Speed control	25	72	70
Multi-stage centrifugal	Inlet valve control	40	60	50
Single-stage centrifugal	Single-point control, standard aerodynamics	50	74	65
Single-stage centrifugal	Dual-point control, custom aerodynamics	65	78	76

Most FGD systems constructed in the recent past consist of a single large absorber vessel treating up to 1000-1200 MW of generating capacity, rather than multiple smaller absorbers. The associated blower configurations vary; however, most designs call for two blowers that can supply 100% of the air requirements for a scrubber (i.e., “2x100%”) instead of a 3x50% configuration. Another common installation is to have 3x100% serving two scrubbers, where all three blowers are connected to an oxidation air distribution header with two blowers operating and one on standby. The 3x100% configuration would usually apply to older systems or to those systems that have chosen to build multiple absorbers for site-specific reasons (e.g., more than 1200-MW of scrubbed capacity).

The cases selected for costing were based on the DOE FOA 403 coal and a stoichiometric ratio of 3 moles O per mole SO_2 (or 3/2 moles of O_2) for the oxidation air relative to the total design sulfur input to the FGD scrubbers. For the oxidation air analysis, the *design* coal sulfur content was increased from 4.0 lb SO_2/MMBtu to 5.5 lb SO_2/MMBtu because many systems will design for higher coal sulfur content to provide additional operational flexibility. A single scrubber was assumed, and two blower configurations were evaluated: 2x100% (Case A) and 3x50% (Case B). In Case B, two blowers operate, and one is a spare.

Table 8-3 presents the blower specifications, the purchased equipment costs, and the estimated total capital cost and annual capital charge for the two blower configurations. The single-stage blower purchased equipment costs were based on quotes obtained in 2012 for similarly-sized equipment. The multi-stage blower purchased equipment costs were scaled from quotes obtained in 2012 for somewhat smaller units and, therefore, may be subject to some discrepancy. All costs are presented in 2012 dollars. As evident by the costs provided in Table 7-3, the capital costs for single-stage blowers are significantly higher than for the corresponding multi-stage systems.

Table 8-3
Specifications and Greenfield Capital Costs for Oxidation Air Blowers

Case	**A**		**B**	
Blower Configuration	2x100%		3x50%	
Design air flow rate, scfm	17,300		8,700	
Blower Quantity	2		3	
Differential Pressure, psi	15		15	
P inlet, psia	14.7		14.7	
Temperature, ºF	85		85	
Est. Power at 100% efficiency, hp/blower	864		432	
	Multi-stage	**Single-stage**	**Multi-stage**	**Single-stage**
Purchased equipment cost, $/blower	135,000	606,000	102,000	369,000
Total purchased equipment cost $/blower	269,000	1,212,000	306,000	1,106,000
Total capital cost, $/plant	1,080,000	4,850,000	1,230,000	4,420,000
Annual capital recovery charge factor , %	17	17	17	17
Annual capital charge, $/yr	183,000	824,000	208,000	752,000
Incremental annual capital charge for 3x50%, $/yr			25,000	-72,000

The operating costs considered in this analysis for the blowers consist only of energy costs. The power requirements were estimated for both types of blowers, each with two different flow control methods. A generic unit load profile was assumed, as shown in Table 8-4. Daytime was assumed to last 15 hours, and night time was assumed to last 9 hours. A constant efficiency was assumed over the range of load conditions for each blower type and flow control combination, equal to the average efficiency shown in Table 8-2 for that combination. Although the efficiencies for multi-stage blowers may vary over the turndown range, the variability of efficiency with turndown is highly dependent on the specific blower model selected and where the design point is located on the blower performance curve. By assigning a constant efficiency to the multi-stage blower, this evaluation presents more favorable energy costs than would likely be the case for many multi-stage blowers.

Table 8-4
Generic Unit Load Profile

	Winter	Spring	Summer	Fall	Annual Avg
Day	100	75	100	75	-
Night	75	50	75	50	-
Seasonal daily average	90.6	65.6	90.6	65.6	78.1

For a 500 MW plant with a 2x100% blower configuration, adding flow control would save on the order of \$80k to \$100k/year based on a levelized cost of electricity of 64 mills/kWh. The increased efficiency gained by switching from multi-stage to single-stage blowers for the 2x100% configuration could reduce energy costs by up to \$135k/year, depending on the specific unit load profile and efficiencies for appropriately sized blowers. Thus, the minimum payback for switching from multi-stage to single-stage is 4 to 5 years, and could be as high as 10 years depending on site-specific conditions.

The above evaluation and payback estimates look solely at the energy savings to justify the selection of oxidation air blower type and flow control method. However, the benefits to managing redox chemistry in the scrubber could far outweigh the savings in electricity costs under some circumstances. For example, if air management and ORP reduction could decrease the formation of selenate to very low levels without creating problems related to sulfite oxidation and gypsum mercury contamination, then costly biological WWT for selenate treatment could be avoided. Inhibiting the formation of selenate in the scrubber could also provide a margin of error to allow for operational upsets in the biological WWT system.

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SUMMARY AND RECOMMENDATIONS

Sample Handling and Analysis for Selenium Speciation

Work conducted under this project evaluated sample handling and analytical methods for selenium speciation in FGD waters. Several analytical techniques were employed: IC/ICP-DRC-MS, HG-CVAA, HG-CVAF, and CSV. Measurements made by the three methods are generally consistent for samples measured at the same storage time and containing predominantly selenite and selenate. Measurements of selenium speciation over time indicated that for accurate selenium speciation, it is best to conduct measurements on unpreserved, filtered samples as soon after sampling as possible (<12 hours). For field locations, it is desirable to have on-site measurement capabilities. After the initial 48 to 72 hours, selenium speciation remains stable for two to three weeks. The impact of sample storage time on speciation depends on the sample matrix and the conditions at the time of testing.

Evaluation of selenium speciation before and after storage impacted the technical conclusions drawn from bench-scale scrubber tests. The trend of increasing selenite oxidation with increasing values of ORP remains valid, though the specific values of ORP that correspond to a particular selenite oxidation level may depend on the sample age at the time of analysis. In light of the day-of-test speciation results, the benefits of DBA are less conclusive, but showed promise. The apparent benefits of other scrubber additives were not affected by the preservation study.

Bench-Scale Scrubber Testing

Bench-scale scrubber tests explored the impacts of oxidation air rate, trace metals, scrubber additives, and natural limestone on selenium speciation in synthetic FGD liquors. Several bench-scale scrubber tests were conducted using samples of field absorber slurries.

The presence and concentration of redox-active chemical species as well as the oxidation air rate contribute to the ORP conditions in FGD scrubbers, and the ORP conditions correlate strongly with liquid-phase selenium speciation and, in some cases, with selenium phase partitioning. Selenite oxidation increases with increasing ORP conditions, and decreases with decreasing ORP conditions. Trace metals, such as manganese and iron, typically enter FGD systems as limestone impurities. These metals significantly impact the range of ORP under which the FGD scrubbers can operate. Under moderately and highly oxidizing conditions, manganese is often oxidized to the solid Mn(IV) state, which is catalytically active and subsequently oxidizes selenite to selenate. Higher concentrations of solid-phase manganese increase selenite oxidation.

Scrubber additives, such as DBA, were tested for their ability to inhibit selenite oxidation. DBA is both a pH buffer and a mild metal complexant; it is thought that the DBA might complex slightly with the manganese and thus inhibit the ability of manganese to oxidize selenite. Though DBA showed promise in early clear liquor bench-scale tests, DBA did not show strong inhibition of selenite oxidation in tests with higher manganese concentrations (e.g., 35 mg/L Mn) and with slurries produced from full-scale wet FGD system feedstocks (natural limestone, pilot host site absorber samples). Other scrubber additives showed similar promise in synthetic liquor tests, but were not successful in tests with more complex field slurries. Further testing of scrubber additives with field solids and at higher metal concentrations may be warranted.

Iron may affect selenium speciation and phase partitioning via two pathways. Solid-phase Fe(III) tends to sorb selenite to the solid phase. Liquid-phase Fe(II) may indirectly oxidize selenite; under forced oxidation conditions, liquid-phase Fe(II) is oxidized to liquid-phase Fe(III), the liquid Fe(III) may then oxidize selenite to selenate and be reduced back to liquid Fe(II). Though liquid-phase Fe(II) is typically not present under the oxidizing conditions of limestone forced-oxidation wet FGD systems, it is possible that some amount of ferrous content may enter with the limestone and exist briefly as the limestone dissolves. Ferric iron is the prevalent oxidation state of iron in limestone forced-oxidation systems, and ferric solids tend to sorb selenite. In bench-scale tests conducted in synthetic liquors, increasing concentrations of ferric solids resulted in increasing selenite reporting to the solid phase. Under high ORP conditions, selenite may oxidize more rapidly before it sorbs to ferric solids. In bench-tests with field liquors, addition of ferric chloride at a 250:1 Fe:Se mass ratio sorbed all added selenite to the solid phase, though addition of ferric salts had no impact on native selenate that already existed in the field slurry sample. If ferric chloride were used to manage scrubber selenium chemistry, process excursions would have to be avoided or rapidly corrected to avoid accumulation of selenate in the scrubber liquor. Any selenate that forms during process excursions would remain until the reaction tank liquor turned over due to blow down.

As might be expected, the oxidizing or reducing conditions in a scrubber, as reflected by the ORP, affect not only selenium, but also other trace elements such as mercury. The impacts of ORP management on the behavior of these other trace elements must also be considered when developing selenium management strategies. In the case of mercury, higher ORP conditions may be desired to limit mercury concentrations in the gypsum byproduct, whereas lower ORP conditions are desirable for limiting selenium oxidation. Research into mercury or selenium management may require a holistic approach that uses both ORP and scrubber additives to define an operating range that maintains SO_2 removal performance, avoids selenite oxidation to less desirable species, and prevents mercury from entering the FGD byproduct gypsum stream. If the mercury cannot be retained in the liquid phase under conditions that prevent selenite oxidation, strategies to direct the mercury to the slurry fine particles (“fines”) and reduce mercury content in the bulk gypsum solids are desirable.

Pilot-Scale Scrubber Testing

Though it was not possible to demonstrate a decrease in selenium concentrations to low levels during pilot testing due to low turnover in the pilot FGD reaction tank, some trends observed in bench-scale testing were evident at the pilot-scale. Specifically, reducing oxidation air and ORP tends to either retain selenium as selenite in the liquor or shift selenium phase partitioning to the solid phase. Oxidation air control may be one option for managing selenium behavior in FGD scrubbers. *Longer-term bench- or pilot-scale tests in field slurries with L/G ratios typical of full-scale scrubbers may allow more accurate testing of ORP control via oxidation air control.* Units that cycle load widely, as did the pilot test host unit, may find it more difficult to impact ORP conditions with oxidation air control. Because decreasing oxidation air to the reaction tank showed that all “new” selenium reported to the solids, the addition of ferric chloride to the pilot scrubber could not show further improvements in selenium behavior. Ferric chloride addition did shift mercury to the slurry solids, specifically to the fine particles. Several competing pathways may govern the reporting of selenium to the slurry solids: co-precipitation with gypsum into the bulk solids and sorption or co-precipitation with iron into the fine particles. The dominance of each pathway in controlling selenium behavior may depend on scrubber operating conditions as well as the concentration and form of iron in the scrubber.

A holistic management strategy for simultaneous selenium and mercury management might comprise operating at the lowest ORP that maintains sulfite oxidation (via management of oxidation air flow) and the use of ferric chloride in the scrubber to direct mercury to the fine particle solids. This approach might reduce selenite oxidation and promote selenite reporting to the solid phase. The selenium would then exit with the bulk byproduct gypsum, and the mercury would predominantly exit with the fine particles in the FGD chloride purge stream, where subsequent precipitation of the mercury could be effected in the FGD WWT system.

Laboratory Wastewater Treatment Tests

Lab-scale WWT tests in synthetic liquors found many additives that could remove selenite. Only high dosages (100 g/L) of elemental iron were successful in removing high percentages of selenate. Low elemental iron dosages (1 g/L) were not very effective. The high elemental iron dosage required for effective selenate removal results in excessive sludge generation, which is undesirable. Lab-scale WWT tests in samples of field liquors generated during pilot scrubber testing showed only modest removal of selenate (<30%) at intermediate elemental iron dosages (10 mg/L and 50 mg/L). Though the kinetics of selenate removal may be improved by adjusting pH or temperature, removal of selenate by physical/chemical treatment with acceptable rates of byproduct generation remains a challenge.

Engineering and Economic Evaluation

The capital and operating costs for two selenium management strategies were considered: ferric chloride addition and oxidation air flow rate control. For ferric chloride addition, as might be expected, the reagent makeup costs dominate the overall costs and range from 0.22 to 0.29 mills/kWh. Impacts on gypsum formation and salability require further evaluation. As part of the evaluation of oxidation air control, blower types and flow control methods typically used for oxidation air blowers were identified. A cursory comparison of capital costs and turndown capabilities for multi-stage and single-stage centrifugal blowers and several flow control methods was completed. For greenfield systems, changing the selection of blower type and flow control method may have payback periods of 4 to 5 years or more if based on energy savings alone. However, the benefits to managing redox chemistry in the scrubber could far outweigh the savings in electricity costs under some circumstances.

Recommendations

As future regulations may limit selenium discharges in the low µg/L range, meeting these guidelines will likely require improvements in our understanding and management of selenium behavior throughout particulate control devices, FGD scrubbers, and the WWT systems.

Given the complexity of selenium chemistry in FGD scrubbers, one approach is to manage the selenium upstream of the FGD scrubber. Recent research evaluated the fate of selenium throughout the coal-fired power plants and identified trends in selenium capture by coal type, particulate control device, and injection additives (Currie, 2011; Senior 2011). Other researchers have looked at the thermodynamic properties of selenium species under the operating conditions typically encountered in the flue gas pathway; their research suggests that selenium capture across scrubbers may be controlled not by FGD chemistry but by mist or aerosol formation, which occurs because the temperature range for the selenous acid dew point coincides with the temperatures through which the inlet flue gas passes in the quench zones of FGD scrubbers (Martin, 2011). An improved understanding of selenium capture in particulate control devices and scrubbers might suggest a way to manage selenium upstream of the scrubbers.

Research conducted under this and related programs has shown that the ORP conditions within FGD scrubbers plays an integral role in the behavior of selenium, mercury, manganese and other trace elements. Within the operating ranges of pH and ORP conditions typically found in forced oxidation FGD scrubbers, numerous trace elements may form and transfer between more than one oxidation state, chemical species, and phase. Consequently, developing an improved understanding of the redox mechanisms in FGD scrubbers will play a key role in managing air, water, and solid discharges of these trace elements. The redox mechanisms also have implications for corrosion, which has become a growing concern in light of recent widespread material failures with the 2205 and other alloys. Much of the research in this program has shown very strong correlations between selenium behavior and the presence, concentration, and phase of other species (manganese, iron, peroxydisulfate, dithionate). However, a clear causation and pathway for selenium species inter-conversion is not yet established. The impending stringent effluent guidelines coupled with the corrosion failures calls for renewed investment in characterizing redox mechanism within FGD scrubbers. Work to this end might comprise a literature review, fundamental lab work with beaker- and bench-scale testing, and perhaps field sampling and analysis. Understanding FGD redox mechanisms may improve the chances of coupling oxidation air control and other approaches to minimize the formation of undesirable species and to manage the phase partitioning of trace elements. The improved knowledge may also lead to corrosion management strategies.

Finally, achieving stringent effluent guidelines may require treatment not only of the “primary” selenium species (i.e., selenite and selenate) but also other less common or unknown selenium species. Some WWT technologies specifically exclude some selenium species from the removal guarantees. Work to address this need could comprise identifying, generating, and conducting treatability studies for “secondary” selenium species.

