FGD Additives to Segregate and Sequester Mercury in Solid Byproducts

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EXECUTIVE SUMMARY

A number of mercury control strategies for U.S. coal-fired power generating plants involve co-benefit capture of oxidized mercury from flue gases treated by wet flue gas desulfurization (FGD) systems. For these processes to be effective at overall mercury control, the captured mercury must not be re-emitted to the atmosphere or into surface or ground water.

The original approach proposed under this project sought to manipulate operating conditions and apply chemical additives within the FGD scrubber such that absorbed mercury remained in the slurry liquid phase and was not re-emitted back into the FGD outlet flue gas. Mercury would exit the FGD system in the chloride purge stream and would subsequently react with precipitating agents to form stable solid byproducts. These solids would be removed via a dewatering step. Thus, the mercury would be captured and concentrated into a small solid waste stream. The FGD gypsum solids formed in the absorber, free of most of the mercury, could then be disposed or processed for reuse as wallboard or in other beneficial reuse such as land application.

The overarching goal of the project was to identify scrubber additive(s) and to define an operating range for FGD scrubbers under which mercury re-emissions would decrease and mercury would remain in the liquor and be blown down from the system in the chloride purge stream. The first step toward this goal comprised extensive bench-scale FGD scrubber tests in Phases I and II of the project. Then, during Phase II, the approaches developed at the bench scale were tested at the pilot scale using an existing skid-mounted pilot wet FGD system. Laboratory wastewater treatment (WWT) tests were conducted to measure the performance of precipitating agents in removing mercury from the chloride purge stream. Finally, the economic viability of the approaches tested was evaluated.

The Phase II bench-scale scrubber test campaign investigated the impacts on mercury behavior of the following FGD parameters: the form and concentration of iron, halogen concentrations, synthetic versus natural limestone, pH, oxidation-reduction potential (ORP), organic carbon, manganese, and several scrubber additives. The bench-scale test program comprised nearly 60 runs ranging in duration from 6 to 32 hours.

The important influence of ORP on mercury phase-partitioning behavior was identified and demonstrated at the bench scale. Increasing the ORP tends to increase the percentage of mercury reporting to the slurry liquor and decrease the percentage reporting to the slurry solids.

Bench-scale testing demonstrated that the limestone used for pH control in FGD systems plays an important role in mercury behavior. Redox-active trace metals, such as iron and manganese, can enter FGD systems as limestone impurities and subsequently catalyze redox reactions and influence the sorption and precipitation of mercury to the slurry solid phase. Other properties of the limestone may influence mercury behavior as well, but were not documented as part of this project.

Numerous scrubber additives were tested in the laboratory under various operating conditions for their ability to complex mercury in the scrubber liquor. No additive showed high fractions of mercury reporting to the slurry liquid phase in tests with natural limestone and total slurry metals concentrations that are typical of full-scale scrubber slurries, or in bench-scale tests with field-

generated slurries. Some additives (e.g., dibasic acid) might be successful for full-scale systems that have low concentrations of redox-active metals, as a result of having less impurities in the limestone and/or having relatively high liquor purge rates.

Bench-scale tests revealed that management of trace metals and metalloids, such as mercury and selenium, is intertwined. While increasing the ORP may be desirable for managing one species, it could be undesirable for managing another species. Management of mercury and selenium may require a holistic approach that uses both ORP and scrubber additives to establish 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. Several bench-scale tests were conducted to measure mercury and selenium behavior simultaneously in an attempt to develop such a holistic approach.

In bench-scale tests in which ferric chloride was added to the scrubber, mercury re-emissions were reduced and the percentage of mercury reporting to the solid phase increased. Though counter-intuitive to the original premise of this program, the results were promising because the mercury preferentially reported to the small solid particles (i.e., "fines") in the slurry. These small particles may exit with the chloride purge stream for systems that employ hydrocyclones for primary dewatering and, in effect, achieve the same goal as retaining mercury in the liquid phase – lowering the mercury content of the product gypsum. Ferric chloride sorbed selenite to the solid phase before the selenite could be oxidized to the undesirable selenate species, which is difficult and costly to remove from FGD waters.

Pilot-scale FGD scrubber testing continued work to develop a strategy that would manage both mercury and selenium behavior in wet FGD systems; the behaviors of both species were measured during pilot testing. Funding for the pilot scrubber testing was provided by this grant and a concurrent research project conducted by project team members on selenium control in FGD systems ("Selenium Speciation and Control Technologies in Sulfate-Rich Wet FGD Systems" funded under Phase II SBIR DOE Grant No. DE-FG02-08ER84948); the pilot test campaign was longer than either program could have supported individually.

Three test conditions were attempted during pilot-scale FGD scrubber testing: high ORP, low ORP, and ferric chloride addition. The first attempt to operate at low ORP conditions ended after one day of operation due to an unplanned outage at the host site facility; that test was repeated later and conducted for the entire five-day duration. However, low ORP conditions were not attainable with reduced load operation of the host site unit which was encountered during this test; therefore, the second test became a natural oxidation test. Oxidation air was turned off within a few hours of beginning the test, yet ORP remained high, above 400 mV, throughout the test.

Mercury phase partitioning between the solid and liquid phases of the slurry was similar under baseline (high ORP) and natural oxidation conditions, most likely because the resulting ORP conditions ended up being similar for the two tests. As with the bench-scale tests, pilot-scale tests with ferric chloride addition indicated that mercury preferentially reports to the slurry fine particles. No decrease in gypsum mercury concentration compared to previous operation was measured by the end of this test; however, mercury concentrations were trending down over time, and it is possible that with continued operation some benefit may have been observed. The three five-day tests showed similar mercury capture across the scrubber, although the natural

oxidation test showed slightly lower mercury capture and slightly higher re-emissions. However, the variability in capture and re-emissions for all tests prevents reaching strong conclusions regarding the impact of ORP and ferric chloride addition on mercury capture and re-emissions. Units that cycle load over a wide range may find it more difficult to control ORP with oxidation air control.

Decreasing oxidation air rates shifted selenium phase partitioning to the solid phase of the scrubber slurry during pilot testing. It was not possible to demonstrate a benefit to selenium behavior by adding ferric chloride to the scrubber because all "newly absorbed" selenium reported to the solid phase in the natural oxidation (reduced oxidation air rate) test, and no further improvement could be demonstrated. Selenium enrichment in the fine particles was modest or negligible. Under low ORP conditions, selenite formed and remained in the slurry liquid phase. However, under these conditions at the pilot scale, concentrations of sulfite remained in the absorber liquor that are undesirable for forced oxidation systems. Because the test was cut short, it was not possible to demonstrate whether appropriate sulfite oxidation levels could be achieved while retaining selenium as selenite in the liquor.

In laboratory wastewater treatment tests, several additives showed high mercury removal performance in synthetic and field liquors, down to concentrations less than 100 nanograms per liter (ng/L). Additional testing with revised additive dosages and revised analytical detection limit targets would be required to demonstrate removal of mercury down to the latest anticipated effluent limits of ~10 ng/L.

Bench-scale tests conducted early in the research program indicated that bromide showed promise for retaining mercury in the liquid phase of synthetic FGD slurries. During 2010, the engineering and economic evaluation was updated for bromide addition to FGD scrubbers. With updated reagent prices, the loss of bromide in the FGD chloride purge stream or "blowdown" was cost-prohibitive; therefore, methods and costs for recovering bromide from the blowdown were evaluated and incorporated into the economic evaluation. In early 2011, bromide was eliminated from further consideration as a scrubber additive due to corrosion concerns based on recent experience in many new U.S. utility FGD systems.

Addition of ferric chloride to FGD scrubbers may provide one option for managing mercury and selenium, given several caveats presented in this report. Therefore, the capital and operating costs for ferric chloride addition were estimated. As would be expected, the reagent makeup costs dominate the economic evaluation and range from approximately 0.22 to 0.29 mills/kWh. Impacts on gypsum formation and salability require further evaluation.

Control of the oxidation air flow rate into the FGD scrubber reaction tank is one option for managing the redox chemistry in FGD scrubbers, though air control alone may be insufficient for some systems. A cursory comparison of capital costs and turndown capabilities for two blower types (i.e., multi-stage and single-stage centrifugal blowers) and several flow control methods was completed. For greenfield systems, changing the selection of blower type and flow control method may have long payback periods if based on energy savings alone. However, the benefits to managing redox chemistry in the scrubber could far outweigh the savings in electricity costs under some circumstances. The ability to improve flow control for retrofit applications is particularly case-specific for multi-stage centrifugal blowers.

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PHASE II PROJECT NARRATIVE

Background

A number of mercury control strategies for U.S. coal-fired power generating plants involve co-benefit capture of oxidized mercury from flue gases treated by wet flue gas desulfurization (FGD) systems. For these processes to be effective at overall mercury control, the captured mercury must not be re-emitted to the atmosphere or into surface or ground water. Measurements reported by URS Group in 2003 indicated that nearly all of the mercury scrubbed from flue gas in many U.S. wet FGD systems ends up in the solid byproducts (EPRI, 2003). Later field measurements taken from a wider variety of limestone forced oxidation (LSFO) scrubbers have shown that the partitioning of mercury between the solid and liquid phases of scrubber slurries is more variable than originally thought (Richardson, 2008). At the project commencement, the factors that influence mercury partitioning between the two phases were not well established; the research supported under this program sought to understand and manage the factors that control the distribution of mercury between re-emitting to the atmosphere, partitioning to the liquid discharges, and partitioning to the solid byproducts of LSFO FGD systems.

In wet FGD absorbers, the oxidized form of mercury (Hg^{+2}) is absorbed from the flue gas into the FGD liquor, while water insoluble elemental mercury (Hg^{0}) is typically not removed. Once absorbed, the oxidized mercury can follow several pathways through the FGD system. The mercury can 1) Undergo chemical reduction reactions while in the FGD liquor to form elemental mercury, which is insoluble and subsequently re-emitted into the FGD outlet flue gas; 2) Partition into the FGD liquor, and potentially become a regulatory compliance issue in FGD blowdown liquor; or 3) Partition into the FGD byproduct solids.

Pathways 1 and 2 are environmentally unfavorable, and pathway 3 may also be problematic depending on the fate of the mercury in the FGD byproduct solids. It is estimated that 70 % of all the FGD byproduct reuse in the U.S. is gypsum used as wallboard feedstock. Testing by URS Group at a number of wallboard production facilities utilizing a variety of byproduct gypsum sources showed appreciable mercury loss, ranging from 2 – 55% of the mercury present in the gypsum, during the wallboard production process (Sanderson, 2007). Furthermore, the presence of the remaining mercury in the wallboard leads to concern over end user exposure to mercury over the life cycle of the wallboard.

In essence, the problem is to capture the mercury before it can be re-emitted from the FGD system and then to concentrate and sequester it in the form of a solid stream, separate from the byproduct gypsum, that is stable enough to prevent release of mercury during subsequent disposal. This approach would help avoid mercury release issues when processing byproduct gypsum to manufacture wallboard, during wallboard end use, and during final disposal in a landfill.

Original Hypothesis and Technical Approach

The original approach proposed under this project sought to manipulate operating conditions and apply chemical additives within the FGD scrubber such that mercury reported to the slurry liquid phase and was not re-emitted back into the FGD outlet flue gas. In the original approach, mercury would exit the FGD system in the chloride purge stream, where the mercury could subsequently react with precipitating agents to form stable solid byproducts. These solids could be removed via a dewatering step. Thus, the mercury would be captured and concentrated into a small solid waste stream. The bulk FGD gypsum solids, free of most of the mercury, could then be disposed or processed for reuse as wallboard or in other beneficial reuse such as land application.

The original hypothesis postulated that scrubber additives could shift chemical reaction equilibria and kinetic mechanisms to result in lower mercury re-emissions from the FGD solution. The additive would also form a strong complex with oxidized mercury that would keep the mercury in the FGD liquor and prevent the mercury from precipitating or adsorbing on the byproduct gypsum solids.

The use of a complexing agent to reduce mercury re-emissions can be illustrated using chloride ion as an example. Re-emission of mercury is thought to occur through the reduction of mercuric ion to elemental mercury by bisulfite ion. The overall reaction can be represented as:

$$Hg^{+2} + HSO_3^- + H_2O \rightarrow Hg^0 \uparrow + SO_4^{-2} + 3H^+ \qquad (1)$$

The main pathway for this reaction may occur through formation of mercuric-sulfite complexes:

$$Hg^{+2} + SO_3^{-2} \leftrightarrow HgSO_3 \qquad (2)$$

$$HgSO_3 + SO_3^{-2} \leftrightarrow Hg(SO_3)_2^{-2} \qquad (3)$$

Excess sulfite favors the $Hg(SO_3)_2^{-2}$ species, but only $HgSO_3$ decomposes to produce elemental mercury:

$$HgSO_3 + H_2O \rightarrow Hg^0 \uparrow + SO_4^{-2} + 2H^+ \qquad (4)$$

Chloride interferes with this pathway by forming a chloro-sulfite complex, $ClHgSO_3^-$. The chlorosulfite complex can still decompose into elemental mercury, but at much slower rates. A second chlorosulfite complex, $Cl_2HgSO_3^{-2}$, may also form reversibly at higher chloride concentrations, but it is believed to decompose into elemental mercury much more slowly based on laboratory testing at URS. As a result, mercury re-emission is inhibited because the mercury is shifted to species that convert more slowly to elemental mercury or possibly not at all. Also, by forming a stable complex with oxidized mercury, the presence of high chloride concentrations can allow the mercury to remain in the FGD liquor and to not precipitate with or adsorb on the byproduct solids.

The overarching goal of the project was to identify scrubber additive(s) and to define an operating range for FGD scrubbers under which mercury re-emissions would decrease and mercury would report to the chloride purge stream. The first step toward this goal comprised extensive bench-scale FGD scrubber tests in Phases I and II of the project. The Phase I project tested the impacts of pH, sulfite concentration, additive type, and additive concentration. Three scrubber additives were tested: chloride, bromide, and commercially available water additive

("Additive A1". Use of Additive A1 caused a moderate decrease in mercury re-emissions but promoted mercury reporting to the slurry solids. Elevated concentrations of chloride and bromide eliminated mercury re-emissions and retained most mercury in the liquid phase.

During the latter part of Phase II, the approaches developed at the bench scale were tested at the pilot-scale using an existing skid-mounted pilot wet FGD system. Laboratory wastewater treatment (WWT) tests measured the performance of precipitating agents in removing mercury from the chloride purge stream, and the economic viability of the approaches was evaluated.

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

In the laboratory:

- Determine the minimum effective concentration of mercury complexing agents using bench-scale scrubber tests;
- Demonstrate the effectiveness of additional scrubber additives in reducing re-emission of elementary mercury from FGD scrubber solutions using bench-scale tests and, particularly, the effectiveness in maintaining complexed mercury in the liquid phase rather than allowing it to precipitate or adsorb on the byproduct gypsum solids;
- Building upon Phase I results, use laboratory-scale precipitation tests to establish optimal precipitation additive dosage, operating conditions, and other important parameters needed for the design of subsequent pilot-scale demonstration tests;

At pilot scale:

- Demonstrate the effectiveness of scrubber additives to reduce mercury re-emissions in coal combustion flue gas and to maintain complexed mercury in the liquid phase; and
- Demonstrate effectiveness of precipitation/filtration treatment approaches developed in Phase I and Phase II laboratory testing.

The Phase II project was originally divided into the following tasks:

Task 1: Bench-scale Scrubber Tests,
Task 2: Laboratory Precipitation and Byproduct Evaluation Tests,
Task 3: Pilot-scale Testing, Site 1,
Task 4: Pilot-scale Testing, Site 2,
Task 5: Engineering and Economic Evaluation, and
Task 6: Management and Reporting.

Task 1 included bench-scale FGD scrubber tests to explore the effects of scrubber operating conditions, liquor constituents, and scrubber additives on mercury complexation in and re-emissions from the scrubber liquor. In Task 2, laboratory-scale precipitation tests sought to optimize the dosage and operating conditions for successful Phase I mercury precipitation additives and to screen new precipitation additives. Tasks 3 and 4 included testing with an existing pilot-scale FGD unit to demonstrate the effectiveness of the mercury complexing and precipitation approach developed at the bench scale. Work under Task 5 included updating the

Phase I economic calculations and expanding the economic and engineering evaluation with approaches and operating conditions developed during Phase II. The final economic calculations conducted at the conclusion of the project reflect Phase II laboratory and field testing. Task 6 included project management and reporting.

Problems Encountered and Departures from Planned Methodology

Challenges Encountered During Bench-scale Scrubber Testing

Prior to commencing Phase II of the project, field measurements indicated that nearly all of the mercury scrubbed from flue gas in many U.S. wet FGD systems ends up in the solid byproducts (EPRI, 2003). In other words, either the mercury was re-emitted, or it reported to the slurry solids. Later field measurements taken from a wider variety of LSFO scrubbers revealed that the partitioning of mercury between the solid and liquid phases of scrubber slurries is more variable than originally thought (Richardson, 2008). It was important to understand the factors that caused this variability and to re-create conditions under which mercury reported completely to the slurry solids. Therefore, the "benchmark" or "baseline" mercury behavior selected for the program was complete reporting of mercury to the slurry solid phase, as was seen in many U.S. wet FGD systems.

The first step in the research process was to demonstrate this baseline behavior at the bench scale under conditions at which mercury has been observed to partition to the solid phase in full-scale scrubbers. Once these "benchmark" conditions were established in the laboratory, operating conditions could be adjusted and scrubber additives could be used to influence mercury behavior in the bench-scale test system with the hopes that similar changes could be effective at full scale. If the fundamental research carried out at the bench-scale showed promise, then the approach would be tested at the pilot scale.

Throughout the beginning of the project and into mid-2010, the "benchmark" conditions under which mercury would consistently and completely partition to the solid phase in bench-scale tests were difficult to establish, despite running at conditions which appear to favor solid-phase partitioning in full-scale systems. Section 3 presents details of the factors and hypotheses tested during this time. As a result of these challenges, pilot testing was delayed and the project period of performance was extended by one year. Bench-scale testing was paused, and a literature review was conducted to identify additional factors for consideration and testing at the bench scale. The literature review confirmed some earlier hypotheses held by project team members: that solid-phase iron is expected to impact mercury phase partitioning behavior. The literature review also revealed the complexity of mercury interactions with other species commonly present in wet FGD systems. Mercury phase-partitioning behavior is influenced not only by the presence and concentration of liquid-phase and solid-phase constituents, but also by the surface characteristics of the slurry solids and by the phase-change behavior of other, non-mercury species.

During the Fall of 2010, benchmark mercury behavior was observed in tests that used natural limestones, in lieu of synthetic reagents, for pH control of the bench-scale reaction tank slurry. Section 3 discusses these results and the possible reasons why natural and synthetic limestones impact mercury behavior differently.

Concurrent research conducted by project team members on selenium control within wet FGD systems has indicated that management of the scrubber oxidizing conditions and oxidation air flow, as measured by the oxidation-reduction potential (ORP), can significantly impact the behavior of trace metals and metalloids such as mercury and selenium. Though ORP was monitored in earlier testing, the significance of its impact was not recognized until later in the program. The bench-scale test method was modified to control ORP by controlling the oxidation air rate fed to the bench-scale scrubber reaction tank.

In December 2010, a work plan modification was requested and granted. The modification extended the bench-scale test campaign and consolidated pilot testing from two sites to one site. The total project budget remained the same.

The extended bench-scale test campaign studied the impacts of ORP, other liquid- and solid-phase constituents, and four scrubber additives. Results from the extended test campaign demonstrated that, above a certain threshold value, increasing ORP tends to increase the fraction of mercury that reports to the slurry liquor. These results confirmed that controlling ORP, via oxidation air flow rate control and management of redox-active chemical species, is another important component of an overall strategy to manage trace metals and metalloids within wet FGD systems.

Challenges Encountered During Pilot-scale Scrubber Testing

Several challenges were encountered during pilot-scale scrubber testing.

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

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

Accomplishments

Bench-scale Testing

The Phase II bench-scale scrubber test campaign investigated the impacts on mercury behavior of the following parameters: the form and concentration of iron in the absorber slurry, halogen concentrations, pH, synthetic versus natural limestone, ORP, organic carbon, manganese, and several scrubber additives. The bench-scale test program comprised 49 standard-length (6-hour) tests, seven intermediate-length (8- to 10-hour) tests, and two successfully completed extended-length (32-hour) tests.

Key accomplishments of the bench-scale test program include the following:

- The important influence of ORP on mercury phase-partitioning behavior was demonstrated at the bench scale.
- Bench-scale testing demonstrated that the limestone used at FGD facilities plays an important role in mercury behavior, influencing mercury behavior in several ways. Redox-active trace metals, such as iron and manganese, can enter FGD systems as limestone impurities. These redox-active metals influence the ORP conditions of the scrubber, can catalyze redox reactions, and can influence the sorption and precipitation of mercury to the solid phase. Additionally, mercury behavior is affected not only by the presence and concentration of the trace metals, but also by the form and surface characteristics of the solid metal species.
- Numerous scrubber additives were tested under various operating conditions for their ability to complex mercury in the scrubber liquor. Some scrubber additives did increase the fraction of mercury reporting to the liquor in (1) tests with synthetic solids and (2) in tests with natural limestone and at low metals concentrations; however, no additive showed high fractions of mercury reporting to the slurry liquid phase in tests with natural limestone and total slurry metals concentrations that are typical of full-scale scrubber slurries or in bench-scale tests with field-generated slurries. Some additives (e.g., dibasic acid [DBA]) might be more successful for full-scale systems that have lower levels of redox active metals as a result of less carryover of fly ash into the FGD system, less impurities in the limestone reagent, and/or higher liquid purge rates from the FGD system.
- Bench-scale tests revealed that management of trace metals and metalloids, such as mercury and selenium, is intertwined and that a holistic management strategy is required. Decreasing the ORP favors the retention of selenium removed from the flue gas as selenite, a form that is more easily removed in conventional FGD WWT systems than the more highly oxidized selenate form. Thus, for selenium management, lower ORP is desirable. However, for mercury management, higher ORP may be desirable to promote mercury partitioning into the liquid phase of the FGD slurry, which would favor the current project's goal of minimizing the mercury content of the gypsum byproduct. Therefore, management of mercury or selenium may require a holistic approach that uses both ORP and scrubber additives to establish an operating range that maintains SO_2 removal performance, avoids selenite oxidation to less desirable species, and minimizes the amount of mercury entering the FGD byproduct gypsum stream.
- Bench-scale tests that simultaneously monitored mercury and selenium behavior suggested one possible holistic management strategy. Addition of ferric chloride to the scrubber reduced mercury re-emissions and increased mercury reporting to the solid phase. Though counter-intuitive to the original premise of this program, the results were promising because the mercury preferentially reported to the small solid particles (i.e., "fines") in the slurry. These small particles may exit with the chloride purge stream for systems that employ hydrocyclones for primary dewatering and, in effect, achieve the same goal as retaining mercury in the liquid phase. Ferric chloride sorbed selenite to the solid phase before the selenite could be oxidized to the undesirable selenate species, which is difficult and costly to remove from FGD waters.

Pilot-scale Testing

Key accomplishments of the pilot-scale scrubber tests are the following:

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

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

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

Laboratory Wastewater Treatment Tests

Laboratory wastewater treatment tests demonstrated that several commercially-available additives (Additive C1, Additive C2, and Additive B1; TMT-15; and Calmet) show high mercury removal performance in synthetic and field liquors to control mercury concentrations below 100 ng/L. Field liquors were generated during pilot testing. Additional testing with revised additive dosages and revised analytical detection limit targets would be required to demonstrate removal of mercury down to the latest anticipated effluent limits of ~10 ng/L.

Engineering and Economic Evaluation

- As part of the engineering and economic evaluation, costs were developed for bromide addition to the scrubber, which included high-level process design of an additive recovery

system. However, industry members began raising concerns with pitting corrosion apparently related to halogen concentrations in FGD absorber liquor in late 2010 and early 2011, and bromide was eliminated from further consideration.

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

Technology Transfer Activities

Selected results describing mercury behavior observed in bench-scale and pilot-scale testing were presented in conjunction with observations of selenium behavior at two conferences during 2011. Citations for the two papers are the following:

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

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

2
BENCH-SCALE FGD SCRUBBER TESTS – EXPERIMENTAL APPROACH

Test Apparatus and Method

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

The reaction tank pH is controlled by makeup of either 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.

The reaction tank can be operated in inhibited, natural or forced sulfite oxidation modes. All tests discussed in this report involved operation in the forced oxidation mode. In limestone forced-oxidation wet FGD systems, the liquor sulfite concentration is controlled to low concentrations, typically less than 1.0 mM (80 mg/L), with the oxidation air rate. Oxidation air is sparged through the reaction tank; the air flow rate may be adjusted manually or controlled automatically up to approximately 6 L/min based on operating parameters. Oxidation air control was added and improved during the Phase II program. Phase I tests used hydrogen peroxide rather than air to control oxidation.

