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Selenium Speciation and Management in Wet FGD Systems

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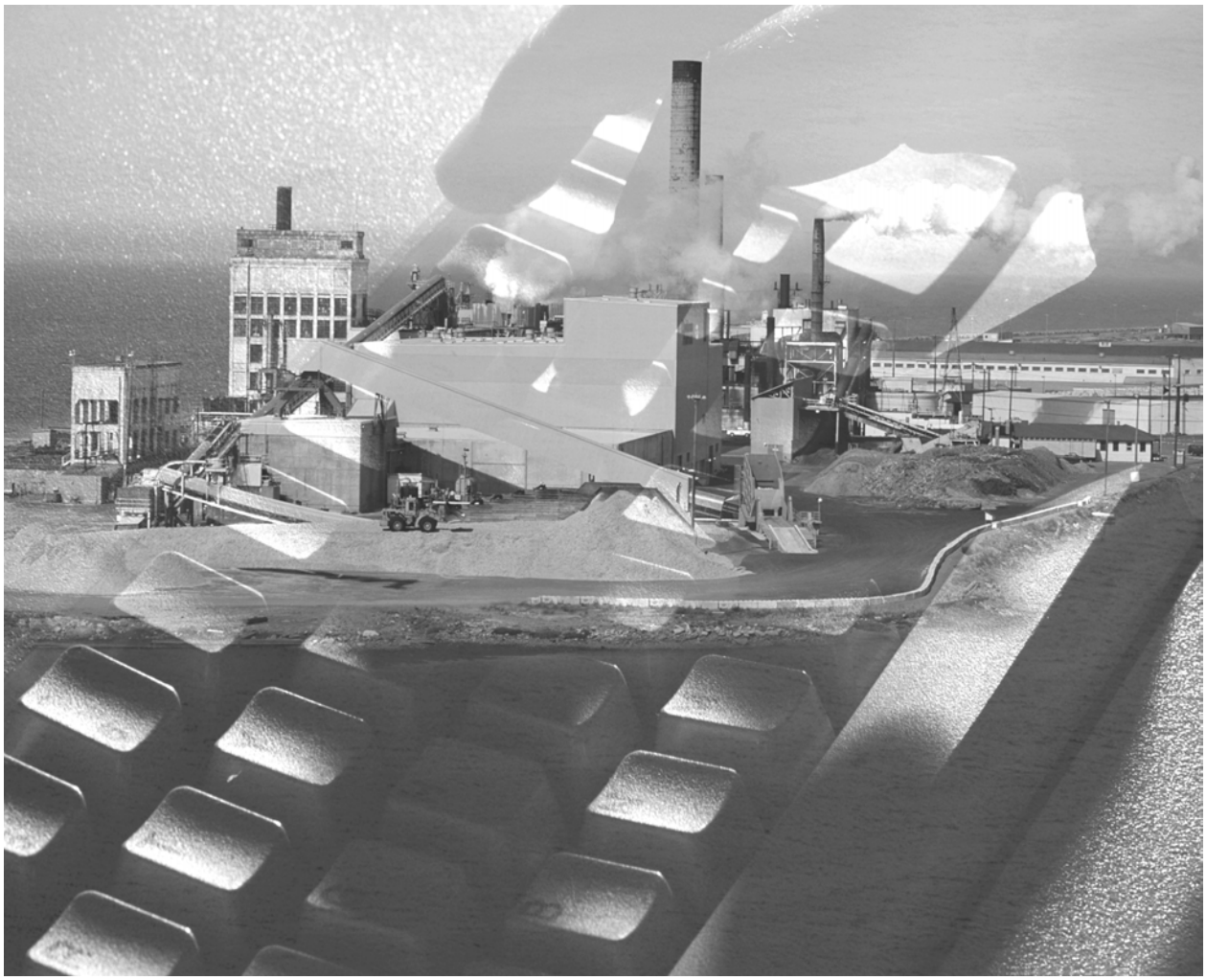

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Technical Update, December 2011

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ABSTRACT

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 (flue gas desulfurization) systems. The selenium chemistry in wet FGDs 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 has successfully demonstrated the avoidance or decrease of selenite oxidation at the bench and pilot scale. The report also includes a discussion of ongoing efforts to improve sample-handling methods for selenium speciation measurements.

Bench-scale scrubber tests explored the impacts of oxidation air rate, trace metals, scrubber additives, and natural limestone in 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 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.

Although it was not possible to demonstrate a decrease in selenium concentrations to levels below the 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 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.

Keywords
Selenium
Selenite
Selenate
Selenosulfate
Speciation
FGD
Wastewater treatment

CONTENTS

LIST OF FIGURES

LIST OF TABLES

1
BACKGROUND

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 negligible to >80%. Scrubber design is a likely 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 may vary widely from site to site, and factors that affect the fate of selenium are currently under evaluation by the 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 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 parts per billion (ppb) to several thousand ppb [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 FGD systems operating at highly oxidizing conditions without organic acids, the

selenite is generally oxidized to selenate. However, selenite does not always 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 laboratories following established standard methods are generally wrong. 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 Chapter 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 Chapter 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 [1]. 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 dilution after leaving the FGD WWT system). A recent draft National Pollution Discharge Elimination

System (NPDES) permit 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) Se. Achieving these selenium discharge levels would be difficult even without the interference of common FGD constituents.

The form of selenium may impact treatability; selenate is not efficiently removed from wastewater using traditional iron co-precipitation while selenite can be. The effectiveness of iron co-precipitation on other selenium forms possibly found in wet FGD systems is not well known. To date, only costly biological treatment approaches have shown high selenate removal efficiencies from FGD wastewaters at larger scales. Recent EPRI pilot studies evaluated metallic iron cementation, which indicated modest selenium removals down to 159 ppb Se. Ongoing work by Southern Company as well as EPRI of a modified zero-valent iron (ZVI) approach by Texas A&M indicates promising results for significant selenite and selenate capture.

Project Approach and Objectives

Ongoing research sponsored by the Electric Power Research Institute (EPRI) and the U.S. Department of Energy (DOE) has investigated the factors that control selenium speciation and phase partitioning in wet FGD systems. EPRI, Trimeric Corporation (Trimeric), URS Corporation (URS), and Trent University (Trent) have teamed on a DOE Small Business Innovation and Research (SBIR) project comprising bench- and pilot-scale wet FGD tests, which have collected data on the rates of selenite conversion to other selenium forms. Bench-scale results from the Phase I SBIR project and earlier EPRI-sponsored bench-scale tests are reported elsewhere [2]. The Phase II project, covered in this report, comprised not only bench- and pilot-scale scrubber testing but also evaluation of several selenium analytical techniques, evaluation of sample handling methods, and laboratory WWT tests.

The primary technical objectives 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.

Report Organization

Chapter 2 describes the bench-scale scrubber test apparatus and test method. Chapter 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 Chapter 4. The equipment and test approach for pilot testing are outlined in Chapter 5, and Chapter 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 Chapter 7. Finally, Chapter 8 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

The schematic of the bench-scale wet FGD system 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 entering the contactor through a central dip tube into a pool of gypsum and limestone slurry or sodium-based scrubbing liquor 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.

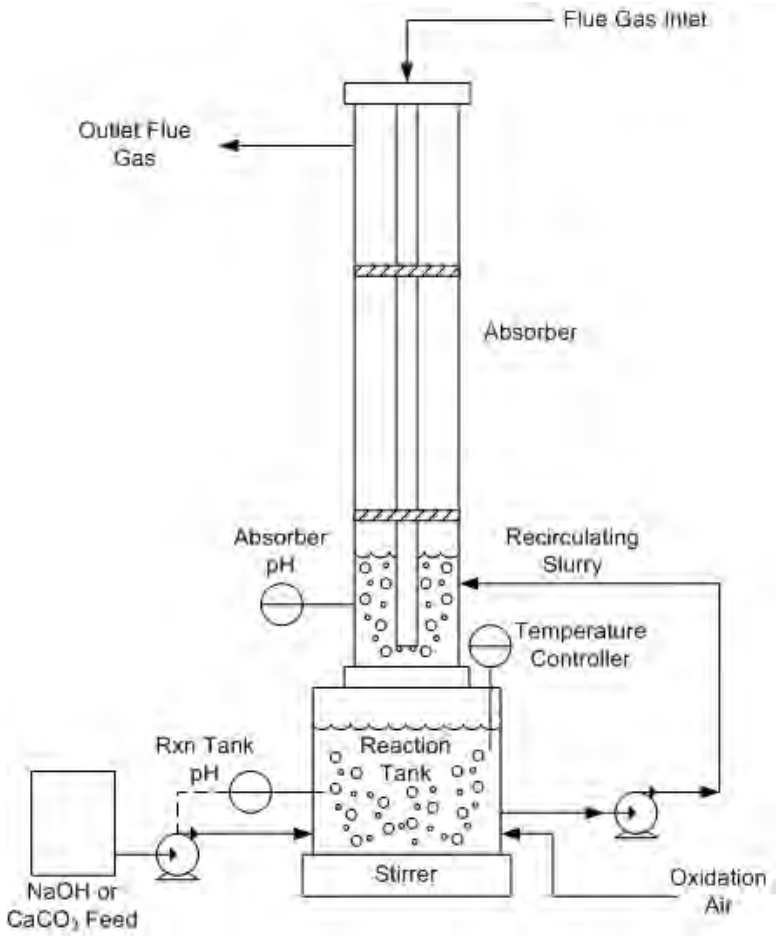

Figure 2-1
Schematic of Bench-scale Wet FGD Scrubber System

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 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.

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
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

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.

In limestone forced-oxidation wet FGD systems, the liquor sulfite concentration is controlled to low concentrations, typically between 0.2 to 1.0 mM, with the oxidation air rate. In Phase I tests, sulfite oxidation was similarly controlled using oxidation air, introduced into the bottom of the reaction tank through a sparger. 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.

In Phase II tests, oxidation-reduction potential (ORP), rather than sulfite concentration, was the parameter being directly controlled. 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 slurry 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. Phase II tests controlled the air rate directly based on ORP values. All ORP measurements shown in this paper 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).

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 Chapter 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 cathodic stripping voltammetry (CSV) instrument for selenium analysis, and same-day sample analysis using Hydride Generation Cold Vapor Atomic Absorption (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; this program tested up to 35 mg/L (ppm) manganese in whole slurry, which more accurately reflects recent field measurements [3]. The range of iron concentrations was extended up to 600 mg/L (ppmw) 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 Chapter 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 ppm Mn @ 150 mV (10 h)	10
ORP and Mn	33	5 ppm Mn @ 150 mV (10 h) Repeat	10
ORP and Mn	34	35 ppm Mn @ 100 mV	6
ORP and Mn	40	35 ppm Mn @ 150 mV	6
ORP and Mn	42	5 ppm Mn with variable ORP (Test 15 re-creation)	6
ORP and Mn	43	5/35 ppm Mn with variable ORP (Complete Oxidation)	6
ORP and Mn	47	35 ppm Mn @ 200 to 400 mV	11
ORP and Mn	49	35 ppm Mn @ 400 mV, 100 mV	10
DBA	30	5 ppm Mn @ 150 mV with DBA (10 h)	10
DBA	50	35 ppm Mn @ 400 mV, 1000 ppm DBA	6
Adipic Acid	32	1000 ppm adipic acid @ 200 mV (5 ppm Mn)	6
Acetic Acid	48	35 ppm Mn @ 400 mV, 1000 ppm Acetic Acid	10
8-HQS	51	35 ppm Mn and 3100 ppm 8-HQS @ 400 mV	6
Selenate	31	Selenate @ 100 mV (5 ppm 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 ppm 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 ppm Fe @ 150 mV with 8% gypsum (actual 115 to 130 mV ORP)	10
Fe + DBA	46	24 ppm Fe @ 150 mV with 8% gypsum and 1000 ppm 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 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, CSV and HG-AA 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, onsite selenium measurement were made using an atomic fluorescence (HG-AF or "AF") instrument in lieu of an atomic absorption instrument; the methods of sample pretreatment for the HG-AA and HG-AF 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 (Inductively Coupled Plasma Mass Spectrometry) 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 (AEC) to measure individual dissolved selenium species. Here, the role of AEC 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.