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A

BENCH-SCALE ANALYTICAL DATA

ICP-MS Day-of-test Data

sample	Time	Actual Total ppb added	TSe	Se(IV)	Se(VI)	SeSO3	Unknowns	Unaccounted
t,injection								
Test 29: 10h, 5 ppm Mn, 175 mV - Unpreserved								
29-1-U	0	992	3	4	0	0		-1
29-2-U	15		1,062	928	115	0		19
29-3-U	90		1,101	736	300	0		65
29-4-U	180		1,077	462	534	0		81
29-5-U	360		1,057	938	148	0		-29
29-6-U	600		1,127	877	159	0		91
29-1-C	0		3	3	0	0		0
29-2-C	15		1,042	560	477	0		5
29-3-C	90		1,064	1053	86	0		-75
29-4-C	180		1,092	178	873	0		41
29-5-C	360		991	736	183	94		-22
29-6-C	600		1,068	823	228	17		0
Test 30: 10h, 5 ppm Mn, 150 mV, 1000 ppm DBA - Unpreserved								
30-1-U	0	988	8	22	0	108		-122
30-2-U	15		1,104	1170	3	109		-178
30-3-U	90		1,138	1160	6	175		-203
30-4-U	180		1,066	1127	9	119		-189
30-5-U	360		1,148	1090	23	30		5
30-6-U	600		1,155	1023	27	55		51
30-1-C	0		9	12	0	11		-14
30-2-C	15		1,190	771	0	267		152
30-3-C	90		1,174	838	7	220		109
30-4-C	180		1,203	810	10	299		84
30-5-C	360		1,200	776	12	272		140
30-6-C	600		1,181	790	17	237		137
Test 31: 1000 ppb SELENATE, 5 ppm Mn, 100 mV - Unpreserved								
31-1-U	0		10	< 2	< 1	6		4
31-2-U	15	990	1,120	3	955	< 2		162
31-3-U	45		1,119	3	1,050	< 2		66
31-4-U	90		1,125	< 2	1,030	< 2		95
31-5-U	180		1,098	6	1,021	< 2		71
31-6-U	360		1,094	2	1,021	< 2		71
31-1-C	0		8	< 2	< 1	6		2
31-2-C	15		1,104	< 2	941	5		158
31-3-C	45		1,097	< 2	968	5		124
31-1-C	90		1,091	< 2	1,036	7		48
31-2-C	180		1,092	< 2	1,017	4		71
31-3-C	360		1,093	< 2	1,006	2		85

sample	Time	Actual Total ppb added	TSe	Se(IV)	Se(VI)	SeSO3	Unknowns	Unaccounted
Test 32: 5 ppm Mn, 200 mV, 1000 ppmw Adipic Acid								
32-1-U	0		6	< 2	2	3		0
32-2-U	15	987	1,063	907	124	< 2		32
32-3-U	45		1,076	975	53	< 2		48
32-4-U	90		1,062	988	18	< 2		56
32-5-U	180		1,069	1,026	18	< 2		25
32-6-U	360		1,103	1,036	25	< 2		42
32-1-C	0		3	< 2	3	3		-3
32-2-C	15		1,058	1,053	23	< 2		-18
32-3-C	45		1,037	1,010	19	< 2		8
32-4-C	90		1,035	1,016	39	< 2		-20
32-5-C	180		1,019	1,021	17	< 2		-19
32-6-C	360		1,011	1,042	23	5		-59
Test 33: 10h, 5 ppm Mn, 150 mV (Repeat)								
33-1-U	0		3	2	1	< 1		0
33-2-U	15	1018	1,197	5	896	< 1		296
33-3-U	90		1,078	336	537	< 1		205
33-4-U	180		1,187	339	525	< 1		323
33-5-U	360		1,003	361	417	< 1		225
33-6-U	600		1,051	641	348	< 1		62
33-1-C	0		2	< 1	1	< 1		1
33-2-C	15		1,082	1,082	6	2		-8
33-3-C	90		1,113	572	417	< 1		124
33-4-C	180		1,113	432	547	< 1		134
33-5-C	360		1,036	504	436	< 1		96
33-6-C	600		1,047	515	514	< 1		18
Test 34: 35 ppm Mn @ 100 mV								
34-1-U	0		7	2	1	< 0.5		4
34-2-U	15	1003	1,103	1,093	7	< 0.5		3
34-3-U	45		1,066	1,032	8	< 0.5		26
34-4-U	90		1,062	949	26	< 0.5		87
34-5-U	180		1,024	918	35	< 0.5		71
34-6-U	360		1,107	1,001	62	< 0.5		44
34-1-C	0		6	1	1	< 0.5		4
34-2-C	15		1,097	780	<0.5	145	13%	172
34-3-C	45		1,110	966	11	35	3%	98
34-4-C	90		1,096	818	28	105	10%	145
34-5-C	180		1,084	716	42	113	10%	213
34-6-C	360		1,073	896	70	10	1%	97

sample	Time	Actual Total ppb added	TSe	Se(IV)	Se(VI)	SeSO3	Unknowns	Unaccounted
Test 35: 24 ppm Fe @ 100 mV								
35-1-U	0		4	2	<0.5	4		-2
35-2-U	15	1013	709	669	2	1		37
35-3-U	45		670	629	3	2		36
35-4-U	90		635	584	4	1		47
35-5-U	180		599	527	8	< 0.5		64
35-6-U	360		602	525	18	< 0.5		59
35-1-C	0		3	0	1	< 0.5		2
35-2-C	15		659	507	<0.5	64		88
35-3-C	45		660	482	<0.5	60		118
35-4-C	90		599	448	<0.5	51		100
35-5-C	180		588	438	<0.5	44		106
35-6-C	360		582	466	18	6		92
Test 36: 24 ppm Fe @ 150 mV								
36-1-U	0		9	1.4	< 0.5	< 0.5		
36-2-U	15	982	740	735	5.3	< 0.5		
36-2-150-U	15		614	611	20.2	< 0.5		
36-3-U	45		644	620	35.5	< 0.5		
36-4-U	90		638	603	55.3	< 0.5		
36-5-U	180		683	554	86.5	< 0.5		
36-6-U	360		729	539	160	< 0.5		
36-1-C	0		6	1.7	0.7	< 0.5		
36-2-C	15		668	167	2.1	6.0		
36-2-150-C	15		604	232	7.3	< 0.5		
36-3-C	45		639	499	45.9	< 0.5		
36-4-C	90		644	527	92.3	< 0.5		
36-5-C	180		574	620	108	< 0.5		
36-6-C	360		714	585	166	< 0.5		
Test 37: 4 ppm Fe @ 150 mV								
37-1-U	0		6	2.4	0.5	0.5		
37-2-U	15	1019	1,010	1049	6.1	0.8		
37-3-U	45		1,020	1094	10	0.6		
37-4-U	90		1,010	1113	14.8	0.9		
37-5-U	180		1,021	1115	33.7	< 0.5		
37-6-U	360		1,031	951	53.5	< 0.5		
37-1-C	0		5	2.5	< 0.5	< 0.5		
37-2-C	15		998	1030	6.3	< 0.5		
37-3-C	45		1,001	984	7.8	< 0.5		
37-4-C	90		993	1003	13.8	< 0.5		
37-5-C	180		987	977	25.1	0.5		
37-6-C	360		999	922	47.1	1.6		

Test 36: 24 ppm Fe @ 150 mV

Sample ID	Test Time	Selenite (ppb)*		Total Liquid-phase		Possible Selenite	
		TD	HG/CVAA	TD	HG/CVAA	TD	HG/CVAA
36-1	0 min	-	<50.0	-	<55.0	-	-
36-2-100mV	15 min	703	707	-	-	-	-
36-2-150mV	15 min	-	617	-	-	-	-
36-3	45 min	-	-	-	-	-	-
36-4	1.5 hr	-	615	-	-	-	-
36-5	3 hr	547	566	-	704	-	20%
36-6	6 hr	560	632	-	740	-	15%

Test 37: 4 ppm Fe @ 150 mV

Sample ID	Test Time	Selenite (ppb)*		Total Liquid-phase		Possible Selenite	
		TD	HG/CVAA	TD	HG/CVAA	TD	HG/CVAA
37-1	0 min	-	<50.0	-	<67.50	-	-
37-2	15 min	1013	956	-	966	-	1%
37-3	45 min	-	935	-	-	-	-
37-4	1.5 hr	-	914	-	-	-	-
37-5	3 hr	1237	911	-	935	-	3%
37-6	6 hr	1190	986	-	1037	-	5%

sample	Time	Actual Total ppb added	TSe	Se(IV)	Se(VI)	SeSO3	Unknowns	Unaccounted
Test 38: 600 ppm Fe @ 100 mV								
38-1-U	0		2	1	< 0.5	9		-8
38-2-U	15	1015	55	50	< 0.5	7		-2
38-3-U	45		35	33	1	5		-3
38-4-U	90		25	23	2	3		-3
38-5-U	180		24	20	4	3		-2
38-6-U	360		31	17	10	1		2
38-1-C	0		< 2	< 0.5	< 0.5	2		
38-2-C	15		52	37	1	11		4
38-3-C	45		33	24	1	5		3
38-4-C	90		27	16	2	5		4
38-5-C	180		20	13	4	4		0
38-6-C	360		29	13	10	4		2
Test 39: 600 ppm Fe and 35 ppm Mn @ 150 mV								
39-1-U	0		< 2	< 0.5	1	< 0.5		
39-2-U	15	1041	16	< 0.5	14	< 0.5		2
39-3-U	45		16	1	14	< 0.5		1
39-4-U	90		20	1	18	< 0.5		2
39-5-U	180		35	1	28	< 0.5		6
39-6-U	360		55	1	47	< 0.5		7
39-1-C	0		< 2	1	1	< 0.5		
39-2-C	15		13	1	12	< 0.5		0
39-3-C	45		16	< 0.5	14	< 0.5		3
39-4-C	90		22	1	17	< 0.5		5
39-5-C	180		32	< 0.5	27	< 0.5		5
39-6-C	360		53	< 0.5	44	< 0.5		9
Test 40: 35 ppm Mn @ 150 mV								
40-1-U	0	988	3	1.2	<1.0	<0.5		
40-2-U	15		1091	976	101	<0.5		
40-3-U	45		1084	601	446	<0.5		
40-4-U	90		1072	1011	81	<0.5		
40-5-U	180		1095	1050	52	<0.5		
40-6-U	360		1040	1019	92	<0.5		
40-1-C	0		3	1.0	<1.0	<0.5		
40-2-C	15		1008	477	595	<0.5		
40-3-C	45		1023	5.2	1079	<0.5		
40-4-C	90		1037	301	814	<0.5		
40-5-C	180		1083	846	51	161		
40-6-C	360		1050	1661	146	230		

Test 38: 600 ppm Fe @ 100 mV

Sample ID	Test Time	Selenite (ppb)*		Total Selenium		Possible Selenite	
		TD	HG/CVAA	TD	HG/CVAA	TD	HG/CVAA
38-1	0 min	-	<50.0	-	<55.0	-	-
38-2	15 min	<155	52.9	-	<55.0	-	<4%
38-3	45 min	-	<50.0	-	<55.0	-	<9%
38-4	1.5 hr	-	<50.0	-	<55.0	-	<9%
38-5	3 hr	<80	<50.0	-	<55.0	-	<9%
38-6	6 hr	<90	<50.0	-	<55.0	-	<9%

Test 39: 600 ppm Fe and 35 ppm Mn @ 150 mV

Sample ID	Test Time	Selenite (ppb)*		Total Selenium		Possible Selenite	
		TD	HG/CVAA	TD	HG/CVAA	TD	HG/CVAA
39-1	0 min	-	<50.0	-	<55.0	-	-
39-2	15 min	123	<50.0	-	<55.0	-	<9%
39-3	45 min	-	<50.0	-	<55.0	-	<9%
39-4	1.5 hr	-	<50.0	-	<55.0	-	<9%
39-5	3 hr	<80	<50.0	-	<55.0	-	<9%
39-6	6 hr	<90	<50.0	-	<55.0	-	<9%

Test 40: 35 ppm Mn @ 150 mV

Sample ID	Test Time	Selenite (ppb)*		Total Liquid-phase		Possible Selenite		
		TD	HG/CVAA	TD	HG/CVAA	TD	HG/CVAA	
40-1	0 min	-	<50.0	-	<55.00	-	-	
40-2	15 min	1290	1098	-	989	-	-11%	
40-3	45 min	-	1030	-	1003	-	-	
40-4	1.5 hr	-	1061	-	997	-	-	
40-5	3 hr	1183	1105	-	973	-	-14%	possible matrix interference
40-6	6 hr	1193	1305	-	999	-	-31%	possible matrix interference

sample	Time	Actual Total ppb added	TSe	Se(IV)	Se(VI)	SeSO3	Unknowns	Unaccounted
Test 41: 100 ppm Fe @ 150 mV								
41-1-U	0	978	9	<0.5	1	<0.5		
41-2-U	15		495	430	5	<0.5		
41-3-U	45		457	401	15	<0.5		
41-4-U	90		515	398	36	<0.5		
41-5-U	180		477	364	76	<0.5		
41-6-U	360		527	326	153	<0.5		
41-1-C	0		5	1	1	<0.5		
41-2-C	15		489	362	6	45		
41-3-C	45		471	364	16	10		
41-4-C	90		463	323	33	39		
41-5-C	180		472	318	72	14		
41-6-C	360		535	314	155	<0.5		
Test 42: 5 ppm Mn @ Variable ORP (200 mV for 3 hours, then 100 mV for 3 hours)								
42-1-U	0	991	4	1	2	<0.5		
42-2-U	15		1186	<0.5	963	<0.5		
42-3-U	45		1193	1	981	<0.5		
42-4-U	90		1196	6	972	1		
42-5-1-U	180		1198	<0.5	950	<0.5		
42-5-2-U	195							
42-5-3-U	225							
42-5-4-U	270		1357	930	108	<0.5		
42-6-U	360		1925	936	104	<0.5		
42-1-C	0		3	<0.5	2	<0.5		
42-2-C	15		1073	<0.5	963	<0.5		
42-3-C	45		1139	1	977	<0.5		
42-4-C	90		1190	1	958	<0.5		
42-5-1-C	180		1150	<0.5	915	<0.5		
42-5-2-C	195							
42-5-4-C	225							
42-5-4-C	270		1343	708	105	142		
42-6-C	360		1335	741	108	132		

Test 41: 100 ppm Fe @ 150 mV

Sample ID	Test Time	Selenite (ppb)*		Total Liquid-phase		Possible Selenite	
		TD	HG/CVAA	TD	HG/CVAA	TD	HG/CVAA
41-1	0 min	-	-	-	<55.0	-	-
41-2	15 min	453	-	-	446.2	-	-2%
41-3	45 min	-	-	-	-	-	-
41-4	1.5 hr	-	-	-	-	-	-
41-5	3 hr	367	-	-	430.0	-	15%
41-6	6 hr	367	-	-	497.2	-	26%

Test 42: 5 ppm Mn @ Variable ORP (200 mV for 3 hours, then 100 mV for 3 hours)

Sample ID	Test Time	Selenite (ppb)*		Total Liquid-phase		Possible Selenite	
		TD	HG/CVAA	TD	HG/CVAA	TD	HG/CVAA
42-1	0 min	-	<55.0	-	<55.00	-	-
42-2	15 min	560	513	-	966	-	47%
42-3	45 min	-	725	-	993	-	27%
42-4	1.5 hr	-	597	-	1001	-	40%
42-5(1)	3 hr	783	653	-	985	-	34%
42-5(2)	3.25 hr	-	901	-	1002	-	10%
42-5(3)	3.75 hr	-	974	-	990	-	2%
42-5(4)	4.5 hr	-	996	-	961	-	0%
42-6	6 hr	1133	1001	-	1019	-	2%