As the Phase II project proceeded, the importance of the ORP to mercury behavior became apparent, and ORP, rather than sulfite concentration, became 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. Tests 35 to 56 controlled the air rate directly based on ORP values; Tests 1 to 34 controlled sulfite to below 1.0 to 2.0 mM. All ORP measurements shown or discussed in this report are relative to a silver/silver chloride reference electrode in 4-M potassium chloride. The reported values should have 200 mV added to put them relative to a standard hydrogen electrode, or 41 mV subtracted to put them relative to a saturated calomel electrode (SCE).

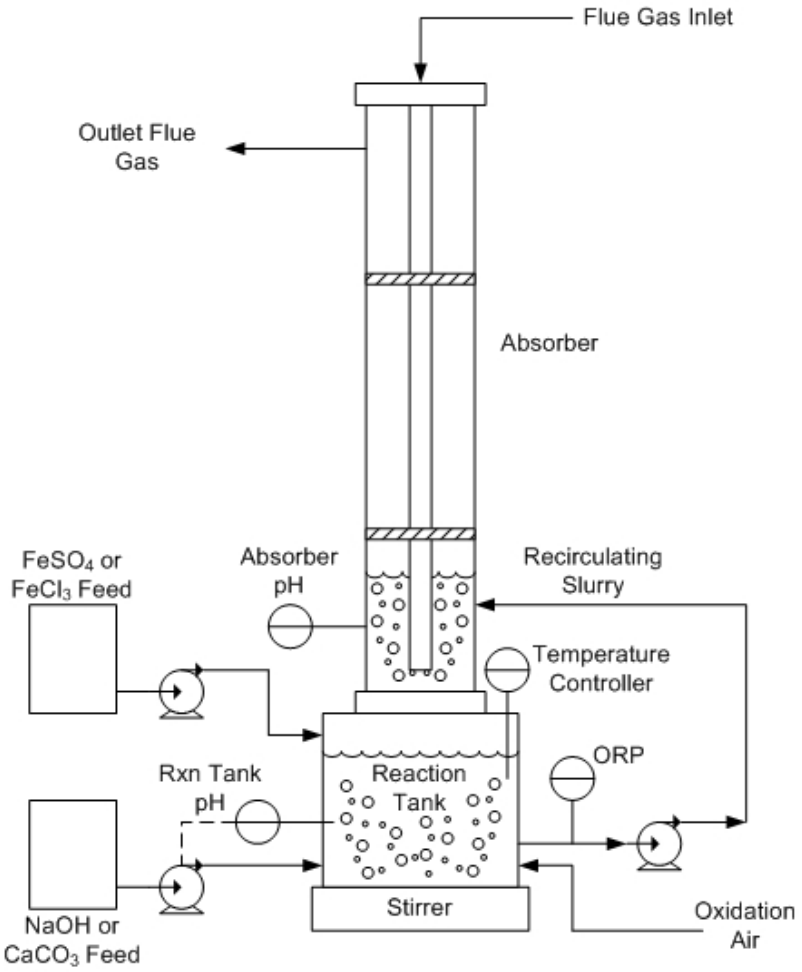

Figure 2-1
Schematic of Bench-scale Wet FGD Scrubber System

Simulated flue gas is mixed from a variety of compressed gases using calibrated rotameters. Figure 2-2 shows the simulation gas mixing apparatus. The dry simulation gas typically contains SO_2, NO_X, HCl, CO_2, oxygen, and nitrogen. Moisture is added to the simulation gas by feeding the oxygen, CO_2, and a portion of the dry nitrogen gas through a water saturator, which is maintained at a predetermined pressure and temperature to achieve the desired humidity level in the wet gas mixture.

Either oxidized or elemental mercury is added to the gas by passing a portion of the dry nitrogen gas makeup through a mercury diffusion cell. The diffusion cell contains either an elemental mercury permeation tube or mercuric chloride ($HgCl_2$) crystals maintained at an elevated temperature (115^o-140^oF). For all tests reported here, the simulation gas was spiked only with oxidized mercury. In actual practice, the oxidized mercury source produces a small amount of elemental mercury in the simulation gas; about 5% of the total mercury in the flue gas entering

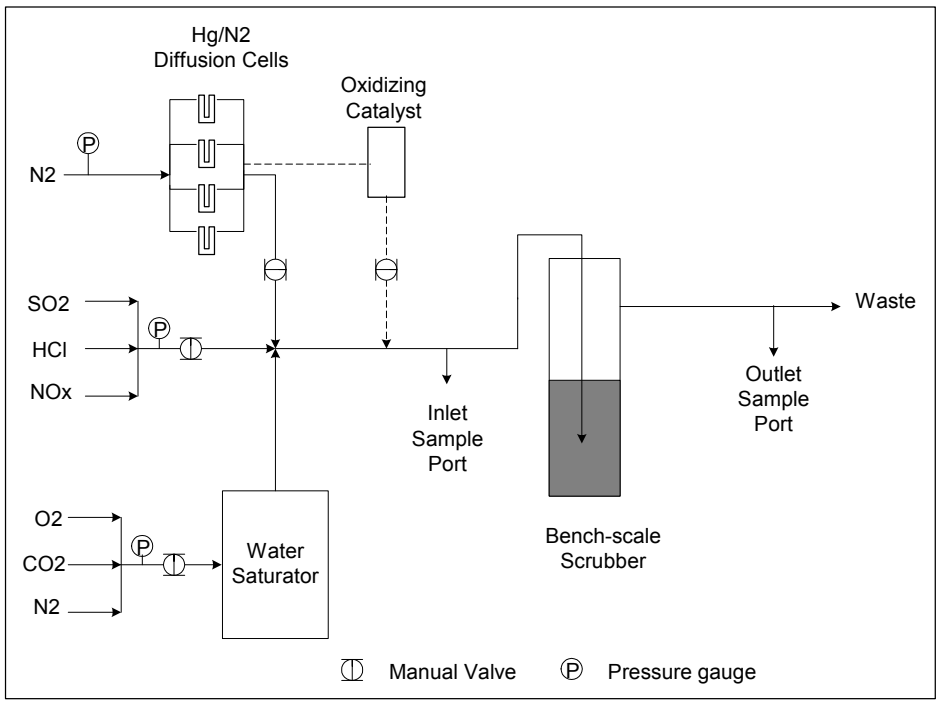

Figure 2-2
Bench-scale Simulated Gas Mixing Apparatus

the scrubber is in the elemental form. Four parallel mercury diffusion cells, each containing mercuric chloride crystals, provide the mercury content of the simulation gas.

The simulated flue gas delivery system to the bench-scale wet FGD system is designed to avoid mercury loss and contamination. A heat-traced simulation gas delivery line allows the use of replaceable Teflon tubing (to deal with any potential mercury contamination), and all fittings and valves in the system have either Teflon or quartz components.

Table 2-1 lists the baseline conditions for bench-scale scrubber tests. 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. Additional chemical species may be spiked into the reaction tank at the beginning of the test, or they may be added gradually as a solution or slurry using a makeup pump. In this manner, a solution containing iron as ferrous sulfate may be added gradually to simulate limestone iron impurities.

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

Parameter	Units	Value
General:		
Reaction Tank pH	-	5.5
Temperature	ºF	131
Liquid Composition:		
NaCl	mM	100
Ca^{2+}	mM	15
$MnSO_4$	mM	0.01
Na_2SO_4	mM	50
Slurry recirculation rate	gpm	~0.3
Solids:		
$CaSO_4$ -2 H_2O	wt%	8
Gas Phase:		
$HgCl_2$	μg/Nm^3	15-30
Hg^0	μg/Nm^3	0.5
CO_2	%	12
O_2	%	3
N_2	balanced	balance
SO_2	ppmv	1000
HCl	ppmv	15
NO_x	ppmv	0
Total Flow	actual L/min	24
Oxidation air rate	L/min @ 60ºF, Patm	≤6

Whereas many Phase I tests began with a simpler clear liquor charge to the reaction tank, all Phase II tests began with an initial charge of solids intended to represent gypsum present in forced oxidation FGD slurries. Tests 1 through 28 used anhydrous calcium sulfate. Review of the literature indicated that anhydrite hydration kinetics to calcium sulfate dihydrate (gypsum) can be slow; therefore, Test 29 and onward used synthetic gypsum as the initial solids charge because LSFO systems produce gypsum, the dihydrate, rather than anhydrite under normal operating conditions. It was unknown what, if any, impact this change would have on the bench-scale results. Synthetic reagents can have different particle size distributions and surface characteristics from their natural counterparts. It was unknown whether the difference between reagent anhydrous calcium sulfate and reagent calcium sulfate dihydrate was significant when

compared to any differences that also exist between reagent calcium sulfate dihydrate and the gypsum produced in full-scale FGD scrubbers.

Typically the simulated scrubber solution is made up with all ingredients added, including trace elements. The reaction tank solution is heated to the steady-state temperature, then acid gas flow through the absorber is started. The pH and sulfite or ORP control are stabilized. When the system is at steady operation, baseline (time = 0) samples are collected. Next, flow of gas-phase mercury is directed to the inlet flue gas mixing system, and the test begins. Gas-phase mercury entering and exiting the bench-scale scrubber is measured semi-continuously, and sulfur dioxide removal across the scrubber is measured periodically. Gas-phase analytical methods are described in the following subsection. Operating parameters (e.g., flue gas temperature, reaction tank temperature, absorber liquid height) are monitored periodically throughout the bench-scale tests. Slurry samples are taken at t = 0 and periodically during the test. Liquid samples were filtered through either 0.45-µm or 0.22-µm pore size filters.

Standard-length tests were conducted for a period of six hours from the time mercury flow to the system begins. For these runs, slurry samples were taken at three hours and six hours after starting mercury flow to the system. Phase II included 49 standard-length tests. In Phase II, seven intermediate-length tests were conducted (one 8-hour test and six 10-hour tests). For the intermediate-length tests, the slurry sample at t = 3 h was replaced by a final sample at t = 8 or 10 h. Three extended-length tests were attempted; of these, one was stopped after 24 hours, and two ran successfully through 32 hours. Slurry samples were taken at t = 0, 12 h, 24 h, and 32 h for extended-length tests.

During Phase II, the bench-scale test method was modified and improved. Methods of sulfite oxidation and ORP control were significantly improved, and the addition of mercury and iron into the system evolved. For example, earlier tests spiked reagent iron compounds and mercury into the reaction tank liquor at the beginning of the run. During all Phase II bench-scale scrubber tests, mercury accumulated gradually in the system via absorption of mercury from the inlet flue gas.

In tests that added iron reagents to the system, the iron was added gradually using a makeup pump. Ferrous sulfate was added via two methods. In the Tests 1 through 17, ferrous sulfate was added to the synthetic limestone slurry used for pH control. In Tests 18 to 25, ferrous sulfate was added directly to the reaction tank at a rate proportional to the synthetic limestone rate such that iron in the ferrous sulfate would equal an amount typical of iron impurities in FGD limestone. Two tests gradually added ferric chloride rather than ferrous sulfate directly to the reaction tank over the course of the test.

A few extended-length, 32-hour tests were conducted during the program. The 32-hour test length falls within the range of typical liquid residence times in full-scale FGD absorbers (24 to 72 hours). Based on assumptions for coal chloride, coal sulfur, and the baseline chloride concentration in the scrubber, a target dissolved mercury concentration was estimated. This mercury concentration assumed that all the mercury remained in the liquid phase, which may not occur under baseline conditions. The test length and conditions were selected to achieve this mercury input into the system within approximately 24 hours. The final eight hours of the test were intended to simulate the steady-state conditions of a full-scale unit. An hour-by-hour material balance was developed for the bench unit to establish water and salt makeup

requirements. Additionally, blowdown requirements after 24 hours were estimated in order to maintain a steady inventory of mercury in the scrubber system. These calculations set the amount of mercury leaving with the blowdown to be equal to the amount of mercury entering the slurry via absorption from the inlet flue gas.

Analytical Methods

Gas-phase mercury measurements were made using two mercury semi-continuous emissions monitors (SCEM) developed for EPRI, as illustrated in Figure 2-3. Flue gas samples were obtained from the bench-scale scrubber inlet or outlet gas at about 1 L/min through a series of impinger solutions using a Teflon-lined pump. To measure *total* mercury in the flue gas, these impinger solutions consist of stannous chloride ($SnCl_2$) followed by a sodium carbonate (Na_2CO_3) buffer and sodium hydroxide (NaOH). The $SnCl_2$ solution reduces all flue gas mercury species to elemental mercury while the latter impinger solutions remove acid gases, thus protecting the downstream, analytical gold surface. Gas exiting the impingers flows through a gold amalgamation column where mercury in the gas is adsorbed at less than 100°C. After adsorbing mercury onto the gold for a fixed period of time, the mercury concentrated on the gold is thermally desorbed (>700°C) from the column into nitrogen. The desorbed mercury is sent as a concentrated stream to a cold-vapor atomic absorption spectrophotometer (CVAAS) for analysis. Thus, the total flue gas mercury concentration is measured semi-continuously, typically with a one- to five-minute sample time followed by a one- to two-minute analytical period. To measure *elemental* mercury in the flue gas, the stannous chloride impinger is replaced with a potassium chloride (KCl) impinger. Two analyzers are used to semi-continuously monitor scrubber inlet and outlet gas mercury concentrations. The analyzers are switched intermittently between sampling for elemental versus total mercury concentrations.

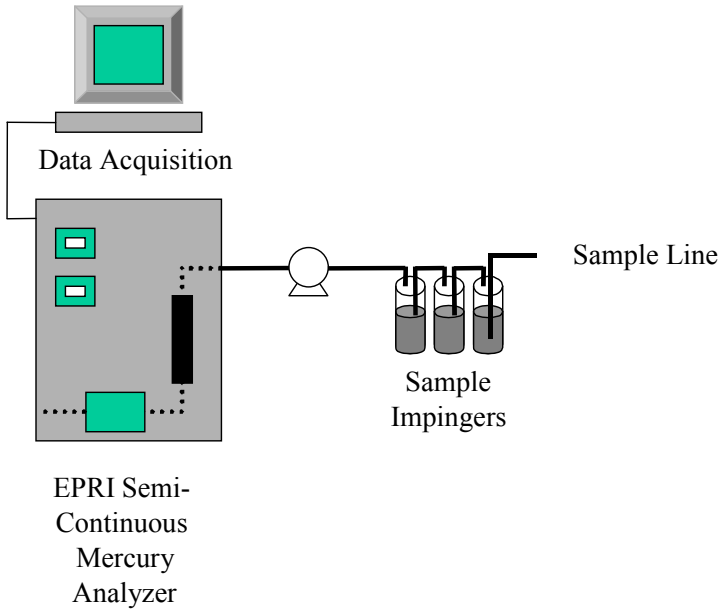

Figure 2-3
Schematic of Mercury SCEM

SO_2 removal across the absorber was quantified at the beginning and end of each test using SO_2 detection tubes. Overall SO_2 removal levels are typically 90% or greater at reaction tank pH of 5.5. For tests with solids, sulfite in the reaction tank was measured using manual iodometric titration with verification via ion chromatography of periodic samples.

3
BENCH-SCALE FGD SCRUBBER TEST RESULTS

Summary of Bench-scale Tests

The Phase II bench-scale scrubber test campaign investigated the impacts on mercury behavior of the following parameters: the form and concentration of iron added to the FGD slurry, halogen concentrations, pH, synthetic versus natural limestone used as a pH control reagent, ORP, organic carbon, manganese, and several scrubber additives. The bench-scale test program comprised 49 standard-length (6-hour) tests, seven intermediate-length (8- to 10-hour) tests, and two successfully completed extended-length (32-hour) tests.

The first challenge of the bench-scale program was to establish and demonstrate baseline mercury behavior. At project commencement, available field data indicated that mercury in most U.S. LSFO FGD systems reports completely to the scrubber slurry solids (EPRI, 2003). Subsequent data, which were sampled from a wider range of FGD systems, indicated that mercury partitioning to the slurry solids varied over a much wider range, from 16% to 99.9% (Richardson, 2008). The premise of this project was to reduce the amount of mercury reporting to the byproduct gypsum. Therefore, the "worst" case baseline conditions are exhibited when essentially all mercury present in the slurry reports to the solid phase.

Project team members hypothesized that mercury partitioning to the solid phase can occur via two pathways: adsorption and co-precipitation. In adsorption, the mercury adsorbs onto a solid particle that already exists. In co-precipitation, the mercury is incorporated into the crystalline lattice as another liquid-phase species precipitates. Previously, several researchers, including project team member URS, have hypothesized and observed that mercury partitioning between the solid and liquid phase of FGD liquors correlates strongly with the presence of iron (Richardson, 2008; Higgins, 2009). Therefore, scrubber tests conducted early in the program focused on tests in which iron was added to the reaction tank and under a range of halogen concentrations. Phase I tests, using a different test method, had shown that elevated concentrations of chloride and bromide tended to retain more mercury in the liquid phase. Mercury would be expected to report to the solids under conditions with moderate or elevated iron concentrations in the slurry solids and low halogen concentrations in the liquor.

Roughly the first half of the program (26 tests) used synthetic limestone (reagent calcium carbonate, $CaCO_3$) for pH control. Of these tests, none demonstrated complete reporting of mercury to the solid phase of the bench-scale scrubber slurry despite adding a variety of reagent iron species via several methods and running tests of longer durations. This discrepancy was significant because complete reporting of mercury to the slurry solids was considered the baseline for the original technical approach of this research program, and it was imperative to determine and create, at the bench-scale, the conditions that lead to nearly complete reporting of mercury to the slurry solids.

Numerous hypotheses were postulated to explain why mercury behavior at the bench scale did not replicate behavior observed at full scale. A literature review was conducted to look for information on mercury-metal sorption, mercury speciation and surface characteristics in FGD

solid byproducts, and the impact of FGD constituents on mercury sorption. The literature review confirmed that other researchers have observed a strong association of mercury with iron in FGD gypsum solids, and that the form and surface characteristics of iron can influence iron-mercury interactions.

Because tests with high concentrations of reagent-grade ferrous and ferric salts did not show mercury reporting to the solid phase and the literature indicated that the form and surface characteristics of the solid phase impacted mercury sorption, the project team elected to use natural limestone in lieu of reagent calcium carbonate for pH control in several bench-scale tests. All but two of the final 32 bench-scale tests used natural limestone, sampled from the supply at a full-scale FGD system, for pH control. Tests with natural limestone demonstrated complete reporting of mercury to the slurry solids at low chloride concentrations (0.005 and 0.1 M Cl [180 and 3500 mg/L]), and thus demonstrated the "baseline" or benchmark behavior. Repeated tests with the natural limestone confirmed this behavior. Moderate concentrations of bromide (0.5 M [40,000 mg/L]) caused 20-27% of the recovered mercury to report to the liquid phase under some conditions tested. Increasing the chloride and bromide concentrations further resulted in modest increases in mercury partitioning to the liquid phase (28-45%).

Based on the promising results observed in tests with natural limestone, the bench-scale test campaign was extended. Several variables were selected for the extended test campaign. Concurrent research conducted by project team members on selenium control in FGD systems ("Selenium Speciation and Control Technologies in Sulfate-Rich Wet FGD Systems" funded under Phase II SBIR DOE Grant No. DE-FG02-08ER84948) has indicated that management of the scrubber oxidizing conditions and oxidation air flow, as measured by the ORP, can significantly impact the behavior of trace metals and metalloids such as mercury and selenium. Therefore, the extended bench-scale test campaign studied the impacts of ORP on mercury behavior. The tests also explored the impacts of chloride, manganese, organic carbon, and four additives on mercury partitioning behavior. The additional tests comprised nominally 14 tests conducted over a relatively short period in early 2011 and four additional tests that measured mercury and selenium behavior simultaneously. Most tests in the extended test campaign used natural limestone; all tests in the group used a higher total slurry concentration of manganese based on field measurements of manganese concentrations in FGD slurries taken in 2006 to 2009 (EPRI 2010).

Results from the extended bench-scale test campaign indicated that ORP significantly impacts mercury behavior in FGD scrubbers and that a holistic approach to mercury and selenium control is warranted. Above a threshold value, increasing the ORP increases the mercury fraction that reports the liquid phase of FGD slurry. ORP impacts the behavior of other trace species as well. For selenium management, lower ORP is desirable. However, for mercury management, higher ORP may be desirable to promote mercury partitioning into the liquid phase of the FGD slurry, which would favor the current project's goal of minimizing the mercury content of the gypsum byproduct. Therefore, research into mercury or selenium management may require a holistic approach that uses both ORP and scrubber additives to determine an operating range that maintains SO_2 removal performance, avoids selenite oxidation to less desirable species, and limits the amount of mercury entering the FGD byproduct gypsum stream.

The tests in the extended bench-scale test campaign also supported the following conclusions:

- Bromide showed limited promise in tests with natural limestone and with the revised, higher slurry manganese concentrations. Low concentrations of bromide showed little impact on mercury partitioning. Moderate concentrations of bromide showed modest increases in mercury liquor fractions for tests with low concentrations of transition metals.
- Several other scrubber additives were tested, but none caused substantial increases in mercury partitioning to the liquid phase in tests with natural limestone and at higher metals concentrations. DBA showed 87% of slurry mercury reporting to the liquid phase in tests with natural limestone and at low manganese concentrations and low ORP conditions. However, when the manganese concentration was increased, DBA showed <18% mercury reporting to the liquor, even at ORP conditions up to 275 mV. A test with citric acid as an alternative to DBA was attempted and stopped due to foaming in the bench-scale scrubber.
- Under the conditions tested, increasing scrubber liquor chloride concentration either has no effect on mercury partitioning or slightly increases the liquid-phase mercury fraction.
- Operating at a higher slurry concentration of manganese had no direct impact under the conditions tested, though the manganese present may have interacted with scrubber additives and thus indirectly affected mercury behavior.
- Organic carbon did not play a key role in mercury behavior under the conditions tested. The presence or absence of organic carbon in the natural limestone had little apparent impact on mercury partitioning. Adding one form of organic carbon to reagent calcium carbonate did not result in the same behavior exhibited under similar conditions in tests with natural limestone.

For tests using natural limestone, no scrubber additives tested have resulted in all or nearly all of the mercury reporting to the liquid phase. Results from bench-scale scrubber tests that monitored both mercury phase partitioning and selenium speciation raised questions surrounding the benefit of one additive, DBA, that had previously shown promise for mercury and selenium management.

The project team significantly reduced the research emphasis placed on bromide after learning in early 2011 that recent experiences in many new U.S. utility FGD systems have raised concerns that bromide would exacerbate corrosion issues, or at least would lessen the acceptance of bromide by the industry. Additional details supporting this change in approach are supplied later in this section.

Six bench-scale scrubber tests were conducted with samples of pilot-host-site slurries during April 2011. The purpose of these screening tests was to run test conditions at the bench scale that were under consideration for pilot testing. During these tests, the behavior of both selenium and mercury were monitored. Results from these tests confirmed that the percentage of mercury reporting to the liquid phase rather than to the solids increases with increasing ORP and vice versa. Selenite oxidation to the undesirable selenate species was inhibited by decreasing the ORP. Addition of ferric chloride to the scrubber reduced mercury re-emissions and increased mercury reporting to the solid phase; mercury preferentially reported to the smaller solid particles. A low dosage of ferric chloride sorbed all incoming selenite to the solid phase, although addition of ferric salts had no impact on selenate that already existed in the field slurry used as the initial charge to the bench-scale scrubber. Results from tests with DBA cast further doubt on the benefits of using DBA for mercury or selenium management in FGD scrubbers.

Tests with DBA resulted in mercury re-emissions and a percentage of mercury reporting to the liquid phase that fell between the baseline, high-ORP test and the low-ORP test results. The oxidation air rates during the DBA test were comparable to the air rates during the high ORP test; the DBA acted as a mild reductant. With that context, the DBA could actually be seen to reduce mercury partitioning to the liquid phase for operation at a given oxidation air rate. Additionally, in these tests with host site materials, DBA did not inhibit selenite oxidation percentages beyond what could be achieved simply by reducing the oxidation air rate. Though it may be possible for DBA to effect the desired mercury and selenium behavior for some systems, that behavior was not evident in bench-scale tests with synthetic liquors at elevated metals concentrations and in tests with field liquors.

The remainder of Section 3 provides data and discussion that support the above summary. Appendix A contains detailed sample analysis data from all Phase II bench-scale tests.

Tests with Synthetic Limestone

Roughly the first half of the program (26 tests) used synthetic limestone (reagent calcium carbonate, $CaCO_3$) for pH control in the bench-scale wet FGD tests conducted.

As noted earlier, field data showed some correlation between mercury and iron concentrations in the gypsum solids, with enrichment of iron and mercury in the smallest particles or “fines”. Therefore, scrubber tests conducted early in the program focused on tests in which iron was added to the reaction tank under a range of halogen concentrations. Phase I tests, using a different test method, had shown that elevated concentrations of chloride and bromide tended to retain more mercury in the liquid phase. Mercury would be expected to report to the solids with moderate or elevated iron concentrations in the slurry solids and with low halogen concentrations in the liquor.

Iron is a transition metal and may be present as elemental iron (0 oxidation state), ferrous iron (+2 oxidation state), and ferric iron (+3 oxidation state). Under the conditions typical of FGD scrubbers (pH 5.5 - 6.5 and oxidizing conditions), iron typically is present in the insoluble ferric state as ferric hydroxides.