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-AA 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) [4]. 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-AA 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-AA.

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 samples after storage.

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-AA 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 ICP-MS technique. The reporting of species other than selenite or selenate, such as selenosulfate and other unknown selenium species, is not well documented or understood at this time. Furthermore, preliminary results obtained in this program indicate that selenosulfate is detected 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-AA 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 the long analysis time, 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 for 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-AA	CSV
Sample digestion	None	Yes (TSe only)	Yes (TSe only)
Selenium species	"Full" speciation	Se(IV), TSe	Se(IV), TSe
Detection limit	1 ppb or less	30 ppb	80-100 ppb
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

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 [2]. 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, which is described next. Ultimately, parallel unpreserved and cryo-preserved samples were analyzed by IC-ICP-DRC-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 described previously: unpreserved, cryo preservation, and borate buffer with formaldehyde ("FBB"). FBB was selected because it "masks" sulfite and might prevent trace levels of sulfite from reacting with selenium species during storage. For selenite and selenate, measurements from unpreserved samples were comparable to other preservation methods. However, for selenosulfate, cryo preservation was favored; analysis of unpreserved samples by 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 order 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 measurement of selenium speciation shortly after sampling, rather than after 48 hours of storage, 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 of storage, and 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 ICP-MS, AA, and CSV measurements were generally consistent with each other for samples measured at the same storage time.

Figures 3-1, 3-2, and 3-3 show the selenite oxidation for tests conducted with 35 ppm manganese only, 35 ppm manganese with 1000 ppm acetic acid, and 35 ppm manganese with 1000 ppm DBA, respectively. All tests were conducted at an ORP value of ~400 mV. 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, the ORP set point was decreased to 100 mV ORP 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 indicate that the selenate did initially convert to selenite, but the final sample at 600 minutes of run time confounds this observation. 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 during storage. Dissolved manganese concentrations 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.

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. 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.

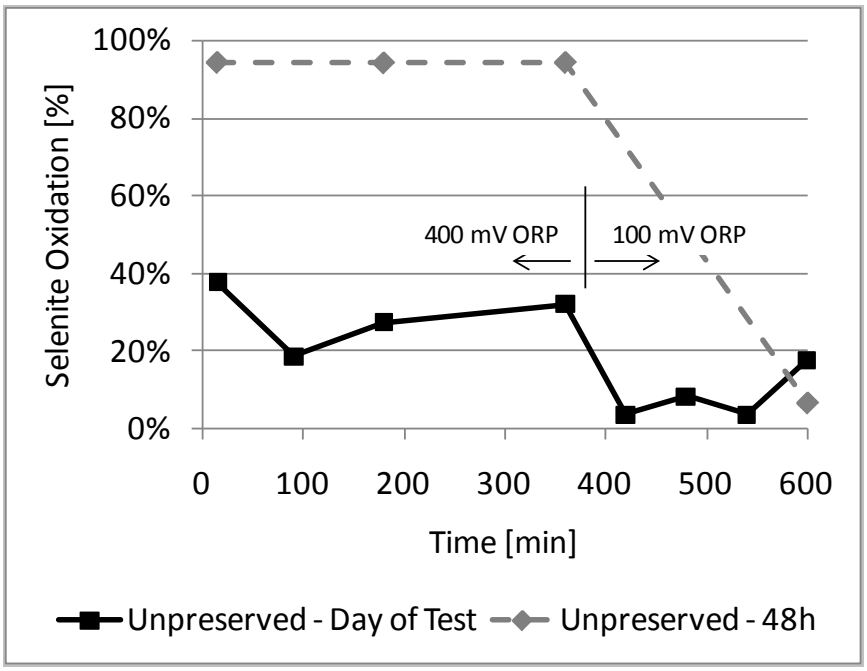

Figure 3-1
Selenite oxidation for 35 ppm Mn only at 400 to 100 mV ORP (Test 49) before and after storage

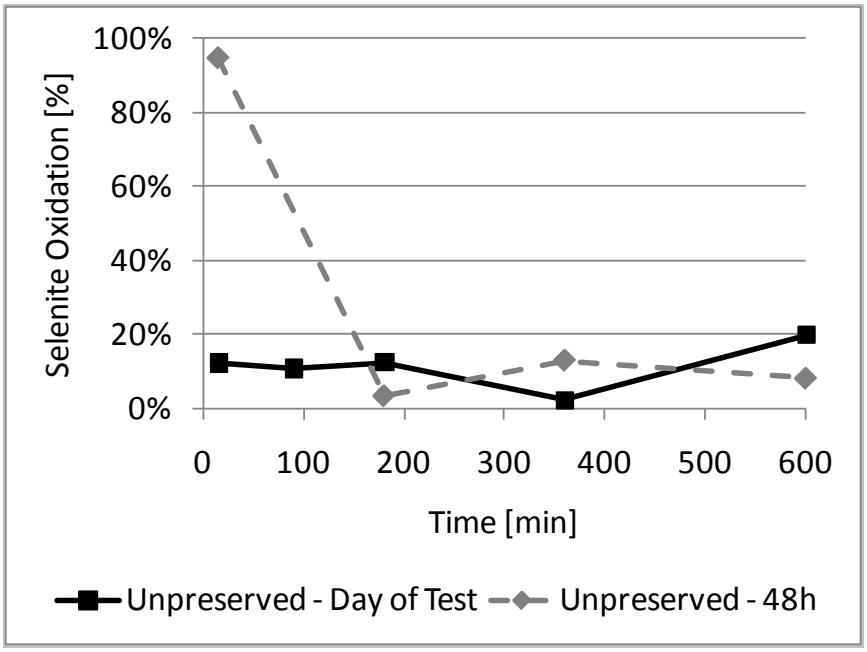

Figure 3-2
Selenite oxidation for 35 ppm Mn and 1000 ppm acetic acid at ~400 mV ORP (Test 48) before and after storage

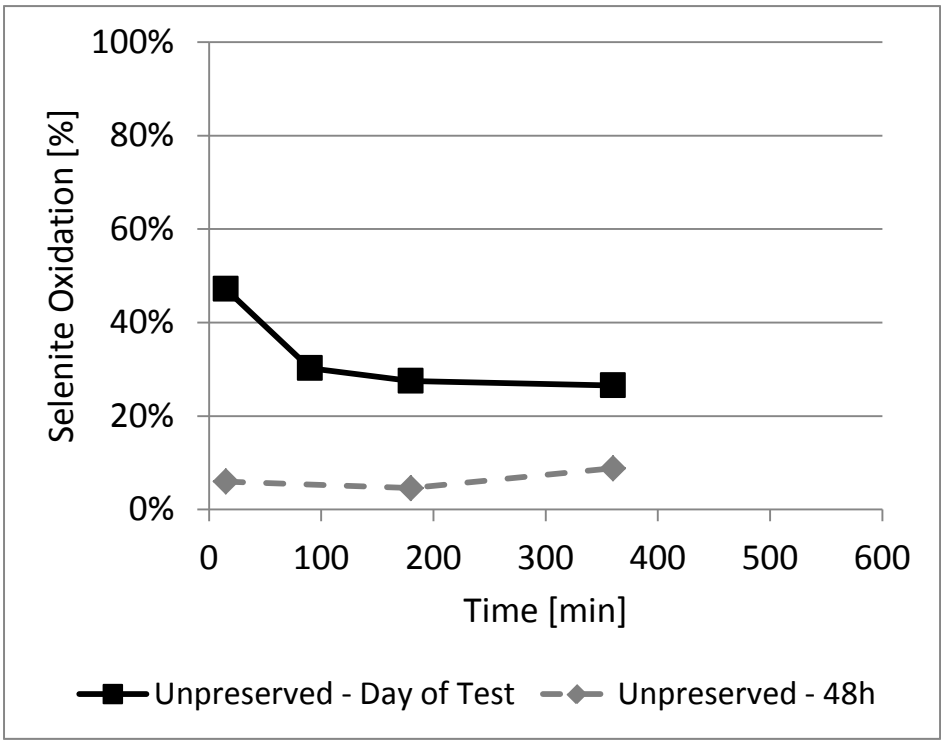

Figure 3-3
Selenite oxidation for 35 ppm Mn and 1000 ppm DBA at ~400 mV ORP (Test 50) before and after storage

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 ICP-MS results for measured selenite (Se^{4+}) and measured 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 liquor. These results indicate that the absolute concentrations change by less than 10%, and often by much less, between nominally two days and several weeks. 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 ICP-MS

	$Se^{(4+)}$ (ppb)		$Se^{(6+)}$ (ppb)		Sum of Species (ppb)	
	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+} (ppb)		
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 storage time.

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 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 before and after storage 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. Analysis should be conducted as rapidly as possible after sampling. After the initial 48 to 72 hours, selenium speciation remains 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 groups of tests that focused on the impacts of manganese and ORP, scrubber additives, iron, natural limestone, and actual FGD liquors. Results from each of these groups are discussed in separate subsections.

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 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 ppb, for a test with 35 ppmw 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 ppmw 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 mixture of adipic, succinic, and glutaric acids. 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.

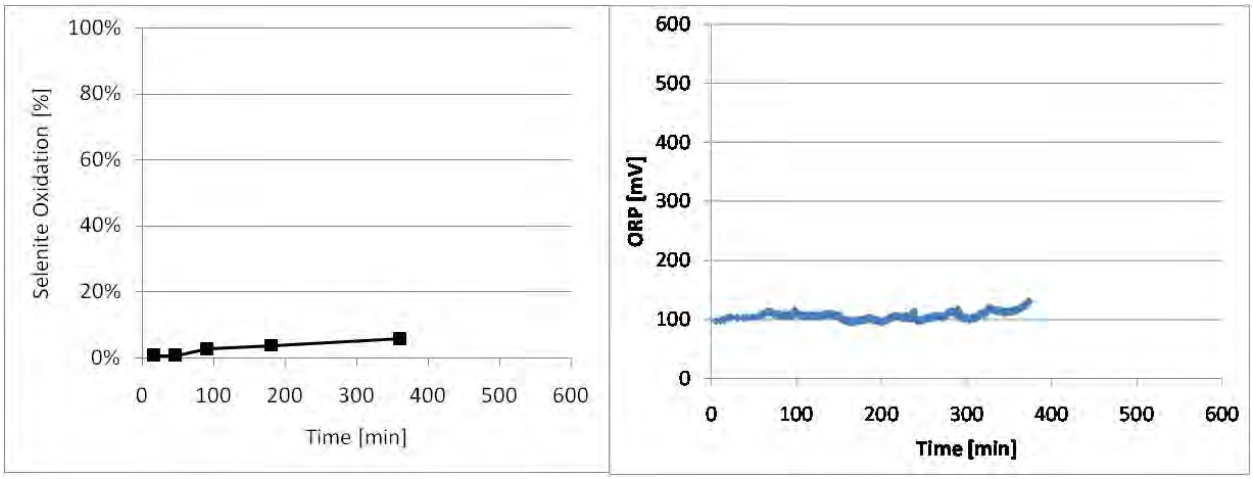

Figure 4-1
Selenite oxidation and ORP for 35 ppmw Mn at 100 mV ORP (Test 34)
(Unpreserved samples measured via ICP-MS after 48h of storage)