ICP-MS Data **sample**	**Time**	**TSe**	**Se(IV)**	**Se(VI)**	**SeSO3**	**Unknowns**	**Unaccounted**
Test 43: 5 ppm Mn, then 35 ppm Mn @ Variable ORP							
1082	ppb Se4						
							Sum of Species
43-1U	0	4	<0.5	2	<0.5		2
43-2U	125	1,232	<0.5	1152	<0.5		1152
43-3U	183	1,215	<0.5	1175	<0.5		1175
43-4U	263	1,272	<0.5	990	<0.5		990
43-5U	360	1,099	<0.5	985	<0.5		985
43-1C	0	2	<0.5	2	<0.5		2
43-2C	125	1,233	3	1164	<0.5		1167
43-3C	183	1,227	3	1165	<0.5		1168
43-4C	263	1,522	<0.5	1013	<0.5		1013
43-5C	360	1,111	<0.5	1045	<0.5		1045
Test 44: 35 ppm Mn @ Variable ORP, 500 ppb Se4 and 500 ppb Se6							
499	ppb Se4						
485	ppb Se6						
50.7	% Se4						
							Sum of Species
44-1U	0	3	<0.5	2	<0.5		2
44-2U	120	1,007	<0.5	934	<0.5		934
44-3U	270	993	<0.5	919	<0.5		919
44-4U	300	997	<0.5	930	<0.5		930
44-5U	415	1,070	450	522	<0.5		971
44-1C	0	5	<0.5	2	<0.5		2
44-2C	120	991	<0.5	937	<0.5		937
44-3C	270	997	3.4	925	<0.5		929
44-4C	300	1,021	<0.5	929	<0.5		929
44-5C	415	1,075	431	533	5.0		970

CSV and AA Data

Test 43: 5 ppm Mn, then 35 ppm Mn @ Variable ORP

AA Day of Test

Sample ID	Test Time	Elapsed Time (min)	Selenite (ppb)*		Total Liquid-phase Selenium (ppb)**		Possible Selenite Oxidation, %	
			TD	HG/CVAA	TD	HG/CVAA	TD	HG/CVAA
T43-1 D0 (T=0) @ 11:07	11:07			<50.00		<55.00		
Injection	11:29							
T43-1A DO @ 11:59	11:59	30		1003.48		1211.06		17
T43-1B DO @ 12:29	12:29	60		1022.24		1223.69		16
T43-1C D0 @13:02	13:02	93		1059.75		1211.77		13
T43-1D D0 @ 13:34	13:34	125		805.96		1185.09		32
T43-2 D0 @ 14:02	14:02	153		710.25		1225.09		42
T43-3 D0 @ 14:32	14:32	183		967.27		1194.22		19
T43-4 D0 @ 15:22	15:22	233		831.54		1166.85		29
T43-5 D0 @ 15:52	15:52	263		657.59		1062.80		38
T43-6 D0 @ 16:22	16:22	293		702.15		1073.36		35
T43-7 D0 @ 17:29	17:29	360		688.65		1074.74		36

Test 44: 35 ppm Mn @ Variable ORP, 500 ppb Se4 and 500 ppb Se6

AA Day of Test

Sample ID	Test Time	Elapsed Time (min)	Selenite (ppb)*		Total Liquid-phase Selenium (ppb)**		Possible Selenite Oxidation, %	
			TD	HG/CVAA	TD	HG/CVAA	TD	HG/CVAA
T44-1 D0 (T=0) @ 10:28	10:28			<50.00		<105.00		
Injection	11:15							
T44-2 D0 @ 11:45	11:45	30		330.16		1062.77		69
T44-3 D0 @ 12:15	12:15	60		278.14		993.14		72
T44-4 D0 @ 12:45	12:45	90		225.50		1015.11		78
T44-5 D0 @ 13:15	13:15	120		86.15		1014.33		92
T44-6 D0 @ 13:45	13:45	150		337.07		1014.38		67
T44-7 D0 @ 14:15	14:15	180		177.05		1025.73		83
T44-8 D0 @ 15:45	15:45	270		297.33		1015.89		71
T44-9 D0 @ 16:15	16:15	300		225.50		1032.49		78
T44-10 D0 @ 16:45	16:45	330		544.53		1052.99		48
T44-11 D0 @ 17:15	17:15	360		551.84		1071.87		49
T44-12 D0 @ 17:45	17:45	390		526.69		1070.37		51
T44-13 D0 @ 18:10	18:10	415		525.21		1094.53		52

AA 48 hour data

Test 43 - AA @ 48 hours

	Selenite (ppb)*	**Total Liquid-phase Selenium (ppb)****	**Possible Selenite Oxidation, %**
	HG/CVAA	**HG/CVAA**	**HG/CVAA**
	<50.00	**<110.00**	
<	**5.00**	**1075.55**	100
<	**100.00**	**1086.55**	91
<	**100.00**	**945.64**	89
<	**100.00**	**951.64**	89

Test 44 - AA @ 48 hours

Selenite (ppb)*	**Total Liquid-phase Selenium (ppb)****	**Possible Selenite Oxidation, %**
HG/CVAA	**HG/CVAA**	**HG/CVAA**
<50.00	**<110.00**	
50	**878.04**	94
50	**876.25**	94
50	**894.07**	94
384.57	**975.72**	61

0.7322295

ICP-MS Data sample	Time	TSe	Se(IV)	Se(VI)	SeSO3	Unknowns	Unaccounted
Test 45: 24 ppm Fe and 150 mV with 8 wt% gypsum (Actual ORP = 115 to 130 mV)							
996	ppb Se4						
							Sum of Species
45-1U	0	2	1	1	<0.5		1
45-3U	90	497	496	10	1.1		506
45-4U	180	523	501	18	2.0		521
45-5U	360	539	501	36	1.1		538
45-6U	600	646	537	47	1.9		586
45-1C	0	1	1	1	<0.5		1
45-3C	90	495	319	8	171.0		498
45-4C	180	744	334	17	166.0		517
45-5C	360	696	303	29	138.2		470
45-6C	600	2,053	385	44	152.7		582
Test 46: 24 ppm Fe, 150 mV, 8 wt% gypsum, 1000 ppmw DBA							
993	ppb Se4						
							Sum of Species
46-1U	0	9	7	<0.5	2.7		10
46-3U	90	795	746	2	8.4		756
46-4U	180	782	800	3	30.0		833
46-5U	360	777	810	4	12.2		826
46-6U	600	792	806	8	7.5		822
46-1C	0	9	1	1	7.6		10
46-3C	90	790	445	1	265.8		712
46-4C	180	793	491	2	286.3		780
46-5C	360	793	476	4	262.0		742
46-6C	600	893	478	5	269.3		752

CSV and AA Data

Test 45: 24 ppm Fe and 150 mV with 8 wt% gypsum (Actual ORP = 115 to 130 mV)
AA Day of Test

Sample ID	Test Time	Elapsed Time (min)	Selenite (ppb)	Total Se (ppb)
45-1	0 min	0	<50.00	<55.00
45-2	15 min	15	483	477
45-3	90 min	90	477	471
45-4	3 hr	180	520	471
45-5	6 hr	360	530	508
45-6	10 hr	600	615	589

Test 46: 24 ppm Fe, 150 mV, 8 wt% gypsum, 1000 ppmw DBA
AA Day of Test

Sample ID	Test Time	Elapsed Time (min)	Selenite (ppb)	Total Se (ppb)
46-1	0 min	0	<50.00	<55.00
46-2	15 min	15	693	787
46-3	90 min	90	706	785
46-4	3 hr	180	787	801
46-5	6 hr	360	755	749
46-6	10 hr	600	808	727

AA 48 hour data

Test 45 - AA @ 48 hours

Selenite (ppb)	Total Se (ppb)	Possible Selenite Oxidation, %
<50.00	<110.00	
498	439	-13
494	454	-9
510	492	-4
605	540	-12

Test 46 - AA @ 48 hours

Selenite (ppb)	Total Se (ppb)	Possible Selenite Oxidation, %
<100.00	<110.00	
766	677	-13
743	668	-11
771	652	-18
764	662	-15

ICP-MS Data sample	Time	TSe	Se(IV)	Se(VI)	SeSO3	Unknowns	Unaccounted
Test 47: 35 ppm Mn @ 200 to 400 mV							
Original run	**7-Oct**						
47-2U	15	1142	214.0	921.0	<0.5		1135.0
47-4U	180	1078	541.0	569.0	<0.5		1110.0
47-5U	360	1159	597.0	546.0	<0.5		1143.0
47-6U	665	1110	<0.5	1,702	<0.5	sample re-run	1702.0
47-2C	15	1026	<0.5	855.1	<0.5		855.1
47-4C	180	1171	550.7	341.9	<0.5		892.6
47-5C	360	1164	1221	563	<0.5	sample re-run	1784.0
47-6C	665	1189	<0.5	840.8	<0.5		840.8
Test 48: 35 ppm Mn @ 400 mV, 1000 ppm Acetic Acid							
Original run	**7-Oct**						
48-2U	15	1187	<0.5	1021	<0.5		1021.0
48-4U	180	1180	961.0	47	<0.5		1008.0
48-5U	360	1169	980.0	75	<0.5		1055.0
48-6U	600	1145	1001.0	89	<0.5		1090.0
48-2C	15	1151	<0.5	891	<0.5		891.0
48-4C	180	1200	931	126	<0.5		1057.0
48-5C	360	1107	981	71	<0.5		1052.0
48-6C	600	1250	1022	71	<0.5		1093.0
Test 49: 35 ppm Mn @ 400 mV, 100 mV							
Original run	**13-Oct**						
49-2U	15	1007	<0.5	861	<0.5		861.0
49-4U	180	962	<0.5	922	<0.5		922.0
49-5U	360	993	<0.5	837	<0.5		837.0
49-6U	600	1113	967	164	<0.5		1131.0
49-2C	15	1038	6	961	<0.5		967.0
49-4C	180	982	8	983	<0.5		991.0
49-5C	360	988	17	825	<0.5		842.0
49-6C	600	1105	821	198	<0.5		1019.0

CSV and AA Data

Test 47: 35 ppm Mn @ 200 to 400 mV

Sample ID	Test Time	Selenite (ppb)*		Selenite, Total		% Se Possible	
		TD	HG/CVAA	TD	HG/CVAA	TD	HG/CVAA
47-1	0	N/A	<50.00	-	<55.00	-	-
47-2	15	N/A	869.9	-	1115	-	22%
47-3	90	N/A	862.8	-	1182	-	27%
47-4	180	N/A	906.9		1189		24%
47-5	360	N/A	921.3	-	1156	-	20%
47-5B	488	N/A	712.9	-	-	-	-
47-5C	553	N/A	722.4	-	-	-	-
47-5D	590	N/A	686.9	-	-	-	-
47-5E	645	N/A	666.3	-	-	-	-
47-6	665	N/A	210.1	-	1217	-	83%

1172

Test 48: 35 ppm Mn @ 400 mV, 1000 ppm Acetic Acid

Sample ID	Test Time	Selenite (ppb)*		Selenite, Total		% Se Possible	
		TD	HG/CVAA	TD	HG/CVAA	TD	HG/CVAA
48-1	0	N/A	<50.0	-	<55.00	-	-
48-2	15	N/A	876.9	-	1000	-	12%
48-3	90	N/A	931.1		1046		11%
48-4	180	N/A	893.3	-	1022	-	13%
48-5	360	N/A	1046.7	-	1074	-	3%
48-6	600	N/A	941.8	-	1173	-	20%

Test 49: 35 ppm Mn @ 400 mV, 100 mV

Sample ID	Test Time	Selenite (ppb)*		Selenite, Total		% Se Possible	
		TD	HG/CVAA	TD	HG/CVAA	TD	HG/CVAA
49-1	0 min	N/A	<50.0	-	<55.00	-	-
49-2	15 min	N/A	574.8	-	923	-	38%
49-3	1.5 hr	N/A	696.8	-	858	-	19%
49-4	3 hr	N/A	636.7	-	878		27%
49-5	6 hr	N/A	629.9	-	928	-	32%
49-5B	-	N/A	949.5	-	-	-	4%
49-5C	-	N/A	960.2	-	1049	-	8%
49-5D	-	N/A	1023	-	1064	-	4%
49-6	10 hr	N/A	856.7	-	1043	-	18%

AA 48 hour data

Test 47 - AA @ 48 hours

Sample ID	Test Time	Selenite (ppb)*			Total Liquor Phase Se (ppb)*		
		day of test	48 hour	RPD	day of test	48 hour	RPD
47-1	0	<50.00	-	-	<55.00	<110.00	-
47-2	15	869.9	<50.00	178.3%	1115	922.12	18.9%
47-4	180	906.9	300.81	100.4%	1189	968.20	20.5%
47-5	360	921.3	519.93	55.7%	1156	984.16	16.1%
47-6	665	210.1	<50.00	123.1%	1217	962.14	23.4%

Test 48 - AA @ 48 hours

Sample ID	Test Time	Selenite (ppb)*			Total Liquor Phase Se (ppb)*		
		day of test	48 hour	RPD	day of test	48 hour	RPD
48-1	0	<50.00	-	-	<55.00	-	-
48-2	15	876.9	<50.00	178.4%	1000	950.1	5.2%
48-4	180	893.3	955.1	6.7%	1022	987.2	3.5%
48-5	360	1047	890.0	16.2%	1074	1022	5.0%
48-6	600	941.8	946.3	0.5%	1173	1029	13.2%

Test 49 - AA @ 48 hours

Sample ID	Test Time	Selenite (ppb)*					Total Liquo
		day of test	48 hour	RPD	pH	ORP	day of test
49-1	0 min	<50.00	-	-	-	-	<55.00
49-2	15	575	<50.00	168.0%			923
49-4	180	637	<50.00	170.9%			878
49-5	360	630	<50.00	170.6%			928
49-6	600	857	836	2.4%			1043

ICP-MS Data sample	Time	TSe	Se(IV)	Se(VI)	SeSO3	Unknowns	Unaccounted
Test 50: 35 ppm Mn @ 400 mV, 1000 ppm DBA							
Original run	**13-Oct**						
50-2U	15	1144	1164	133	<0.5		1297.0
50-4U	90	1101	1193	42	<0.5		1235.0
50-5U	180	1133	1372	79	<0.5		1451.0
50-6U	360	1186	2126	171	<0.5	rerun 2x agair	2297.0
50-2C	15	1221	520	522	<0.5	No SeSO3 species present in reruns	1042.0
50-4C	90	1105	924	40	<0.5		964.0
50-5C	180	1163	1080	62	<0.5		1142.0
50-6C	360	1192	1009	95	<0.5		1104.0

		Se(IV)	Se(VI)	SeSO3	Σ of species	Enchancement correction factor
50-2c	Original run data	1221	1046	4.3	2281	0.438
50-4c		1941	78	10	2042	0.45
50-5c		1384	78	11.5	1488	0.673
50-6c		2000	154	53	2226	0.45

Corrected results

Se(iV)	Se(VI)	SeSO3
535	458	4.3
873	35	10
931	52	11.5
900	69	53

CSV and AA Data

Test 50: 35 ppm Mn @ 400 mV, 1000 ppm DBA

Sample ID	Test Time	Selenite (ppb)*		Selenite, Total		% Se Possible	
		TD	HG/CVAA	TD	HG/CVAA	TD	HG/CVAA
50-1	0	N/A		-		-	-
50-2	15	N/A	546.2	-	1034	-	47%
50-3	45	N/A	320.7	-	996		68%
50-4	90	N/A	736.9	-	1057	-	30%
50-4b	120	N/A	670.1	-	1044	-	36%
50-5	180	N/A	735.9	-	1015	-	28%
50-6	360	N/A	825.5	-	1124	-	27%

AA 48 hour data

Test 50 - AA @ 48 hours

Sample ID	Test Time	Selenite (ppb)*					Total Liquo
		day of test	48 hour	RPD	pH	ORP	day of test
50-1	0	<50.00	-	-	-	-	<55.00
50-2	15	546.2	929	82.3%			1034
50-3	90	736.9	-	-			1057
50-4	180	735.9	920	40.0%			1015
50-5	360	825.5	931	22.7%			1124

"=" indicates equial to Se Clear Liquor Baseline value.