Iron Addition Method #1

It was believed that iron enters an FGD system primarily as an impurity in the limestone reagent. Therefore, in Tests 1 to 17 iron was added with the synthetic limestone used for pH control. In this manner, the iron was added gradually over the course of the test. The test matrix for tests using this iron addition method is shown in Table 3-1. Tests 1 through 17 were six-hour tests, and these tests were conducted with an initial charge of reagent calcium sulfate (anhydrite) to achieve 8 wt% suspended solids in the reaction tank.

With this method, measurements revealed that virtually all of the soluble ferrous sulfate added to the calcium carbonate slurry was oxidized and precipitated to the solid ferric state prior to entering the bench-scale reaction tank. Thus, this test method accounted for adsorption of mercury onto solid iron particles, but not co-precipitation of mercury with iron.

Table 3-1
Bench-scale Scrubber Test Matrix with Iron Addition Method 1

Run #	Ferrous Sulfate Content in 5 wt% Limestone Slurry	Chloride (M)	Bromide (M)
Baseline Conditions	None	0.1	0
1	4000 µg Fe / g slurry	0.1	1
2	8000 µg Fe / g slurry	0.1	1
3	4000 µg Fe / g slurry	0.1	0.5
4	8000 µg Fe / g slurry	0.1	1
5	4000 µg Fe / g slurry	1	0
6	4000 µg Fe / g slurry	0.5	0
7	4000 µg Fe / g slurry	0.1	0.25
8	4000 µg Fe / g slurry	0.1	0.1
9	4000 µg Fe / g $CaCO_3$	0.1	0.25
10	4000 µg Fe / g $CaCO_3$	0.5	0
11	4000 µg Fe / g $CaCO_3$	0.1	0.1
12	8000 µg Fe / g $CaCO_3$	0.1	0.1
13	4000 µg Fe / g $CaCO_3$	0.1	0
14	4000 µg Fe / g $CaCO_3$	0.1	0.5
15	4000 µg Fe / g $CaCO_3$	0.1	0
16	4000 µg Fe / g $CaCO_3$	0.1	0.25
17	4000 µg Fe / g $CaCO_3$	0.85 (30,000 mg/L)	0

Phase I tests used bromide concentrations of 0.5 M and 1.0 M (40,000 mg/L and 80,000 mg/L). However, at these high concentrations, an updated economic evaluation indicated that the bromide chemical makeup costs are unacceptably high without recovering bromide from the FGD blowdown stream. Therefore, lower concentrations of 0.1 M and 0.25 M (8,000 and 20,000 mg/L) bromide were tested in Phase II. Tests at the previous, higher concentrations of bromide were retained in the test matrix in order to evaluate the impacts of iron and test method and because additive recovery is possible.

Tests 1 through 8 were conducted on 4000 to 8000 µg Fe /g of synthetic limestone makeup slurry, with that range selected based on a range of field measurements for iron concentrations in limestone slurry. Subsequent clarification of the reporting basis from the field measurements led

to a correction in the iron addition rate, and Tests 9 through 17 were conducted with 4000 µg Fe /g synthetic limestone *solids*. This resulted in approximately 20 to 40 times less iron added than in Tests 1 through 8. Because those first eight tests were conducted at unrealistic iron concentration relative to full-scale FGD operation, those results are not presented in this report.

Table 3-2 shows selected mercury partitioning results from bench-scale tests 9 through 17. Despite the presence of iron, tests with a relatively low baseline chloride concentration of 0.1 M (3500 mg/L) showed 75-81% of the mercury remaining in the liquid, and elevated concentrations of chloride had little effect on mercury partitioning. Tests with bromide showed varied results. Contrary to expectations, a similar molar concentration of bromide (0.1 M [8000 mg/L]) showed less than 30% of the mercury remaining in the liquid, and more than 70% of the mercury reporting to the solids. This low percentage remaining in the liquor was not expected, especially because bromide is known to form stronger liquid-phase complexes with oxidized mercury than chloride at similar molar concentrations. However, tests with 0.25-M and 0.5-M bromide (20,000 and 40,000 mg/L) exhibited 72 to 92% of the mercury reporting to the liquor (only 8 to 28% of mercury reporting to the solids), more like what was expected based on Phase I results. The results were confounding, and conditions leading to complete reporting of mercury to the slurry solids were not identified. In particular, note that the baseline chloride concentration was moderately low compared to the range seen in full-scale LSFO wet FGD systems, but even the lowest bromide concentration tested (0.1-M or 8000 mg/L) was higher than what is typically seen in LSFO systems as a result of coal bromine levels.

Table 3-2
Mercury Partitioning Results for Tests with Iron Addition Method 1

Run #	Description	Ferrous Sulfate Addition (µg Fe / g $CaCO_3$)	Chloride (M)	Bromide (M)	% recovered Hg in liquid phase	% recovered Hg in solid phase	% of Hg recovered from inlet gas
9	0.25 M (20,000 mg/L) Br	4000	0.1	0.25	85%	15%	77%
10	0.5 M (18,000 mg/L) Cl	4000	0.5	0	83%	17%	75%
11	0.1 M (8000 mg/L) Br	4000	0.1	0.1	27%	73%	115%
12	0.1 M Br, higher Fe	8000	0.1	0.1	13%	87%	84%
13	Iron Baseline	4000	0.1	0	75%	25%	41%
14	0.5 M (40,000 mg/L) Br	4000	0.1	0.5	92%	8%	91%
15	Iron Baseline (repeat)	4000	0.1	0	81%	19%	103%
16	0.25 M (20,000 mg/L) Br (Test 9 repeat)	4000	0.1	0.25	72%	28%	83%
17	0.85 M (30,000 mg/L) Cl	4000	0.85	0	n/a	n/a	n/a

Iron Addition Method #2

Anecdotal information suggests that iron impurities in limestone may contain not only ferric but also ferrous ions in the limestone matrix. As the limestone used for pH control in the FGD scrubber dissolves in the slurry, it may release ferrous and ferric material. The ferric materials will remain in the solid phase and the ferrous material will dissolve, be oxidized, and then precipitate as a ferric hydroxide. Thus, mercury absorbed into the scrubber liquor may partition to the solid phase by either adsorbing to ferric oxides and hydroxides already present in the slurry, or by co-precipitating with ferrous ions as they are introduced by limestone dissolution then oxidized and precipitated. Therefore, the test method was modified to reflect phenomena expected in full-scale scrubbers. In Tests 18 to 25, ferrous sulfate was added directly to the reaction tank at a rate proportional to the synthetic limestone makeup such that iron in the ferrous sulfate would equal an amount typical of iron impurities contained in FGD limestone reagent. This revised method attempted to account for both adsorption and co-precipitation of mercury. The test duration was also extended to allow more mercury to accumulate in the slurry to the point of observing re-emissions, which would more closely approximate full-scale steady-state conditions. Several intermediate- and extended-length tests were conducted. The test matrix for tests conducted with the second iron addition method is shown in Table 3-3.

Table 3-3
Bench-scale Scrubber Test Matrix with Iron Addition Method 2

Test #	Test Length (hours)	Iron (µg Fe / g $CaCO_3$)	Cl (M)	Br (M)	Mn (mg/L)	Purpose
18	10	4000	0.1	0	0.5	Intermediate-length baseline test with 2nd iron addition method (iron added separately as Fe(II)SO_4)
19	10	4000	0.1	0.5	0.5	Intermediate-length test with moderate bromide concentration
20	10	4000	0.85	0	0.5	Intermediate-length test with high chloride concentration
21	10	4000	0.1	0.25	0.5	Intermediate-length test with lower bromide concentration
22	32	4000	0.1	0	0.5	Achieve steady-state baseline conditions via extended test
23	24	4000	0.1	0.5	0.5	Achieve steady-state conditions with bromide via extended test (1st attempt)
23B	32	4000	0.1	0.5	0.5	Achieve steady-state conditions with bromide via extended test
24	10	4000	0.50	0	0.5	Test effects of pH with chloride
25	10	4000	0.50	0.5	0.5	Test effects of pH with bromide
26	6	40,000 µg Fe / g Reaction Tank Solids	0.10	0	0.5	Test very high levels of iron

During the intermediate-length tests, slurry samples were taken at 6 hours and 10 hours after introduction of mercury to the system. Intermediate-length tests under baseline conditions (i.e., no scrubber additives) showed 56-78% of mercury reporting to the solids. Though tests at 0.85-M chloride (30,000 mg/L) and 0.25-M bromide (20,000 mg/L) showed marginal improvement relative to the baseline, a test conducted with 0.5-M bromide (40,000 mg/L) showed marked improvement over the baseline conditions with 88-95% of the mercury remaining in the liquid phase. Under baseline conditions, some mercury re-emissions would be expected. However, the intermediate-length baseline test exhibited only very low re-emissions at the end of the test.

At this point in the project, the team believed that additional data would likely be required to secure a pilot host site. Therefore, a limited number of extended-length tests were conducted; longer tests would have a greater chance at observing mercury behavior that is similar to full-scale steady-state behavior. A test length of 32 hours was selected; this test length falls within the range of typical liquid residence times in full-scale FGD absorbers (24 to 72 hours). The test method was modified, as previously described in Section 2. The test length and conditions were selected to achieve steady-state conditions within 24 hours such that the final eight hours of the test simulated the steady-state operations of a full-scale system. Two test conditions were selected to run: one at baseline conditions and one with 0.5-M bromide. The first attempted test with bromide had numerous operational problems, and was terminated after 24 hours; a second attempt successfully operated for 32 hours.

Newly available iron data from full-scale wet FGD systems were reviewed prior to the 32-h tests in order to select a target solid-phase iron concentration. An iron addition rate was selected to achieve the target solid-phase concentration within 24 hours. Table 3-4 presents mercury, iron, and particle size data for two full-scale systems in which nearly all mercury partitioned to the solid phase. PHCOF indicates "primary hydrocyclone overflow" and "D_{10}" indicates the particle size at which 10% of the particles are smaller. For the 32-h tests, the target iron concentration of ~3500 µg Fe/g $CaCO_3$ was selected to be equal to the iron concentration in the bulk absorber solids.

Table 3-4
Iron, Mercury, and PSD Data for Full-Scale Wet FGD Systems in which Mercury Was Found Partitioned Primarily to the Absorber Slurry Solids

Site	Absorber Slurry Liquor Hg (µg/L)	Absorber Slurry Solid Hg (µg/g)	Suspended Solids Loading (wt%)	% of Hg in Solid Phase	Iron in Bulk Absorber Solids (µg/g)	Iron in PHCOF (µg/g)	PHCOF D_{10} (µm)
Site A (URS, 2008)	<0.2 - 0.2	0.5 - 0.8	15.0 - 16.5	>99.8	1650	13,600 - 17,100	2
Site B (URS, 2009)	<0.3 - 1.4	0.6 - 0.9	9.3 - 12.9	>99.3	3650	20,600 - 42,900	2.5

Table 3-5 shows the solid- and liquid-phase mercury and iron concentrations measured for both the intermediate- and extended-length bench-scale scrubber tests. Figure 3-1 shows the percentage of recovered mercury measured in the solid phase, in the liquid phase, as re-

emissions, or as sampling losses. In contrast to the 10-h baseline test results, the 32-h baseline test did not show a large percentage of mercury partitioning to the solid phase. The final samples from the 10-h baseline test had an iron concentration within ~15% of the 24-h sample from the baseline 32-h test; however, the 24-h sample had significantly less mercury per unit of iron than the sample from the intermediate-length test. The operating parameters (e.g., pH) were generally steady and consistent between the 10-h and 32-h baseline tests. It was not clear at that time what caused the discrepancy between the intermediate- and extended-length test results.

The test method and conditions used in the long-term baseline test did not cause mercury to partition to the solid phase under operating conditions where full-scale systems might expect to see a greater fraction of mercury in the solids. Data for full-scale FGD systems in which mercury did partition to the solid phase were re-visited. More recent Spring 2010 data suggested that iron concentrations in the absorber and PHCOF solids may reach ~8000 µg Fe/g solids and ~60,000 µg Fe/g solids, respectively in some full-scale systems. The full-scale systems with large fractions of mercury in the solids typically had high recycle through the PHCOF back to the scrubber, and the "fines" particles (< 10 µm) that recirculate with the PHCOF contained much higher iron concentrations than the bulk scrubber slurry solids. Thus, a few additional regular-length (6-h) bench scale scrubber tests were conducted at higher iron addition rates such that the final iron concentration in the slurry solids would approach the high end of iron concentrations observed in bulk absorber solids and the low end of iron concentrations observed in PHCOF fines (~10,000 µg Fe/g solids). However, these tests did not show mercury partitioning to the solid phase either. Iron concentrations in the fines could not be determined for the bench-scale tests because the bench-scale system does not have slurry dewatering equipment. A suitable technique was not available at the time to simulate a primary hydrocyclone and separate fine solids from the bulk solids in sufficient quantity to conduct chemical analyses. Later tests and analyses benefitted from a wet-sieving system acquired for this purpose.

At this point in the program, the reasons for the discrepancy between the bench-scale behavior and full-scale behavior were not fully understood. Several differences between the bench-scale system and typical full-scale systems were identified as possible causes:

- Higher solids loading and solids surface area per volume of slurry in full-scale systems,
- Differences in particle size distribution (PSD),
- Differences between the ratio of crystal nucleation and crystal growth/attrition rates, and
- Differences in solid surface characteristics.

Table 3-5
Liquid and Solid Phase Mercury Concentrations during Intermediate- and Extended-Length Tests

Run #	**-**	**18**	**22**	**19**	**23**	**23B**
Liquor Matrix	**-**	**Baseline**	**Baseline**	**0.5 M Br**	**0.5 M Br**	**0.5 M Br**
Length	**hours**	**10**	**32**	**10**	**32 (Note 1)**	**32**
Liquid Phase Hg						
0 h	µg/L	<0.381	5.32	9.20	0.88	0.28
6 h	µg/L	11.8	22.2	57.7	11.2	24.6
10 h *(Note 2)*	µg/L	50.6	37.1	98.8	32.6	45.5
24 h	µg/L	n/a	37.4	n/a	63.0	82.3
32 h	µg/L	n/a	47.5	n/a	n/a	91.6
Liquid Phase Fe						
0 h	mg/L	<2	n/a	<2	<3	<0.4
6 h	mg/L	<2	<1	<2	<1	<0.2
10 h *(Note 2)*	mg/L	<2	<1	<2	<1	<0.2
24 h	mg/L	n/a	<2	n/a	<1	<0.2
32 h	mg/L	n/a	<1	n/a	n/a	<0.1

Table 3-5 (continued)
Liquid and Solid Phase Mercury Concentrations During Intermediate- and Extended-Length Tests

Run #	**-**	**18**	**22**	**19**	**23**	**23B**
Liquor Matrix	**-**	**Baseline**	**Baseline**	**0.5 M Br**	**0.5 M Br**	**0.5 M Br**
Length	**hours**	**10**	**32**	**10**	**32 (Note 1)**	**32**
Solid Phase Hg						
6 h	µg/g	0.402	0.053	0.080	0.083	0.151
10 h *(Note 2)*	µg/g	0.647	0.064	0.062	0.095	0.171
24 h	µg/g	n/a	0.118	n/a	0.102	0.227
32 h	µg/g	n/a	0.147	n/a	n/a	0.239
Solid Phase Fe						
6 h	µg/g	701	548	390	1050	530
10 h *(Note 2)*	µg/g	1695	1170	642	2460	1350
24 h	µg/g	n/a	1960	n/a	3820	2260
32 h	µg/g	n/a	2010	n/a	n/a	2240

Note 1: Test 23 was ended at 24 hours due to operational difficulties.
Note 2: Sample at 12 h for 32-h tests.
Note 3: "n/a" indicates not applicable.

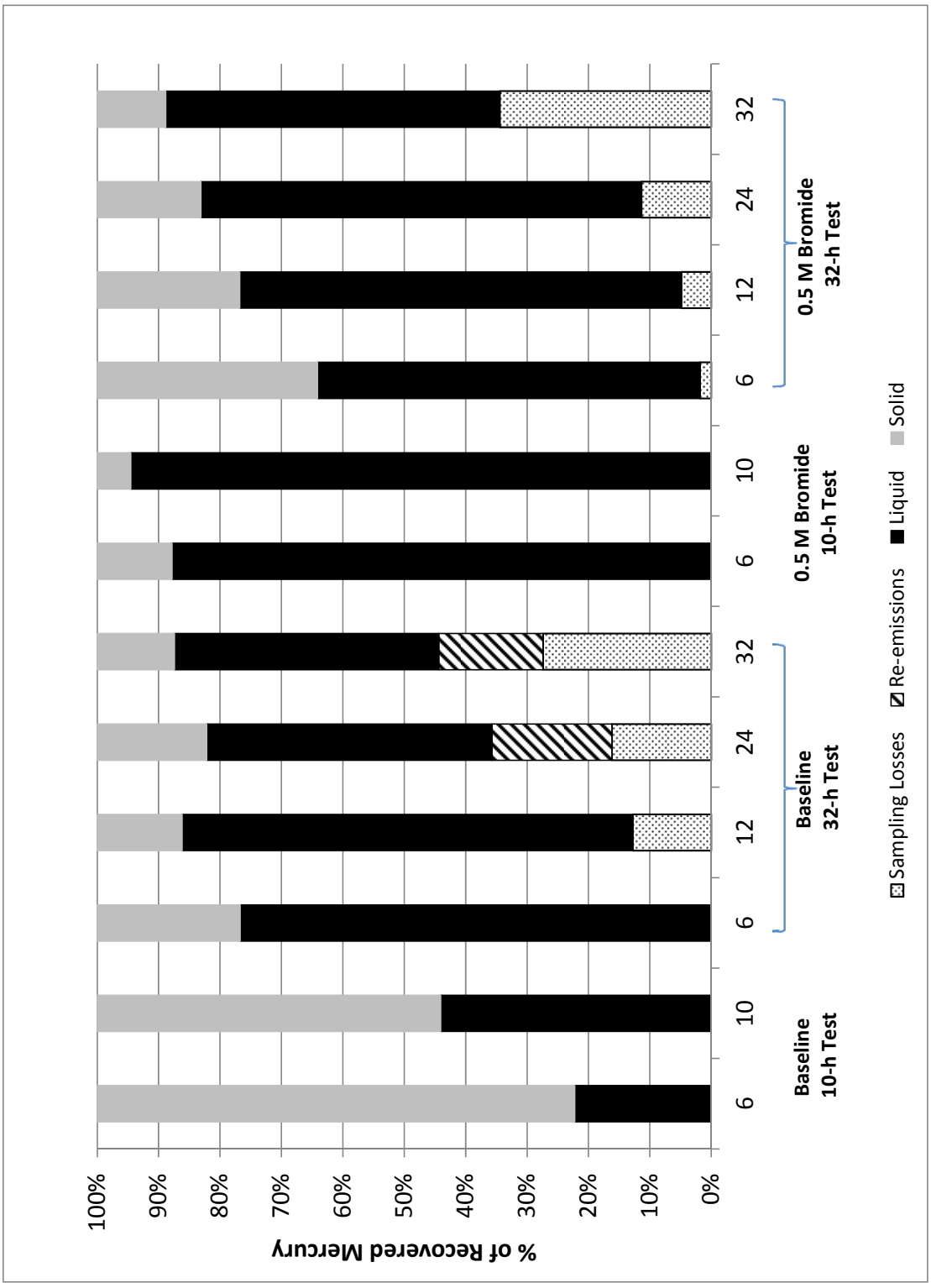

Figure 3-1
Mercury Phase Partitioning for Intermediate- and Extended-length Tests

The available surface area of iron-enriched fines per unit of slurry may be much lower in the bench-scale system. The solids loading in the recirculating slurry of the bench scrubber is lower (~8 wt%) than that of typical full-scale scrubbers (12-25 wt%) because of agitator limitations. Thus, for a given particle size distribution, the higher solids loadings in full-scale systems would provide more solid surface area per unit of slurry than the bench unit; in some cases, a full-scale system with high solids loading may have up to five times the solid surface area available in the bench unit. The solids loading in the bench unit is limited by particle settling in the absorber. With the bench-scale scrubber design, it is not possible to use a top-mount mechanical agitator, so a magnetic agitator is used. This agitator is not as robust as the side-mount agitators in full-scale wet FGD reaction tanks.

Differences in PSD might also contribute to differences in behavior between the solid particles and liquid-phase constituents. PSD data from a limited number of bench-scale tests indicate that solids loading in the bench unit increases via crystal growth, but less so by crystal nucleation (formation of new crystals). Larger crystals are not crushed into fines by recirculating equipment in the bench unit, as they are by pumps and mechanical agitators in full-scale systems over their 24-h to 72-h solids residence time. The lack of recycle of PHCOF fine solids back to the absorber in the bench-scale tests also contributes to differences in PSD between the bench-scale unit and full-scale wet FGD systems.

In addition to differences of PSD and the resulting available solid surface area, the surface characteristics of the solids in the bench unit may differ from those of full-scale units. Specifically, the bench unit does not have dewatering from which iron-enriched fines are recycled to the scrubber. Thus, in full-scale FGD systems, the slurry has more fine solids, and those solids are richer in iron concentration than in the bench-scale tests.

Solid-phase iron concentrations can be much higher in the fine particles that are returned from dewatering to the scrubber via the PHCOF in systems with hydrocyclones, as was shown in Table 3-4. It was postulated that the solid-phase iron concentrations observed in the fine particles might be required to demonstrate mercury reporting to the solid phase in the bench unit. Therefore, one more attempt was made to find conditions under which mercury reports to the solid phase with the addition of ferric oxide. The target solid-phase iron concentration of 40,000 µg Fe / g solids (40,000 ppm Fe) for this test was selected based on the field measurements of the PHCOF fines shown in Table 3-4. For this test, ferric oxide was used because the oxidation of ferrous ions to ferric ions can sometimes be slow, especially at pH conditions below 6. Additionally, all of the ferric oxide was added at the beginning of the test rather than added gradually throughout the test. The intent was to provide the maximum amount of ferric hydroxide surface area for the greatest portion of test time. Approximately 81% of the recovered mercury remained in liquid phase, though the recovery of mercury added via the inlet gas was low (42%). These results may indicate one or more of the following:

- The form of iron and its surface characteristics may be more important than the solid-phase iron concentration,
- Other operating parameters, such as ORP, or other constituents may have a stronger impact on mercury behavior than iron concentrations,
- The bench unit may not accurately replicate the solids characteristics of full-scale units,

- The presence of iron in the FGD solids may only coincide with rather than cause mercury partitioning to the solid phase, or
- Solid fines that adsorbed to equipment walls may have contained the unrecovered Hg.

In the absence of bench-scale conditions that show partitioning of mercury to the solid phase, which is commonly observed at full-scale, the performance of scrubber additives could not be adequately demonstrated at the bench scale. Therefore, testing was paused and a literature review ensued that looked for information on mercury-metal sorption, mercury speciation and surface characteristics in FGD solid byproducts, and the impact of FGD constituents on mercury sorption.

Literature Review

The literature review sought information on mercury-iron sorption behavior, the mechanism of mercury adsorption and co-precipitation, and the form of adsorbed mercury on various substrates such as iron, gypsum, and other common FGD constituents. Key lessons from the literature review include the following:

- Other research groups have documented that mercury in FGD solid byproducts associates with iron found in the byproducts (Al-Abed, 2008) and that mercury can sorb strongly to certain forms of iron (Kim, 2004a; Kim, 2004b).
- Not only the presence but also the form and surface characteristics of transition metals in the FGD slurry can impact mercury sorption behavior (Ibid.).
- Other common FGD constituents, such as chlorides and sulfates, can exhibit complex impacts on mercury sorption behavior that is further influenced by the presence of metals (Ibid.).
- Other research groups have observed enrichment of metals in the fine particles of the FGD slurry (Al-Abed, 2008).

The literature review confirms that iron is expected to play an important role in mercury behavior within FGD scrubbers, and that the form of iron could be important. Iron can enter FGD scrubbers as a limestone impurity, via attrition of limestone ball mill grinding media, via fly ash carryover, and/or via makeup water; therefore, running bench-scale tests with limestone, fly ash, or makeup water samples from a full-scale FGD system was considered.

Tests with Natural Limestone

Bench-scale scrubber tests with high solid-phase iron concentrations formed from reagent-grade iron compounds did not show mercury reporting to the solid phase to the extent seen at full-scale wet FGD installations. The literature indicated that the form and surface characteristics of the solid-phase iron impacted mercury sorption. Therefore, the project team elected to use natural limestone in lieu of reagent calcium carbonate for pH control in several bench-scale tests with the expectation that the iron impurities and other trace elements present in the natural limestone would have characteristics that promote sorption of Hg. Tests were conducted with anhydrous calcium sulfate (anhydrite) and calcium sulfate dihydrate (synthetic gypsum) as the initial solids

charge to the scrubber; the solids loading added at the beginning of each test was 7-8 wt% (e.g., 400 g of solid in 5 L of solution).