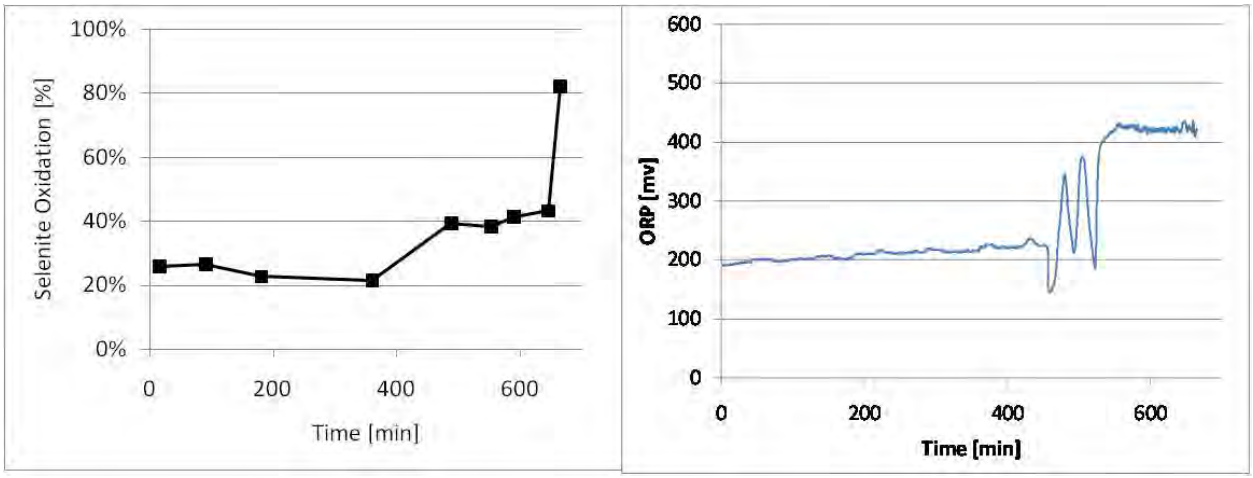

Figure 4-2
Selenite oxidation and ORP for 35 ppmw Mn at Variable ORP (Test 47)

Figure 4-3 shows the effects of DBA and storage time on selenite oxidation for tests with 35 ppmw manganese at 400 mV ORP; these results are also shown in Figures 3-1 and 3-2 for 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 has been 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. The speciation change during storage is confounding because it is unknown whether the DBA will decrease selenite oxidation with time after blow down from the absorber in full-scale FGD systems.

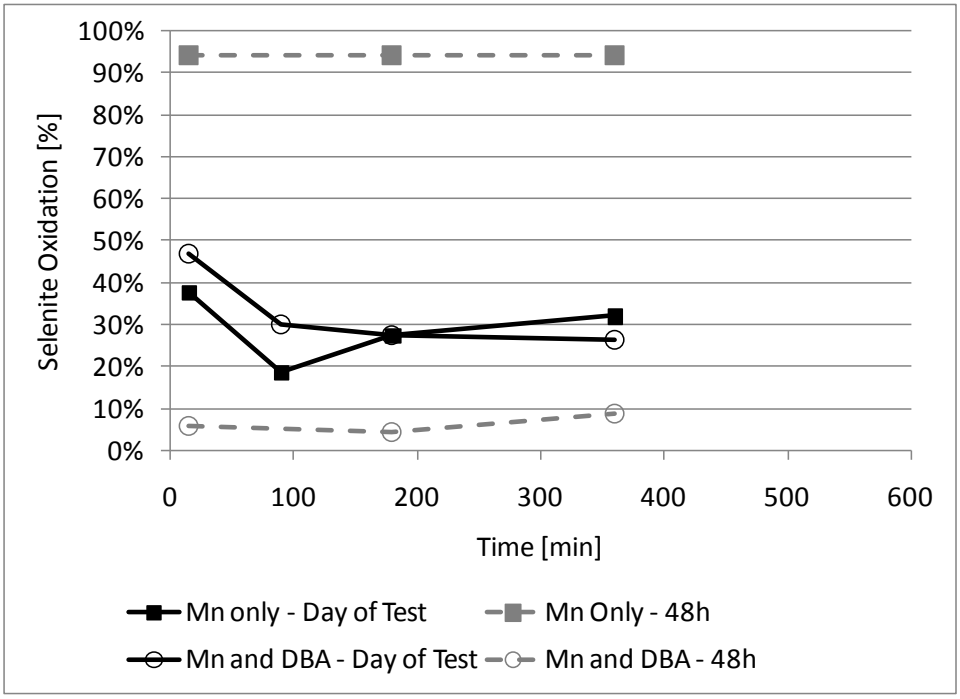

Figure 4-3
Effects of DBA and storage time on selenite oxidation for tests with 35 ppmw Mn at 400 mV ORP

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 ppmw manganese and adipic acid at 200 mV ORP showed little to no selenite oxidation in samples analyzed by 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 ppmw 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 oxidation during storage 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 another 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.

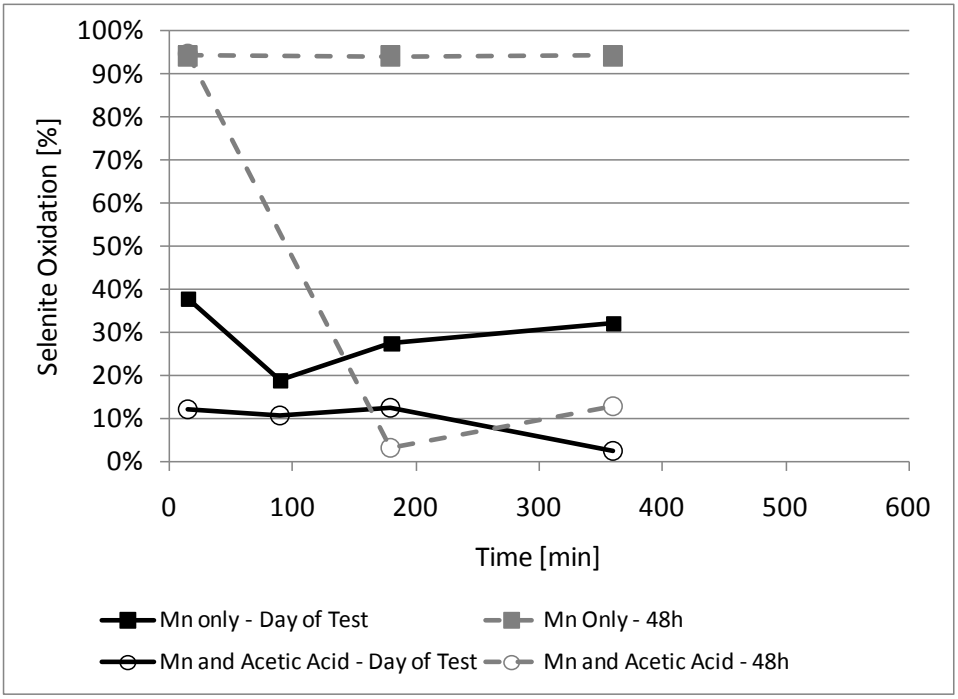

Figure 4-4
Effect of acetic acid and storage on selenite oxidation for tests with 35 ppmw Mn at 400 mV ORP

Iron

Bench-scale testing has demonstrated that various forms of iron can effectively adsorb 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. Adsorbed selenium 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 ppm 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.

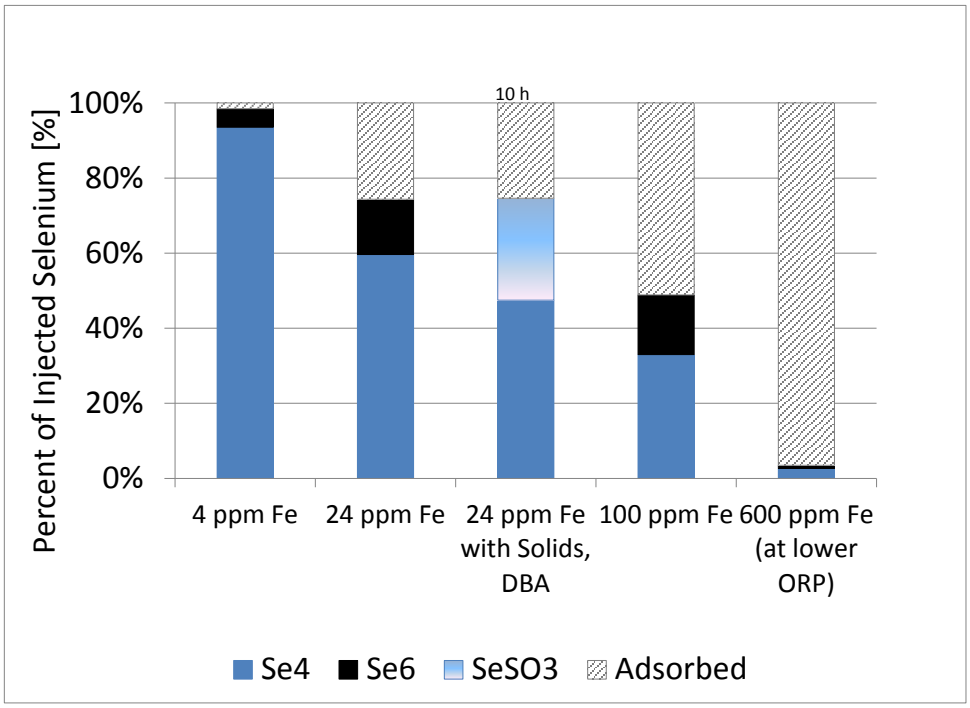

Figure 4-5
Selenium distribution for tests with iron at moderate ORP conditions

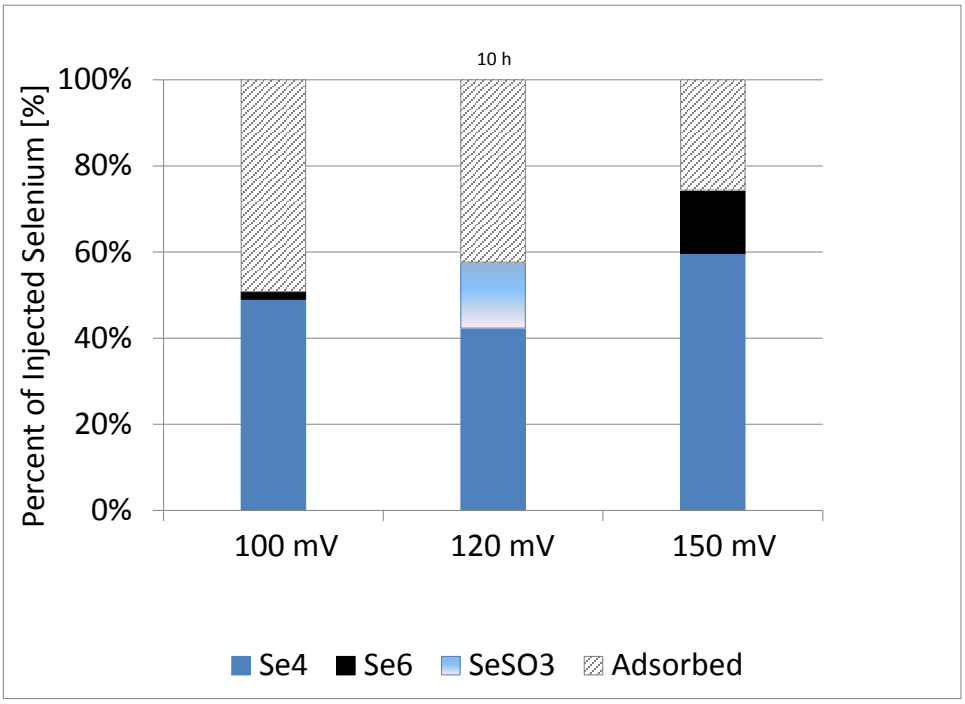

Figure 4-6
Impact of ORP on Selenium distribution for tests with 24 ppm Iron

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 [5]. Pilot testing with iron under this program may seek to observe the stability of sorbed selenium.