	Units			
Run #		**29**	**30**	**31**
Test		**Mn @ 150 mV (10 h)**	**Mn @ 150 mV with DBA (10 h)**	**Selenate @ 100 mV (5 ppm Mn)**
Test Date		4/26/2010	4/27/2010	5/3/2010
Speciation Analysis Date		4/29/2010	4/29/2010	5/6/2010
Test length (hours)		10	10	6
Test Matrix Variables:				
Operating Conditions:				
pH (reaction tank)	-	5.5	5.5	5.5
ORP	mV	150	150	100
Selenium Species:				
Na_2SeO_3 (Se IV)	ppb as Se	1000	1000	
Na_2SeO_4 (Se VI)	ppb as Se			1000
Other (List)	ppb as Se			
Constituents:				
Ferric Hydroxide				
DBA			1000 ppmw	
$MnSO_4$ (aq)		5 ppm as Mn	5 ppm as Mn	5 ppm as Mn
Adipic Acid	ppmw			
Acetic Acid	ppmw			
8-HQS	ppmw			

Run #		**29**	**30**	**31**

LIQUID PHASE RESULTS
"-" indicates "not applicable" or "not analyzed"

Seleniun Speciation (See separate file for detailed results)
c =cryo, u = unpreserved, qa/qc = data under review

0 min		c, u	c, u	c, u
15 min		c, u	c, u	c, u
45 min		-	-	c, u
1.5 h		c, u	c, u	c, u
3 h		c, u	c, u	c, u
6 h		c, u	c, u	c, u
10 h		c, u	c, u	-

Seleniun Speciation - URS (See separate file for detailed results)
Trace Detect, qa/qc = data under review

Day Of Test		-	-	-
48 hour samples		-	-	-

Seleniun Speciation - URS (See separate file for detailed results)
Borohydride atomic absorption, qa/qc = data under review

Day Of Test		-	-	-
48 hour samples		-	-	-

Metals - Mn (Trent analyses are at the bottom of the worksheet)

0 h	ppm Mn	4.41	4.68	5.11
15 min	ppm Mn	-	-	-
45 min	ppm Mn	-	-	-
1.5 h	ppm Mn	-	-	-
3 h	ppm Mn	-	-	-
6 h	ppm Mn	-	-	5.30
10 h	ppm Mn	4.45	4.96	-

Metals - Mn (48 hour unpreserved)

0 h	ppm Mn	-	-	-
15 min	ppm Mn	-	-	-
45 min	ppm Mn	-	-	-
1.5 h	ppm Mn	-	-	-
3 h	ppm Mn	-	-	-
6 h	ppm Mn	-	-	-
10 h	ppm Mn	-	-	-

Metals - Fe

0 h	ppm Fe	-	-	-
15 min	ppm Fe	-	-	-
1.5 h	ppm Fe	-	-	-
3 h	ppm Fe	-	-	-
6 h	ppm Fe	-	-	-
10 h	ppm Fe	-	-	-

Run #		**29**	**30**	**31**

Sulfite DF

15 min	mM SO3	-	-	-
1.5 h	mM SO3	-	-	-
3 h	mM SO3	-	4.93	-
6 h	mM SO3	-	-	1.00
10 h	mM SO3	0.23	8.60	-

Sulfite DF - 48 hour unpreserved

15 min	mM SO3	-	-	-
1.5 h	mM SO3	-	-	-
3 h	mM SO3	-	-	-
6 h	mM SO3	-	-	-
10 h	mM SO3	-	-	-

Sulfate (SO4)

15 min	ppm SO4	-	-	-
1.5 h	ppm SO4	-	-	-
3 h	ppm SO4	-	10422	-
6 h	ppm SO4	-	-	13680
10 h	ppm SO4	19051	17723	-

Dithionate (S2O6)

15 min	ppm S2O6	-	-	-
1.5 h	ppm S2O6	-	-	-
3 h	ppm S2O6	-	32.59	-
6 h	ppm S2O6	-	-	9.29
10 h	ppm S2O6	21.24	75.77	-

Dithionate (S2O6) - 48 hour unpreserved

15 min	ppm S2O6	-	-	-
1.5 h	ppm S2O6	-	-	-
3 h	ppm S2O6	-	-	-
6 h	ppm S2O6	-	-	-
10 h	ppm S2O6	-	-	-

Persulfate (S2O8)

15 min	ppm S2O8	-	-	-
1.5 h	ppm S2O8	-	-	-
3 h	ppm S2O8	-	<2	-
6 h	ppm S2O8	-	-	2.36
10 h	ppm S2O8	35.94	<2	-

Persulfate (S2O8) - 48 hour unpreserved

15 min	ppm S2O8	-	-	-
1.5 h	ppm S2O8	-	-	-
3 h	ppm S2O8	-	-	-
6 h	ppm S2O8	-	-	-
10 h	ppm S2O8	-	-	-

Run #		29	30	31
Chloride DF				
6 h	mM	-	-	99.9
10 h	mM	99.3	102	-
DBA				
0 h				
Succinic	ppm	-	159	-
Glutaric	ppm	-	731	-
Adipic	ppm	-	138	-
6 h				
Succinic	ppm	-	-	-
Glutaric	ppm	-	-	-
Adipic	ppm	-	-	-
10 h				
Succinic	ppm	-	150	-
Glutaric	ppm	-	682	-
Adipic	ppm	-	126	-
Acetate				
0 h	ppm	-	-	-
10 h	ppm	-	-	-

"=" indicates equial to Se Clear Liquor Baseline

	Units				
Run #		**32**	**33**	**34**	**35**
Test		**Adipic Acid @ 200 mV (5 ppm Mn)**	**Mn @ 150 mV (10 h) Repeat**	**High Mn @ 100 mV**	**Med Fe @ 100 mV**
Test Date		5/4/2010	5/16/2010	6/7/2010	6/8/2010
Speciation Analysis Date		5/6/2010	5/19/2010	6/10/2010	6/10/2010
Test length (hours)		6	10	6	6
Test Matrix Variables:					
Operating Conditions:					
pH (reaction tank)	-	5.5	5.5	5.5	5.5
ORP	mV	200	150	100	100
Selenium Species:					
Na_2SeO_3 (Se IV)	ppb as Se	1000	1000	1000	1000
Na_2SeO_4 (Se VI)	ppb as Se				
Other (List)	ppb as Se				
Constituents:					
Ferric Hydroxide					24 ppmw as Fe
DBA					
$MnSO_4$ (aq)		5 ppm as Mn	5 ppm as Mn	35 ppm as Mn	0
Adipic Acid	ppmw	1000			
Acetic Acid	ppmw				
8-HQS	ppmw				

Run #		**32**	**33**	**34**	**35**

LIQUID PHASE RESULTS
"-" indicates "not applicable" or "not analyzed"

Seleniun Speciation (See separate file for detaile
c =cryo, u = unpreserved, qa/qc = data under re

0 min		c, u	c, u	c, u	c, u
15 min		c, u	c, u	c, u	c, u
45 min		c, u	na	c, u	c, u
1.5 h		c, u	c, u	c, u	c, u
3 h		c, u	c, u	c, u	c, u
6 h		c, u	c, u	c, u	c, u
10 h		-	c, u	-	-

Seleniun Speciation - URS (See separate file for
Trace Detect, qa/qc = data under review

Day Of Test		-	-	-	-
48 hour samples		-	-	-	-

Seleniun Speciation - URS (See separate file for
Borohydride atomic absorption, qa/qc = data un

Day Of Test		-	-	-	-
48 hour samples		-	-	-	-

Metals - Mn (Trent analyses are at the bottom of

0 h	ppm Mn	4.43	4.89	36.7	-
15 min	ppm Mn	-	-	35.6	-
45 min	ppm Mn	-	-	35.6	-
1.5 h	ppm Mn	-	-	35.8	-
3 h	ppm Mn	-	5.00	35.4	-
6 h	ppm Mn	4.47	4.66	34.7	-
10 h	ppm Mn	-	4.62	-	-

Metals - Mn (48 hour unpreserved)

0 h	ppm Mn	-	-	-	-
15 min	ppm Mn	-	-	-	-
45 min	ppm Mn	-	-	-	-
1.5 h	ppm Mn	-	-	-	-
3 h	ppm Mn	-	-	-	-
6 h	ppm Mn	-	-	-	-
10 h	ppm Mn	-	-	-	-

Metals - Fe

0 h	ppm Fe	-	-	-	0.21
15 min	ppm Fe	-	-	-	0.24
1.5 h	ppm Fe	-	-	-	0.23
3 h	ppm Fe	-	-	-	0.28
6 h	ppm Fe	-	-	-	0.35
10 h	ppm Fe	-	-	-	-

Run #		**32**	**33**	**34**	**35**
Sulfite DF					
15 min	mM SO3	-	-	0.36	1.05
1.5 h	mM SO3	-	-	-	-
3 h	mM SO3	-	-	-	-
6 h	mM SO3	0.43	-	0.26	0.36
10 h	mM SO3	-	0.12	-	-
				70	77
Sulfite DF - 48 hour unpreserved					
15 min	mM SO3	-	-	-	-
1.5 h	mM SO3	-	-	-	-
3 h	mM SO3	-	-	-	-
6 h	mM SO3	-	-	-	-
10 h	mM SO3	-	-	-	-
Sulfate (SO4)					
15 min	ppm SO4	-	-	6705	7378
1.5 h	ppm SO4	-	-	-	-
3 h	ppm SO4	-	-	-	-
6 h	ppm SO4	14759	17629	14668	14936
10 h	ppm SO4	-	-	-	-
				153	156
Dithionate (S2O6)					
15 min	ppm S2O6	-	-	<3	1.7
1.5 h	ppm S2O6	-	-	5.8	2.2
3 h	ppm S2O6	-	-	9.1	2.6
6 h	ppm S2O6	5.09	-	16.5	3.0
10 h	ppm S2O6	-	7.43	-	-
				7.640384423	
Dithionate (S2O6) - 48 hour unpreserved					
15 min	ppm S2O6	-	-	-	-
1.5 h	ppm S2O6	-	-	-	-
3 h	ppm S2O6	-	-	-	-
6 h	ppm S2O6	-	-	-	-
10 h	ppm S2O6	-	-	-	-
Persulfate (S2O8)					
15 min	ppm S2O8	-	-	1.8	2.7
1.5 h	ppm S2O8	-	-	2.6	4.3
3 h	ppm S2O8	-	-	3.1	6.2
6 h	ppm S2O8	5.16	-	5.5	8.1
10 h	ppm S2O8	-	19.86	-	-
Persulfate (S2O8) - 48 hour unpreserved					
15 min	ppm S2O8	-	-	-	-
1.5 h	ppm S2O8	-	-	-	-
3 h	ppm S2O8	-	-	-	-
6 h	ppm S2O8	-	-	-	-
10 h	ppm S2O8	-	-	-	-

Run #		**32**	**33**	**34**	**35**
Chloride DF					
6 h	mM	96.7	-	89.9	100.0
10 h	mM	-	95.1	-	-
DBA					
0 h					
Succinic	ppm	-	-	-	-
Glutaric	ppm	-	-	-	-
Adipic	ppm	827	-	-	-
6 h					
Succinic	ppm	-	-	-	-
Glutaric	ppm	-	-	-	-
Adipic	ppm	704	-	-	-
10 h					
Succinic	ppm	-	-	-	-
Glutaric	ppm	-	-	-	-
Adipic	ppm	-	-	-	-
Acetate					
0 h	ppm	-	-	-	-
10 h	ppm	-	-	-	-

"=" indicates equial to Se Clear Liquor Baseline Begin TD and AA measurements

	Units				
Run #		**36**	**37**	**38**	**39**
Test		**Med Fe @ 150 mV**	**Low Fe @ 150 mV**	**High Fe @ 100 mV**	**High Fe and High Mn @ 150 mV**
Test Date		6/14/2010	6/15/2010	6/21/2010	6/22/2010
Speciation Analysis Date		6/16/2010	6/16/2010	6/23/2010	6/23/2010
Test length (hours)		6	6	6	6
Test Matrix Variables:					
Operating Conditions:					
pH (reaction tank)	-	5.5	5.5	5.5	5.5
ORP	mV	200 (actual 150)	200 (actual 150)	100	150
Selenium Species:					
Na_2SeO_3 (Se IV)	ppb as Se	1000		1000	1000
Na_2SeO_4 (Se VI)	ppb as Se				
Other (List)	ppb as Se				
Constituents:					
Ferric Hydroxide		24 ppmw as Fe	4 ppmw as Fe	600 ppmw as Fe	600 ppmw as Fe
DBA					
$MnSO_4$ (aq)		0	0	0	35 ppm as Mn
Adipic Acid	ppmw				
Acetic Acid	ppmw				
8-HQS	ppmw				

Run #		36	37	38	39

LIQUID PHASE RESULTS
"-" indicates "not applicable" or "not analyzed"

Seleniun Speciation (See separate file for detaile
c =cryo, u = unpreserved, qa/qc = data under re

0 min		c, u	c, u	c, u	c, u
15 min		c, u	c, u	c, u	c, u
45 min		c, u	c, u	c, u	c, u
1.5 h		c, u	c, u	c, u	c, u
3 h		c, u	c, u	c, u	c, u
6 h		c, u	c, u	c, u	c, u
10 h		-	-	-	-

Seleniun Speciation - URS (See separate file for
Trace Detect, qa/qc = data under review

Day Of Test		Se4	Se4	Se4	Se4
48 hour samples		-	-	-	-

Seleniun Speciation - URS (See separate file for
Borohydride atomic absorption, qa/qc = data un

Day Of Test		Se4, TSe	Se4, TSe	Se4, TSe	Se4, TSe
48 hour samples		-	-	-	-

Metals - Mn (Trent analyses are at the bottom of

0 h	ppm Mn	-	-	-	31.4
15 min	ppm Mn	-	-	-	29.6
45 min	ppm Mn	-	-	-	-
1.5 h	ppm Mn	-	-	-	28.2
3 h	ppm Mn	-	-	-	26.7
6 h	ppm Mn	-	-	-	23.6
10 h	ppm Mn	-	-	-	-

Metals - Mn (48 hour unpreserved)

0 h	ppm Mn	-	-	-	-
15 min	ppm Mn	-	-	-	-
45 min	ppm Mn	-	-	-	-
1.5 h	ppm Mn	-	-	-	-
3 h	ppm Mn	-	-	-	-
6 h	ppm Mn	-	-	-	-
10 h	ppm Mn	-	-	-	-

Metals - Fe

0 h	ppm Fe	0.20	0.23	0.36	0.23
15 min	ppm Fe	0.23	0.16	0.20	0.23
1.5 h	ppm Fe	0.22	0.18	0.23	0.23
3 h	ppm Fe	0.25	0.23	0.25	0.25
6 h	ppm Fe	0.31	0.25	0.29	0.29
10 h	ppm Fe	-	-	-	-

Run #		36	37	38	39
Sulfite DF		0.96 mM SO3-- at 100 mV 15 minutes			
15 min	mM SO3	0.12	0.05	1.78	0.07
1.5 h	mM SO3	-	-	-	-
3 h	mM SO3	-	-	-	-
6 h	mM SO3	0.07	0.09	0.80	0.09
10 h	mM SO3	-	-	-	-
		88	65	78	99
Sulfite DF - 48 hour unpreserved					
15 min	mM SO3	-	-	-	-
1.5 h	mM SO3	-	-	-	-
3 h	mM SO3	-	-	-	-
6 h	mM SO3	-	-	-	-
10 h	mM SO3	-	-	-	-
Sulfate (SO4)		7206 ppm at 100 mV and 15 minutes			
15 min	ppm SO4	8479	6208	7521	9538
1.5 h	ppm SO4	-	-	-	-
3 h	ppm SO4	-	-	-	-
6 h	ppm SO4	16262	13487	14838	16645
10 h	ppm SO4	-	-	-	-
		169	140	155	173
Dithionate (S2O6)		0.8	<-- @ 100 mV		
15 min	ppm S2O6	-	<6	2.4	7.90
1.5 h	ppm S2O6	-	<6	2.7	16.2
3 h	ppm S2O6	1.0		3.5	30.3
6 h	ppm S2O6	1.1	<6	4.5	58.2
10 h	ppm S2O6	-	-	-	-
Dithionate (S2O6) - 48 hour unpreserved					
15 min	ppm S2O6	-	-	-	-
1.5 h	ppm S2O6	-	-	-	-
3 h	ppm S2O6	-	-	-	-
6 h	ppm S2O6	-	-	-	-
10 h	ppm S2O6	-	-	-	-
Persulfate (S2O8)		2.01	<--- @ 100 mV		
15 min	ppm S2O8	3.66	2.46	1.20	3.33
1.5 h	ppm S2O8	-	3.90	2.56	4.50
3 h	ppm S2O8	7.57	5.76	2.90	7.76
6 h	ppm S2O8	11.4	8.70	3.99	14.2
10 h	ppm S2O8	-	-	-	-
Persulfate (S2O8) - 48 hour unpreserved					
15 min	ppm S2O8	-	-	-	-
1.5 h	ppm S2O8	-	-	-	-
3 h	ppm S2O8	-	-	-	-
6 h	ppm S2O8	-	-	-	-
10 h	ppm S2O8	-	-	-	-