Table 3-6 shows the test matrix for the natural limestone scrubber tests. Baseline conditions were shown earlier in Table 2-1. The initial solids charge for bench-scale scrubber Tests 1 through 28 used anhydrous calcium sulfate ("anhydrite"). Review of the literature indicated that anhydrite hydration kinetics to calcium sulfate dihydrate (gypsum) can be slow; therefore, Tests 29 and onward used synthetic gypsum as the initial solids charge because LSFO systems produce gypsum, the dihydrate, rather than anhydrite, under normal operating conditions. It was unknown what, if any, impact this change would have on the bench-scale results. Synthetic reagents can have different particle size distributions and surface characteristics from their natural counterparts. It was unknown whether the difference between reagent anhydrous calcium sulfate and reagent calcium sulfate dihydrate would be significant when compared to any differences there may be between reagent calcium sulfate dihydrate and the gypsum produced in full-scale FGD scrubbers. During Tests 27 and 28, the limestone was used "as received," meaning solids recovered from limestone slurry ground at the full-scale site were used to prepare the bench-scale reagent slurry. Plugging problems in the feed line to the scrubber were encountered, possibly due to agglomeration of the recovered solids; therefore, all subsequent tests used re-ground limestone; all tests with an initial solids charge of synthetic gypsum (dihydrate) used re-ground limestone. PSD data for the re-ground natural limestone and several scrubber solid samples are presented later.

Table 3-6
Test Matrix for Natural Limestone Bench-scale Scrubber Tests

Test Number	27	28	29	30	31	32	33	34
Chloride (M)	0.005	0.005	0.005	0.1	0.1	0.1	0.5	1.0
(mg/L)	180	180	180	3500	3500	3500	18,000	35,000
Bromide (M)	-	0.5	-	-	0.5	0.5	0.5	1.0
(mg/L)	-	40,000	-	-	40,000	40,000	40,000	80,000
Solids initial charge	Anhydrite		Synthetic Gypsum					
Natural Limestone Condition	As-received		Re-ground					

Figure 3-2 shows the percentage of recovered mercury that reports to each of the slurry phases for bench-scale tests that used natural limestone for pH control. The phase distribution is based on final measurements of slurry suspended solids loading, liquid-phase mercury concentrations, and solid-phase mercury concentrations. Results for Tests 27 and 28, the two anhydrite tests, are shown at left, and the gypsum tests are shown in the middle and at right. Test 27, which had 0.005-M Cl (180 mg/L) and no bromide, showed mercury reporting completely to the solid phase. Tests 29 and 30 with natural limestone and synthetic gypsum at low and moderate chloride levels also showed mercury reporting completely to the solid phase. Figure 3-2 also shows the results of using bromide in the bench-scale scrubber tests. The target conditions of Test 28 were the same as Test 27, except 0.5-M bromide (40,000 mg/L) was added. In Test 28, bromide had no apparent effect on mercury partitioning in comparison to Test 27; mercury partitioned completely to the solid phase in both tests. Tests 27 through 30 are the first bench-

scale tests with a gradual accumulation of mercury in the system in which the mercury partitioned completely to the solid phase; those conditions therefore served as a “baseline” for additive performance in subsequent tests.

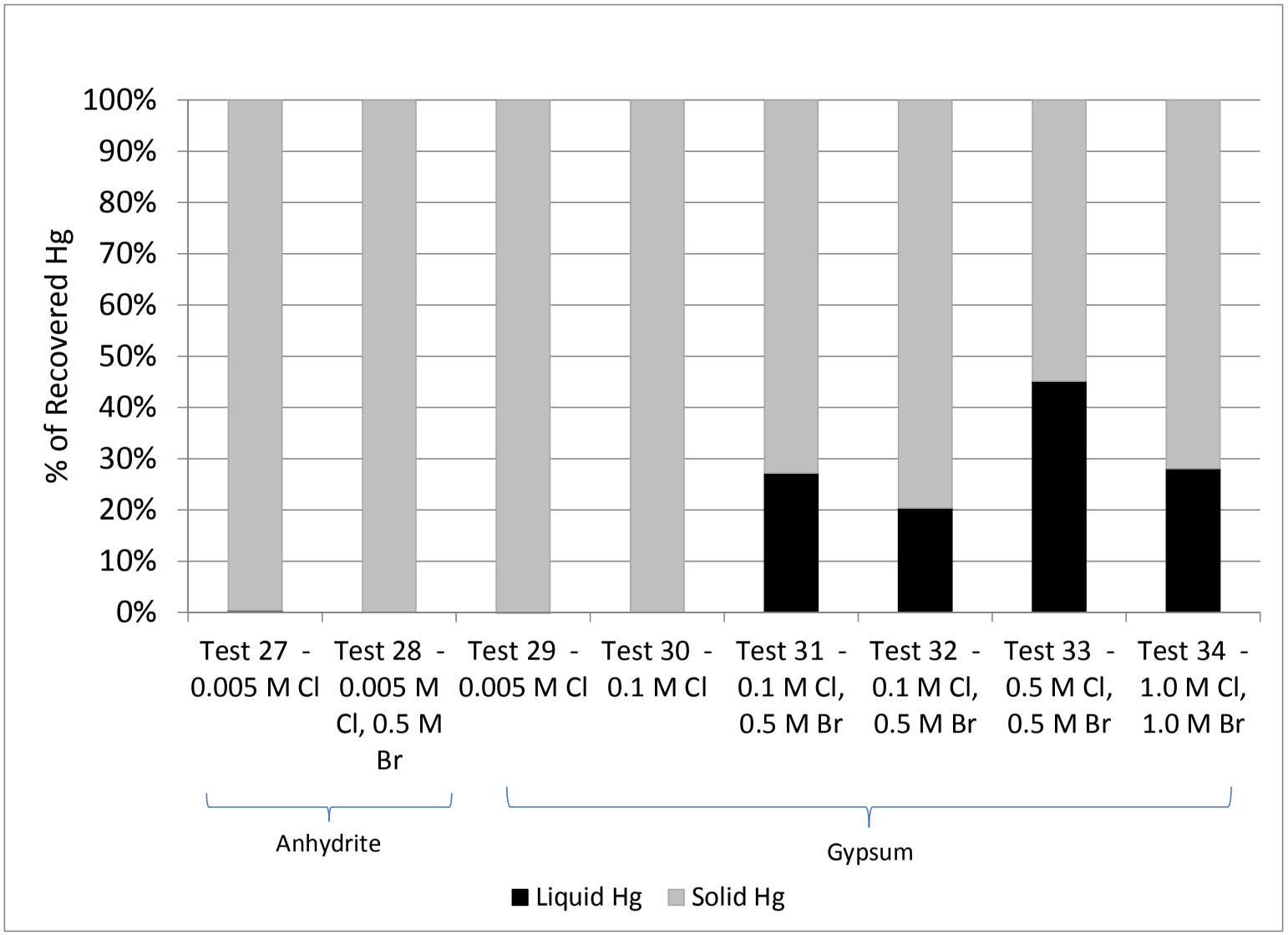

Figure 3-2
Mercury Phase Partitioning in Bench-scale Tests with Natural Limestone

In contrast, Tests 31 and 32, which used synthetic gypsum and re-ground limestone, showed that adding 0.5-M bromide (40,000 mg/L) caused 20-27% of the mercury to report to the liquid phase, which was promising. Increasing the concentrations of chloride to 0.5 M (18,000 mg/L) in conjunction with 0.5-M bromide resulted in modest increases in mercury partitioning to the liquid phase; 45% of mercury reported to the liquid phase in Tests 33. However, further increasing the concentrations of chloride and bromide did not increase mercury reporting to the liquid phase, as shown in the Test 34 results; the percent of recovered, liquid-phase mercury actually decreased slightly. The Test 34 results indicate that some factor other than chloride and bromide concentration may have impacted mercury behavior during the test, or that higher concentrations of these species may favor mercury sorption. Operating data for Tests 33 and 34 were compared, and no conclusive explanations were found. The literature indicates that chloride can exhibit complex interactions with mercury. Chloride may form soluble species with mercury and promote mercury reporting to the liquid phase; however, under some circumstances, chloride may react with mercury in the presence of iron oxides to form a solid compound, FeOHgCl (Kim, 2004b).

Bromide retained some mercury in the liquid phase in Tests 31 through 34, but not in Test 28. The higher chloride concentrations of Tests 31 through 34 likely contribute to this difference, though the grinding of the limestone may also impact mercury partitioning.

With re-ground limestone, the baseline 0.1-M chloride concentration (3500 mg/L) did not by itself cause mercury partitioning to the liquid, but when bromide and the baseline chloride concentration were used, some mercury did report to the liquor, as shown by the results for Tests 31 to 34. It may be possible to couple the use of bromide with chloride levels and changes in operating conditions to retain a greater fraction of mercury in the liquid phase in tests with natural limestone.

Operating conditions of the natural limestone scrubber tests were reviewed to ensure that they did not confound the results. Sulfur oxidation was maintained for all tests; liquid-phase sulfite concentrations remained below 0.5 mM (40 mg/L) for all tests with natural limestone. The ORP for the tests tended to be mildly oxidizing, with most tests operating between 100 mV and 160 mV ORP. Bench tests achieved 700-1300 ppm Fe in solids at 6 hours of run time and up to 1800 ppm at 10 hours of run time. The solid-phase iron concentrations measured in the bench scrubber solids are low relative to the iron measured in the bulk solids of many full-scale units. This result emphasizes that the form of the iron may be key, or that factors and constituents other than iron are also playing a key role in mercury behavior.

In an attempt to understand what characteristics of the limestone led to a change in mercury behavior, additional sample characterization was conducted for some of the natural limestone tests (Tests 27 to 34). Specifically, the natural limestone and the bench scrubber solids were analyzed for a series of trace metals as well as PSD, and liquid samples from several bench scrubber tests were analyzed for trace metals.

Particle size distributions (PSDs) were measured for the re-ground natural limestone, used in Tests 29 to 34, and for the scrubber solids sampled from several bench-scale scrubber tests with natural limestone. Figures 3-3 through 3-7 show the PSD results. Particle size is shown along the x-axis. The sigmoidal line corresponds to the left-hand y-axis of cumulative volume percent of the particles passing through a sieve with a given particle cut size. The columns at each particle size represent the volume percent of particles that are retained in each sieve size range

(i.e., "% Channel", shown in the right-hand y-axis.). Note that these analyses were conducted with a Microtrac Model S3500 particle size analyzer and not literally using wet sieving, so the sieve sizes are "virtual," and are based on an assumption of spherical particles.

Figure 3-3 shows the PSD for re-ground limestone, which reveals that the ground limestone contained a large fraction of particles smaller than 10-µm in diameter, including appreciable quantities of submicron-diameter particles.

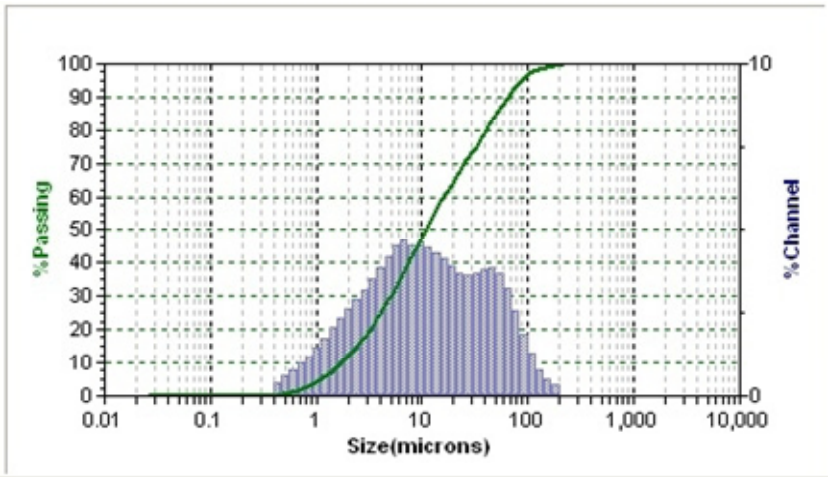

Figure 3-3
PSD for Ground Natural Limestone

The PSD for the final solids from Test 27 is shown in Figure 3-4. The PSD shows no submicron particles and very few particles below 10-µm in diameter. The PSD for Test 28, which was a repeat of Test 27 with an addition of 0.5 M bromide, was nearly identical to the PSD for Test 27, which indicates that bromide did not influence PSD under Test 28 conditions. Figures 3-5 and 3-6 show the PSDs for solid samples taken during Test 30 at the beginning of the run and at the end of the run (six hours of run time). The Test 30 results show that the PSD was not changing appreciably during the test. The PSD shows a moderate fraction of particles with <10 µM diameter, though no submicron particles were observed. Figure 3-7 shows the PSD for the final solids sample taken after six hours of run time in Test 31, which added 0.5 M bromide to the conditions used in Test 30. Comparison of Figures 3-6 and 3-7 shows that bromide had little impact on PSD under the conditions tested.

The salient points from the PSD data include the following:

- The collective PSD results indicate that small particles, in and of themselves, are not necessary for mercury to report to the solid phase of FGD slurries.
- PSD is not changing appreciably during the short-term (6-hour) tests.
- Bromide has little impact on PSD within the test durations and under the conditions tested.

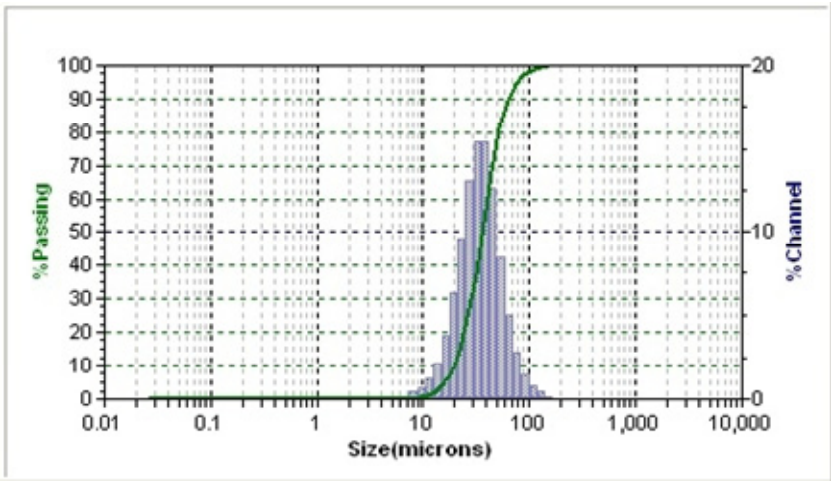

Figure 3-4
PSD for Test 27 (Anhydrite with 0.005 M Chloride) at t = 6 hours

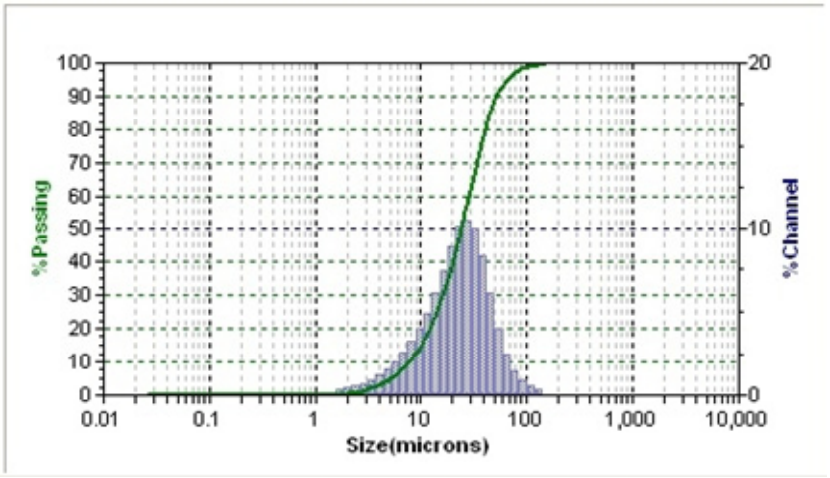

Figure 3-5
PSD for Test 30 (Synthetic Gypsum, Ground Limestone, 0.1 M Cl) at t = 0 hours

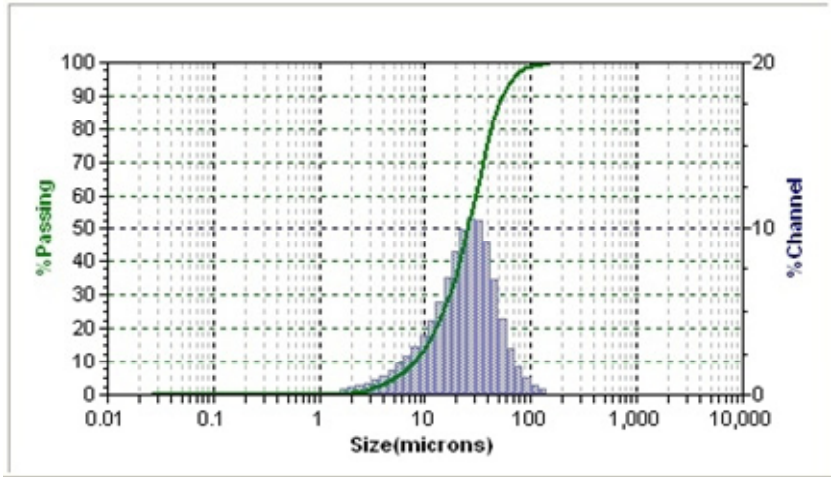

Figure 3-6
PSD for Test 30 (Synthetic Gypsum, Ground Limestone, 0.1 M Cl) at t = 6 hours

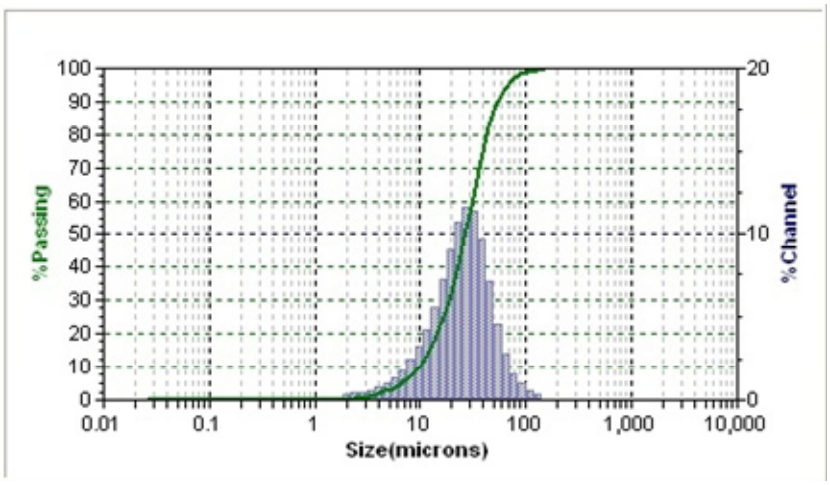

Figure 3-7
PSD for Test 31 (Synthetic Gypsum, Ground Limestone, 0.1 M Cl, and 0.5 M Br) at t = 6 hours

Extended Bench-scale Test Campaign

Based on the promising results observed in tests with natural limestone, the bench-scale test campaign was extended. The extended bench-scale test campaign studied the impacts on mercury behavior of ORP, chloride, manganese, organic carbon, and four scrubber additives. The additional tests comprised nominally 14 tests conducted over a relatively short period in early 2011 and four additional tests that measured mercury and selenium behavior simultaneously.

Table 3-7 shows the test matrix for tests with mercury only. The rationale for the selected test matrix is presented, and the salient results are discussed.

Table 3-7
Test Matrix and Partitioning Results for Mercury-Only Bench-Scale Scrubber Tests

Test #	Reagent LS	Natural LS	Cl (M)	Mn (mg/L)	Additive	Target ORP (mV)	Actual ORP (mV)	Purpose	% Hg in Liquor	% Hg in Solid
35		X	0.1	0.5		-	150	Baseline with improved ORP control	1%	99%
36		X	0.5	0.5		150	150	Effect of chloride with improved ORP control	1%	99%
36 @ 8hrs		X	0.5	0.5		200	200	Run for extra two hours at higher ORP	32%	68%
37		X	0.1	35	-	150	100	Natural limestone at new "Baseline 2" manganese concentration and low ORP	0%	100%
38		X	0.1	35	-	300	275	Effect of increased ORP	Note 1	Note 1
39		X	0.1	35	1000 mg/L Citric Acid	300	100	Effect of citric acid	Note 1	Note 1
40		X	0.5	35	-	300	250	Effect of chloride	62%	38%
41		X	0.1	35	0.25 M Bromide	300	170	Effect of bromide	2%	98%
42	X		0.1	35	2 mg/L Organic Carbon	300	100	Test whether organic carbon is key component in natural limestone by adding a form of organic carbon to reagent limestone	92%	8%
43	X		0.1	35	20 mg/L Organic Carbon	100	100	Test second concentration of organic carbon with reagent limestone	88%	12%
44		X	0.1	0.5	1000 mg/L DBA	100	150 (low excursion)	Effect of DBA at older baseline conditions	87%	13%
45	X		0.1	0.5	1000 mg/L DBA	150	150	Test whether DBA can act as source of organic carbon with reagent limestone	100%	0%
46	X		0.1	35	20 mg/L Organic Carbon	300	275	Effect of ORP in the presence of organic carbon and reagent limestone.	90%	10%

Table 3-7 (continued)
Test Matrix and Partitioning Results for Mercury-Only Bench-Scale Scrubber Tests

Test #	Reagent LS	Natural LS	Cl (M)	Mn (mg/L)	Additive	Target ORP	Actual ORP	Purpose	% Hg in Liquor	% Hg in Solid
47		X	0.1	35	-	300	300	Test 38 repeat (effect of increased ORP)	44%	56%
48		Baked	0.1	35	-	150	140	Test natural limestone after "baking" the limestone to remove organic carbon	2%	98%

Note 1: Results are not reported due to operational excursions that call the results into question.

The baseline concentration for manganese was adjusted for the majority of tests in the extended test campaign. In tests conducted prior to December 2010, the typical "baseline" manganese concentration was 0.01 mM, or roughly 0.55 mg/L Mn in solution. The original objective was to provide just enough manganese to maintain the kinetics of sulfite oxidation to sulfate as is observed in full-scale FGD systems; in the absence of a catalyst material such as manganese the oxidation reaction kinetics are very slow. Field measurements conducted by URS from 2006 to 2009 have indicated that the total slurry concentration of manganese typically is a higher value, if all the manganese found both in the liquid and solid phases were expressed as a concentration in the liquid phase (EPRI, 2010). Results from the selenium SBIR program revealed that manganese and other catalytically active transition metals play a key role not only in sulfite oxidation but also in selenium speciation and oxidation, and that the impacts can depend on manganese concentration. Thus, the selenium program began using a higher manganese concentration (35 mg/L or approximately 35 ppm Mn) in the reaction tank and observing how the manganese partitioned between the phases, and how this partitioning impacted selenium speciation and behavior. In a similar vein, for the recent mercury bench-scale tests, the majority of tests employed the new manganese baseline concentration of 35 mg/L.

Effects of ORP

Above a threshold value, increasing ORP increases mercury partitioning to the liquid phase. Higher ORP conditions indicate a more oxidizing environment, which would tend to favor soluble, oxidized forms of mercury (e.g., Hg^{2+}). Figure 3-8 qualitatively shows the impacts of ORP on mercury partitioning. Comparison of results from Test 30 and Test 35 shows that increasing the ORP from ~100 mV to ~150 mV had no effect on mercury phase partitioning. Test 36, a test at 0.5 M chloride, ran at 150 mV ORP value for the standard test length of six hours. Then, the ORP was increased to 200 mV and the test was extended for two hours. With the increase in ORP, the mercury partitioning changed such that 32% was found in the liquor as compared to only 1% while operating at an ORP of 150 mV. At the new, higher manganese baseline concentration, increasing the ORP from 100 mV (Test 37) to 300 mV (Test 47) increased the percent of mercury in the liquor from 0% to 44%.

Effects of Bromide

The bench-scale test results suggest that the promise of bromide for controlling mercury re-emissions and phase partitioning is limited and somewhat complex. Figure 3-9 shows the mercury partitioning data for tests at lower metals concentrations; the results indicate that both bromide and ORP can increase the liquor mercury fraction. Comparison of Test 36 and Test 33 results show that bromide increases the liquor mercury fraction. The decrease in liquor mercury fraction at 1.0-M Br (Test 34) is confounded by low ORP conditions. Taken as a whole, the data shown in Figure 3-9 indicate that bromide increases mercury liquor fraction under various test conditions, though the improvement is limited to less than 50% mercury in the liquor. At higher metals concentrations, the desired effect of bromide is hindered; as presented in Table 3-7, Test 37 (35 mg/L Mn at 100 mV ORP) reported no mercury in the liquor phase, and Test 41 (35 mg/L Mn at 170 mV ORP, 300 mV target) reported negligible mercury in the liquor phase. Thus, the limited promise of using bromide to maintain mercury in the liquor phase is itself called into question.