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 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, and 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 particulates (“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 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 at larger scales. 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 results 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. 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	200	Effect of DBA at new manganese baseline and moderate ORP	0%	100%
50	DBA	300	Effect of DBA at high ORP	12%	88%
51	DBA	150	Effect of DBA at moderate ORP	0%	100%
52	Acetic acid	300	Effect of acetic acid at high 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 - $MnSO_4$	ppm as Mn	35
Chloride - NaCl	M	0.1
Selenite - Na_2SeO_3 (Se IV)	ppb 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 ppbw (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 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 absolute selenate concentration did not increase after the initial 15-minute sample; at 300 mV ORP, selenate did increase throughout the tests for DBA and acetic acid. The final, absolute 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.

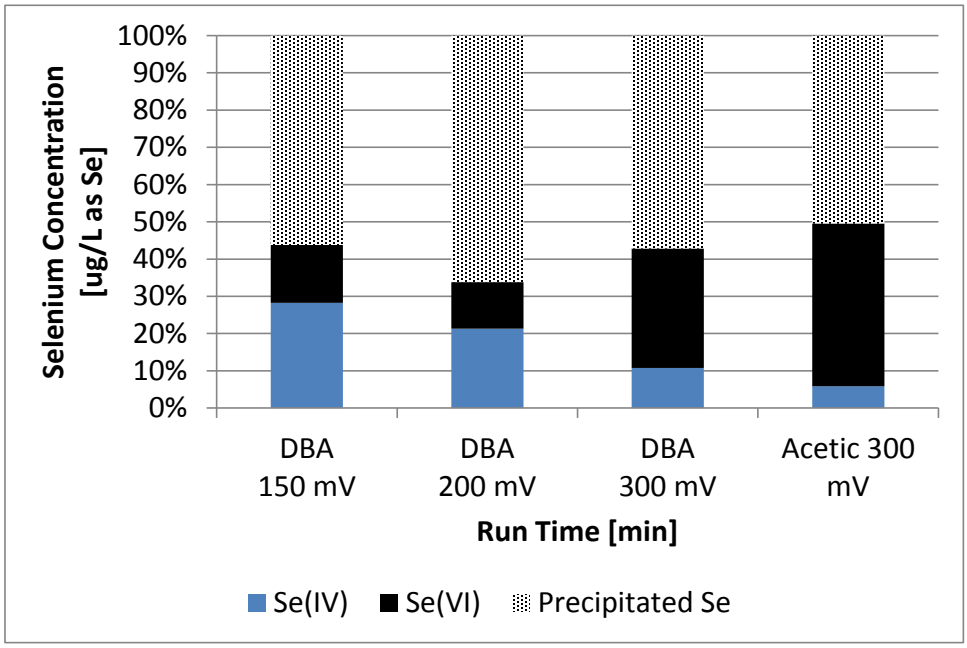

Figure 4-7
Selenium Speciation and Partitioning for Tests with Natural Limestone

At medium to high ORP conditions, the 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 the 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 DBA may be warranted to try and understand why it shows beneficial mercury partitioning and selenium speciation under some circumstances but not others.

Tests with Field Liquors

During April 2011, six bench-scale screening tests were conducted using FGD scrubber slurry and limestone slurry from the pilot host facility. The purpose of the screening tests was to run conditions at the bench scale that were under consideration for pilot testing. Results from the screening tests could give a preliminary indication of selenium behavior in the more complex matrices (i.e., slurries) encountered in full-scale systems. 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 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 with 8 wt% of host site absorber solids. The pH was controlled using host site limestone slurry that was filtered and re-combined to achieve 10 wt% solids. 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.

The selenium addition for these tests differed from tests in synthetic liquors. The pilot host site liquor contains nominally 3000 ppbw of “native” selenate; therefore, the selenite “spike” amount was increased to 2000 ppbw 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 ppb.

As shown in Table 4-3, 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 ppbw and no detected selenite.

Decreasing the ORP decreased the rate of selenite oxidation; 740 ppbw of selenium remained as selenite at the end of Test 54. DBA does not show a clear benefit to inhibit selenite oxidation when compared with decreasing the ORP. Addition of ferric chloride reduces total liquid phase selenium, and presumably adsorbs or precipitates the selenium. Increasing the ferric chloride dosage rate increased the amount of selenium leaving the liquid phase, presumably by adsorption or co-precipitation with the iron.

Table 4-3
Final Selenium Speciation for 6-hour Tests with Pilot Host-Site Feedstocks

Run #	Test	ORP	Se^{4+}	Se^{6+}	TSe
		mV	ppbw as Se	ppbw as Se	ppbw as Se
53	Plant ORP (Baseline)	450	<50	4526	4576
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	3068
57	Ferric Chloride (Concentration 2)	100 - 200	<50	2022	2072
58	DBA at Low ORP and variable pH	200	nr	nr	nr

"nr" indicates not reported

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.

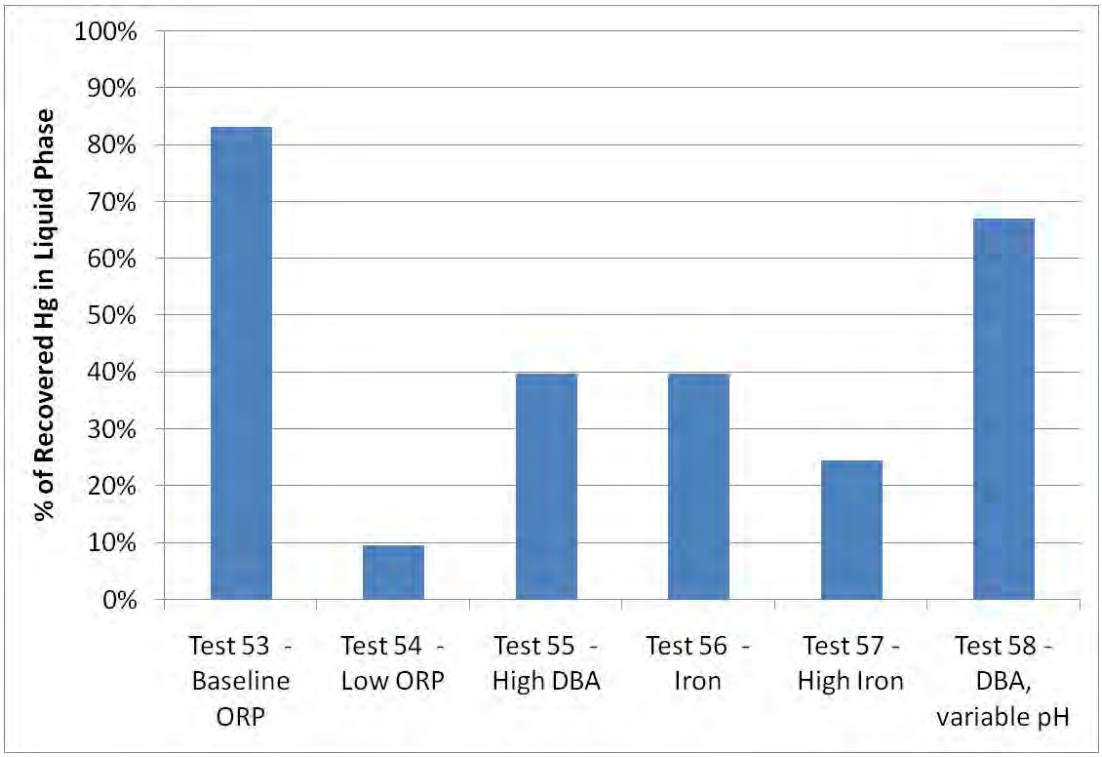

Figure 4-8
Mercury Phase Partitioning for Tests with Pilot Host-Site Feedstocks

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, the mercury phase-partitioning generally agrees with the full-scale measurements: approximately 80% of the mercury reports to the liquor. Decreasing the ORP shifts mercury partitioning to the solid phase of the slurry. 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 resulted in Hg re-emissions and Hg shifting into the solid phase. Further testing with DBA indicated that the re-emissions observed with DBA may be a brief transient effect as the system re-equilibrates. The impact of DBA on Hg re-emissions is inconclusive. Lower pH conditions may promote Hg partitioning to the solid phase. Addition of ferric chloride to the scrubber reduces Hg re-emissions, and promotes conditions under which Hg shifts to the solid phase. Increasing the ferric chloride increases the rate of Hg reporting to the liquid phase; however, at the higher iron addition rate, 24% of the mercury remained in the liquid phase.

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 residence time of liquid and solids through 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 and shorter FGD residence times. 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 particulates ("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.

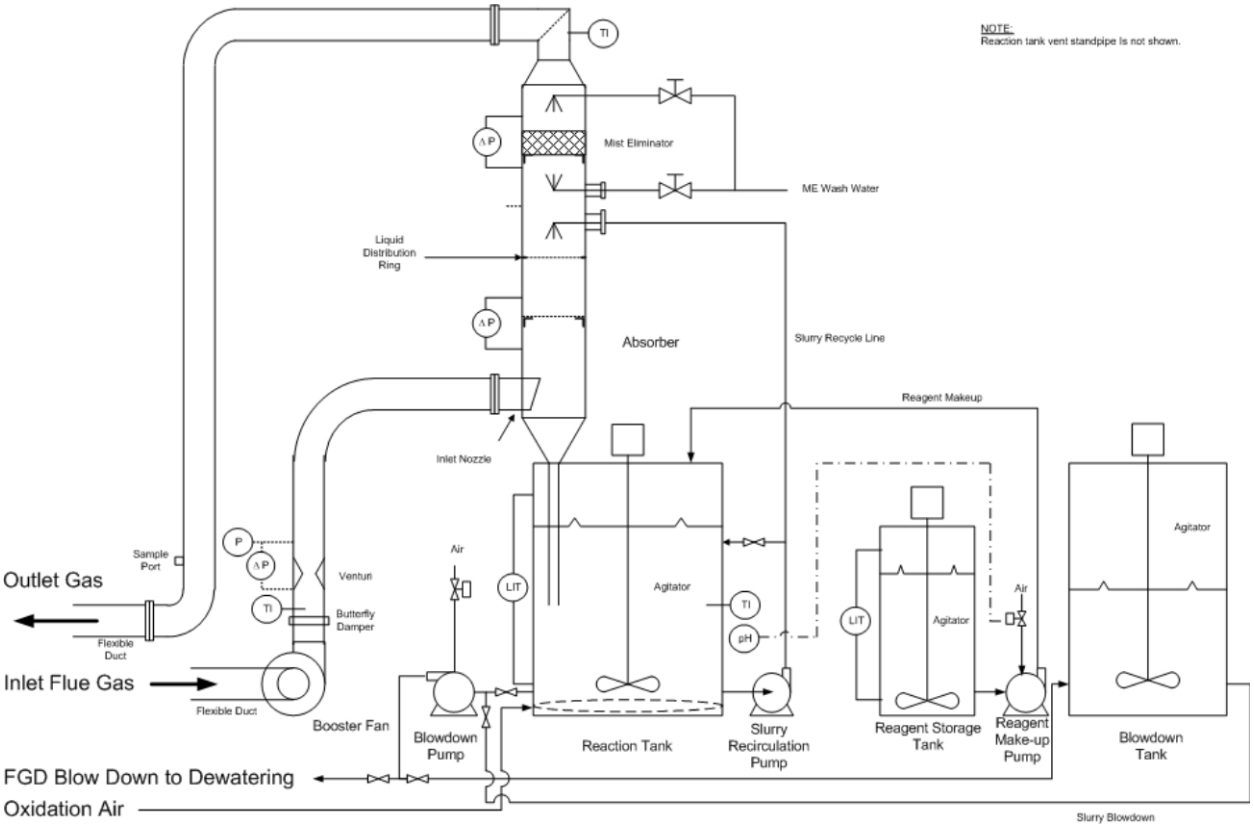

Figure 5-1
Schematic of Pilot FGD Scrubber System

A schematic of the pilot hydrocyclone is shown in Figure 5-2. The pilot hydrocyclone is used periodically (nominally once or twice per day) to blow down reaction tank slurry to control the solids loading. The hydrocyclone is used to separate the fine particulates, which exit in the overflow, from the larger particles, which exit in the underflow. In full-scale systems, 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.