Run #		**36**	**37**	**38**	**39**
Chloride DF					
6 h	mM	99.1	92.1	92.5	95.3
10 h	mM	-	-	-	-
DBA					
0 h					
Succinic	ppm	-	-	-	-
Glutaric	ppm	-	-	-	-
Adipic	ppm	-	-	-	-
6 h					
Succinic	ppm	-	-	-	-
Glutaric	ppm	-	-	-	-
Adipic	ppm	-	-	-	-
10 h					
Succinic	ppm	-	-	-	-
Glutaric	ppm	-	-	-	-
Adipic	ppm	-	-	-	-
Acetate					
0 h	ppm	-	-	-	-
10 h	ppm	-	-	-	-

"=" indicates equial to Se Clear Liquor Baseline

	Units				
Run #		**40**	**41**	**42**	
Test		**High Mn @ 150 mV**	**100 ppm Fe @ 150 mV**	**Mn with variable ORP (Test 15 re-creation)**	
Test Date		7/14/2010	7/19/2010	7/20/2010	
Speciation Analysis Date		7/15/2010	7/21/2010	7/21/2010	
Test length (hours)		6	6	6	
Test Matrix Variables:					
Operating Conditions:					
pH (reaction tank)	-	5.5	5.5	5.5	
ORP	mV	150	150	Start at 200. Decrease to 100 after 3 h samples	
Selenium Species:					
Na_2SeO_3 (Se IV)	ppb as Se	1000	1000	1000	
Na_2SeO_4 (Se VI)	ppb as Se				
Other (List)	ppb as Se				
Constituents:					
Ferric Hydroxide			100 ppmw as Fe		
DBA					
$MnSO_4$ (aq)		35 ppm as Mn		5 ppm as Mn	
Adipic Acid	ppmw				
Acetic Acid	ppmw				
8-HQS	ppmw				

Run #		**40**	**41**	**42**	

LIQUID PHASE RESULTS
"-" indicates "not applicable" or "not analyzed"

Seleniun Speciation (See separate file for detaile
c =cryo, u = unpreserved, qa/qc = data under re

0 min		c, u	c, u	c, u	
15 min		c, u	c, u	c, u	
45 min		c, u	c, u	c, u	
1.5 h		c, u	c, u	c, u	
3 h		c, u	c, u	c, u	
6 h		c, u	c, u	c, u	
10 h		-	-	-	

Seleniun Speciation - URS (See separate file for
Trace Detect, qa/qc = data under review

Day Of Test		Se4	Se4	Se4	
48 hour samples		-	-	-	

Seleniun Speciation - URS (See separate file for
Borohydride atomic absorption, qa/qc = data un

Day Of Test		Se4, TSe	Se4 only	Se4, TSe	
48 hour samples		-	-	-	

Metals - Mn (Trent analyses are at the bottom of

0 h	ppm Mn	34.9	-	3.7	0
15 min	ppm Mn	35.4	-	3.4	125
45 min	ppm Mn	-	-	-	183
1.5 h	ppm Mn	35.8	-	3.2	263
3 h	ppm Mn	36.5	-	2.7	360
6 h	ppm Mn	36.9	-	4.5	
10 h	ppm Mn	-	-	-	

Metals - Mn (48 hour unpreserved)

0 h	ppm Mn	-	-	-	
15 min	ppm Mn	-	-	-	
45 min	ppm Mn	-	-	-	
1.5 h	ppm Mn	-	-	-	
3 h	ppm Mn	-	-	-	
6 h	ppm Mn	-	-	-	
10 h	ppm Mn	-	-	-	

Metals - Fe

0 h	ppm Fe	-	0.29	-	
15 min	ppm Fe	-	0.29	-	
1.5 h	ppm Fe	-	0.29	-	
3 h	ppm Fe	-	0.32	-	
6 h	ppm Fe	-	0.36	-	
10 h	ppm Fe	-	-	-	

Run #		**40**	**41**	**42**	

Sulfite DF

15 min	mM SO3	0.09	0.18	<0.04	
1.5 h	mM SO3	-	-	-	
3 h	mM SO3	-	-	-	
6 h	mM SO3	0.88	0.10	0.48	
10 h	mM SO3	-	-	-	

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Sulfite DF - 48 hour unpreserved

15 min	mM SO3	-	-	-	
1.5 h	mM SO3	-	-	-	
3 h	mM SO3	-	-	-	
6 h	mM SO3	-	-	-	
10 h	mM SO3	-	-	-	

Sulfate (SO4)

15 min	ppm SO4	6130	6882	6087	
1.5 h	ppm SO4	-	-	-	
3 h	ppm SO4	-	-	-	
6 h	ppm SO4	13623	13965	13844	
10 h	ppm SO4	-	-	-	

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Dithionate (S2O6)

15 min	ppm S2O6	3.3	<3	5.5	
1.5 h	ppm S2O6	13.1	<3	6.4	
3 h	ppm S2O6	24.8	<3	6.6	
6 h	ppm S2O6	39.7	<3	8.8	
10 h	ppm S2O6	-	-	-	

Dithionate (S2O6) - 48 hour unpreserved

15 min	ppm S2O6	-	-	-	
1.5 h	ppm S2O6	-	-	-	
3 h	ppm S2O6	-	-	-	
6 h	ppm S2O6	-	-	-	
10 h	ppm S2O6	-	-	-	

Persulfate (S2O8)

15 min	ppm S2O8	2.0	1.6	9.9	
1.5 h	ppm S2O8	4.0	3.3	15.7	
3 h	ppm S2O8	6.1	5.1	22.6	
6 h	ppm S2O8	8.8	8.5	23.5	
10 h	ppm S2O8	-	-	-	

Persulfate (S2O8) - 48 hour unpreserved

15 min	ppm S2O8	-	-	-	
1.5 h	ppm S2O8	-	-	-	
3 h	ppm S2O8	-	-	-	
6 h	ppm S2O8	-	-	-	
10 h	ppm S2O8	-	-	-	

Run #		40	41	42	
Chloride DF					
6 h	mM	94.7	99.1	98.4	
10 h	mM	-	-	-	
DBA					
0 h					
Succinic	ppm	-	-	-	
Glutaric	ppm	-	-	-	
Adipic	ppm	-	-	-	
6 h					
Succinic	ppm	-	-	-	
Glutaric	ppm	-	-	-	
Adipic	ppm	-	-	-	
10 h					
Succinic	ppm	-	-	-	
Glutaric	ppm	-	-	-	
Adipic	ppm	-	-	-	
Acetate					
0 h	ppm	-	-	-	
10 h	ppm	-	-	-	

"=" indicates equial to Se Clear Liquor Baseline

	Units			
Run #		**43**		**44**
Test		**Mn with Variable ORP (Complete Oxidation)**		**Mn with Variable ORP (50% Se4, 50% Se6, Complete Oxidation)**
Test Date		8/9/2010		8/10/2010
Speciation Analysis Date		8/11/2010		8/11/2010
Test length (hours)		6		6
Test Matrix Variables:				
Operating Conditions:				
pH (reaction tank)	-	5.5		5.5
ORP	mV	Increase to ORP at which AA measures complete oxidation of Se4 to Se6 (start with 300 mV), operate at that ORP for 90 minutes, then decrease to 100 mV and operate for 4 hours		Use same ORP progression as Test 43
Selenium Species:				
Na_2SeO_3 (Se IV)	ppb as Se	1000		500
Na_2SeO_4 (Se VI)	ppb as Se			500
Other (List)	ppb as Se			
Constituents:				
Ferric Hydroxide				
DBA				
$MnSO_4$ (aq)		5 ppm as Mn (30 ppm added at ~200 min)		35 ppm as Mn
Adipic Acid	ppmw			
Acetic Acid	ppmw			
8-HQS	ppmw			

Run #		**43**		**44**

LIQUID PHASE RESULTS
"-" indicates "not applicable" or "not analyzed"

Seleniun Speciation (See separate file for detaile
c =cryo, u = unpreserved, qa/qc = data under re

0 min		c,u at all times		c,u at all times
15 min				
45 min				
1.5 h				
3 h				
6 h				
10 h		-		-

Seleniun Speciation - URS (See separate file for
Trace Detect, qa/qc = data under review

Day Of Test		-		-
48 hour samples		-		-

Seleniun Speciation - URS (See separate file for
Borohydride atomic absorption, qa/qc = data un

Day Of Test		Se4, TSe		Se4, TSe
48 hour samples		Se4, TSe		Se4, TSe

Metals - Mn (Trent analyses are at the bottom of

		Times are specific to Test 43		Times are specific to Test 44
0 h	ppm Mn	0.90	0	24.60
15 min	ppm Mn	1.12	120	3.53
45 min	ppm Mn	1.27	270	1.25
1.5 h	ppm Mn	0.12	300	1.27
3 h	ppm Mn	0.88	411	42.42
6 h	ppm Mn	-		-
10 h	ppm Mn	-		-

Metals - Mn (48 hour unpreserved)

0 h	ppm Mn	-		-
15 min	ppm Mn	-		-
45 min	ppm Mn	-		-
1.5 h	ppm Mn	-		-
3 h	ppm Mn	-		-
6 h	ppm Mn	-		-
10 h	ppm Mn	-		-

Metals - Fe

0 h	ppm Fe	-		-
15 min	ppm Fe	-		-
1.5 h	ppm Fe	-		-
3 h	ppm Fe	-		-
6 h	ppm Fe	-		-
10 h	ppm Fe	-		-

Run #		**43**		**44**

Sulfite DF

15 min	mM SO3	<0.04		<0.04
1.5 h	mM SO3	-		-
3 h	mM SO3	-		-
6 h	mM SO3	<0.04		2.49
10 h	mM SO3	-		-

Sulfite DF - 48 hour unpreserved

15 min	mM SO3	-		-
1.5 h	mM SO3	-		-
3 h	mM SO3	-		-
6 h	mM SO3	-		-
10 h	mM SO3	-		-

Sulfate (SO4)

15 min	ppm SO4	9163		6364
1.5 h	ppm SO4	-		-
3 h	ppm SO4	-		-
6 h	ppm SO4	12957		13928
10 h	ppm SO4	-		-

Dithionate (S2O6)

15 min	ppm S2O6	3.3	0	37.2
1.5 h	ppm S2O6	3.2	270	67.9
3 h	ppm S2O6	12.4	300	69.3
6 h	ppm S2O6	13.7	411	77.1
10 h	ppm S2O6	-		-

Dithionate (S2O6) - 48 hour unpreserved

15 min	ppm S2O6	-		-
1.5 h	ppm S2O6	-		-
3 h	ppm S2O6	-		-
6 h	ppm S2O6	-		-
10 h	ppm S2O6	-		-

Persulfate (S2O8)

15 min	ppm S2O8	24.2	0	5.0
1.5 h	ppm S2O8	28.3	270	16.1
3 h	ppm S2O8	37.4	300	27.8
6 h	ppm S2O8	53.3	411	21.4
10 h	ppm S2O8	-		-

Persulfate (S2O8) - 48 hour unpreserved

15 min	ppm S2O8	-		-
1.5 h	ppm S2O8	-		-
3 h	ppm S2O8	-		-
6 h	ppm S2O8	-		-
10 h	ppm S2O8	-		-

Run #		**43**		**44**
Chloride DF				
6 h	mM	98.2		100.3
10 h	mM	-		-
DBA				
0 h				
Succinic	ppm	-		-
Glutaric	ppm	-		-
Adipic	ppm	-		-
6 h				
Succinic	ppm	-		-
Glutaric	ppm	-		-
Adipic	ppm	-		-
10 h				
Succinic	ppm	-		-
Glutaric	ppm	-		-
Adipic	ppm	-		-
Acetate				
0 h	ppm	-		-
10 h	ppm	-		-

"=" indicates equial to Se Clear Liquor Baseline

	Units			
Run #		**45**	**46**	**47**
Test		**24 ppm Fe @ 150 mV with 8% gypsum *(actual 115 to 130 mV ORP)***	**24 ppm Fe @ 150 mV with 8% gypsum and 1000 ppm DBA**	**35 ppm Mn @ 200 to 400 mV**
Test Date		8/16/2010	8/17/2010	10/4/2010
Speciation Analysis Date		8/19/2010	8/19/2010	10/7/2010
Test length (hours)		10	10	11
Test Matrix Variables:				
Operating Conditions:				
pH (reaction tank)	-	5.5	5.5	5.5
ORP	mV	150	150	200 mV (first 9 hours), 400 mV last two hours
Selenium Species:				
Na_2SeO_3 (Se IV)	ppb as Se	1000	1000	1000
Na_2SeO_4 (Se VI)	ppb as Se			
Other (List)	ppb as Se			
Constituents:				
Ferric Hydroxide		24 ppmw as Fe	24 ppmw as Fe	
DBA			1000 ppmw	
$MnSO_4$ (aq)				35 ppm as Mn
Adipic Acid	ppmw			
Acetic Acid	ppmw			
8-HQS	ppmw			

Run #		**45**	**46**	**47**

LIQUID PHASE RESULTS
"-" indicates "not applicable" or "not analyzed"

Seleniun Speciation (See separate file for detaile
c =cryo, u = unpreserved, qa/qc = data under re

0 min		-	-	c,u at all times
15 min		-	-	
45 min		-	-	
1.5 h		c,u	c,u	
3 h		c,u	c,u	
6 h		c,u	c,u	
10 h		c,u	c,u	

Seleniun Speciation - URS (See separate file for
Trace Detect, qa/qc = data under review

Day Of Test		-	-	-
48 hour samples		-	-	-

Seleniun Speciation - URS (See separate file for
Borohydride atomic absorption, qa/qc = data un

Day Of Test		Se4, TSe	Se4, TSe	Se4, TSe
48 hour samples		Se4, TSe	Se4, TSe	Se4, TSe

Metals - Mn (Trent analyses are at the bottom of

0 h	ppm Mn	-	-	37.9
15 min	ppm Mn	-	-	36.5
45 min	ppm Mn	-	-	-
1.5 h	ppm Mn	-	-	-
3 h	ppm Mn	-	-	37.4
6 h	ppm Mn	-	-	36.5
10 h	ppm Mn	-	-	7.1

Metals - Mn (48 hour unpreserved)

0 h	ppm Mn	-	-	-
15 min	ppm Mn	-	-	35.7
45 min	ppm Mn	-	-	-
1.5 h	ppm Mn	-	-	-
3 h	ppm Mn	-	-	36.1
6 h	ppm Mn	-	-	35.7
10 h	ppm Mn	-	-	6.7

Metals - Fe

0 h	ppm Fe	-	-	-
15 min	ppm Fe	-	-	-
1.5 h	ppm Fe	-	-	-
3 h	ppm Fe	0.29	0.26	-
6 h	ppm Fe	0.31	0.39	-
10 h	ppm Fe	0.34	0.35	-

Run #		**45**	**46**	**47**

Sulfite DF

15 min	mM SO3	0.50	2.78	<0.038
1.5 h	mM SO3	-	-	-
3 h	mM SO3	0.56	3.29	<0.038
6 h	mM SO3	0.43	3.41	<0.038
10 h	mM SO3	1.00	2.62	<0.038