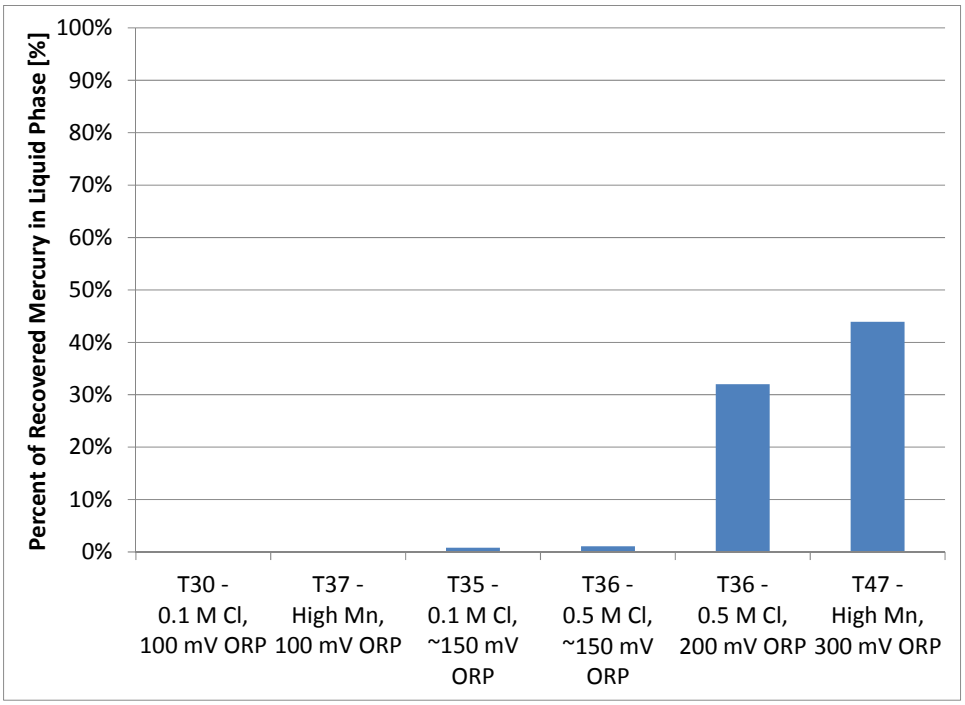

Figure 3-8
Effect of ORP on Mercury Partitioning

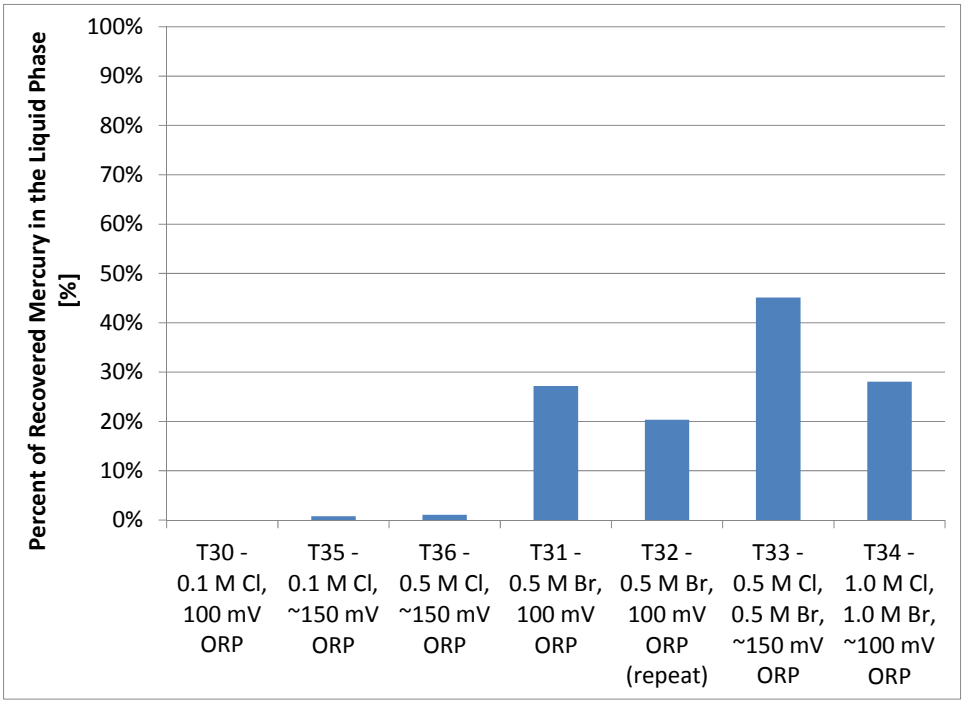

Figure 3-9
Effect of Bromide on Mercury Partitioning (Low Metals Concentrations)

During 2010 and 2011, numerous utilities reported premature material failures due to pitting corrosion in FGD absorber vessels using Alloy 2205 and other alloys with similar chloride pitting resistance ratings (EPRI 2011). This alloy is the predominant alloy used for FGD installations during the past five years such that 19% of FGD systems in operation now or in design/construction have scrubbers constructed with Alloy 2205. Considering other alloys that may be susceptible to similar failures, the percentage is over 25%. These failures have heightened the sensitivity of utilities to corrosion issues and may hinder the application of bromide except in a smaller subset of FGD systems that use very corrosion-resistant materials of construction. Bench-scale scrubber tests with bromide in the extended test campaign have shown only modest improvements in directing mercury to the liquid phase; therefore, the project team significantly decreased the research emphasis placed on bromide.

Effects of DBA

At low metals concentrations, DBA was observed to increase mercury partitioning to the liquid phase. For example, Test 35 was conducted at ~150 mV ORP with natural limestone and the earlier, lower manganese baseline concentration. Nearly all of the mercury reported to the solid phase. Test 44 was conducted under similar conditions, but with the addition of DBA. In Test 44, 87% of the mercury reported to the liquid phase. DBA has also shown benefits for selenium management in bench-scale scrubber tests with synthetic liquors. Therefore, DBA addition was selected as a condition for the tests that monitored mercury and selenium behavior simultaneously.

Effects of Organic Carbon

The interactions of organic carbon and mercury were considered and tested. As described earlier, many researchers have noted that mercury tends to associate with iron in FGD byproduct gypsum. However, previous bench-scale tests that added reagent iron to the scrubber and used reagent "limestone" (i.e., calcium carbonate) for pH control did not show mercury reporting to the solid phase under many test conditions and iron concentrations. Many hypotheses were proposed for this apparent discrepancy in behavior. One possible reason is that other species present in the natural limestone may promote the association of mercury with iron in the slurry solids. It is well established that mercury can form strong complexes with fulvic and humic substances, particularly in natural waters (Salbu and Steinnes, 1995). Some research has noted that humic substances (i.e., organic carbon) may increase mercury sorption to goethite, an iron oxide (Backstrom, 2002). Therefore, the project team hypothesized that organic carbon might be the "missing link", and several measurements and tests were conducted to explore the impacts of organic carbon on mercury phase partitioning in the bench-scale system.

The total organic carbon (TOC) concentration was measured in the feedstock materials and in bench-scale slurry samples from tests conducted using natural limestone as a reagent. Table 3-8 presents the organic carbon content for the solid feedstocks. Reagent calcium carbonate had negligible organic carbon, and the natural limestone contained 0.28 wt% organic carbon. Some of the natural limestone was heated at 500 °C in the presence of air for six hours to drive off the organic carbon. The organic carbon of this "baked" limestone was measured to decrease to below detection limits.

Table 3-8
Organic Carbon Content of Solid Feedstocks

Sample	TOC (wt%)
Reagent calcium carbonate	<0.05
Natural limestone	0.28
Baked natural limestone	<0.05

Figure 3-10 shows mercury partitioning results for the tests exploring the impacts of organic carbon. Test 48 was conducted at low ORP with baked natural limestone for pH control. Previous tests (e.g., Test 37) showed virtually all of the mercury reporting to the solid phase when using natural limestone at these ORP conditions. Similarly, in Test 48, only 2% of the recovered mercury reported to the liquid phase. Thus, removing the organic carbon from the natural limestone did not prevent the mercury from reporting to the solid phase under the conditions tested.

In Tests 42 and 43, two concentrations of humic acid were added to the reaction tank, and reagent calcium carbonate was used for pH control. With reagent calcium carbonate used for pH control, previous test results showed the mercury absorbed staying primarily in the slurry liquor. These tests might reveal whether organic carbon, in the form of humic acid, would promote mercury sorption to the slurry solids formed using reagent calcium carbonate. Despite the low ORP conditions, more than 80% of the mercury reported to the liquid phase. Thus, the form of organic carbon tested did not, on its own, promote mercury reporting to the solid phase. These results may indicate that organic carbon is not the deciding factor of mercury behavior in FGD scrubbers.

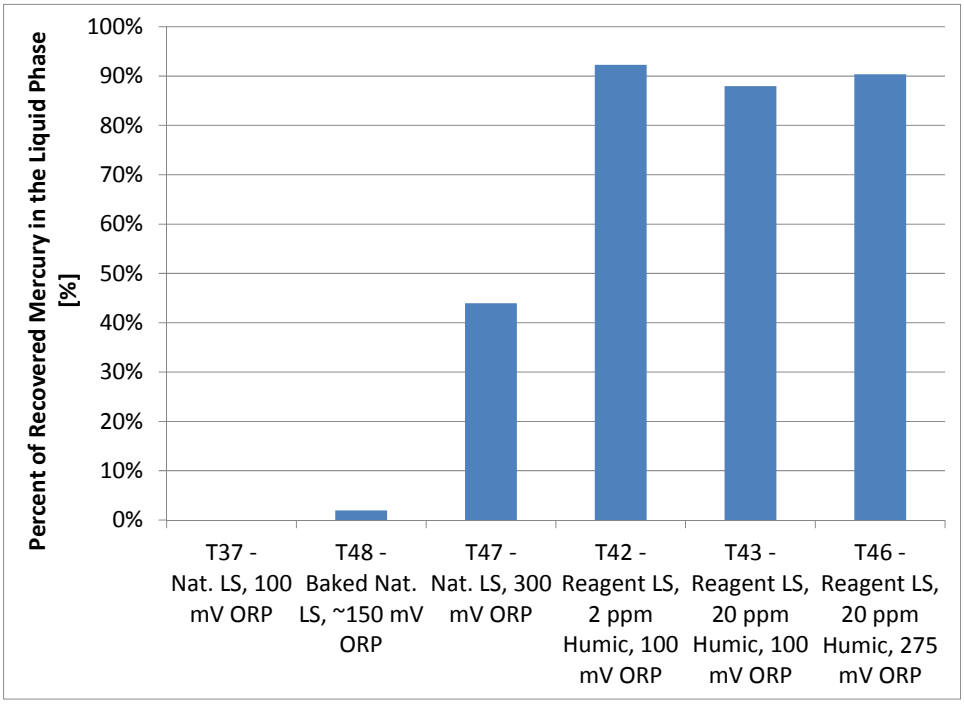

Figure 3-10
Mercury Partitioning for "Organic Carbon" Tests

Team member URS has conducted other bench-scale FGD tests for EPRI to determine why natural limestone behaves differently than reagent-grade calcium carbonate with respect to mercury partitioning. One area of testing has involved dissolving limestone with weak acid solutions at scrubber pH values and recovering the small percentage of inert residues that do not dissolve at these pH conditions. These test results indicate that the residues can be added in tests conducted with reagent-grade calcium carbonate to achieve mercury partitioning results similar to those with natural limestone. Further work, funded separately by EPRI, is underway to elucidate what factors in the insoluble residues control mercury partitioning behavior (Blythe, 2011).

Tests with Simultaneous Measurement of Mercury and Selenium

Research conducted under this program 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. Research conducted under a concurrent Phase II SBIR project on selenium management has shown that reducing the ORP favors formation of a selenium species (selenite) that is more easily removed in conventional FGD WWT systems. Thus, for selenium management, lower ORP is desirable, while for mercury management, higher ORP may be desirable. These competing priorities suggest that simultaneous measurement and management of mercury and selenium will be required to develop an approach that does not create a problem for one species while solving a problem for the other species.

Results from both the mercury and the selenium programs indicated that DBA may promote the targeted behavior of both mercury and selenium. For mercury, this is reflected in the results of Test 44, which showed 87% mercury reporting to the liquid phase in the presence of DBA under conditions that would otherwise result in mercury reporting nearly completely to the solid phase, such as was reflected in the results for Test 35. In tests with synthetic liquors, DBA has inhibited the oxidation of selenite to selenate under several conditions (Searcy, 2011). Therefore, several tests were conducted with DBA in which the behaviors of mercury and selenium were monitored simultaneously at the bench scale. One test with acetic acid was conducted under high ORP conditions. Table 3-9 shows the test conditions that are common to the four runs, and Table 3-10 presents the related test matrix.

Table 3-9
Test Conditions for Bench-Scale Tests with Simultaneous Mercury and Selenium Measurement

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

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

Table 3-10
Test Matrix and Mercury Partitioning Results for Bench-Scale Scrubber Tests with Mercury and Selenium

Test #	Reagent LS	Natural LS	Cl (M)	Mn (mg/L)	Additive	Actual ORP (mV)	Purpose	% Hg in Liquor	% Hg in Solids
49		X	0.1	35	DBA	175 – 200	Effect of DBA at new manganese baseline and 200 mV ORP	0%	100%
50		X	0.1	35	DBA	250 – 275	Effect of DBA at 300 mV ORP	12%	88%
51		X	0.1	35	DBA	150	Effect of DBA at 150 mV ORP	0%	100%
52		X	0.1	35	Acetic acid	300	Effect of acetic acid at 300 mV ORP	18%	82%

At ORP conditions ranging from 150 mV to 300 mV, the percentage of mercury reporting to the liquid phase was low (<18%). The primary difference between Test 44, 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.

Figure 3-11 shows the selenium results from the four tests. At the beginning of each test, 1000 µg/L (as Se) of selenite was injected into the reaction tank. The liquid-phase selenite and total selenium concentrations were measured; selenate was estimated by difference. These were the first tests conducted with selenium in the presence of natural limestone. 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. The selenite oxidation rates in the presence of natural limestone 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 host site liquor under the conditions tested. Nearly all dissolved selenium was oxidized to selenate during the six-hour test.

Given the positive results shown by the earlier Test 44 and other tests conducted for the selenium program, further evaluation of DBA was warranted to try and understand why DBA shows beneficial mercury partitioning and selenium speciation under some circumstances but not others.

Tests with Pilot Host Site Liquor

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

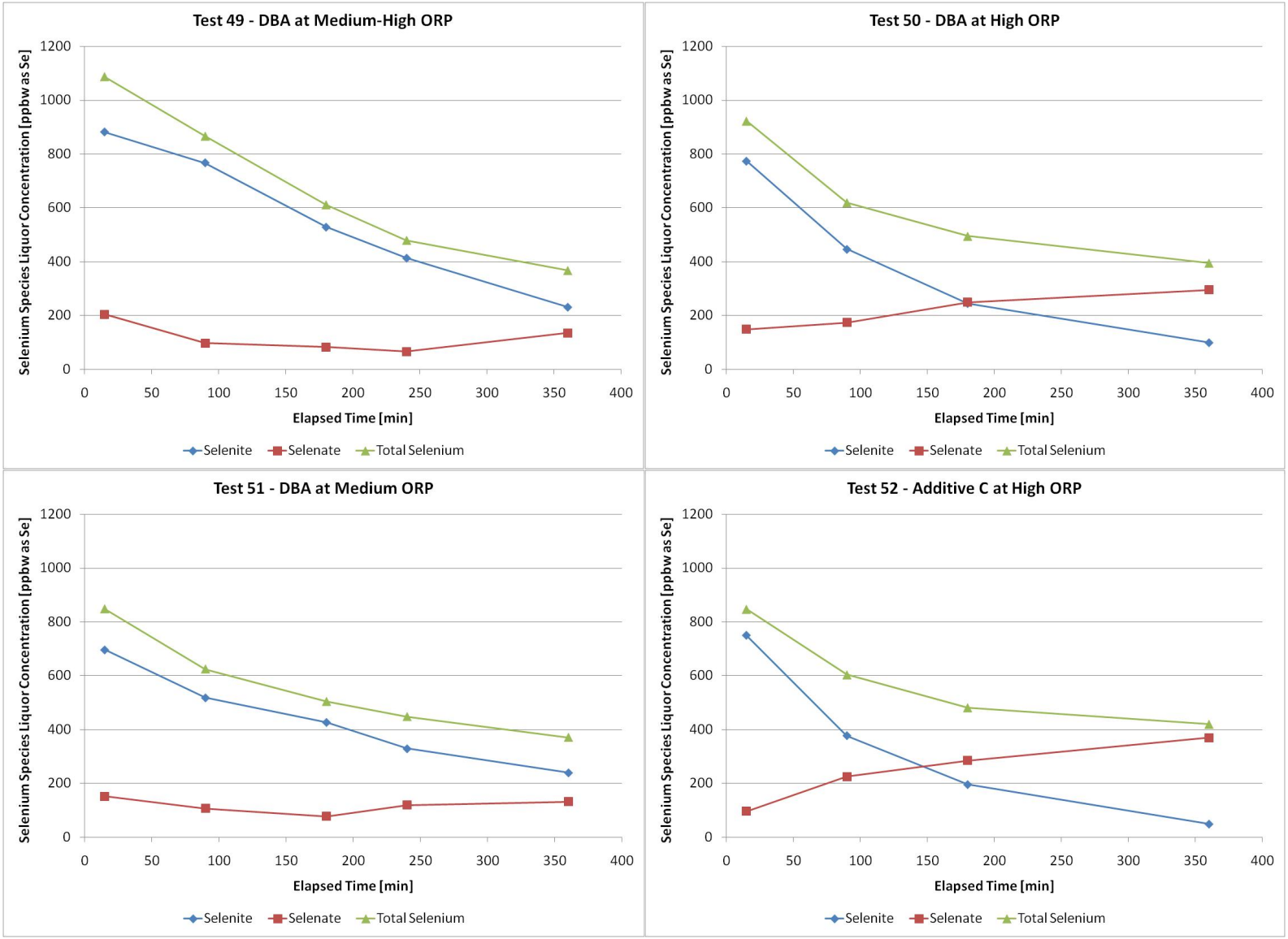

Figure 3-11
Selenium Results for Bench-Scale Tests with Mercury and Selenium

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

Table 3-11 shows the test matrix for the screening tests as well as the mercury phase partitioning and re-emissions results. 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 mercury and selenium behavior. The target ferric chloride addition rate was selected for both mercury and selenium management; in this case, selenium was the controlling case, so the "Low" and "High" target addition rates were 250:1 and 500:1 g Fe:g Se, respectively. The ferric chloride addition rate was based on estimates for the amount of selenite added into the bench-scale scrubber.

Table 3-11
Final Mercury Phase Partitioning and Re-emissions for Bench-scale Tests with Pilot Host-Site Feedstocks

Test Description	ORP (mV)	% 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	450	83%	17%	2%	1%
Test 54 - Low ORP	200	10%	90%	5%	2%
Test 55 - High DBA	200	40%	60%	13%	7%
Test 56 - Iron	100 - 200	40%	60%	1%	1%
Test 57 - High Iron	100 - 200	24%	76%	2%	1%
Test 58 - DBA, variable pH	200	67%	33%	11%	5%

Figure 3-12 shows the mercury phase partitioning behavior observed during these six tests. Under baseline conditions (Test 53), the mercury phase partitioning generally agrees with the full-scale measurements: approximately 80% of the mercury reports to the liquor. Decreasing the ORP (Test 54) shifts mercury partitioning to the solid phase of the slurry, as would be expected based on earlier bench-scale scrubber tests. Due to operational problems, little mercury was added to the system during the low ORP test. Therefore, the impacts of ORP on mercury re-emissions cannot be established conclusively from this data set. The conditions with high DBA and moderate ORP (Test 55) resulted in mercury re-emissions and a percentage of mercury reporting to the liquid phase that fell between the baseline, high-ORP test and the low-ORP test percentages. It should be noted that the oxidation air rates during the DBA test were comparable to the air rates during the high ORP test. The DBA acted as a mild reductant, in that the ORP was lowered at the high-ORP air rate and the percentage of mercury partitioning to the liquid phase was reduced. Further testing with DBA (Test 58) indicated that the re-emissions observed with DBA may be a brief transient effect as the system re-equilibrates. Therefore, the impact of DBA on mercury re-emissions is inconclusive. Lower pH conditions may promote mercury partitioning to the solid phase. Addition of ferric chloride to the scrubber (Test 56) reduced mercury re-emissions, and promoted conditions under which mercury shifts to the solid phase. Increasing the ferric chloride rate (Test 57) increased the percentage of mercury reporting to the solid phase; however, even at the higher iron addition rate, 24% of the mercury remained in the liquid phase. Subsequent sample analyses from the pilot-scale testing determined the extent to which the mercury and iron concentrated in the fines.

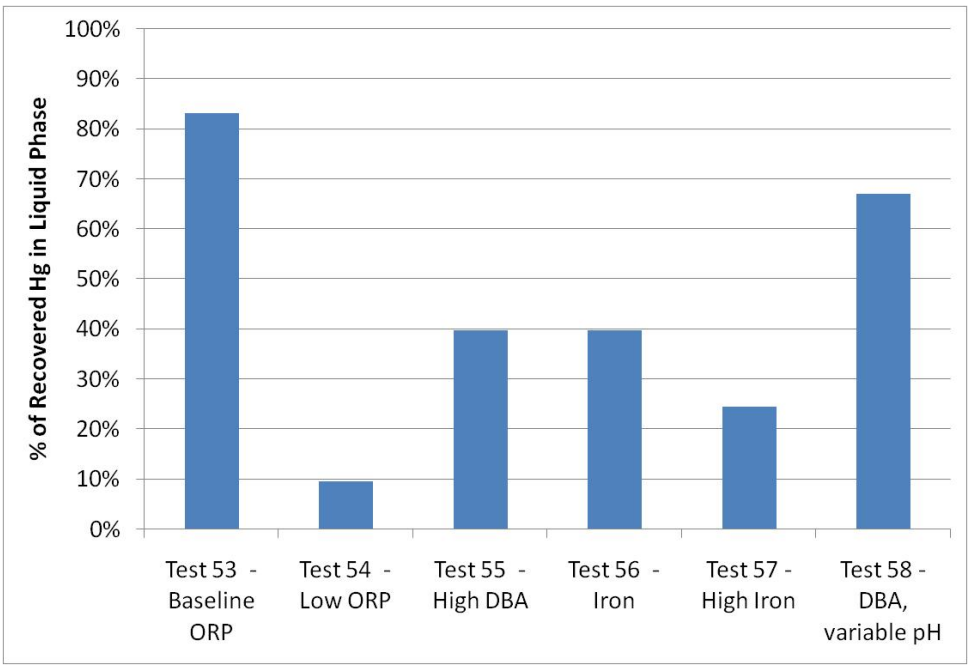

Figure 3-12
Mercury Phase Partitioning for Bench-scale Tests with Pilot Host-Site Feedstocks

Table 3-12 presents the final selenium speciation as measured on the day of test for these six tests. At least some of the selenite spiked into solution left the liquid phase for all tests, presumably reporting to the solid phase. However, total selenium measurements showed variability and scatter, making it difficult to quantify selenium phase partitioning and selenite oxidation. Under baseline conditions, the selenium speciation generally agreed with the full-scale measurements: all selenite was oxidized to selenate, which is reflected by the final total dissolved selenium concentration of over 4500 µg/L and no detected selenite.

Table 3-12
Final Selenium Speciation for 6-hour Bench-scale Tests with Pilot Host-Site Feedstocks

Run #	Test	ORP (mV)	Se^{4+} (µg/L as Se)	Se^{6+} (µg/L as Se)	Total Se (µg/L as Se)
53	Plant ORP (Baseline)	450	<50	4526	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

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

CH2MHill has a patent application (#20090130013) for the use of various iron salts in LSFO FGD scrubbers to adsorb selenium and several heavy metals (e.g., mercury) such that the trace metals report to the solid phase of FGD slurries. The SBIR research reported here complements the CH2MHill work by exploring whether trace metals management techniques developed under the two concurrent SBIR projects, such as changes to operating conditions or the use of scrubber additives, could enhance mercury or selenium reporting to the solid phase or inhibit that sorption process under the specific test conditions of this program.

4
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 4-1 is a simplified schematic for the system.

A pilot-scale hydrocyclone is used periodically (nominally once or twice per day) to blow down reaction tank slurry to control its solids loading. The hydrocyclone is used to separate most of the water and fine particles in the feed slurry, which exit in the overflow, from the bulk of the particles (mostly larger particles) and the remaining water in the feed slurry, which exit in the underflow. A schematic of the pilot hydrocyclone is shown in Figure 4-2.