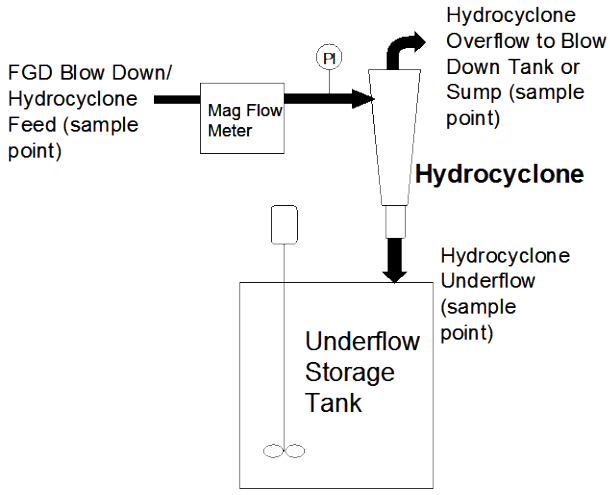

Figure 5-2
Schematic of Pilot Hydrocyclone

Test Method

For this program, the pilot wet FGD system was operated to treat a target flow rate of 1700 acfm of 300 °F flue gas from the full-scale wet FGD inlet flue gas. 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 1/3 full-scale wet FGD reaction tank slurry and 2/3 service (makeup) water with an initial spike of chloride salts to achieve expected steady-state concentrations. 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 the underflow slurry representing the byproduct gypsum solids from the pilot system, and the overflow slurry of fine solids returning to the pilot absorber reaction tank. The liquor associated with the underflow slurry represents the chloride purge water stream from the FGD system, to control chloride buildup resulting from HCl removal from the inlet flue gas.

Test Plan

During operation, the pilot FGD inlet and outlet flue gas were monitored for SO_2 concentration. The pH and ORP of the recycle slurry were continuously monitored. At each blowdown episode, a suite of slurry, liquor and solids 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, total selenium in the slurry solids and liquor, other trace elements, and selenium speciation in the liquor phase.

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

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

Host Site Description

The pilot host site is a facility firing low-to-medium-sulfur bituminous coal located in the Southeastern United States. The full-scale FGD system operates in forced oxidation mode and does not currently use scrubber additives. The absorber operates at elevated ORP conditions, and absorber liquid-phase selenium concentrations are nominally 1500-2000 ppbw as Se, all selenate.

Targeted Pilot Test Conditions

The targeted test conditions for pilot testing are shown in Table 3. 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 between 250:1 and 500:1 Fe:Se on a mass basis.

Table 5-1
Targeted Pilot Test Conditions

Test	ORP [mV]
Baseline	450
Low ORP	200
Ferric Chloride	200

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: baseline 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. 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 not only selenium speciation and phase partitioning in the scrubber slurries, but also 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. Also discussed with the pilot-scale results are highlighted pilot scrubber performance indicators (e.g., sulfur removal and oxidation, limestone utilization).

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 feeds and to observe full-scale trends in selenium behavior. Coal and ash samples were obtained almost daily. 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. A limited number of samples were taken at the full-scale FGD secondary hydrocyclone overflow (WWT inlet) and at the WWT system outlet. Analysis of full-scale samples focused on operations at the beginning of each of the three five-day pilot tests.

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 roughly consistent at the beginning of the three tests. In all cases, the dissolved selenium consisted completely of selenate; 40-45% of the total selenium in the absorber slurry had reported to the liquid phase. Liquid-phase mercury concentrations in the full-scale absorber slurry remained high at around 2000 µg/L. Mercury reported predominantly to the liquor (>90%) for the latter two samples. The solid-phase mercury measurement for the Baseline test suffered from poor precision, and may be suspect, calling into question the lower fraction of mercury estimated in the liquid phase for that sample. As would be expected, manganese remained predominantly in the solid phase under the consistently high ORP conditions; iron reported completely to the solid phase as well. Both peroxydisulfate and dithionate concentrations were relatively high in the baseline sample, and

both species were measured at lower concentrations in subsequent tests. Dithionate concentrations were significantly lower in the final sample used for initial charge of the ferric chloride test. Dissolved total organic carbon (TOC) was low in all samples.

Figure 6-1
Pilot Wet FGD System

Table 6-1
Host Site Full-Scale Absorber Samples

Description	Units	Baseline	Natural Oxidation	Iron
Sample Date		6/15/2011	7/13/2011	7/19/2001
Temperature	ºF	125	125	121
pH (reaction tank)	-	5.34	5.14	5.23
ORP	mV	605	621	n/a
Dissolved Selenium (HG-CVAA)				
Total Selenium	µg/L as Se	1614	2124	na
Selenite	µg/L as Se	nd	nd	na
Selenate (by difference)	µg/L as Se	1614	2124	na

Description	Units	Baseline	Natural Oxidation	Iron
Dissolved Selenium (IC-ICP-DRC-MS)				
Total Selenium	µg/L as Se	1530	1797	1616
Selenite	µg/L as Se	<0.5	<0.5	<0.5
Selenate	µg/L as Se	1530	1797	1612
Solid Selenium	µg/g	10.93	10.01	11.12
% 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	1866	1602	1825
Manganese				
Liquor Mn	mg/L	0.32	3.93	0.14
Solid Mn	µg/g	158.5	116	167
% Mn in Liquor		1%	12%	0%
Sulfur Species				
Sulfite (SO_3)	mg/L	<2	<2	<2
Sulfate (SO_4)	mg/L	1301	1306	1514
Dithionate (S_2O_6)	mg/L	1042	684	259
Peroxydisulfate (S_2O_8)	mg/L	1072	946	805
Halogens				
Bromide	mg/L	33	80	80
Chloride	mg/L	5261	5429	4775
Solids content	wt% solids	17.1	19.4	17.9
Liquor TOC (total organic carbon)	mg/L	7	8	8

The dewatering system at the host site comprises a primary hydrocyclone, a purge hydrocyclone, and a centrifuge. Underflow from the primary hydrocyclone feeds the centrifuge. Centrate flows from the centrifuge to a transfer tank and then returns to the absorber tower. Gypsum solids from the centrifuge are disposed offsite. The overflow from the primary hydrocyclone feeds the purge hydrocyclone. Underflow from the purge hydrocyclone returns to the absorber tower, and the overflow flows to the WWT system.

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 roughly 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	Se4 (µg/L)	Se6 (µg/L)	Sum of 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.

Pilot Scrubber Results

The behavior of selenium and numerous other species was measured throughout the pilot test campaign to test the effectiveness of the two control strategies selected for testing: (1) reduce ORP by decreasing oxidation air rate and (2) add ferric chloride to the scrubber. 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 preferentially reported to smaller particles or dispersed through the bulk slurry solids.

Process operating conditions, flows and system performance indicators were also monitored. 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 balances revealed that the liquid turnover and sulfur input into 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 (e.g., 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 duration could not be extended. The end result is that the changes in liquid-phase selenium 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 selenium 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.

Liquid-phase Selenium Results

Baseline Test

Selenium behavior observed during the baseline test in the pilot scrubber was roughly consistent with behavior observed in the full-scale scrubber. During the baseline test, pH and SO_2 removal targets were maintained; ORP ran slightly higher than in the full-scale unit. Pilot FGD ORP values are shown in Figure 6-2.

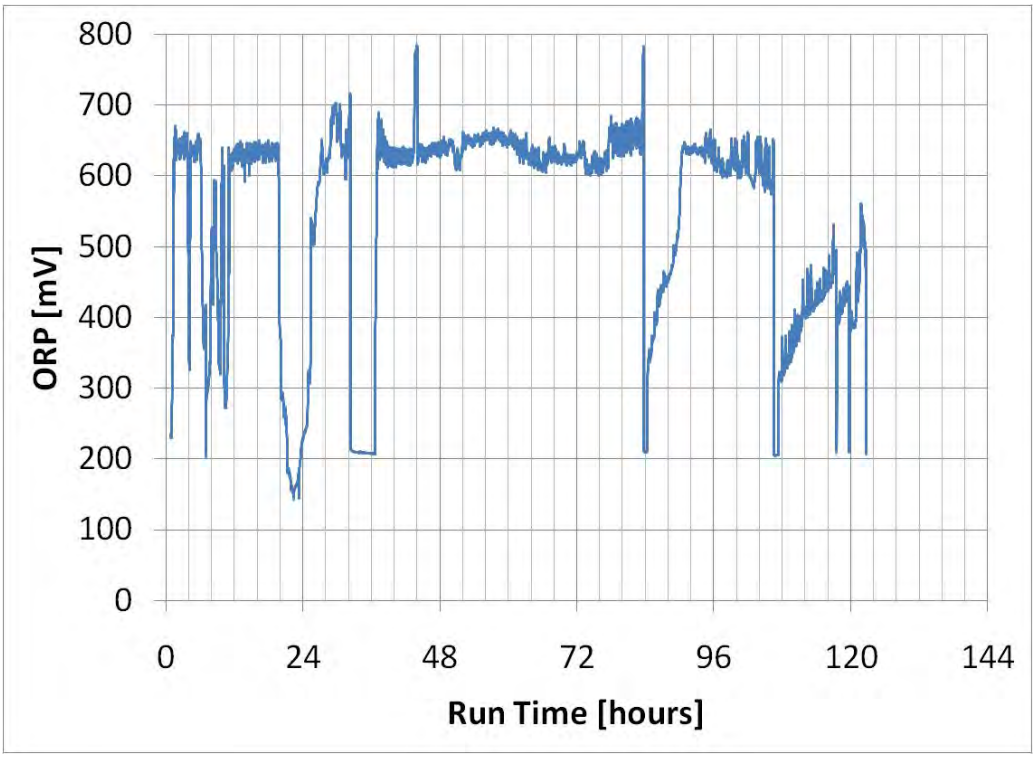

Figure 6-2
ORP – Baseline Test

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 Baseline test. "BD" indicates a blowdown event. All dissolved selenium was measured as selenate throughout the test. Due to the fluctuations in solids loading and liquid levels, 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, though a modest fraction (~20-25%) accumulated in the liquor as selenate. The estimated fraction reporting to the solids is somewhat higher than the full-scale system, in which slightly less than 60% of the slurry selenium reports to the solid phase.

Table 6-3
Baseline - Scrubber Selenium Measurements

Event	Run Time	Suspended Solids Loading	Total Se in Liquor	Total Se in Bulk Solids
	h	wt%	µg/L	µg/g
Full-Scale				
	0	17.1	1,570	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

Low ORP Test

The second target test condition was 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 oxidation performance were maintained. 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.