Sulfite DF - 48 hour unpreserved

15 min	mM SO3	-	-	<0.05
1.5 h	mM SO3	-	-	-
3 h	mM SO3	-	-	<0.038
6 h	mM SO3	-	-	<0.038
10 h	mM SO3	-	-	<0.038

Sulfate (SO4)

15 min	ppm SO4	5974	6087	7680
1.5 h	ppm SO4	-	-	-
3 h	ppm SO4	-	-	-
6 h	ppm SO4	-	-	-
10 h	ppm SO4	18173	18244	22974

final sample at 11 hours

Dithionate (S2O6)

15 min	ppm S2O6	<4	2.3	9.0
1.5 h	ppm S2O6	-	-	-
3 h	ppm S2O6	<6	10.8	29.4
6 h	ppm S2O6	3.6	19.9	53.5
10 h	ppm S2O6	14.3	32.3	126

final sample at 11 hours

Dithionate (S2O6) - 48 hour unpreserved

15 min	ppm S2O6	-	-	9.8
1.5 h	ppm S2O6	-	-	-
3 h	ppm S2O6	-	-	26.5
6 h	ppm S2O6	-	-	51.6
10 h	ppm S2O6	-	-	123

Persulfate (S2O8)

15 min	ppm S2O8	2.7	<1.5	2.22
1.5 h	ppm S2O8	-	-	-
3 h	ppm S2O8	8.7	<1.5	5.83
6 h	ppm S2O8	14.3	<1.5	12.66
10 h	ppm S2O8	16.6	<1.5	32.57

Persulfate (S2O8) - 48 hour unpreserved

15 min	ppm S2O8	-	-	2.10
1.5 h	ppm S2O8	-	-	-
3 h	ppm S2O8	-	-	5.79
6 h	ppm S2O8	-	-	12.29
10 h	ppm S2O8	-	-	32.18

Run #		**45**	**46**	**47**
Chloride DF				
6 h	mM	-	-	-
10 h	mM	106	103	3759
DBA				
0 h				
Succinic	ppm	-	98	-
Glutaric	ppm	-	753	-
Adipic	ppm	-	111	-
6 h				
Succinic	ppm	-	-	-
Glutaric	ppm	-	-	-
Adipic	ppm	-	-	-
10 h				
Succinic	ppm	-	67	-
Glutaric	ppm	-	648	-
Adipic	ppm	-	106	-
Acetate				
0 h	ppm	-	-	-
10 h	ppm	-	-	-

"=" indicates equial to Se Clear Liquor Baseline

Test Terminated

	Units				
Run #		**48**	**49**	**50**	**51**
Test		**35 ppm Mn @ 400 mV, 1000 ppm Acetic Acid**	**35 ppm Mn @ 400 mV, 100 mV**	**35 ppm Mn @ 400 mV, 1000 ppm DBA**	**35 ppm Mn and 3100 ppm 8-HQS @ 400 mV**
Test Date		10/5/2010	10/11/2010	10/12/2010	10/19/2010
Speciation Analysis Date		10/7/2010	10/13/2010	10/13/2010	
Test length (hours)		10	10	6	6
Test Matrix Variables:					
Operating Conditions:					
pH (reaction tank)	-	5.5	5.5	5.5	5.5
ORP	mV	400 mV	400 mV (1st six hours), 100 mV last four hours	400 mV	400 mV
Selenium Species:					
Na_2SeO_3 (Se IV)	ppb as Se	1000	1000	1000	1000
Na_2SeO_4 (Se VI)	ppb as Se				
Other (List)	ppb as Se				
Constituents:					
Ferric Hydroxide					
DBA				1000	
$MnSO_4$ (aq)		35 ppm as Mn	35 ppm as Mn	35 ppm as Mn	35 ppm as Mn
Adipic Acid	ppmw				
Acetic Acid	ppmw	1000			
8-HQS	ppmw				3100

Run #		**48**	**49**	**50**	**51**

LIQUID PHASE RESULTS
"-" indicates "not applicable" or "not analyzed"

Seleniun Speciation (See separate file for detaile
c =cryo, u = unpreserved, qa/qc = data under re

0 min		c,u at all times	c,u at all times	c,u at all times
15 min				
45 min				
1.5 h				
3 h				
6 h				
10 h				

Seleniun Speciation - URS (See separate file for
Trace Detect, qa/qc = data under review

Day Of Test		-	-	attempted; problems with analyzer
48 hour samples		-	-	-

Seleniun Speciation - URS (See separate file for
Borohydride atomic absorption, qa/qc = data un

Day Of Test		Se4, TSe	Se4, TSe	Se4, TSe
48 hour samples		Se4, TSe	Se4, TSe	Se4, TSe

Metals - Mn (Trent analyses are at the bottom of

0 h	ppm Mn	19.3	16.0	19.1
15 min	ppm Mn	18.4	12.2	13.4
45 min	ppm Mn	-	-	-
1.5 h	ppm Mn	-	1.6	3.2
3 h	ppm Mn	4.4	1.5	3.6
6 h	ppm Mn	4.7	1.5	4.8
10 h	ppm Mn	6.1	50.4	-

Metals - Mn (48 hour unpreserved)

0 h	ppm Mn	-	-	-
15 min	ppm Mn	19.9	13.0	13.4
45 min	ppm Mn	-	-	-
1.5 h	ppm Mn	-	-	2.1
3 h	ppm Mn	4.5	1.4	2.6
6 h	ppm Mn	4.9	1.5	3.8
10 h	ppm Mn	6.3	48.6	-

Metals - Fe

0 h	ppm Fe	-	-	-	-
15 min	ppm Fe	-	-	-	-
1.5 h	ppm Fe	-	-	-	-
3 h	ppm Fe	-	-	-	-
6 h	ppm Fe	-	-	-	-
10 h	ppm Fe	-	-	-	-

Run #		**48**	**49**	**50**	**51**
Sulfite DF					
15 min	mM SO3	<0.038	<0.038	<0.038	-
1.5 h	mM SO3	-	-	<0.038	-
3 h	mM SO3	0.14	<0.038	<0.038	-
6 h	mM SO3	0.59	<0.038	0.06	-
10 h	mM SO3	1.11	1.25	-	-
Sulfite DF - 48 hour unpreserved					
15 min	mM SO3	<0.038	<0.038	<0.038	-
1.5 h	mM SO3	-	-	<0.038	-
3 h	mM SO3	0.07	<0.05	<0.038	-
6 h	mM SO3	0.42	<0.038	<0.038	-
10 h	mM SO3	0.81	0.23	-	-
Sulfate (SO4)					
15 min	ppm SO4	6684	7465	7821	-
1.5 h	ppm SO4	-	-	-	-
3 h	ppm SO4	-	-	-	-
6 h	ppm SO4	-	-	16157	-
10 h	ppm SO4	20752	20970	-	-
Dithionate (S2O6)					
15 min	ppm S2O6	36.2	61.6	42.7	-
1.5 h	ppm S2O6	-	-	51.7	-
3 h	ppm S2O6	49.2	68.0	53.1	-
6 h	ppm S2O6	50.5	68.1	52.5	-
10 h	ppm S2O6	50.6	82.0	-	-
Dithionate (S2O6) - 48 hour unpreserved					
15 min	ppm S2O6	35.8	61.9	42.3	-
1.5 h	ppm S2O6	-	-	51.4	-
3 h	ppm S2O6	49.3	66.8	52.2	-
6 h	ppm S2O6	49.8	67.1	52.4	-
10 h	ppm S2O6	51.1	90.0	-	-
Persulfate (S2O8)					
15 min	ppm S2O8	5.36	10.26	5.85	-
1.5 h	ppm S2O8	-	-	8.50	-
3 h	ppm S2O8	11.96	20.43	8.85	-
6 h	ppm S2O8	12.44	28.78	7.53	-
10 h	ppm S2O8	13.49	12.35	-	-
Persulfate (S2O8) - 48 hour unpreserved					
15 min	ppm S2O8	5.40	10.24	6.44	-
1.5 h	ppm S2O8	-	-	8.23	-
3 h	ppm S2O8	11.88	19.56	8.87	-
6 h	ppm S2O8	12.38	28.87	7.22	-
10 h	ppm S2O8	12.98	11.83	-	-

Run #		**48**	**49**	**50**	**51**

Chloride DF

6 h	mM	-	-	3487	-
10 h	mM	3782	3511	-	-

DBA

0 h

Succinic	ppm	-	-	161	-
Glutaric	ppm	-	-	729	-
Adipic	ppm	-	-	128	-

6 h

Succinic	ppm	-	-	207	-
Glutaric	ppm	-	-	604	-
Adipic	ppm	-	-	95	-

10 h

Succinic	ppm	-	-	-	-
Glutaric	ppm	-	-	-	-
Adipic	ppm	-	-	-	-

Acetate

0 h	ppm	803	-	-	-
10 h	ppm	703	-	-	-

B

FULL-SCALE SYSTEM COAL AND ASH DATA

The following tables comprise Appendix B:

- Host site coal data
- Host site ash data

Table B-1
Host Site Coal Data

				Concentration (Wt%, AD Basis)		Wt%, Dry Basis			BTU/lb, Dry Basis		Concentration (ug/g, Dry Basis)			
Lab Sample Number	Description	Date	Customer Sample Number	Total Moisture	Residual Moisture	Ash	Sulfur	Chlorine	Heating Value	MAF Heating Value	Selenium	Mercury	Mercury	Mercury RPD%
20114469	Coal	6/14/2011	A021-C-1	4.52	2.09	13.62	1.41	0.0725	12879	14910	2.19	0.040	0.038	5.3
20114470	Coal	6/16/2011	A021-C-2	7.22	2.25	18.23	1.70	0.0552	12005	14681	2.06	0.065	0.061	6.5
20114471	Coal	6/21/2011	A021-C-3	5.91	2.30	10.43	1.60	0.0911	13398	14958	2.59	0.052	0.055	5.7
20114472	Coal	7/13/2011	A021-C-4	6.39	2.07	12.19	1.76	0.0796	12992	14796	2.07	0.059	0.058	1.7
20114473	Coal	7/15/2011	A021-C-5	7.38	2.06	25.32	1.23	0.0551	10944	14655	2.32	0.036	0.036	0.0
20114474	Coal	7/17/2011	A021-C-6	7.97	2.45	12.33	1.16	0.0820	13005	14834	1.78	0.034	0.031	9.5
20114475	Coal	7/18/2011	A021-C-7	7.03	2.08	15.89	1.37	0.0633	12510	14873	2.24	0.049	0.052	6.1
20114476	Coal	7/23/2011	A021-C-8	6.54	2.38	17.26	1.23	0.0594	12305	14872	2.16	0.034	0.036	5.9
20114477	Coal	7/24/2011	A021-C-9	6.53	2.53	16.56	1.34	0.0718	12329	14776	1.83	0.071	0.074	4.3

Table B-2
Host Site Ash Data

Date	Condition	Field	Hg (µg/g)	TSe (µg/g)
6/17/2011	Baseline Test	A	0.048	4.30
6/17/2011	Baseline Test	B	0.058	5.31
6/21/2011	Baseline Test	A	<0.044	4.28
6/21/2011	Baseline Test	B	<0.044	3.20
7/14/2011	Low ORP - trial 2	A	0.053	5.81
7/14/2011	Low ORP - trial 2	B	0.075	6.42
7/16/2011	Low ORP - trial 2	A	0.064	5.37
7/16/2011	Low ORP - trial 2	B	0.088	8.28
7/18/2011	Low ORP - trial 2	A	0.046	3.61
7/18/2011	Low ORP - trial 2	B	0.114	7.02
7/19/2011	Fe injection Test - 1	A	0.048	3.80
7/19/2011	Fe injection Test - 1	B	0.050	7.26
7/23/2011	Fe injection Test - 1	A	0.108	5.59
7/23/2011	Fe injection Test - 1	B	0.076	5.46
7/25/2011	Fe injection Test - 1	A	0.082	5.08
7/25/2011	Fe injection Test - 1	B	0.057	4.88

C

METALS DATA FOR FULL-SCALE AND PILOT-SCALE SYSTEMS

Table C-1
Trace Metals Data for Full-scale and Pilot-Scale Systems

Date	6/9/2011				6/15/2011				6/16/2011			
Time					**Day = 0**				**Day = 0**			
Test Condition	**Baseline**				**Baseline**				**Baseline**			
Location	**Liquor Fe (µg/L)**	**Flag**	**Solid Fe (mg/kg)**	**Flag**	**Liquor Fe (µg/L)**	**Flag**	**Solid Fe (mg/kg)**	**Flag**	**Liquor Fe (µg/L)**	**Flag**	**Solid Fe (mg/kg)**	**Flag**
Full scale Abs					<548		1866					
Pilot Abs							1889					
LS slurry											2437	
Location	**Liquor Mn (µg/L)**	**Flag**	**Solid Mn (mg/kg)**	**Flag**	**Liquor Mn (µg/L)**	**Flag**	**Solid Mn (mg/kg)**	**Flag**	**Liquor Mn (µg/L)**	**Flag**	**Solid Mn (mg/kg)**	**Flag**
Full scale Abs					319		158.5					
Pilot Abs					671		126.5					
LS slurry									75		213	
MUW					<53							
Location	**Liquor Hg (µg/L)**	**Flag**	**Solid Hg (µg/g)**	**Flag**	**Liquor Hg (µg/L)**	**Flag**	**Solid Hg (µg/g)**	**Flag**	**Liquor Hg (µg/L)**	**Flag**	**Solid Hg (µg/g)**	**Flag**
Full scale Abs					196		0.487					
Pilot Abs					21.2		0.11				0.10	
LS slurry									<0.160		0.060	
Make-up water					0.48							
WWT inlet	156		11.165									
WWT outlet	0.79											
Full scale Abs >20µm							<0.052					
Full scale Abs <20µm							0.63					
FB	<0.17											
Location	**Liquor TSe (µg/L)**	**Flag**	**Solid Se (µg/g)**	**Flag**	**Liquor TSe (µg/L)**	**Flag**	**Solid Se (µg/g)**	**Flag**	**Liquor TSe (µg/L)**	**Flag**	**Solid Se (µg/g)**	**Flag**
Full scale Abs							10.930					
Pilot Abs							11.41					
LS slurry											0.801	
Make-up water												
WWT inlet			70.03									

Date	**6/17/2011**				**6/19/2011**				**6/21/2011**			
Time	**BD = 1**				**BD = 2**				**BD = 4**			
Test Condition	**Baseline**				**Baseline**				**Baseline**			
Location	**Liquor Fe (µg/L)**	**Flag**	**Solid Fe (mg/kg)**	**Flag**	**Liquor Fe (µg/L)**	**Flag**	**Solid Fe (mg/kg)**	**Flag**	**Liquor Fe (µg/L)**	**Flag**	**Solid Fe (mg/kg)**	**Flag**
Pilot Abs							2222		<538		2854	
Pilot HCOF							9232				8376	
Pilot HCUF							599				674	
Location	**Liquor Mn (µg/L)**	**Flag**	**Solid Mn (mg/kg)**	**Flag**	**Liquor Mn (µg/L)**	**Flag**	**Solid Mn (mg/kg)**	**Flag**	**Liquor Mn (µg/L)**	**Flag**	**Solid Mn (mg/kg)**	**Flag**
Pilot Abs					86		127		105		137	
Pilot HCOF							450				362	
Pilot HCUF							59				52	
Location	**Liquor Hg (µg/L)**	**Flag**	**Solid Hg (µg/g)**	**Flag**	**Liquor Hg (µg/L)**	**Flag**	**Solid Hg (µg/g)**	**Flag**	**Liquor Hg (µg/L)**	**Flag**	**Solid Hg (µg/g)**	**Flag**
Pilot Abs	66.7		0.17		89.7		0.24		76.0		0.22	
Pilot HCOF							0.79				0.68	
Pilot HCUF							<0.084				<0.087	
Pilot Abs >20µm											0.056	J
Pilot Abs <20µm											1.22	
Location	**Liquor TSe (µg/L)**	**Flag**	**Solid Se (µg/g)**	**Flag**	**Liquor TSe (µg/L)**	**Flag**	**Solid Se (µg/g)**	**Flag**	**Liquor TSe (µg/L)**	**Flag**	**Solid Se (µg/g)**	**Flag**
Full scale Abs												
Pilot Abs			8.1145				7.568				7.17	
Pilot HCOF							9.01				11.31	
Pilot HCUF							8.00				7.07	