Test Method

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

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

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

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

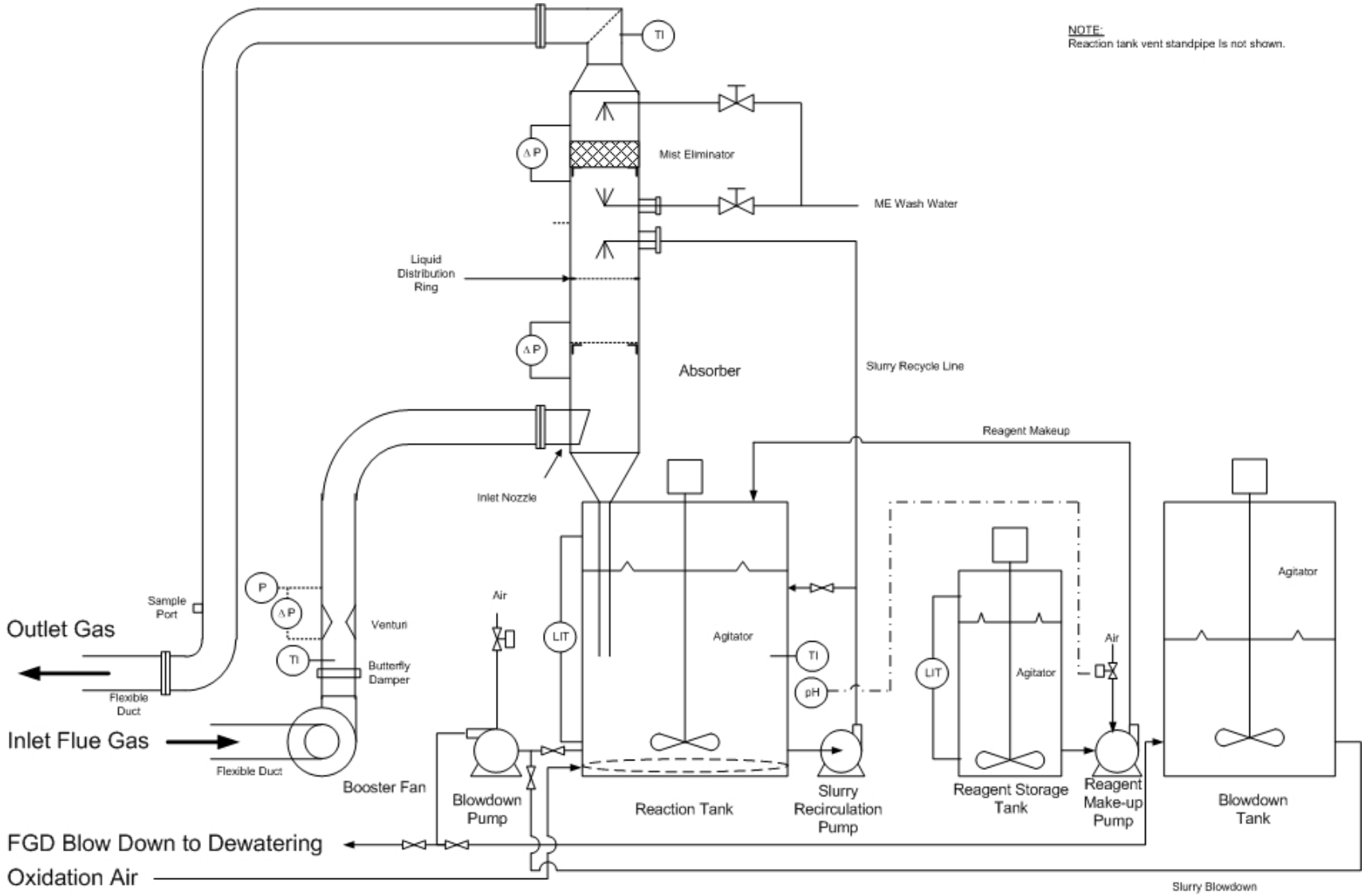

Figure 4-1
Schematic of Pilot FGD Scrubber System

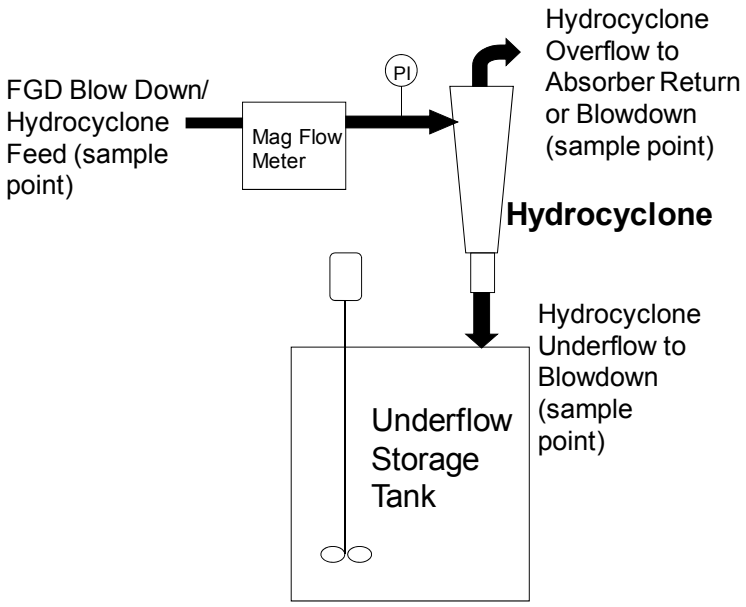

Figure 4-2
Schematic of Pilot Hydrocyclone

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

Test Plan

During operation, the pilot FGD inlet and outlet flue gas were monitored for mercury concentration and SO_2 concentration. Gas-phase mercury concentrations were measured using semi-continuous emission monitors (SCEMs), as described in Section 2, with some modifications to allow for long-term operation in the field. SO_2 concentration was originally slated to be measured using a continuous emissions monitor (CEM), but repeated problems with the instrument precluded its use. Therefore, SO_2 was measured periodically using gas detection stain tubes. A data logger continuously recorded numerous operating parameters such as flue gas temperatures, pressures, and flow rate; reaction tank slurry pH, ORP, and tank level; and others.

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

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

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

Host Site Description

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

Targeted Pilot Test Operating Conditions

The targeted test conditions for pilot testing are shown in Table 4-1. The baseline, high ORP case is actually a desired condition for mercury management when the goal is to retain mercury in the liquid phase. For the host site, decreasing the ORP might benefit selenium management but could create a problem for mercury management by shifting mercury to the gypsum byproduct. The low ORP pilot-scale test, which was expected to result in mercury partitioning to the pilot slurry solids but a reduction in selenate production, was intended to serve as a baseline to be improved upon for the mercury program and the desired condition for the selenium program. The goal of the test with ferric chloride addition to the scrubber was to measure whether ferric chloride could direct mercury preferentially to the fine particles, rather than to the

product gypsum solids, and simultaneously adsorb or co-precipitate selenite that was absorbed from the flue gas before it became oxidized to selenate.

Table 4-1
Targeted Pilot Test Conditions

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

It should be noted that, as discussed in Section 5, the targeted ORP conditions for the low ORP and ferric chloride addition tests could not be attained. The low ORP test became a natural oxidation test, but the measured slurry ORP remained above 400 mV, while the ferric chloride addition was also conducted at ORP values higher than intended.

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

5
PILOT-SCALE TEST RESULTS

Pilot-scale scrubber tests occurred during June and July 2011. Figure 5-1 shows the pilot FGD skid during installation at the host facility. During the pilot test campaign, three five-day tests were conducted: high ORP, low ORP, and ferric chloride addition. The first attempt to operate at low ORP conditions ended after one day of operation due to an unplanned outage at the host site facility; that test was repeated later and conducted for the entire five-day duration.

Figure 5-1
Pilot Wet FGD System

The following subsections describe operations of the full-scale host facility during pilot testing, results for each of the tests, and operational challenges encountered. Discussion of pilot-scale results includes not only mercury capture, re-emissions, and phase partitioning in the scrubber slurries, but also results for the behavior of other trace metals (i.e., iron, and manganese) and a metalloid (selenium). The trace metal behavior may impact mercury behavior across and within the pilot scrubber, and it may correlate with or cause selenium oxidation and sorption. 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 after leaving FGD systems.

Host Site Data and Operations

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

Table 5-1 presents analytical results for samples taken from the full-scale scrubber at the beginning of each five-day test. Operation of the full-scale scrubber was relatively consistent at the beginning of the three tests. Liquid-phase mercury concentrations in the full-scale absorber slurry remained high at around 200 µg/L. Mercury was found predominantly in the liquor (>90%) for the samples collected at the beginning of the low ORP (natural oxidation) and ferric chloride addition tests. The solid-phase mercury measurement for the initial, high ORP test suffered from poor precision, and may be suspect, calling into question the lower fraction of mercury calculated to have remained in the liquid phase for that sample. In all cases, the dissolved selenium consisted completely of selenate, and 40-45% of the total selenium in the absorber slurry remained in the liquid phase. As would be expected based on a typical Pourbaix diagram, manganese remained predominantly in the solid phase under the consistently high ORP conditions; iron reported completely to the solid phase as well. Dissolved total organic carbon (TOC) was low in all samples.

Table 5-1
Host Site Full-Scale Absorber Samples from the Beginnings of the Three Pilot FGD Tests

Description	Units	Baseline High ORP	Natural Oxidation	Ferric Chloride Addition
Sample Date		6/15/2011	7/13/2011	7/19/2011
Temperature	ºF	125	125	121
pH (reaction tank)	-	5.34	5.14	5.23
ORP	mV	605	621	n/a
Selenium:				
Dissolved Selenium (HG-CVAA)				
Total Selenium	µg/L as Se	1610	2120	na
Selenite	µg/L as Se	nd	nd	na
Selenate (by difference)	µg/L as Se	1610	2120	na
Dissolved Selenium (IC-ICP-DRC-MS)				
Total Selenium	µg/L as Se	1530	1800	1620
Selenite	µg/L as Se	<0.5	<0.5	<0.5
Selenate	µg/L as Se	1530	1800	1610

Table 5-1 (continued)
Host Site Full-Scale Absorber Samples from the Beginnings of the Three Pilot FGD Tests

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

The host site WWT system comprises a conventional physical/chemical system followed by constructed wetlands. Samples were collected at the WWT inlet and upstream of the constructed wetlands from an equalization basin. The samples were collected prior to beginning each pilot-scale test at approximately the same time samples were collected from the full-scale absorber. The wastewater is diluted 4:1 to control the chloride concentration entering the wetlands. Table 5-2 presents the mercury data collected at the WWT inlet and in the equalization basin. Total mercury removal across the physical/chemical portion of the WWT system was relatively high, ranging from 88% to 98%, assuming a constant dilution factor. At the WWT inlet, the liquid selenium was almost completely selenate. 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 5-2
Mercury Content at WWT Inlet and at Downstream Equalization Tank

Full-Scale Sample Point	Liquid Hg (μg/L)	Solid Hg (μg/g)	wt% solids (g solids/g total)	Solid Hg (μg/L)	Total Hg (μg/L)	% Hg Removal
Baseline Test						
WWT Inlet	155.7	11.2	0.62	69.2	224.9	98%
Equalization Basin	0.79	n/a	0.00	n/a	0.79	
Equalization Basin (Pre-Dilution)	3.95	n/a	0.00	n/a	3.95	
Natural Oxidation Test						
WWT Inlet	169.1	1.42	1.12	15.8	184.9	88%
Equalization Basin	0.57	132.0	0.0028	3.7	4.3	
Equalization Basin (Pre-Dilution)	2.86	132.0	0.0140	18.5	21.4	
$FeCl_3$ Test						
WWT Inlet	272.1	2.93	0.55	16.0	288.1	95%
Equalization Basin	1.13	315.5	0.0005	1.6	2.7	
Equalization Basin (Pre-Dilution)	5.67	315.5	0.0026	8.1	13.7	

Note 1: Exact dilution ratios at each sample time were not available; an approximate 4:1 dilution factor was used to estimate undiluted concentrations.
Note 2: "n/a" indicates not available.

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

Pilot Scrubber Results

The behavior of mercury and numerous other species was measured throughout the pilot test campaign to test the impacts of ORP and ferric chloride addition on mercury behavior. The mercury 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 mercury preferentially reported to smaller particles or dispersed through the bulk slurry gypsum solids.

Process operating conditions, flow rates and system performance indicators were also monitored in order to completely characterize the test conditions. Data on other species may serve to correlate with or explain mercury and selenium behavior. Operating data can reveal whether or

not the pilot scrubber was operating as desired and may provide some explanation for mercury behavior.

Operational Challenges

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

Summary of Test Operations

During the initial, high ORP test, pH and SO_2 removal targets were maintained; ORP ran slightly higher than in the full-scale unit. Pilot FGD ORP values for the baseline test are shown in Figure 5-2. The second test condition was intended to be a low ORP test. However, low ORP conditions were not attainable; therefore, the second test became a natural oxidation test; ORP conditions for this run are shown in Figure 5-3. Oxidation air was turned off within a few hours of beginning the test, yet ORP remained above 400 mV throughout the test. Sulfur removal and sulfite oxidation performance were maintained. These conditions may result from lower than anticipated average inlet SO_2 concentrations, higher than expected flue gas oxygen concentrations, and low flue gas flow rates, which could enhance the relative O_2 to SO_2 pickup rates across the pilot scrubber. In the third test, ferric chloride salts were added continuously to the scrubber via the recirculating slurry stream. Figure 5-4 shows the ORP conditions during this test; the ORP during this test also remained above 400 mV.

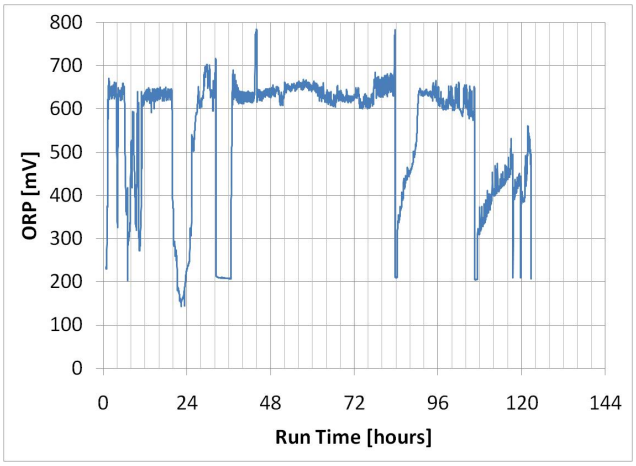

Figure 5-2
ORP – Baseline High ORP Test

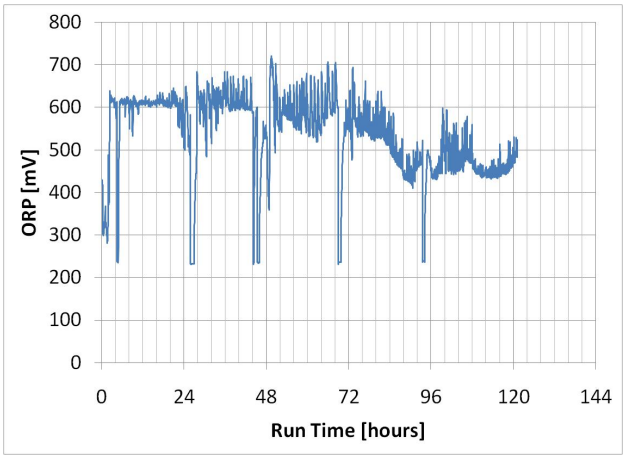

Figure 5-3
ORP – Natural Oxidation Test

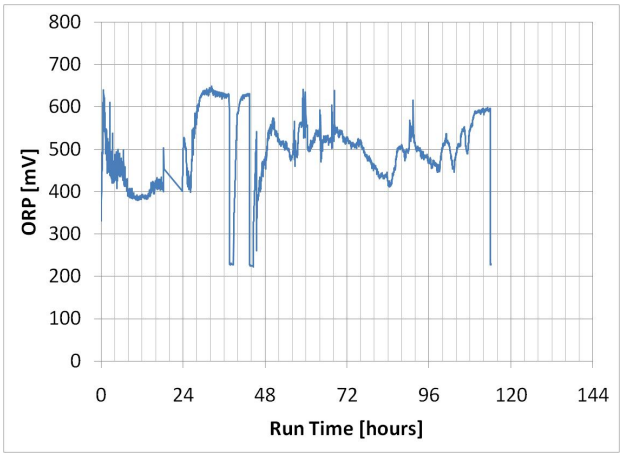

Figure 5-4
ORP – Ferric Chloride Addition Test

Mercury Results

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

The data for capture and re-emissions of mercury across the scrubber for each of the four tests (including the initial low ORP test that was stopped after one day by a unit outage) are summarized as test averages and standard deviations in Table 5-3. Detailed mercury concentration data are presented graphically for the baseline high ORP test; detailed data for the other tests are included in Appendix D. For the baseline high ORP test, Figure 5-5 shows the vapor-phase total mercury concentrations in the flue gas entering and exiting the pilot scrubber. Figure 5-6 shows the vapor-phase elemental mercury concentrations, Figure 5-7 shows the calculated mercury capture percentage across the scrubber, and Figure 5-8 shows the mercury re-

emissions percentage. The mercury removal across the scrubber is calculated as a percentage of total inlet mercury, and the mercury re-emission is the percentage of inlet oxidized gas-phase mercury that is chemically reduced in the scrubber and re-emitted as elemental gas-phase mercury. For all tests, the inlet flue gas mercury oxidation averaged above 90%, with concentrations of total mercury typically at or below 5 $\mu g/Nm^3$ (corrected to 3% O_2 and reported on a dry basis); the concentrations were considerably lower on a wet and actual air dilution basis, particularly when the flue gas O_2 concentration was in the range of 10%. As reflected in Table 5-3, 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 5-3
Average Mercury Removal and Re-emissions Percentages across Pilot Scrubber

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

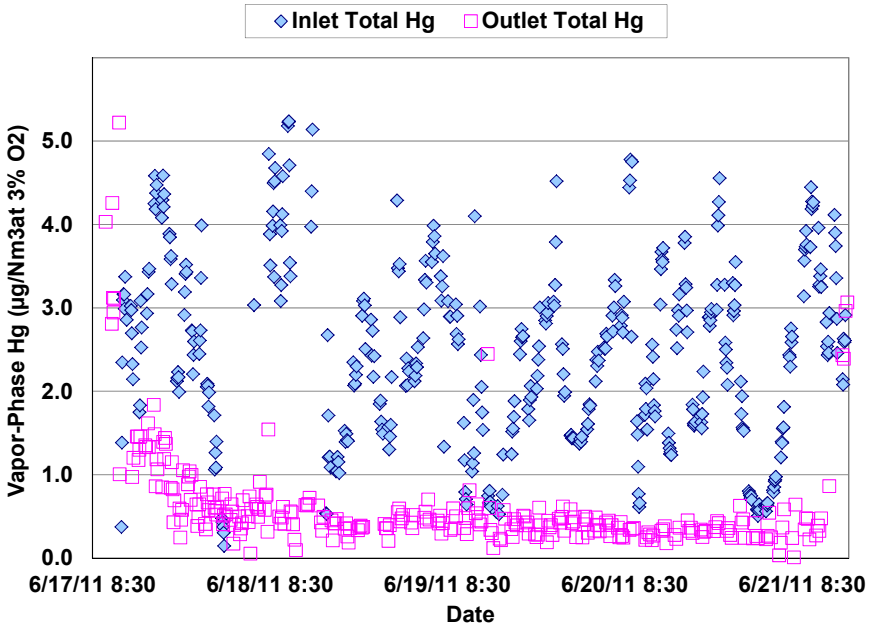

Figure 5-5
Vapor-phase Total Mercury in Pilot Inlet and Outlet Flue Gas Streams (Baseline High ORP Test)

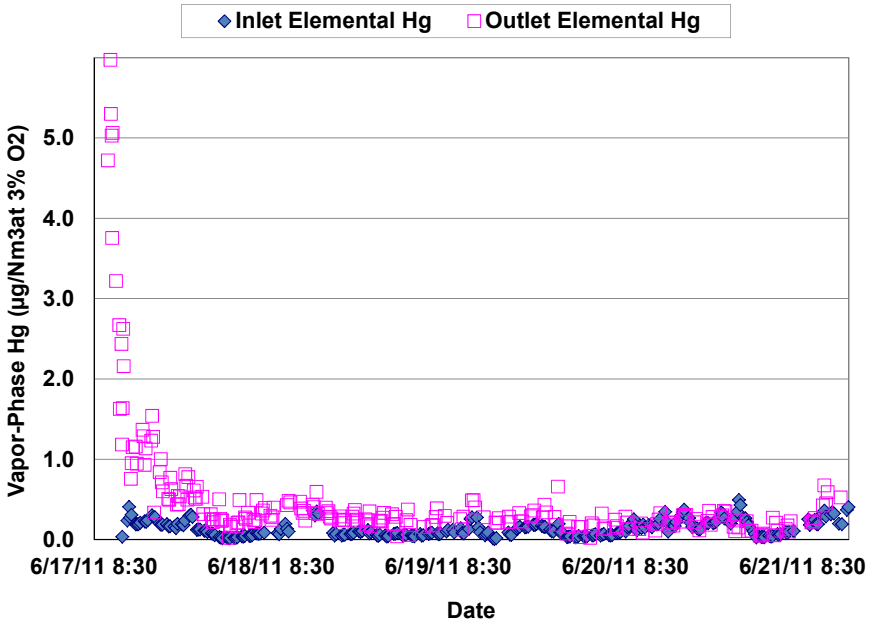

Figure 5-6
Vapor-phase Elemental Mercury in Pilot Inlet and Outlet Flue Gas Streams (Baseline High ORP Test)

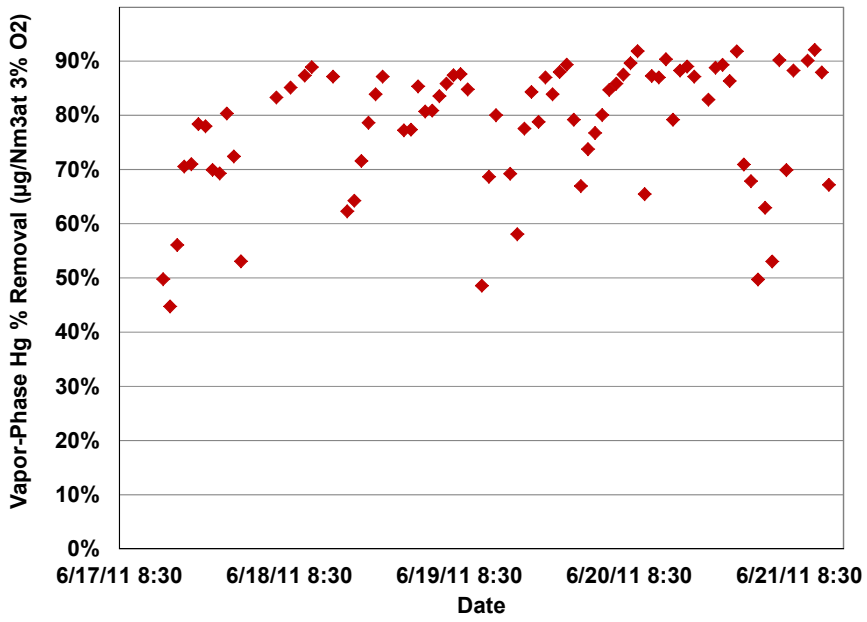

Figure 5-7
Mercury Removal across Pilot-scale Scrubber (Baseline High ORP Test)

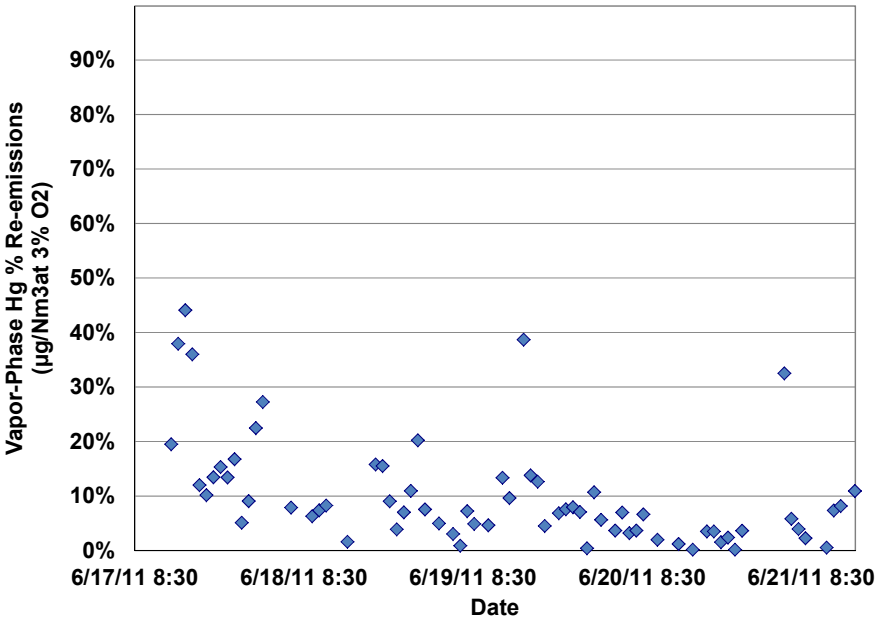

Figure 5-8
Mercury Re-emissions across Pilot-scale Scrubber (Baseline High ORP Test)

Table 5-4 shows the mercury concentrations and the phase partitioning for mercury in the pilot absorber slurry as well as in the hydrocyclone overflow and underflow streams during blowdown events. In the baseline, high ORP test and in the natural oxidation test, about 70 to 80% of the mercury remained in the liquor, while 20 to 30% reported to the solids. In contrast, in the full-

scale absorber, approximately 90% of the mercury reports to the slurry liquor, so the pilot high ORP test, which was intended to mimic the full-scale operation, shows a lower fraction of mercury reporting to the liquor. A lower fraction reporting to the liquor was expected during the natural oxidation test. In fact, a much lower fraction was expected but was not achieved, likely because the measured pilot absorber slurry ORP never dropped below 400 mV.