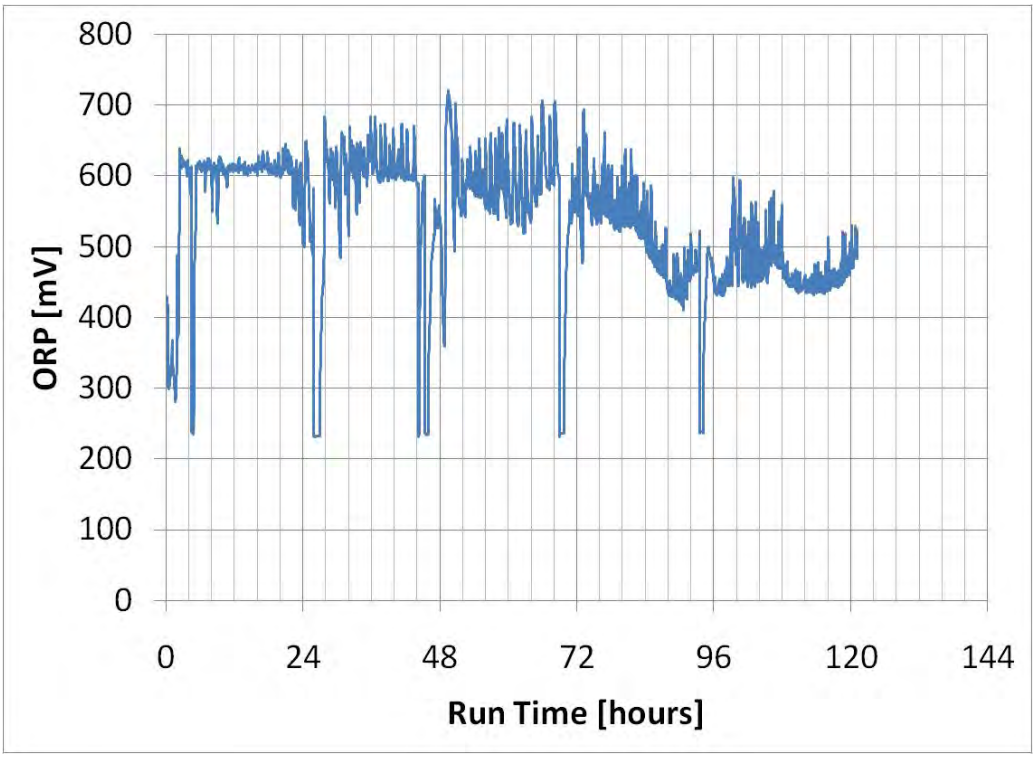

Figure 6-3
ORP – Natural Oxidation Test

Table 6-4 shows the measured total selenium in the slurry liquor and solids for the low ORP (actually conducted under natural oxidation) test. As with the baseline test, all dissolved selenium was selenate. 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	Suspended Solids Loading	Total Se in Liquor	Total Se in Bulk Solids
	h	**wt%**	**µg/L**	**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

Iron Addition Test

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, and Table 6-5 presents the selenium measured in the liquid and solid phases of the pilot scrubber slurry. The ORP during this test 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 confirmed that all iron reported to the solid phase of the pilot slurry, and the mass ratio of added iron to accumulating selenium was roughly 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 ppbw as Se). Given that the natural oxidation test showed nearly all “new” 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.

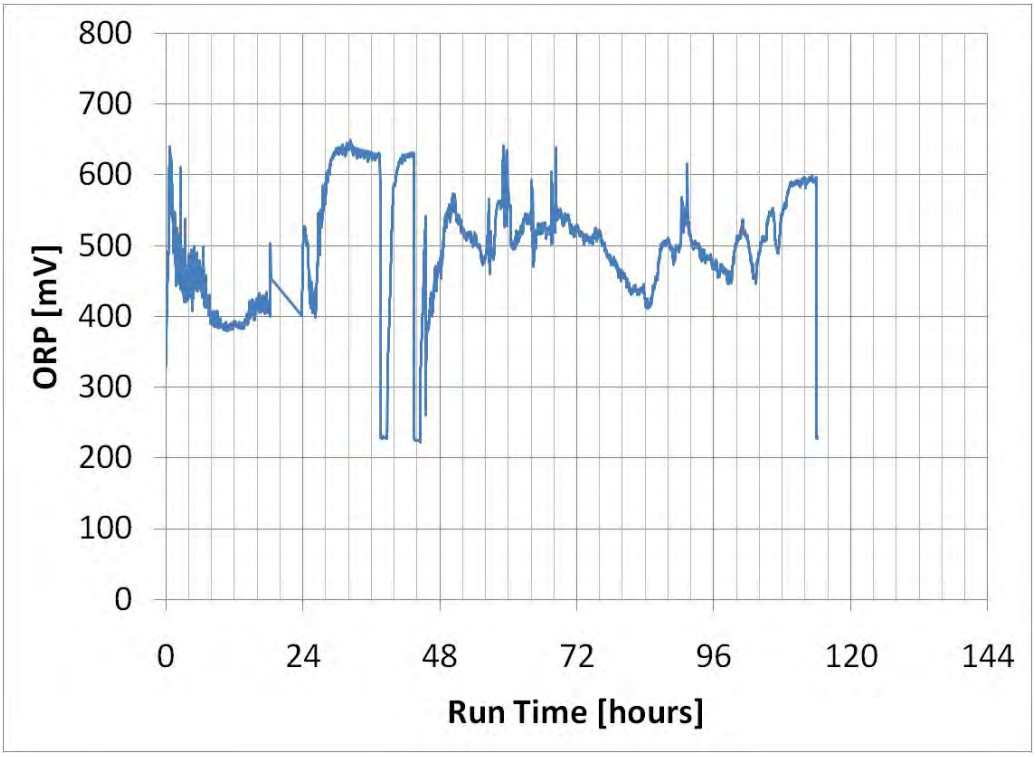

Figure 6-4
ORP – Ferric Chloride Test

Table 6-5
Ferric Chloride Test - Scrubber Selenium Measurements

Event	Run Time	Suspended Solids Loading	Total Se in Liquor	Total Se in Bulk Solids
	h	wt%	µg/L	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 at the host

facility. 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 ppb as Se) was measured in the final pilot absorber samples. Examination of operating data explains how the low ORP conditions were achieved during this test; the operating data indicate that L/G ratios closer to typical full-scale values and lower flue gas oxygen concentrations might have allowed lower ORP operations in other tests. The results may also indicate that oxidation air flow control may comprise one part of a scrubber selenium management approach, though this approach might be less 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 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 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.

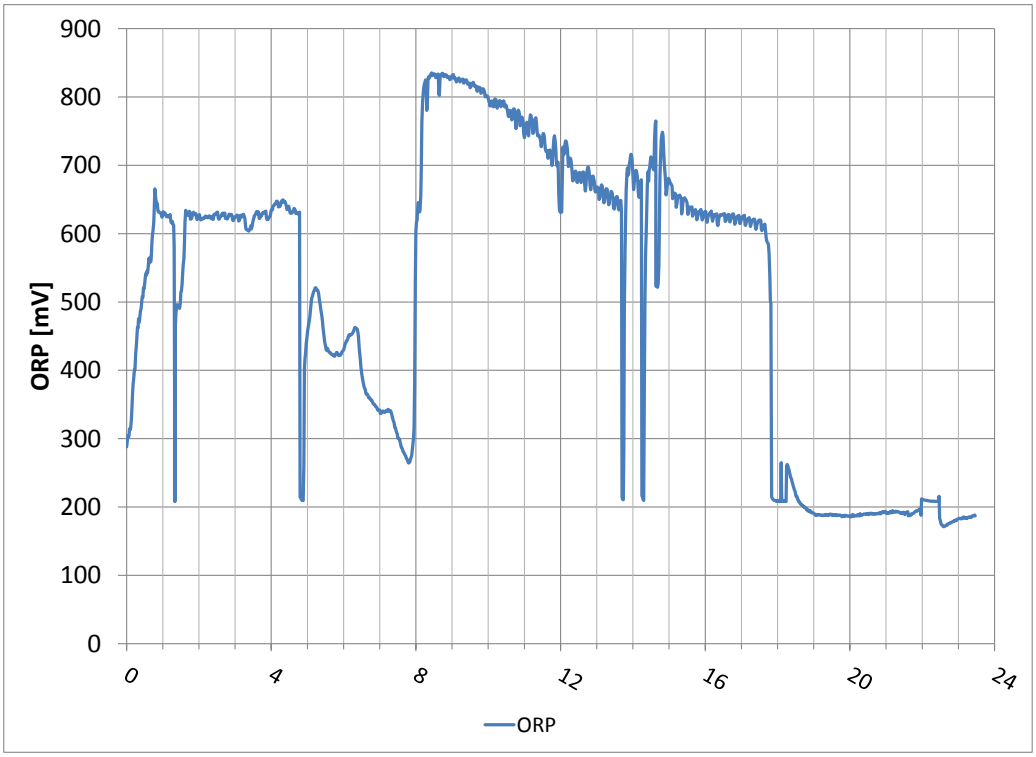

Figure 6-5
ORP – First Attempt at Low ORP

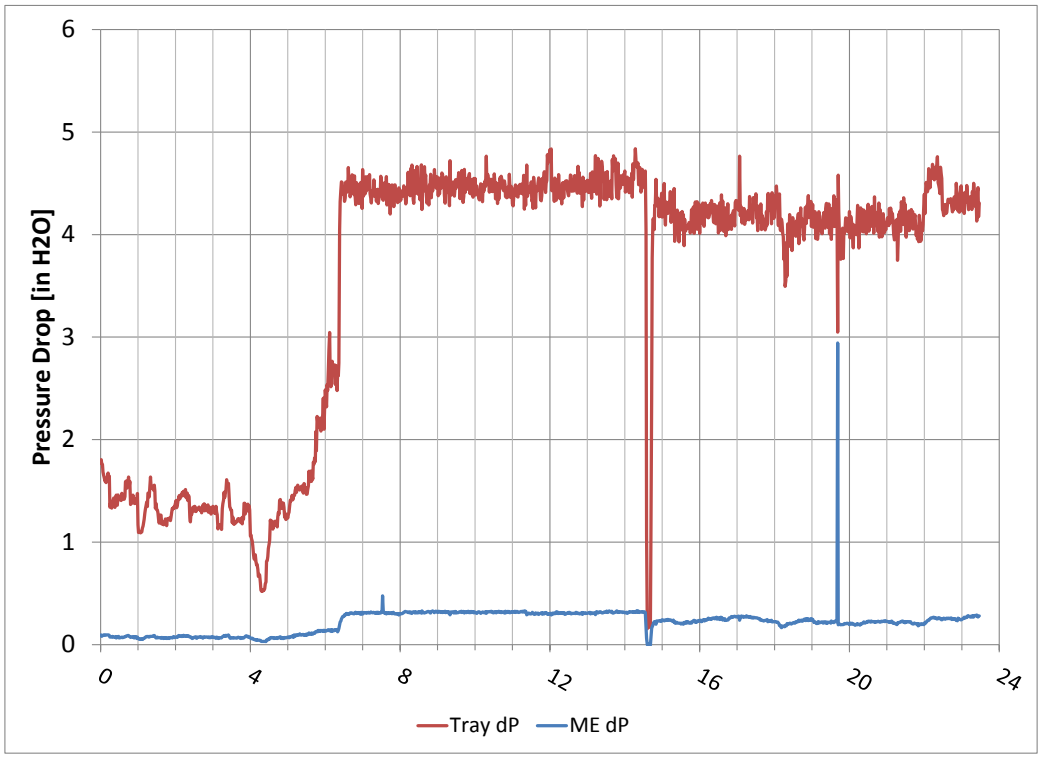

Figure 6-6
Absorber Tray Pressure Drop – First Attempt at Low ORP

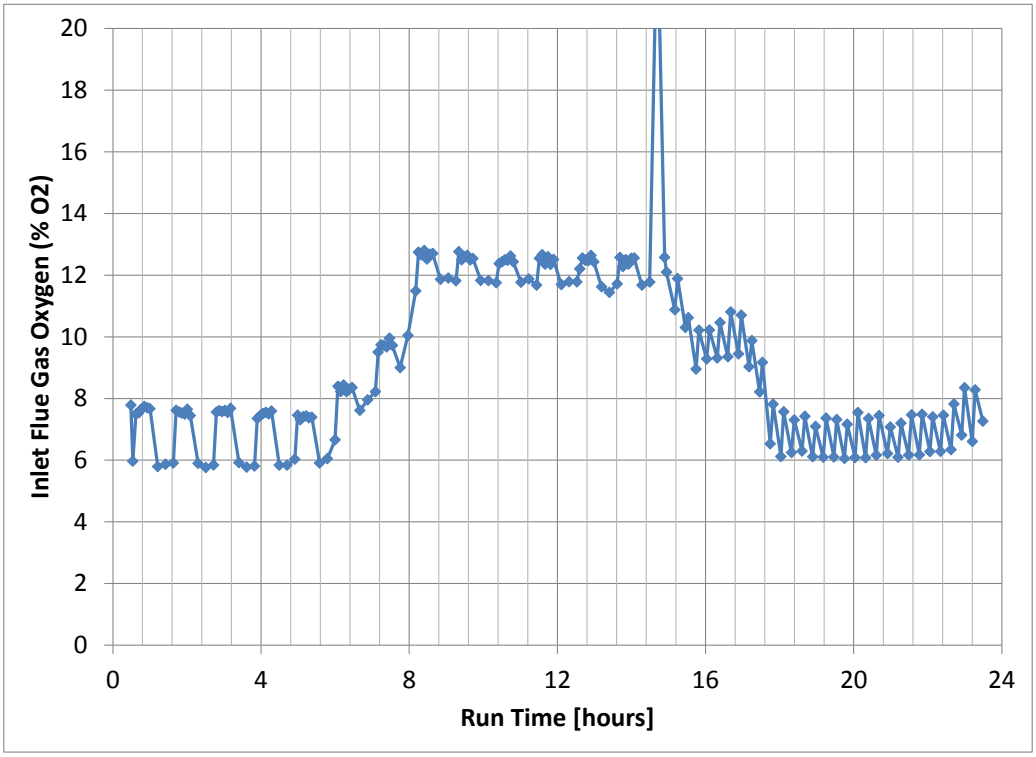

Figure 6-7
Flue Gas Oxygen Concentration – First Attempt at Low ORP

As noted earlier, the final pilot absorber sample for this one-day test contained 68 ppb 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 forced oxidation conditions. This result 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 under low ORP that ultimately operated in "natural oxidation" mode.