Date	**7/13/2011**				**7/14/2011**				**7/16/2011**			
Time	**Day = 0**				**BD = 1**				**BD = 3**			
Test Condition	**Low ORP - trial 2**				**Low ORP - trial 2**				**Low ORP - trial 2**			
Location	**Liquor Fe (µg/L)**	**Flag**	**Solid Fe (mg/kg)**	**Flag**	**Liquor Fe (µg/L)**	**Flag**	**Solid Fe (mg/kg)**	**Flag**	**Liquor Fe (µg/L)**	**Flag**	**Solid Fe (mg/kg)**	**Flag**
Full scale Abs	<541		1602									
Pilot Abs			1575				1534				1857	
Pilot HCOF							4499				6815	
Pilot HCUF							568				568	
LS slurry					1953		2057					
Location	**Liquor Mn (µg/L)**	**Flag**	**Solid Mn (mg/kg)**	**Flag**	**Liquor Mn (µg/L)**	**Flag**	**Solid Mn (mg/kg)**	**Flag**	**Liquor Mn (µg/L)**	**Flag**	**Solid Mn (mg/kg)**	**Flag**
Full scale Abs	121		116									
Pilot Abs	<54		145		1328		121		80		124	
Pilot HCOF							289				308	
Pilot HCUF							71				<23	
LS slurry	62		204		<50		198					
MUW	58											
Location	**Liquor Hg (µg/L)**	**Flag**	**Solid Hg (µg/g)**	**Flag**	**Liquor Hg (µg/L)**	**Flag**	**Solid Hg (µg/g)**	**Flag**	**Liquor Hg (µg/L)**	**Flag**	**Solid Hg (µg/g)**	**Flag**
Full scale Abs	211		0.097									
Pilot Abs	52.3		0.31		79.3		0.16		97.2		0.18	
Pilot HCOF							0.41				0.65	
Pilot HCUF			<0.083				<0.084				0.047	J
LS slurry	<0.26		0.030									
Make-up water	<0.28											
WWT inlet	169		1.42									
WWT outlet	<0.57		132									
Full scale Abs >20µm			0.053	J								
Full scale Abs <20µm			1.08									
FB					<0.16							
Location	**Liquor TSe (µg/L)**	**Flag**	**Solid Se (µg/g)**	**Flag**	**Liquor TSe (µg/L)**	**Flag**	**Solid Se (µg/g)**	**Flag**	**Liquor TSe (µg/L)**	**Flag**	**Solid Se (µg/g)**	**Flag**
Full scale Abs			10.010									
Pilot Abs			<9.230				8.4245				7.0605	
Pilot HCOF							10.89				8.98	
Pilot HCUF							8.14				7.22	
LS slurry			<0.600									
WWT inlet			75.6335									
WWT outlet			ND									
U1 full scale HCUF			10.28									

Date	7/18/2011				7/19/2011				7/21/2011			
Time	BD = 5				Day = 0				BD = 1			
Test Condition	Low ORP - trial 2				Fe injection Test - 1				Fe injection Test - 1			
Location	**Liquor Fe (µg/L)**	**Flag**	**Solid Fe (mg/kg)**	**Flag**	**Liquor Fe (µg/L)**	**Flag**	**Solid Fe (mg/kg)**	**Flag**	**Liquor Fe (µg/L)**	**Flag**	**Solid Fe (mg/kg)**	**Flag**
Full scale Abs					<0.556		1825					
Pilot Abs	<543		2212		<278		1860		<275		2593	
Pilot HCOF			6142								4646	
Pilot HCUF			652								833	
LS slurry							2063					
Location	**Liquor Mn (µg/L)**	**Flag**	**Solid Mn (mg/kg)**	**Flag**	**Liquor Mn (µg/L)**	**Flag**	**Solid Mn (mg/kg)**	**Flag**	**Liquor Mn (µg/L)**	**Flag**	**Solid Mn (mg/kg)**	**Flag**
Full scale Abs					142		167					
Pilot Abs	91		128		362		136		118		125	
Pilot HCOF			283								166	
Pilot HCUF			58								63	
LS slurry					62		196					
MUW					57							
Location	**Liquor Hg (µg/L)**	**Flag**	**Solid Hg (µg/g)**	**Flag**	**Liquor Hg (µg/L)**	**Flag**	**Solid Hg (µg/g)**	**Flag**	**Liquor Hg (µg/L)**	**Flag**	**Solid Hg (µg/g)**	**Flag**
Full scale Abs					232		0.12					
Full scale HCUF							0.04	J				
Pilot Abs	89.3		0.19		83.2		0.1435		113		0.19	
Pilot HCOF			0.60								0.29	
Pilot HCUF			0.047	J							0.049	J
LS slurry					<0.26		0.051					
Make-up water					<0.26							
WWT inlet					272		2.93					
WWT outlet					<1.13		316					
Full scale Abs >20µm							<0.041					
Full scale Abs <20µm							0.61					
Pilot Abs >20µm			0.067	J								
Pilot Abs <20µm			1.26									
Location	**Liquor TSe (µg/L)**	**Flag**	**Solid Se (µg/g)**	**Flag**	**Liquor TSe (µg/L)**	**Flag**	**Solid Se (µg/g)**	**Flag**	**Liquor TSe (µg/L)**	**Flag**	**Solid Se (µg/g)**	**Flag**
Full scale Abs							11.12					
Pilot Abs			6.09				9.26				8.5365	
Pilot HCOF			8.09								10.91	
Pilot HCUF			5.74								9.62	
LS slurry							0.587					
WWT inlet							25.56					
WWT outlet							<34.48					
U1 full scale HCUF							14					

Date	7/23/2011				7/25/2011			
Time	**BD = 3 (PM samples)**				**BD = 5 (PM samples)**			
Test Condition	**Fe injection Test - 1**				**Fe injection Test - 1**			
Location	**Liquor Fe (µg/L)**	**Flag**	**Solid Fe (mg/kg)**	**Flag**	**Liquor Fe (µg/L)**	**Flag**	**Solid Fe (mg/kg)**	**Flag**
Pilot Abs	<273		2797		<275		5986	
Pilot HCOF			16,017				21,461	
Pilot HCUF			503				640	
FB							<270	
Location	**Liquor Mn (µg/L)**	**Flag**	**Solid Mn (mg/kg)**	**Flag**	**Liquor Mn (µg/L)**	**Flag**	**Solid Mn (mg/kg)**	**Flag**
Pilot Abs	112		111		122		159	
Pilot HCOF			368				513	
Pilot HCUF			55				60	
Location	**Liquor Hg (µg/L)**	**Flag**	**Solid Hg (µg/g)**	**Flag**	**Liquor Hg (µg/L)**	**Flag**	**Solid Hg (µg/g)**	**Flag**
Pilot Abs	96.0		0.19		67.19		0.51	
Pilot HCOF			0.99				2.33	
Pilot HCUF			0.084				0.12	
Pilot Abs >20µm							0.10	J
Pilot Abs <20µm							5.48	
FB					<0.30		<0.012	
Location	**Liquor TSe (µg/L)**	**Flag**	**Solid Se (µg/g)**	**Flag**	**Liquor TSe (µg/L)**	**Flag**	**Solid Se (µg/g)**	**Flag**
Pilot Abs			7.8585				6.75	
Pilot HCOF			14.25				11.20	
Pilot HCUF			8.05				5.58	

D

GAS-PHASE MERCURY DATA FOR PILOT SCRUBBER TESTS

Gas-phase mercury data for the baseline pilot test was presented in Section 5. Data for the remaining pilot scrubber tests are presented below.

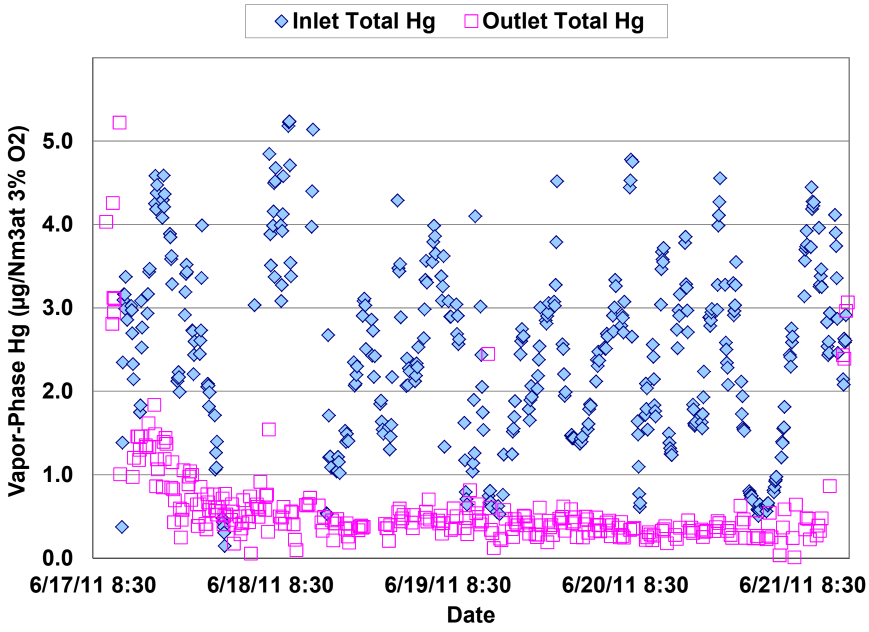

Figure D-1
Inlet and Outlet Flue Gas Total Mercury (Pilot Scrubber) for Baseline High ORP Test

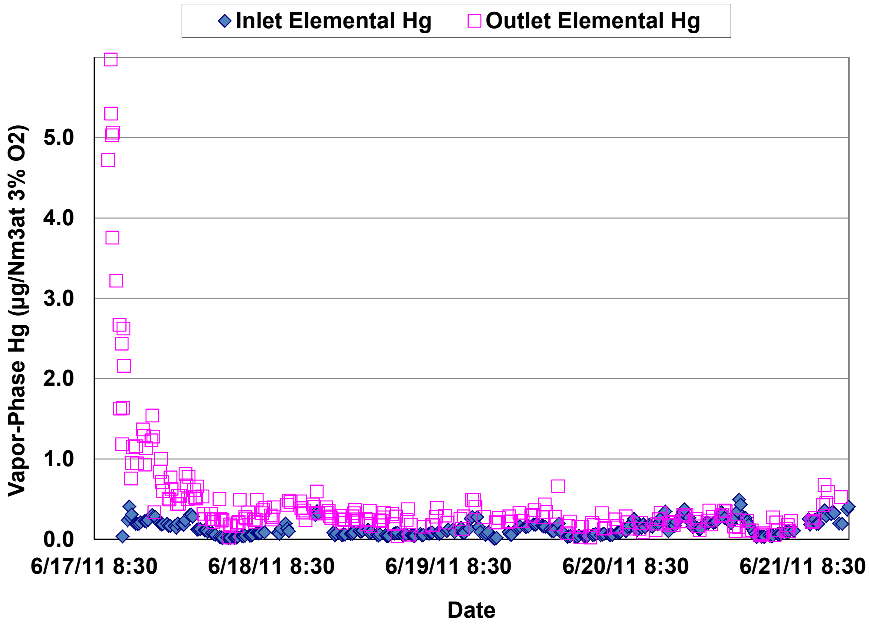

Figure D-2
Inlet and Outlet Flue Gas Elemental Mercury (Pilot Scrubber) for Baseline High ORP Test

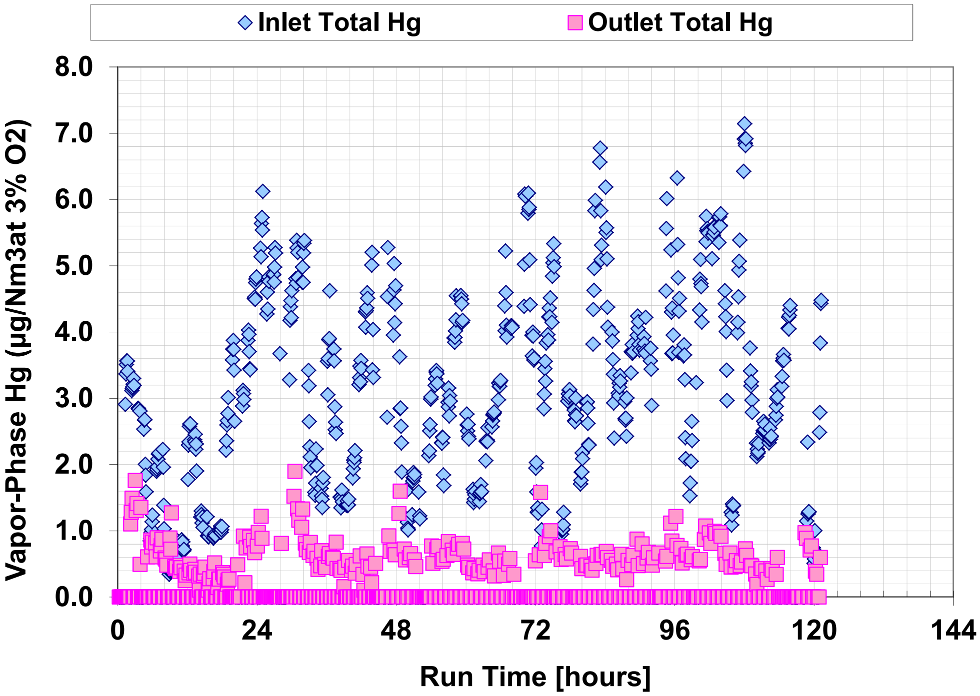

Figure D-3
Inlet and Outlet Flue Gas Total Mercury (Pilot Scrubber) for Low ORP Trial 2 (Natural Oxidation)

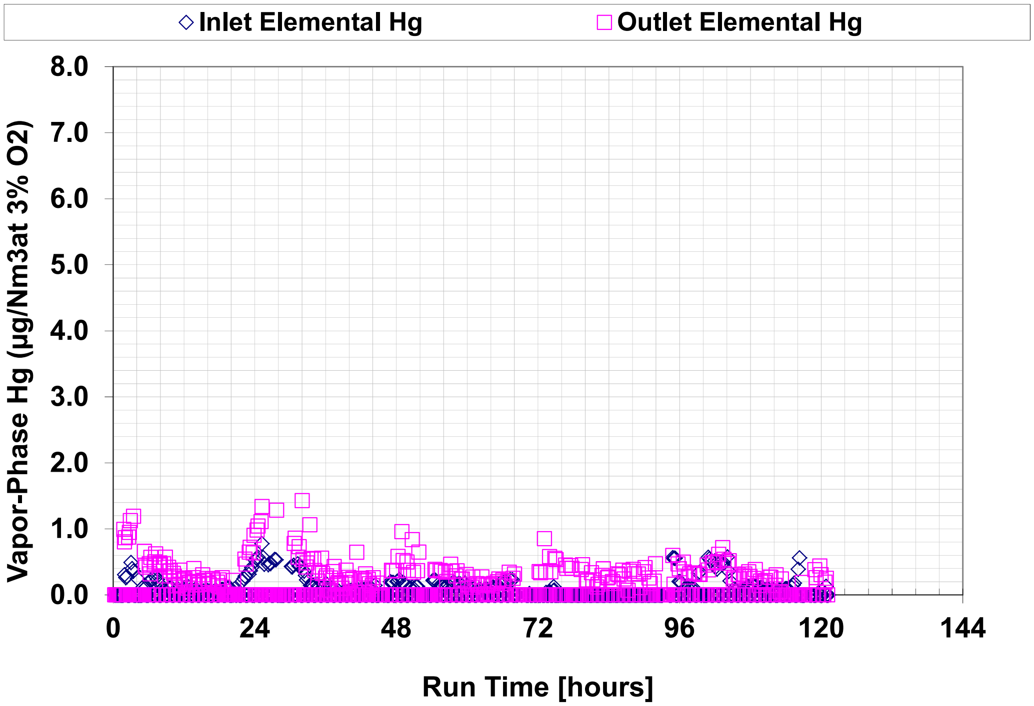

Figure D-4
Inlet and Outlet Flue Gas Elemental Mercury (Pilot Scrubber) for Low ORP Trial 2 (Natural Oxidation)