Table 5-4
Mercury Phase Partitioning in Bulk Pilot Absorber Slurry, HCOF, and HCUF Streams

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

During the ferric chloride test, the percentage of mercury in the slurry found in the solids rather than the liquor was observed to increase over time, from 13% at the beginning of the test to over 50% at the end. This likely reflects an increased inventory of iron in the slurry solids available to adsorb/co-precipitate mercury as time progressed and the iron addition continued. This effect is substantiated by the iron concentration data presented later in this section. It is possible that with continued operation, and if steady state were achieved, an even higher percentage of mercury in the slurry would have reported to the solids. While higher partitioning of mercury to the solids goes counter to the initial premise of this research program (keeping the mercury in the liquor and not in the gypsum byproduct), the data also show that the mercury was preferentially

accumulating in the fine particles over the course of the ferric chloride test. The slurry blowdown at 38 hours was marked by an abnormally high suspended solids content in the hydrocyclone overflow, which skews this comparison, but the remaining results show that the percentage of mercury found in the fine overflow solids was increasing over time. This would mean the percentage of the mercury reporting to the underflow (product gypsum) was decreasing, and may have continued to decrease as steady state was achieved. This observation supports a hypothesis that mercury associates with the enriched iron fractions in the fines during ferric chloride addition, and may have the effect of lowering the product gypsum mercury concentration. However, because of the reduced turnover of solids and liquor in the pilot wet FGD system, for the reasons described above, this effect was not clearly demonstrated; the end-of-test partitioning of solid-phase mercury between the hydrocyclone overflow and underflow was similar for all three tests.

Mercury concentrations were measured in solid absorber slurry samples that were wet sieved to produce fractions comprising particles >20 µm (primarily product gypsum) and particles <20 µm (fines). Solid samples from the initial charge of full-scale absorber slurry and from the final pilot-scale absorber slurry were wet sieved; the results for mercury distribution are presented in Figure 5-9 and Table 5-5. The mercury wet-sieve results are consistent with the mercury measurements in the hydrocyclone overflow and underflow streams during blowdown events. Mercury behavior under baseline and natural oxidation tests showed only minor differences, and the use of ferric chloride appears to promote mercury reporting to the solid phase, specifically to the fine particles.

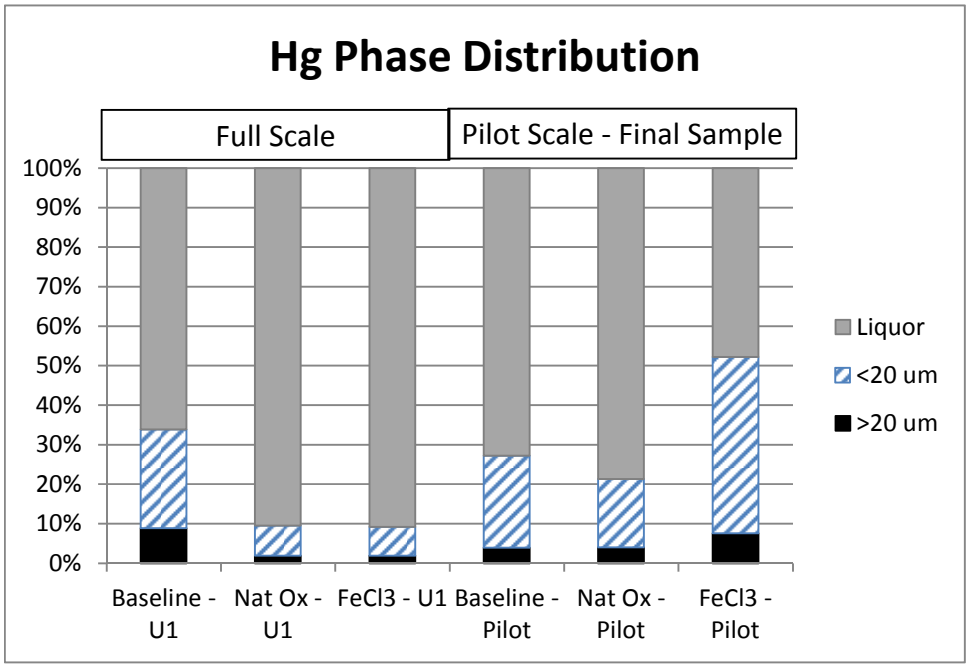

Figure 5-9
Mercury Phase Partitioning in Full-scale and Pilot-scale Absorber Samples

Table 5-5
Solid-phase Mercury Results in Wet-Sieved Samples

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

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

Selenium Results

Baseline High ORP Test

Selenium behavior observed during the baseline test in the pilot scrubber was relatively consistent with behavior observed in the full-scale scrubber. Table 5-6 shows the measured total selenium in the liquid and solid phases of the slurry for the initial charge of full-scale scrubber slurry and for the pilot-scale scrubber slurry over the course of the High ORP test. "BD" indicates a blowdown event. All dissolved selenium was measured as selenate throughout the test. Due to the fluctuations in slurry suspended solids loading and level in the pilot FGD reaction tank, a material balance is required to present a complete picture of the selenium phase partitioning. Material balances indicate that most (~75-80%) selenium that was added to the pilot system from the flue gas reported to the slurry solids, although a modest fraction (~20-25%) accumulated in the liquor as selenate. The estimated fraction reporting to the solids is somewhat higher than in the full-scale system, in which slightly less than 60% of the slurry selenium reports to the solid phase.

Table 5-6
Baseline High ORP Test - Scrubber Selenium Measurements

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

Natural Oxidation Test

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

Table 5-7 shows the measured total selenium in the slurry liquor and solids for the natural oxidation test. As with the baseline test, all dissolved selenium was found in the selenate form. A material balance indicates that nearly all "new" selenium that accumulated in the slurry from

the flue gas reported to the solid phase of the slurry. Thus, lowering the oxidation air rate may cause a shift of selenium partitioning from the slurry liquor to the slurry solids.

Table 5-7
Natural Oxidation - Scrubber Selenium Measurements

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

Ferric Chloride Addition Test

In the third test, ferric chloride salts were added continuously to the scrubber via the recirculating slurry stream. The ORP remained above 400 mV. A material balance indicates that selenium absorbed from the flue gas into the slurry reported almost entirely to the solid phase, as with the natural oxidation test. Measurements of liquid- and solid-phase iron concentrations confirmed that all iron reported to the solid phase of the pilot slurry, and the mass ratio of added iron to accumulating selenium was nominally 500:1. Due to the low liquid turnover during the test, it was not possible to demonstrate reduction of dissolved selenium concentrations to low levels (e.g., <50 µg/L as Se). Given that the natural oxidation test showed nearly all "newly absorbed" selenium entering the system reporting to the solid phase, it was not possible to demonstrate the benefits of ferric chloride addition to the scrubber for selenium management in these tests. Slurry liquor and solid selenium concentrations during this test are summarized in Table 5-8.

Table 5-8
Ferric Chloride Addition Test - Scrubber Selenium Measurements

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

Low ORP Test, First Attempt

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

The results also indicate that oxidation air flow control may represent one part of a scrubber selenium management approach, though this approach might not be effective for plants that cycle load over a wide range. Figure 5-10 shows the ORP conditions for this test, Figure 5-11 shows the absorber tray pressure drop, and Figure 5-12 shows the flue gas oxygen concentration. During this test, problems with the pilot FGD flue gas control valve were encountered, and the valve opened fully just after six hours of operation. The valve opening is reflected by the sharp increase in absorber tray pressure drop at that time; due to flow meter problems during this time, the higher actual flow rate was not accurately reflected by recorded flow rates. As more SO_2 was absorbed into the system as sulfite, the ORP began dropping rapidly. Then, just after eight hours of operation, the plant began decreasing load, the flue gas oxygen content increased, and the ORP increased simultaneously. After 18 hours of operation, the unit began cycling up in load, the flue gas oxygen decreased, and ORP dropped to nominally 200 mV, where the ORP remained for the last five hours of the test.

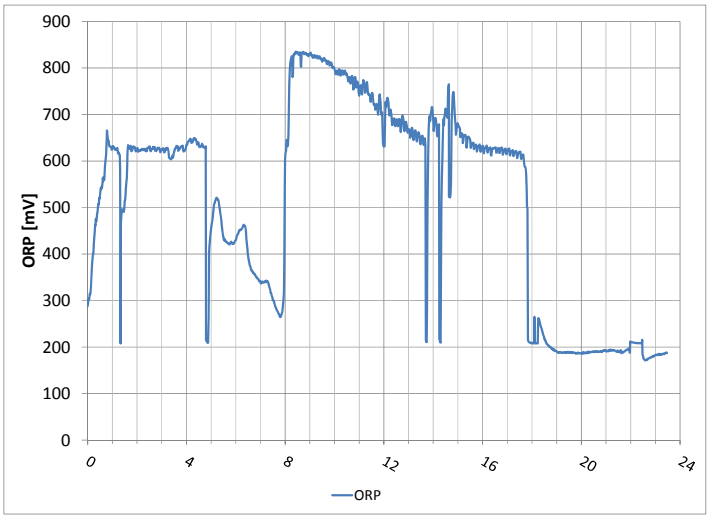

Figure 5-10
ORP – First Attempt at Low ORP

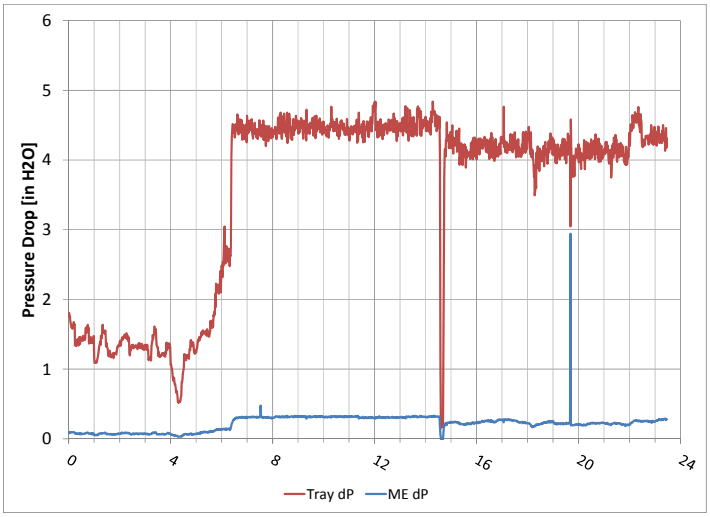

Figure 5-11
Absorber Tray Pressure Drop – First Attempt at Low ORP

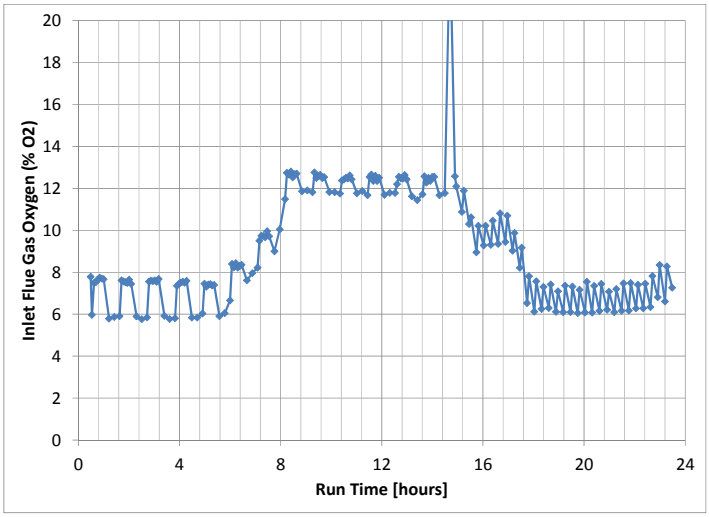

Figure 5-12
Flue Gas Oxygen Concentration – First Attempt at Low ORP

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

Solid-phase Selenium Results

The distribution of solid-phase selenium within different particle size fractions of the pilot scrubber slurry solids was measured during pilot testing. Two measurement approaches were used: (1) distribution between pilot HCOF and HCUF streams during blowdown events and (2) distribution between different size fractions in the absorber slurry based on wet-sieved slurry solid samples. Table 5-9 presents the solid selenium measured in pilot HCOF and HCUF streams.

Table 5-9
Solid Selenium in Pilot Hydrocyclone Underflow and Overflow

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

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

Wet sieving of solid samples separated fractions comprised of particles >20 µm (bulk solids) and particles <20 µm (fines). Solid samples from the initial charge of full-scale absorber slurry and from the final pilot-scale absorber slurry were wet-sieved; the results are presented in Figure 5-13 and Table 5-10.

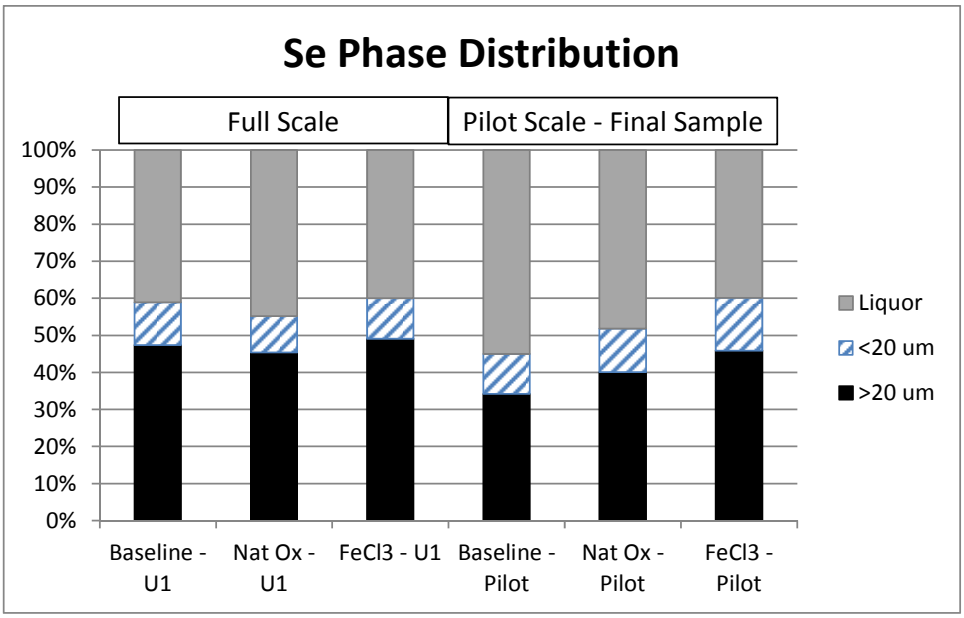

Figure 5-13
Selenium Phase Partitioning in Full-scale and Pilot-scale Absorber Samples

Table 5-10
Solid-phase Selenium Results in Wet-Sieved Samples

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

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

Iron and Manganese

Iron remained almost completely in the solid phase throughout pilot testing, as would be expected. Iron is typically found with greater than 99% in the slurry solid phase at typical wet FGD pH and ORP conditions. Table 5-11 shows the iron concentrations and the phase partitioning for iron in the absorber slurry as well as in the hydrocyclone overflow and underflow streams during blowdown events. The percentages of iron found in the solid phase of the absorber slurry are not shown, but with the liquid-phase concentrations all below the reported detection limits, the percentages in the solids were all calculated to be greater than 99.8% or higher. Iron enrichment in the fines was also high with 72 to 92% of the absorber slurry iron reporting to the hydrocyclone overflow solids.

Table 5-11
Iron Phase Partitioning in Bulk Pilot Absorber Slurry, HCOF, and HCUF Streams

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

During all tests, the manganese remained predominantly in the oxidized Mn(IV) solid state. Table 5-12 shows the manganese concentrations and the phase partitioning for manganese in the absorber slurry as well as in the hydrocyclone overflow and underflow streams during blowdown events. These results show that manganese tends to concentrate in the smaller particles found in the overflow. Manganese enrichment in the fines is greater than was seen for selenium, but generally less than was seen for iron.

Table 5-12
Manganese Phase Partitioning in Bulk Pilot Absorber Slurry, HCOF, and HCUF Streams

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

Other FGD Analytes

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

correlations may be drawn between the presence of the secondary sulfur species and selenium behavior based on the pilot testing data set.

Summary

Key findings of the pilot-scale scrubber tests are the following:

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

was cut short, it was not possible to demonstrate appropriate sulfite oxidation levels while retaining selenium as selenite in the liquor.

Despite numerous operational challenges, some trends from bench-scale scrubber testing were evident during pilot testing. Specifically, the use of ferric chloride as a scrubber additive may prove useful in controlling mercury behavior within FGD scrubbers. Additionally, reducing oxidation air rate and ORP tends to either retain selenium as selenite in the liquor or shift selenium to the solid phase. A holistic strategy for simultaneous mercury and selenium 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 solids. This approach would likely reduce selenite oxidation and promote selenite reporting to the solid phase. The selenium would then exit with the bulk byproduct gypsum, and the mercury would predominantly exit with the fine particles in the FGD chloride purge stream; subsequent precipitation of remaining liquid-phase mercury and separation of the mercury-rich solids could be effected in the FGD WWT system.

6
LABORATORY WASTEWATER TREATMENT TESTS

Laboratory wastewater treatment tests were conducted in synthetic and field FGD liquors during the Phase II program. Earlier Phase I precipitation testing demonstrated that two additives, Additive B1 and TMT-15 (2,4,6-trimercapto-s-triazine trisodium salt), successfully precipitated nearly all of the mercury in tests with synthetic liquors when either chloride (at 0.5 M concentration) or bromide (at 1.0 M concentration) was used to complex the mercury upstream in the FGD system. Phase II tests with synthetic liquors tested the ability of a wider range of commercially available precipitating agents to remove mercury from bromide-laden liquors. Laboratory precipitation tests measured the ability of numerous commercially available precipitation agents to remove dissolved mercury from field liquors generated during pilot scrubber testing. The following subsections present the test conditions and results for the precipitation tests conducted in synthetic and field-generated liquors.

Tests in Synthetic Liquors

The purpose of the precipitation study was to demonstrate removal of mercury from the FGD chloride purge stream and thus prevent mercury discharges from the FGD WWT system. The Phase II precipitation test method included improved control and monitoring of operating parameters. Five precipitation agents were tested at two pH conditions. Some agents were tested at a single agent concentration or dosing rate, and some were tested at two concentrations. All tests were conducted in a synthetic baseline FGD liquor (previously shown in Table 2-1) with 0.5 M NaBr added. If bromide is used to retain mercury in the scrubber liquid phase, the precipitation agents used in the WWT system must be stronger precipitating agents for mercury than bromide is a complexing agent. As noted in Section 3, the emphasis on using bromide as a complexing agent for mercury declined substantially as halogen-related corrosion concerns became evident for many of the recent FGD installations. However, this knowledge was not available when the precipitation tests in synthetic liquors occurred, and bench-scale tests with bromide had shown promise for retaining mercury in the liquid phase.

For each test condition, the synthetic FGD liquor was prepared at the beaker scale, heated to ~100 ºF, pH adjusted, and spiked with mercuric chloride. The initial "t=0" liquid sample was the collected. Then, the precipitation agent was added and the pH was adjusted to the desired value. The solution was agitated for 30 additional minutes, and the final liquor sample was taken for mercury analysis. The difference in liquid phase mercury concentrations between the initial and final samples divided by the initial concentration yielded the mercury removal percentage.

Table 6-1 shows results from the Phase II precipitation study. The agent, TMT-15, has been tested previously, and the excellent removal results were confirmed with the improved test method; performance was similar at both pH 7 and 9. Additives C1 and C2 are similar, though not identical, to precipitation agents previously tested; the agent supplier requested that the updated products be tested. Additives B1, C1, and C2 were provided by a large wastewater treatment company. Both Additive C1 and Additive C2 were successful in reducing liquid mercury concentrations to less than 10 µg/L. The sodium decanoate and Calmet, a calcium

polysulfide, had not previously been tested in the SBIR program and were identified via a literature review during the previous reporting period. Sodium decanoate was not successful at precipitating mercury from solution. Calmet was successful, with slightly better performance at pH 7 than pH 9. Thus, several mercury precipitation agents showed promise for testing the pilot scale FGD wastewater.

Table 6-1
Mercury Removal by Several Precipitation Agents in the Presence of 0.5 M Bromide

			Hg Concentration (µg/L)		
Agent	**Concentration (mg/L)**	**Desired pH**	**t = 0 min**	**t = 30 min**	**% Hg Removed**
TMT-15	30	7	2170	0.51	99.98
TMT-15	30	9	2150	0.41	99.98
Additive C1	10	7	2010	4.91	99.76
Additive C1	100	7	2020	4.76	99.76
Additive C2	10	7	1980	6.53	99.67
Sodium Decanoate	40	7	2020	2030	-0.48
Sodium Decanoate	40	9	2060	2020	1.88
Calmet	30	7	1910	0.45	99.98
Calmet	30	9	1950	0.39	99.98
Calmet	150	7	2010	1.19	99.94
Calmet	150	9	2040	6.04	99.70

Tests in Field Liquors

At the end of the field pilot-scale test program, a portion of the final HCOF was reserved for later WWT testing. Aliquots (200 mL) for testing were filtered through a 0.45-µm pore size filter prior to conducting the WWT tests. Prior to adding the precipitation agents, filtered samples were taken to re-confirm the initial liquid-phase mercury concentration. Next, the precipitation agent was added and the solution was agitated with a stir bar for 30 minutes. Then, final samples were taken and filtered to establish mercury removal efficiency. The pH conditions were monitored, though not adjusted, throughout the test.

Table 6-2 shows the WWT test matrix conducted on the pilot HCOF samples from the baseline test. The baseline liquor samples contained 76 µg/L of mercury in the liquid phase when initially sampled. Later samples contained 59 and 47 µg/L of mercury, which indicates that mercury may be precipitating very slowly from solution in the HCOF slurry. In precipitation tests conducted on synthetic, laboratory-generated liquors, as described above, Additive C1, Additive C2, TMT-15, and Calmet showed greater than 99.6% removal of mercury. Therefore, these four additives were selected for testing on samples generated in the pilot-scale scrubber. Additional additives

were tested primarily for selenium removal under the concurrent selenium management SBIR project. The incremental cost was minimal to test for mercury removal with those additives; therefore, mercury removal efficiency with three other additives (ferric chloride, Additive B1, and two dosages of elemental iron) are reported. The removal efficiencies for elemental iron was tested not only at 30 minutes residence time, but also at 60 minutes.

Table 6-2
Test Conditions for Beaker-Scale Precipitation Tests in Field Liquors

Additive	Target pH	Target Dosage (g/l)	Hg Conc. (µg/L)			Hg Removal (%)	
			t = 0 min	t = 30 min	t = 60 min	t = 30 min	t = 60 min
Additive C1	7	0.10	46.5	0.080	n/a	99.83%	n/a
Additive C2	7	0.10	46.5	0.052	n/a	99.89%	n/a
TMT-15	7	0.03	46.5	0.064	n/a	99.86%	n/a
Calmet	9	0.03	59.3	0.038	n/a	99.94%	n/a
$FeCl_3$	5.5	0.05	59.3	38.2	n/a	35.66%	n/a
Additive B1	5	0.5	59.3	0.062	n/a	99.89%	n/a
Fe(0)	5.5	10	59.3	1.50	1.43	97.48%	97.58%
Fe(0)	5.5	50	59.3	3.51	3.10	94.08%	94.77%

"n/a" indicates not analyzed.

The mercury removal performance of Additive C1, Additive C2, and TMT-15 in field liquors was consistent with performance in synthetic liquors; all showed greater than 99.8% removal of mercury with final mercury concentrations below 0.100 µg/L (100 ng/L). Additional testing would be required to demonstrate whether removals to ~10 ng/L could be achieved with higher dosages or longer reaction time. Ferric chloride showed poor removal performance. Additive B1 performance was similarly high compared to the Additive C1 and Additive C2 agents. Elemental iron removed more than 90% of the iron but did not achieve mercury concentrations below 100 ng/L.

Summary

Several additives (Additive C1, Additive C2, and Additive B1; TMT-15; and Calmet) have shown high mercury removal performance in synthetic and field liquors. Additional testing would be required to demonstrate removal of mercury down to the latest anticipated effluent limits of ~10 ng/L.

7
ENGINEERING AND ECONOMIC EVALUATION

The capital and operating costs for several mercury management strategies were considered: bromide addition, ferric chloride addition, and oxidation air flow rate control. The evaluations of ferric chloride addition and oxidation air flow rate control have not been presented in prior reports; therefore, a greater level of detail is presented here than for results presented previously.

Bromide Addition and Recovery

Bench-scale tests conducted early in the research program indicated that bromide showed promise for retaining mercury in the liquid phase of synthetic FGD slurries. Therefore, during 2010, the engineering and economic evaluation was updated for bromide addition to FGD scrubbers. With updated reagent prices, the loss of bromide in the FGD chloride purge stream or "blowdown" was cost-prohibitive; therefore, methods for recovering bromide from the blowdown were evaluated and incorporated into the economic evaluation. In early 2011, the project team significantly reduced the research emphasis placed on bromide after learning that recent experience in many new U.S. utility FGD systems has raised concerns that bromide would exacerbate corrosion issues, or at least would lessen the acceptance of bromide by the industry. Because bromide was eliminated from further consideration, the details of the economic evaluation are presented in Appendix F, rather than in the body of the report, to serve as a record of the work conducted. Appendix F contains an excerpt of the May 2010 progress report, which summarizes the economics for bromide addition and the most promising bromide recovery option. In the excerpt, "Additive A" refers to bromide; the solvent recovery method was chlorination.