Solid-phase Selenium Results

The reporting of selenium to various slurry solid size fractions may provide insight into the mechanisms impacting selenium phase partitioning. Management of the selenium reporting between different solid size fractions might also offer a means to manage the fate of selenium exiting the FGD systems. Therefore, 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 hydrocyclone overflow and underflow streams during blowdown events and (2) distribution between different size fractions in the absorber slurry based on wet-sieved solid samples. Table 6-6 presents the solid selenium measured in pilot hydrocyclone overflow and underflow streams.

In all cases, the selenium concentrations measured in the fine particulates, 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 smaller overflow solids to concentration in the underflow solids was less than two in all but the final blowdown samples from the ferric chloride test. The percent of selenium reporting to the fine particulates 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.

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

		HC Underflow		HC Overflow		
Test Condition	**Run Time [h]**	**Se in Solids (µg/g)**	**Wt % Solids**	**Se in Solids (µg/g)**	**Wt % Solids**	**% of Solid Se in HCOF solids**
Baseline	84	8.0	61.0	9.0	2.7	16%
Baseline	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	38	9.6	61.9	10.9	5.9	25%
Ferric Chloride	68	8.1	60.6	14.3	2.5	14%
Ferric Chloride	114	5.6	61.1	11.2	4.0	39%

Wet sieving of solid samples separated solid samples into fractions comprising 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.

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 reports to the fines during the ferric chloride test is similar to other tests despite a much higher selenium *concentration* in the fines, because the fines in the ferric chloride test are a smaller portion of the total solids content of the slurry. Enrichment of other trace metals (e.g., Fe, Hg) 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 selenium co-precipitates with the gypsum rather than associating with iron impurities in the limestone. Other researchers have found evidence supporting the formation of calcium-selenium solid complexes in FGD systems [5]. 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 particulates. The dominance of these pathways in controlling selenium behavior may depend on scrubber operating conditions.

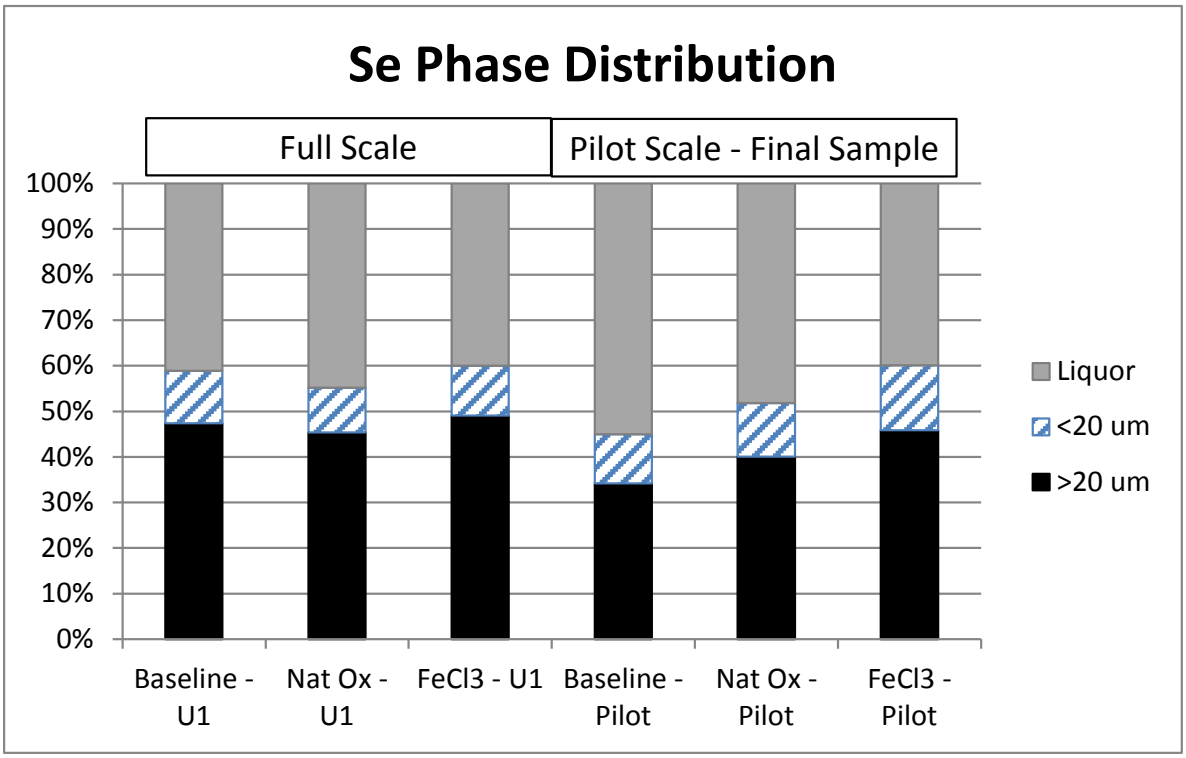

Figure 6-8
Selenium Phase Partitioning in Full-scale and Pilot-scale Absorber Samples

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

Master Sample	Se Conc. (>20 µm)	Se Conc. (<20 µm)	<20 µm	<20 µm	% Se in Solids	% Se in >20 µm	% Se in <20 µm	% Se in Liquor
	µg/g	µg/g	wt% of solids in size range	% of solid Se	% total Se	% total Se	% total Se	% total Se
Full-scale								
Baseline	9.69	10.17	19%	20%	59%	47%	12%	41%
Natural Oxidation	9.18	10.11	16%	18%	55%	45%	10%	45%
Ferric Chloride	10.20	9.02	20%	18%	60%	49%	11%	40%
Pilot-scale								
Baseline	6.34	7.40	21%	24%	45%	34%	11%	55%
Natural Oxidation	5.20	6.72	18%	23%	52%	40%	12%	48%
Ferric Chloride	4.80	14.02	10%	24%	60%	46%	14%	40%

Iron and Manganese

Iron remained completely in the solid phase throughout pilot testing, as would be expected. Table 6-8 shows the iron concentrations and the phase partitioning for iron in the bulk absorber slurry as well as in the hydrocyclone overflow and underflow streams during blowdown events. Iron enrichment in the fines was high with roughly 70 to 90% of the absorber slurry iron reporting to the HCOF solids.

Table 6-8
Iron Phase Partitioning in Bulk Pilot Absorber Slurry, HCOF, and HCUF Streams

		Bulk Absorber Slurry			HC Underflow		HC Overflow		
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**	**% of Solid Fe in HCOF solids**
Baseline									
	0		1889	6.1					
	84		2222	11.3	599	61.0	9232	2.7	79%
	123	<538	2854	11.3	674	59.7	8376	3.4	82%
Natural Oxidation									
	0		1575	7.0					
	26		1534	11.0	568	63.0	4499	3.1	72%
	69		1857	10.2	568	62.0	6815	2.6	76%
	121	<543	2212	11.3	652	60.9	6142	3.4	78%
Ferric Chloride									
	0	<278	1860	9.0					
	38	<275	2593	15.0	833	61.9	4646	5.9	79%
	68	<273	2797	12.7	503	60.6	16,017	2.5	85%
	114	<275	5986	12.7	640	61.1	21,461	4.0	92%

During all tests, the manganese remained predominantly in the oxidized Mn(IV) solid state. Table 6-9 shows the manganese concentrations and the phase partitioning for manganese in the bulk 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 HCOF. Manganese enrichment in the fines is higher than selenium, but lower than iron.

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

		Bulk Absorber Phase Partitioning				HC Underflow		HC 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 HCOF solids
Baseline										
	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	1506	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										
	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	

Mercury

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

The capture and re-emissions of mercury across the scrubber are summarized in Table 6-10. The mercury removal across the scrubber is calculated as a percentage of total inlet mercury, and the mercury re-emissions is the percentage of inlet oxidized gas-phase mercury that is chemically reduced in the scrubber and re-emitted as elemental gas-phase mercury. The inlet gas mercury averaged above 90% oxidized mercury, with concentrations of total mercury typically at or below 5 µg/Nm^3. 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 6-10
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%

Detailed material balance calculations for the three five-day tests revealed that roughly 50% of the mercury capture from the flue gas slipstream reported to the slurry liquor under baseline and natural oxidation conditions. In the full-scale absorber, approximately 90% of the mercury reports to the slurry liquor, so the pilot baseline conditions show a lower fraction of mercury reporting to the liquor. Material balances also indicated that during the ferric chloride test, nearly all mercury accumulating from the flue gas into the pilot slurry reported to the solid phase.

Table 6-11 shows the mercury concentrations and the phase partitioning for mercury in the bulk pilot absorber slurry as well as in the hydrocyclone overflow and underflow streams during blowdown events. The final mercury concentration in the bulk absorber solids during the ferric chloride test indicates the complete reporting of "new" mercury to the absorber solids. The data also show that the mercury is preferentially reporting to the fine particulates, which may support the hypothesis that mercury associated with the enriched iron fractions in the fines during the ferric chloride test.

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

		Bulk Absorber Phase Partitioning				HC Underflow		HC Overflow		
Test	Run Time (h)	Hg in Liquor (µg/L)	Hg in Solids (µg/g)	Wt % Solids	% Hg in Solids	Hg in Solids (µg/g)	Wt % Solids	Hg in Solids (µg/g)	Wt % Solids	% of Solid Hg in HCOF solids
Baseline										
	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										
	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%

Mercury was measured in the solid absorber slurry samples that were wet-sieved to produce fractions comprising 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 for mercury are presented in Figure 6-9 and Table 6-12. The mercury wet sieve results are consistent with the mercury measurements in the HCOF and HCUF 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 particulates.