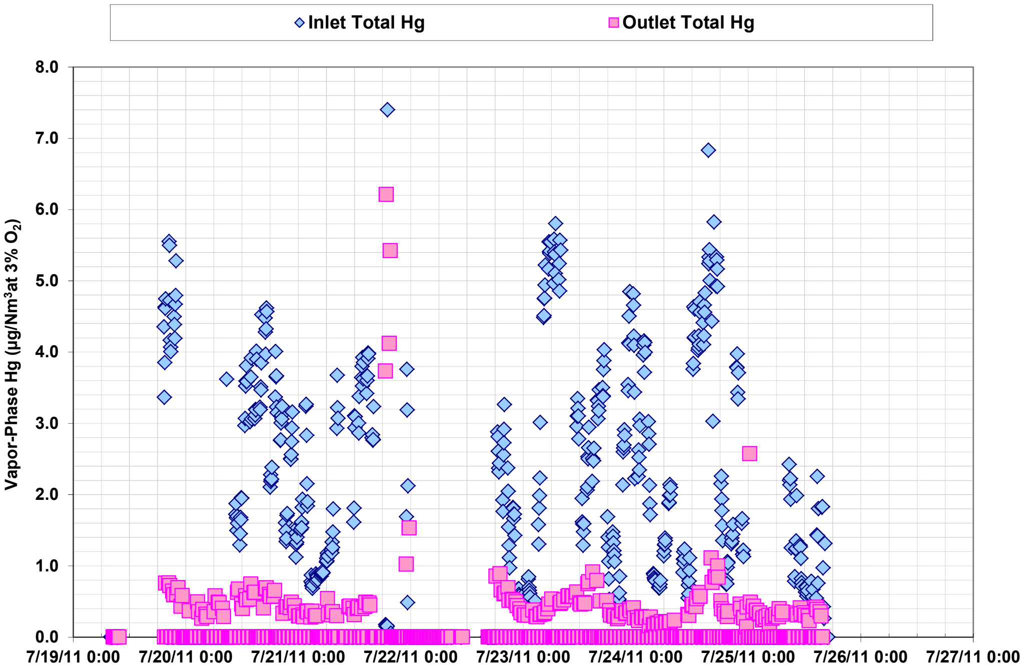

Figure D-5
Inlet and Outlet Flue Gas Total Mercury (Pilot Scrubber) for Ferric Chloride Test

Figure D-6
Inlet and Outlet Flue Gas Elemental Mercury (Pilot Scrubber) for Ferric Chloride Test

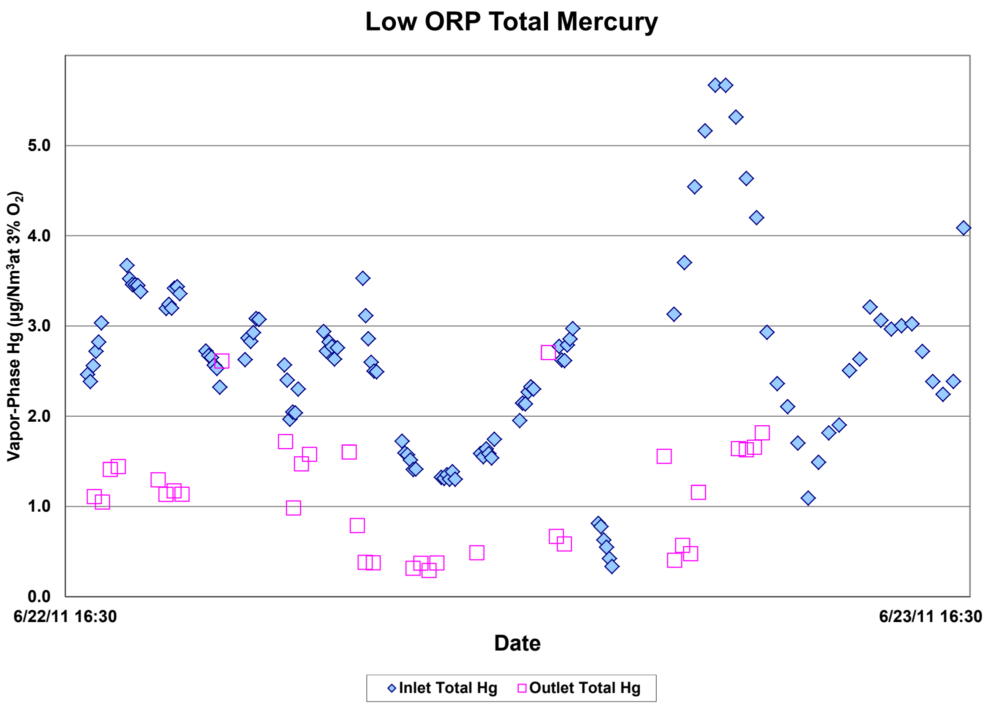

Figure D-7

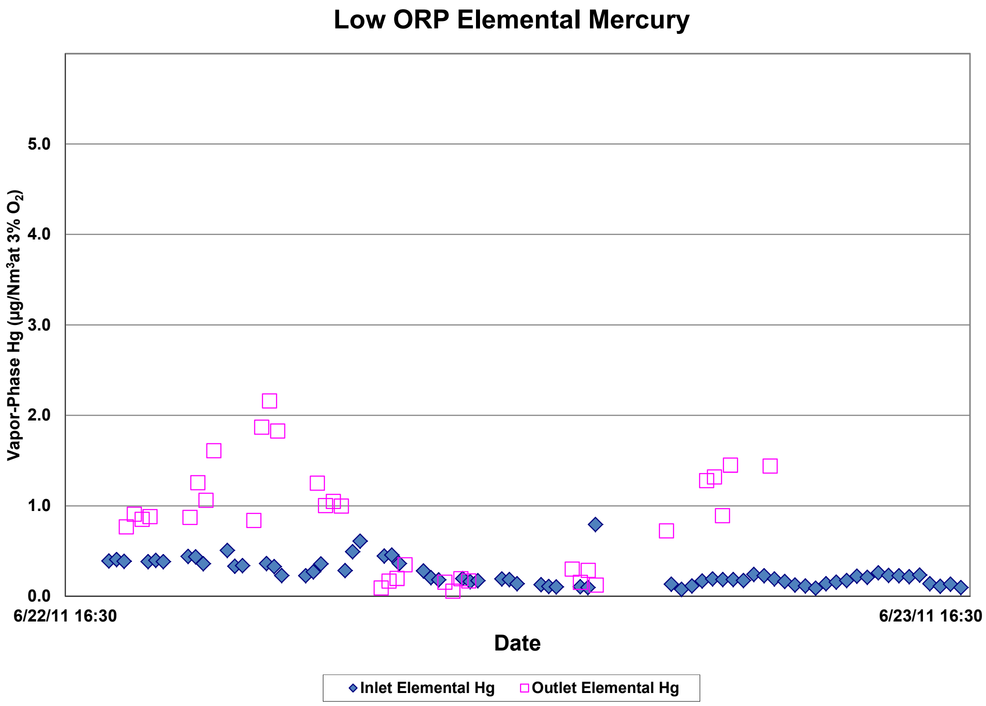

Figure D-8
Inlet and Outlet Flue Gas Elemental Mercury (Pilot Scrubber) for One-day Low ORP Trial 1

E

FGD MAJOR ANALYTES - FULL-SCALE AND PILOT-SCALE SCRUBBER DATA

Table E-1
FGD Major Analytes – Full-scale and Pilot-scale Absorber Sample Data

Test				Baseline	Baseline	Baseline	Baseline	Baseline	Baseline
Run Time				0	0	32	84	107	123
Description	Full Scale	WWIn	WWOut	Full Scale	Pilot Unit	Pilot Unit	Pilot Unit	Pilot Unit	Pilot Unit
Blowdown					0	1	2	3	4
Date	6/9/2011	6/9/2011	6/9/2011	6/15/2011	6/15/2011	6/17/2011	6/19/2011	6/20/2011	6/21/2011
Time	14:00	11:22	11:42	11:45	15:00	19:30	23:50	22:50	14:45
pH	5.18	6.19	7.36	5.34	7.19	5.53	5.96	5.60	5.55
Temperature, C	52.7	48.9	35.2	51.9	31.2	62.3	46	46.7	47.8
ORP, mV	570	390	370	605	324	595	720	703	615
SOLID RESULTS									
Ca, mm/g	No solids analysis requested	No solids analysis requested	No solids analysis requested	5.79	5.75	No solids analysis requested	5.74	No solids analysis requested	5.96
Mg, mm/g				0.0036	0.0034		0.01		0.02
SO3, mm/g				<0.005	<0.005		<0.005		<0.005
SO4, mm/g				5.51	5.59		5.42		5.46
CO3, mm/g				0.02	0.04		0.09		0.10
inerts, wt%				1.81	1.84		2.30		2.89
solids, wt%				17.09	6.10		11.31		11.26
oxidation, %				100.0	100.0		100.0		100.0
utilization, %				98.2	98.6		97.0		95.9
Closures									
Weight, %				-2.2	-1.2		-2.6		-0.5
Molar, %				2.3	1.2		2.2		3.6
LIQUID RESULTS									
Ca, mm/L				72.2	62.4		95.6		100.8
Mg, mm/L				27.0	8.4		19.7		21.9
Na, mm/L				3.2	2.3		3.8		3.9
Br, mm/L				0.4	0.8		0.9		1.0
Cl, mm/L	131.1	142.8	28.4	148.4	112.9	144.0	184.0	199.6	203.1
CO3, mm/L				2.4	0.9		2.4		2.9
SO3, mm/L	<0.05			<0.03	<0.03	<0.02	<0.02	<0.02	<0.03
SO4, mm/L				13.5	11.2		12.1		15.2
S2O6, mm/L				6.5	1.9		5.3		5.4
S2O8, mm/L	1.6			5.6	1.7	0.4	2.1	2.2	0.3
Tot Hyd SO4, mm/L				23.3	21.0		23.4		22.3
S/N, mm/L (other than SO3 and SO4)				9.8	9.8		11.3		7.1
Charge Imbalance									
Calculated, %				4.0	-0.9		2.9		1.5
TOC, mg/L				7					9

Test	Low ORP 1	Low ORP 1	Low ORP 1	Low ORP 1
Run Time	0	0	0	
Description	Full Scale	WWIn	WWOut	Pilot Unit
Blowdown				
Date	6/22/2011	6/22/2011	6/22/2011	6/23/2011
Time	16:15	16:05	16:00	17:30
pH	5.45	6.25	7.30	4.93
Temperature, C	52.8	49	34.4	49
ORP, mV	597	458	510	183
SOLID RESULTS				
Ca, mm/g	5.78	No solids analysis requested	No solids analysis requested	5.73
Mg, mm/g	0.01			0.01
SO3, mm/g	<0.005			<0.005
SO4, mm/g	5.52			5.59
CO3, mm/g	0.03			0.18
inerts, wt%	2.53			1.95
solids, wt%	13.84			11.03
oxidation, %	100.0			100.0
utilization, %	98.1			97.0
Closures				
Weight, %	-1.2			-0.2
Molar, %	2.0			-0.2
LIQUID RESULTS				
Ca, mm/L	73.7			87.0
Mg, mm/L	28.9			13.1
Na, mm/L	3.2			3.8
Br, mm/L	0.5			0.8
Cl, mm/L	152.9	149.3	37.4	165.1
CO3, mm/L	2.1			2.9
SO3, mm/L	<0.03			4.70
SO4, mm/L	12.9			11.9
S2O6, mm/L	5.6			2.8
S2O8, mm/L	5.3			<0.02
Tot Hyd SO4, mm/L	30.2			18.2
S/N, mm/L (other than SO3 and SO4)	17.3			1.6
Charge Imbalance				
Calculated, %	2.9			1.9
TOC, mg/L				

Test	Nat Ox	Nat Ox	Nat Ox	Nat Ox	Nat Ox
Run Time	0	0	26	69	121
Description	Full Scale	Pilot Unit	Pilot Unit	Pilot Unit	Pilot Unit
Blowdown					
Date	7/13/2011	7/13/2011	7/14/2011	7/16/2011	7/18/2011
Time	15:37	9:20	13:25	16:42	13:20
pH	5.14				
Temperature, C	51.8				
ORP, mV	621				
SOLID RESULTS					
Ca, mm/g	5.62				5.77
Mg, mm/g	<0.003				0.013
SO3, mm/g	<0.005	<0.005	<0.005	<0.005	<0.005
SO4, mm/g	5.57	5.58	5.40	5.44	5.45
CO3, mm/g	0.08				0.16
inerts, wt%	1.14				1.73
solids, wt%	19.42	6.98	10.98	10.25	11.27
oxidation, %	100.0				100.0
utilization, %	98.7				96.2
Closures					
Weight, %	-2.4				-2.2
Molar, %	-0.2				1.5
LIQUID RESULTS					
Ca, mm/L	73.0				74.3
Mg, mm/L	27.7				17.0
Na, mm/L	3.2				3.5
Br, mm/L	1.0	1.2	1.5	1.5	1.5
Cl, mm/L	153.1	120.8	147.0	150.1	152.8
CO3, mm/L	2.1				2.4
SO3, mm/L	<0.02	<0.02	<0.02	<0.02	<0.02
SO4, mm/L	13.6	14.4	11.9	12.8	14.3
S2O6, mm/L	4.27	1.42	1.73	1.87	1.87
S2O8, mm/L	4.92	1.44	0.89	0.55	1.20
Tot Hyd SO4, mm/L	28.3	17.3	15.3	15.8	18.1
S/N, mm/L (other than SO3 and SO4)					
Charge Imbalance					
Calculated, %	6.1				0.8
TOC, mg/L	8				7

Test	Iron	Iron	Iron	Iron	Iron
Run Time	0	0	38	68	114
Description	Full Scale	Pilot Unit	Pilot Unit	Pilot Unit	Pilot Unit
Blowdown					
Date	7/19/2011	7/19/2011	7/21/2011	7/23/2011	7/25/2011
Time	8:45	19:15	8:30	PM	PM
pH	5.23				
Temperature, C	49.5				
ORP, mV	n/a				
SOLID RESULTS					
Ca, mm/g	5.57				5.64
Mg, mm/g	<0.003				0.01
SO3, mm/g	<0.005	<0.005	<0.005	<0.005	<0.005
SO4, mm/g	5.56	5.59	5.50	5.65	5.51
CO3, mm/g	<0.006				0.15
inerts, wt%	1.26				1.93
solids, wt%	17.90	8.99	14.95	12.69	12.68
oxidation, %	100.0				100.0
utilization, %	100.0				97.4
Closures					
Weight, %	-3.1				-1.8
Molar, %	0.1				0.0
LIQUID RESULTS					
Ca, mm/L	66.5				89.6
Mg, mm/L	27.8				20.8
Na, mm/L	3.4				3.6
Br, mm/L	1.0	1.1	1.5	1.4	1.6
Cl, mm/L	134.7	119.6	160.5	160.5	188.4
CO3, mm/L	1.8				2.3
SO3, mm/L	<0.02	<0.02	<0.04	<0.04	<0.03
SO4, mm/L	15.8	12.5	14.1	12.7	11.8
S2O6, mm/L	1.62	1.55	1.97	1.76	1.98
S2O8, mm/L	4.19	1.24	1.00	1.08	1.24
Tot Hyd SO4, mm/L	31.5	17.4	17.9	16.3	16.3
S/N, mm/L (other than SO3 and SO4)					
Charge Imbalance					
Calculated, %	6.9				2.5
TOC, mg/L	8				7