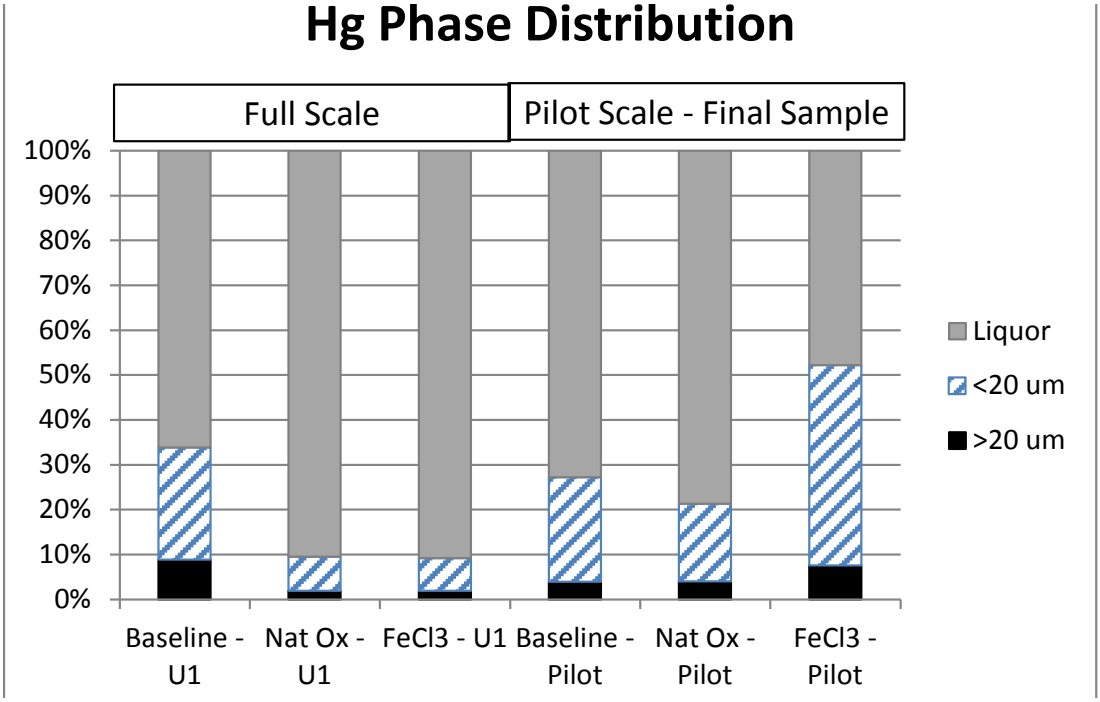

Figure 6-9
Mercury Phase Partitioning in Full-scale and Pilot-scale Absorber Samples

Table 6-12
Solid-phase Mercury Results in Wet-Sieved Samples

Master Sample	Hg Conc. (>20 µm)	Hg Conc. (<20 µm)	<20 µm	<20 µm	% Hg in Solids	% Hg in >20 µm	% Hg in <20 µm	% Hg in Liquor
	µg/g	µg/g	wt% of solids in size range	% of solid Hg	% total Hg	% total Hg	% total Hg	% total Hg
Full-scale								
Baseline	<0.052	0.63	81%	19%	34%	9%	25%	66%
Natural Oxidation	0.053	1.08	84%	16%	10%	2%	8%	90%
Ferric Chloride	<0.041	0.61	80%	20%	9%	2%	7%	91%
Pilot-scale								
Baseline	0.056	1.22	79%	21%	27%	4%	23%	73%
Natural Oxidation	0.067	1.26	82%	18%	21%	4%	17%	79%
Ferric Chloride	0.100	5.48	90%	10%	52%	8%	45%	48%

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, halogens, and secondary sulfur species (e.g., dithionate and peroxydisulfate) were monitored. 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 low ORP attempt. Limestone utilization remained above 96% in all tests. Dithionate and peroxydisulfate were monitored; little accumulation or reaction 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

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 "new" 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 particulates.
- Selenium enrichment in the fine particulates 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 particulates. 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, levels of sulfite formed 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.
- 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 ppb 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 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 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 particulates in the FGD chloride purge stream, where subsequent precipitation of the mercury 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. 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 ppmw Mn + baseline
Mn + DBA	35 ppmw Mn + 1000 ppmw DBA + baseline
Mn + Acetic Acid	35 ppmw Mn + 1000 ppmw 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
	Nalco 14850	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
	Nalco 14850	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 additives (ferric chloride, ferric chloride with copper sulfate, Nalco 14850, 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.

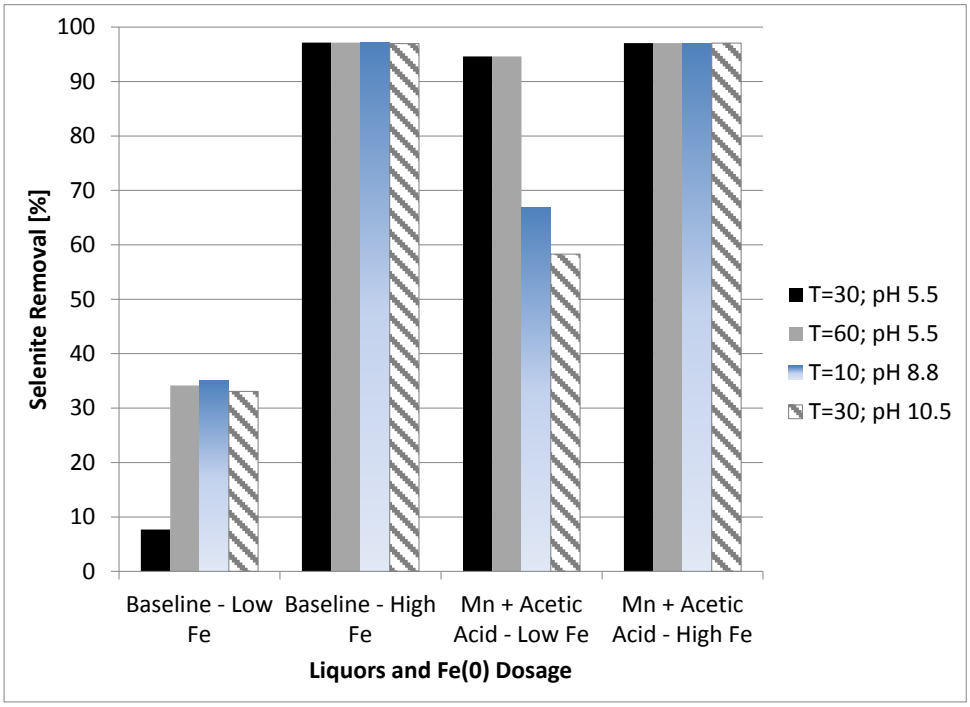

Figure 7-1
Selenite Removal in Synthetic Liquors with Elemental Iron

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.

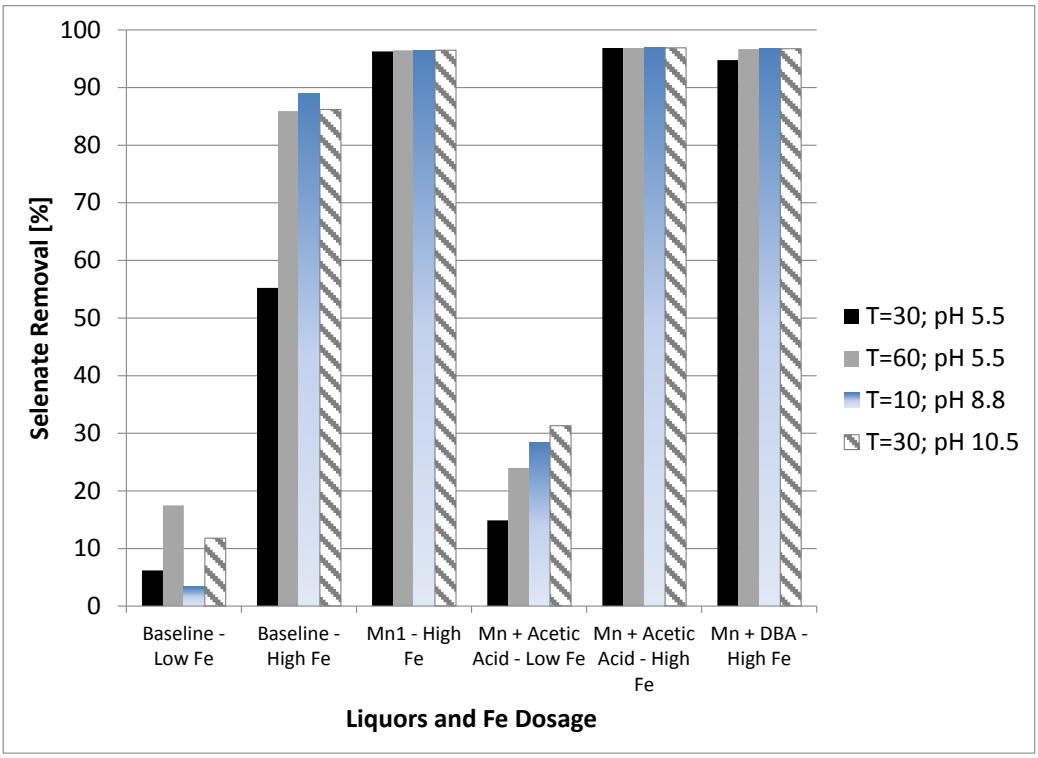

Figure 7-2
Selenate Removal in Synthetic Liquors with Elemental Iron

Tests in Field Liquors

At the end of the field pilot-scale tests, a portion of the final hydrocyclone overflow (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	Nalco 14850	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.

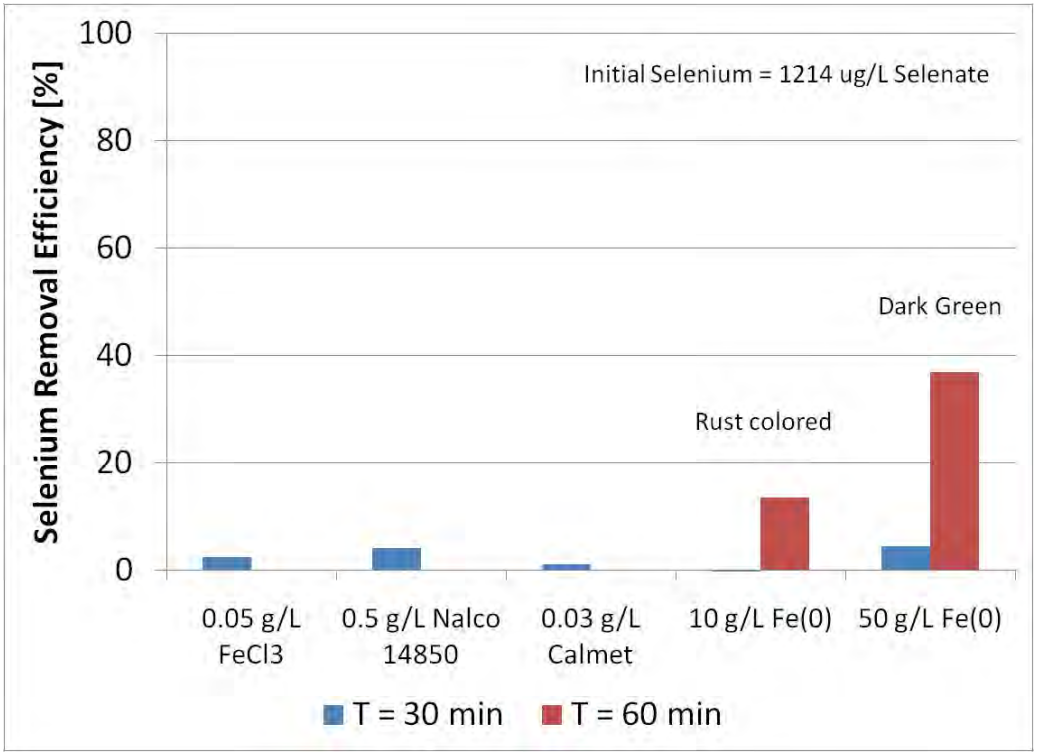

Figure 7-3
Beaker-scale WWT Test Results using Final HCOF sample from Baseline Pilot-Scale Test

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
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, AA, AF, 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 in selenium speciation in synthetic FGD liquors. Several bench-scale scrubber tests were conducted in 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 ppm 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 particulates (“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 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.

Recommendations

As future regulations may limit selenium discharges in the low ppb 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 [6,7]. 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 only by FGD chemistry but also by mist or aerosol formation, which occurs because the temperature range for the selenous acid dewpoint coincides with the inlet quench temperatures of FGD scrubbers [8]. 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 interconversion 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.

9
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