Ferric Chloride Addition

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

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

To conduct an economic analysis of ferric chloride addition, two cases were considered: a model plant similar to the host site for the pilot testing, and a DOE standard example case for Illinois #6 bituminous coal ("FOA 403" coal). For each coal, the coal characteristics were first assembled.

For the host unit coal, the actual coal data from samples collected of the host unit's feedstock were averaged for parameters including heat and ash content, and concentrations of sulfur, chloride, mercury, and selenium. These values were specified by DOE for the FOA 403 coal, other than the selenium concentration. The selenium concentration for that coal was assumed to be the average of data for a subset of sites selected for the 2009/2010 Information Collection Request (ICR) for non-mercury metals analyses. A 2010 EPRI project conducted selenium balances across the same subset of power plants that were chosen for the ICR.

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

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

Table 7-1 shows the coal data and other inputs used to estimate the ferric chloride addition rates, which are also shown in Table 7-1. The makeup costs assume a 78% capacity factor for the generating units, as presented later in the generic unit load profile (Table 7-4).

Table 7-1
Inputs and Results for Estimating Ferric Chloride Addition Rates

Description	Units	Pilot Host Site	DOE Illinois #6 Coal
Coal heating value	Btu/lb	12,500	12500
Coal composition (dry basis)			
Hg	ppm	0.0489	0.15
Se	ppm	2.14	4.05
Cl	ppm	700	3000
S	wt%	1.42	2.5
Ash	wt%	15.76	9.7
Gross generating capacity	MW	500	500
F-factor	dscf/MMBtu	9,780	9,780
Heat rate	Btu/kWh	10,000	10,000
% of coal Hg to FGD inlet flue gas	%	80%	80%
% of Hg to FGD liquor	%	81%	81%
% of Coal Se to FGD liquor	%	24.1%	5.1%
Coal Hg	lb/Tbtu	3.92	12.00
Coal Se	lb/Tbtu	171.4	324.0
Hg to FGD liquor	lb/Tbtu	2.54	7.78
Se to FGD liquor	lb/Tbtu	41.31	16.52
Fe:Hg mass ratio		2000	2000
Fe:Se mass ratio		500	500
$FeCl_3$ rate based on Hg	lb Fe/TBtu	14,700	45,200
$FeCl_3$ rate based on Se	lb Fe/TBtu	60,000	24,000
Concentrated “42 Be” $FeCl_3$ solution makeup rate	gpm	1.12	0.93
	gal/week	11,260	9,330
Reagent unit cost	$/gal	2.2	2.2
$FeCl_3$ Makeup Costs	$/year	1,010,000	760,000
$FeCl_3$ Makeup Costs	mills/kWh	0.29	0.22

Table 7-1 (continued)
Inputs and Results for Estimating Ferric Chloride Addition Rates

Purchased Equipment Costs	$	100,000	84,000
Capital Cost Multiplier		4	4
Total Capital Cost	$/kW	0.80	0.67

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

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

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

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

Oxidation Air Control

Control of the oxidation air flow rate into the FGD absorber reaction tank is one option for managing the redox chemistry in FGD scrubbers, though air control alone may be insufficient for some systems. The oxidation air system is sized to handle the air requirement at the design coal sulfur content and at an established ratio of air to sulfur input to the FGD scrubbers. Often, plants may operate firing coal below the design coal sulfur level, and many plants may operate below design load at night and in the Spring and Fall. Many oxidation air systems currently in place do not control the flow rate to a large extent and simply operate the blowers at maximum

flow rate on a continuous basis, particularly in older FGD systems. For systems that operate at maximum air output, the air rate is often much higher than what is required to maintain sulfite oxidation, thus wasting power. Beyond the benefits attributed to ORP control, control of oxidation air flow also reduces energy costs for the blowers.

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

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

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

The control of a single-stage unit is typically achieved via the use of inlet vanes, an outlet diffuser with vanes, or a combination of both. Single-stage blowers are usually equipped with a VFD that operates in conjunction with the inlet and outlet vanes. An advantage of a single-stage unit is that the efficiency remains more consistent over the turn down range when both inlet vanes and an outlet diffuser are used, and single-stage units typically have a wider turndown range. For example, one supplier documented that over a turn down from 100 to 50% of the design flow rate, the efficiency of a single stage unit would remain constant at 78%. When turning down a corresponding multi-stage unit, the efficiency would drop from 78 to approximately 60%. Figure 7-1 shows the efficiencies and turndown capabilities of the two blower types, each with two flow control options. The turndown is expressed as percentage decrease from maximum flow. It should be noted that the figure was supplied in the promotional

materials of a single-stage blower supplier (Turblex, 2008). Table 7-2 shows the turndown and efficiency values selected from Figure 7-1 for use in the economic analysis.

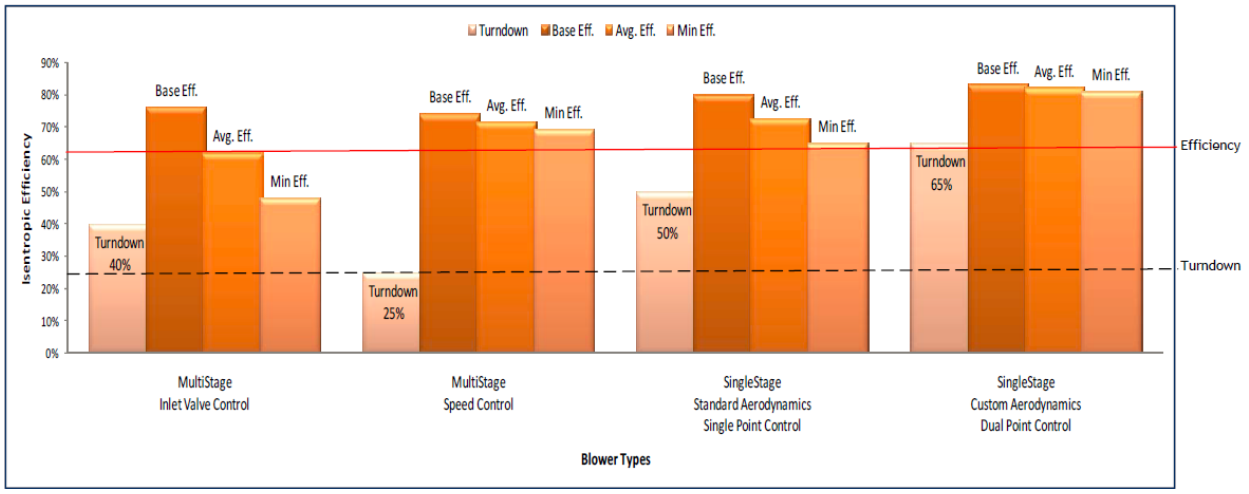

Figure 7-1
Efficiency and Turndown for Multi-stage and Single-stage Blowers

Table 7-2
Turndown and Efficiencies for Centrifugal Blowers using Several Flow Control Methods

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

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

The cases selected for costing were based on the DOE FOA 403 coal and a stoichiometric ratio of 3 moles O per mole SO_2 (or 3/2 moles of O_2) for the oxidation air relative to the total design

sulfur input to the FGD scrubbers. For the oxidation air analysis, the *design* coal sulfur content was increased from 4.0 lb SO_2/MMBtu to 5.5 lb SO_2/MMBtu because many systems will design for higher coal sulfur content to provide additional operational flexibility. A single scrubber was assumed, and two blower configurations were evaluated: 2x100% (Case A) and 3x50% (Case B). In Case B, two blowers operate, and one is a spare.

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

Table 7-3
Specifications and Greenfield Capital Costs for Oxidation Air Blowers

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

The operating costs considered in this analysis for the blowers consist only of energy costs. The power requirements were estimated for both types of blowers, each with two different flow control methods. A generic unit load profile was assumed, as shown in Table 7-4. Daytime was assumed to last 15 hours, and night time was assumed to last 9 hours. A constant efficiency equal to the average maintainable efficiency shown in Table 7-2 was assigned for each blower type and flow control combination. Although the efficiencies for multi-stage blowers may vary over the

turndown range, the variability of efficiency with turndown is highly dependent on the specific blower model selected and where the design point is located on the blower performance curve. By assigning a constant efficiency to the multi-stage blower, this evaluation presents more favorable energy costs than would likely be the case for multi-stage blowers.

Table 7-4
Generic Unit Load Profile

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

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

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

8
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A
BENCH-SCALE ANALYTICAL DATA

Table A-1
Data for Tests 1 through 17

Run #		**1**	**2**	**3**	**4**	**5**	**6**
Date		**2/5/2009**	**3/3/2009**	**3/4/2009**	**3/5/2009**	**3/11/2009**	**3/12/2009**
Test		**High bromide, low iron**	**High bromide, medium iron**	**Medium bromide, medium iron**	**High bromide, medium iron**	**High chloride, medium iron**	**Medium chloride, medium iron**
Test Matrix Variables:							
Ferrous sulfate	ppmw	4000	8000	4000	8000	4000	4000
Gypsum solids - $CaSO_4$ -2 H_2O (s)	wt%	8	8	8	8	8	8
Bromide (NaBr)	M	1	1	0.5	1	0	0
Chloride (NaCl)	M	0.1	0.1	0.1	0.1	1.0	0.5
Inlet flue gas Hg	ug/Nm3						
Outlet flue gas Hg	ug/Nm3						
Liquor Hg							
t = 0 h	ug/L	<0.316	n/a	0.738	1.10	<0.387	<0.390
t = 3 h	ug/L	11.92	n/a	8.86	16.41	8.21	<0.387
t = 6 h	ug/L	24.51	n/a	20.94	n/a	4.23	43.92
Liquor Fe							
t = 0 h	ug/L		n/a	<1.3	<1.2	<1.7	<1.8
t = 3 h	ug/L		n/a	<1.3	<1.0	<0.9	<1.0
t = 6 h	ug/L		n/a	5.68		<0.9	<1.4
Solid Hg							
t = 3 h	ug/g	n/a	n/a	0.076	<0.051	0.14	0.2225
t = 6 h	ug/g	<0.025	n/a	0.083	0.08	0.386	0.082
Solid Fe				mg/g	mg/g	mg/g	mg/g
t = 3 h	ug/g	n/a	n/a	5295	8890	1519	3433
t = 6 h	ug/g	1.55	n/a	7904	11072	4713	6619
Wt% Solids	wt%	n/a	n/a	n/a	n/a	n/a	n/a
Chloride DF (t = 6 h)*	mM	97.86	n/a	92.37	94.53	915.7	506.6
Bromide DF (t = 6 h)*	mM	905.6	n/a	432.6	917.2	-	-
Sulfite DF (t = 6 h)*	mM	0.575	n/a	<0.04	<0.03	0.18	0.136

Run #		**7**	**8**	**9**	**10**	**11**	**12**
Date		**4/30/2009**	**5/1/2009**	**5/6/2009**	**5/7/2009**	**5/15/2009**	**5/21/2009**
Test		**0.25 M Bromide with 4000 ppm Fe**	**0.1 M Bromide with 4000 ppm Fe**	**0.25 Bromide with 4000 ppm Fe of solids**	**0.5 M Chloride with 4000 ppm Fe of solids**	**0.1 Bromide with 4000 ppm Fe of solids**	**0.1 Bromide with 8000 ppm Fe of solids**
Test Matrix Variables:							
Ferrous sulfate	ppmw	4000	4000	4000ug Fe/g CaCO3	4000ug Fe/g CaCO3	4000ug Fe/g CaCO3	8000ug Fe/g CaCO3
Gypsum solids - $CaSO_4$ -2 H_2O (s)	wt%	8	8	8	8	8	8
Bromide (NaBr)	M	0.25	0.1	0.25	0	0.1	0.1
Chloride (NaCl)	M	0.1	0.1	0.1	0.5	0.1	0.1
Inlet flue gas Hg	ug/Nm3		>=15	38	27	22.75	21.5
Outlet flue gas Hg	ug/Nm3		<1	<1	<1	<1	<1
Liquor Hg							
t = 0 h	ug/L	1.73	<0.382	1.95	0.931	1.02	1.45
t = 3 h	ug/L	7.75	2.97	23.02	11.53	1.79	3.52
t = 6 h	ug/L	18.52	3.62	43.79	23.23	11.06	5.41
Liquor Fe							
t = 0 h	ug/L	<3	<2	<2	<2	<2	<2
t = 3 h	ug/L	<2	<2	<2	<2	<2	<2
t = 6 h	ug/L	2.08	<2	<2	<2	<2	<3
Solid Hg							
t = 3 h	ug/g	0.073	0.081	0.030	<0.026	0.15	0.14
t = 6 h	ug/g	0.186	0.234	0.083	0.051	0.2815	0.25
Solid Fe		ug/g	ug/g	ug/g	ug/g		
t = 3 h	ug/g	3208	5616	365	314		530
t = 6 h	ug/g	9682	8966	463	522		811
Wt% Solids	wt%	10.35	10.6	8.53	8.93	9.51	9.59
Chloride DF (t = 6 h)*	mM	103.3	94.5	88.3	415.3	80.8	81
Bromide DF (t = 6 h)*	mM	242.4	94.57	219.8	n/a	82.45	81.1
Sulfite DF (t = 6 h)*	mM	1.085	0.542	<0.03	<0.05	0.072	0.124

Run #		**13**	**14**	**15**	**16**	**17**
Date		**5/22/2009**	**5/29/2009**	**7/23/2009**	**7/30/2009**	**8/13/2009**
Test		**4000 ppm Fe of solids (Iron Baseline)**	**0.5 M Bromide with 4000 ppm Fe of solids**	**4000 ppm Fe of solids (Iron Baseline Duplicate)**	**0.25 Bromide with 4000 ppm Fe of solids (Duplicate of Test 9)**	**0.85 M Chloride with 4000 ppm Fe**
Test Matrix Variables:						
Ferrous sulfate	ppmw	4000ug Fe/g CaCO3	4000ug Fe/g CaCO3	4000ug Fe/g CaCO3	4000ug Fe/g CaCO3	4000ug Fe/g CaCO3
Gypsum solids - $CaSO_4$ -2 H_2O (s)	wt%	8	8	8	8	8
Bromide (NaBr)	M	0	0.5	0	0.25	0
Chloride (NaCl)	M	0.1	0.1	0.1	0.1	0.85 (30,000 ppm)
Inlet flue gas Hg (nominal)	ug/Nm3	22.5	18	27.3	31.2	
Outlet flue gas Hg (nominal)	ug/Nm3	<1	<1	<1	~2	
Liquor Hg						
t = 0 h	ug/L	<0.639	7.41	<0.319	1.09	
t = 3 h	ug/L	9.42	22.32	13.88	9.05	
t = 6 h	ug/L	11.32	39.8	34.06	25.81	
Liquor Fe						
t = 0 h	ug/L	<2	<2			
t = 3 h	ug/L	<2	<2			
t = 6 h	ug/L	<2	<2			
Solid Hg						
t = 3 h	ug/g	<0.027	<0.027	0.031	0.042	
t = 6 h	ug/g	0.069	0.027	0.085	0.106	
Solid Fe						
t = 3 h	ug/g	329	259	304.8	275.5	
t = 6 h	ug/g	775	385	355.9	339.5	
Wt% Solids	wt%	5.08	9.68			
Chloride DF (t = 6 h)*	mM	75.6	90.1	95.56	102.8	
Bromide DF (t = 6 h)*	mM	n/a	449.8	-	258	
Sulfite DF (t = 6 h)*	mM	0.049	<0.05	<0.02	0.045	

Table A-2
Data for Tests 18 through 52

Test Length	**Units**	**10 hour**	**10 hour**	**10 hour**	**10 hour**	**32 hour**
Run #		**18**	**19**	**20**	**21**	**22**
Date		**8/27/2009**	**9/10/2009**	**10/1/2009**	**10/6/2009**	**11/23/2009**
Test		4000 ppm Fe of solids (Iron Baseline) Iron added separately as Fe(II)SO4	0.5 M Bromide with 4000 ppm Fe of solids (new iron addition method)	0.85 M Cl with 4000 ppm Fe of solids (new iron addition method)	0.25 M Bromide with 4000 ppm Fe of solids (new iron addition method)	Baseline Long-Term Test with new iron addition method
Test Matrix Variables:						
pH (Default is 5.5)						
Ferrous sulfate	ppmw	4,000 ug Fe/g CaCO3	4,000 ug Fe/g CaCO3	4,000 ug Fe/g CaCO3	4,000 ug Fe/g CaCO3	4,000 ug Fe/g CaCO3
Gypsum solids - $CaSO_4$ -2 H_2O (s)	wt%	8	8	8	8	8
Bromide (NaBr)	M	0	0.5	=	0.25	=
Chloride (NaCl)	M	=	=	0.85	=	=
Liquor Hg						
t = 0 h	ug/L	<0.381	9.20	0.64	0.78	5.32
t = 3 h	ug/L					
t = 6 h	ug/L	11.82	57.71	15.63	15.745	22.15
t = 10 h (12 h for 32-h tests)	ug/L	50.56	98.84	37.04	30.599	37.05
t = 24 h	ug/L	n/a	n/a	n/a	n/a	37.36
t = 32 h	ug/L	n/a	n/a	n/a	n/a	47.45
Liquor Fe						
t = 0 h	mg/L	<2	<2	<2	<1	n/a
t = 3 h	mg/L					
t = 6 h	mg/L	<2	<2	<2	<2	<1
t = 10 h (12 h for 32-h tests)	mg/L	<2	<2	<2	<2	<1
t = 24 h	mg/L	n/a	n/a			<2
t = 32 h	mg/L	n/a	n/a			<1
Solid Hg						
t = 0 h	ug/g					
t = 3 h	ug/g					
t = 6 h	ug/g	0.402	0.080	0.159	0.141	0.053
t = 10 h (12 h for 32-h tests)	ug/g	0.647	0.062	0.141	0.272	0.064
t = 24 h	ug/g	n/a	n/a	n/a	n/a	0.118
t = 32 h	ug/g	n/a	n/a	n/a	n/a	0.147

Test Length	Units	10 hour	10 hour	10 hour	10 hour	32 hour
Run #		**18**	**19**	**20**	**21**	**22**
Date		**8/27/2009**	**9/10/2009**	**10/1/2009**	**10/6/2009**	**11/23/2009**
Solid Fe						
t = 0	ug/g					
t = 3 h	ug/g					
t = 6 h	ug/g	701	390	581	378	548
t = 10 h (12 h for 32-h tests)	ug/g	1695	642	436	627	1168
t = 24 h	ug/g	n/a	n/a			1958
t = 32 h	ug/g	n/a	n/a			2011
Chloride DF	M					
t = 0 h						
t = 6 h						0.095
t = 10 h (12 h for 32-h tests)		0.09	0.09	0.78	0.11	0.094
t = 24 h						0.091
t = 32 h						0.094
Bromide	M					
t = 0 h						
t = 6 h						
t = 10 h (12 h for 32-h tests)			0.429		0.236	
t = 24 h						
t = 32 h						
Sulfite DF (t = 0 h)						
Sulfite DF (t = 6 h)	mM					0.02
Sulfite DF (t = 10 h) (12-h for 32-h tests)		0.16	0.12	0.57	0.12	0.04
Sulfite DF (t = 24 h)						0.37
Sulfite DF (t = 32 h)						0.31
Wt% Solids	wt%					
t = 0 h						
t = 6 h						9.48
t = 10 h (12 h for 32-h tests)				9.83	10.38	9.29
t = 24 h						10.41
t = 25 h						
t = 26 h						
t = 27 h						10.33
t = 28 h						10.20
t = 29 h						9.97
t = 30 h						9.76
t = 31 h						9.29

Test Length	**Units**	**10 hour**	**10 hour**	**10 hour**	**10 hour**	**32 hour**
Run #		**18**	**19**	**20**	**21**	**22**
Date		**8/27/2009**	**9/10/2009**	**10/1/2009**	**10/6/2009**	**11/23/2009**
t = 32 h						9.25
Hg/Fe mass ratio in solids	ug Hg/g Fe					
t = 3 h		-	-	-	-	-
t = 6 h		574	205	274	372	97
t = 10 h (12 h for 32-h tests)		381	97	322	434	55
t = 24 h						60
t = 32 h						73
Fe/Hg mass ratio in solids	g Fe/gHg					
t = 3 h		-	-	-	-	-
t = 6 h		1742	4875	3654	2687	10320
t = 10 h (12 h for 32-h tests)		2621	10355	3103	2305	18250
t = 24 h						16593
t = 32 h						13727
Iron Mass Balance						
ppm Fe at t=0		3517	3690	3598	3617	3914
ppm Fe at t=12 h		3887	3830	3655	3725	3842
ppm Fe at t=24 h						
ppm Fe at t=32 h						3916
ppm Fe avg		3702	3760	3626	3671	3891
Initial FeSO4 wt [g]		335.4		343.3	347	708.3
Final FeSO4 wt [g]		197.7	255.9	260.7	271.3	269.5
FeSO4 added [g]		137.7		82.6	75.7	438.8
g Fe added		0.51		0.30	0.28	1.71
Fe in slurry liquor if all Fe had remained in liquid		127441		74884	69474	355692
Sample time		12 h	10 h	~10h	~10h	~32h
Solids wt%	wt%	9	9	9	9	9.25
g solids		414	414	360	360	444
g Fe in solids		0.61		0.16	0.23	0.89
g Fe in solids removed for sampling						0.37
Rough Fe recovery		**120%**		**52%**	**81%**	**74%**

Test Length	**Units**	**32 hour**	**32 hour**	**10 hour**	**10 hour**	**6 hour**
Run #		**23**	**23B**	**24**	**25**	**26b**
Date		**12/2/2009**		**4/13/2010**	**4/14/2010**	**6/28/2010**
Test		0.5 M Bromide with 4000 ppm Fe of solids (new iron addition method)	0.5 M Bromide with 4000 ppm Fe of solids (new iron addition method)	0.5 M Cl @ pH 6	0.5 M Cl and 0.5 M Br @ pH 6	40,000 ppm Fe in solids
Test Matrix Variables:						
pH (Default is 5.5)				6	6	
Ferrous sulfate	ppmw	4,000 ug Fe/g CaCO3	4,000 ug Fe/g CaCO3	4,000 ug Fe/g CaCO3	4,000 ug Fe/g CaCO3	40,000 ug Fe / g CaCO3
Gypsum solids - $CaSO_4$ -2 H_2O (s)	wt%	8	8	8	8	8
Bromide (NaBr)	M	0.5	0.5	=	0.5	0
Chloride (NaCl)	M	=	=	0.50	0.50	0.10
ORP range	mV					~125
Absorber pH						4.5
Liquid-phase TOC	mg/L = ppmw					
t = 0 (combustion method)	mg/L					
t = 6 h (persulfate method)	mg/L				ND (2 mg/L DL)	
t = 6 h (combustion method)	mg/L				0.7 (0.5 mg/L DL)	
Liquor Hg						
t = 0 h	ug/L	0.88	0.28	0.81	0.78	0.305
t = 3 h	ug/L					5.585
t = 6 h	ug/L	11.17	24.56	25.76	21.55	12.51
t = 10 h (12 h for 32-h tests)	ug/L	32.58	45.53	38.83	34.20	
t = 24 h	ug/L	63.00	82.25	n/a	n/a	
t = 32 h	ug/L	n/a	91.57	n/a	n/a	

Test Length	**Units**	**32 hour**	**32 hour**	**10 hour**	**10 hour**	**6 hour**
Run #		**23**	**23B**	**24**	**25**	**26b**
Date		**12/2/2009**		**4/13/2010**	**4/14/2010**	**6/28/2010**
Liquor Fe						
t = 0 h	mg/L	<3	<0.4	<0.8	<1.0	<0.6
t = 3 h	mg/L					
t = 6 h	mg/L	<1	<0.2	<0.8	<1.0	<0.5
t = 10 h (12 h for 32-h tests)	mg/L	<1	<0.2	<1.0	<1.0	<0.5
t = 24 h	mg/L	<1	<0.2			
t = 32 h	mg/L	n/a	<0.1			
Solid Hg						
t = 0 h	ug/g					0
t = 3 h	ug/g					0
t = 6 h	ug/g	0.083	0.151	0.063	0.025	0.039
t = 10 h (12 h for 32-h tests)	ug/g	0.095	0.171	0.083	0.030	
t = 24 h	ug/g	0.102	0.227	n/a	n/a	
t = 32 h	ug/g	n/a	0.239	n/a	n/a	
Solid Fe						
t = 0	ug/g					36,747
t = 3 h	ug/g					
t = 6 h	ug/g	1052	530	5204	5749	30,305
t = 10 h (12 h for 32-h tests)	ug/g	2456	1350	7900	9544	25,555
t = 24 h	ug/g	3822	2262			
t = 32 h	ug/g	n/a	2238			
Chloride DF	M					
t = 0 h		0.089	0.087			
t = 6 h		0.087	0.083			
t = 10 h (12 h for 32-h tests)		0.088	0.081			0.93
t = 24 h		0.083	0.082			
t = 32 h			0.092			
Bromide	M					
t = 0 h		0.442	0.429			
t = 6 h		0.419	0.408			
t = 10 h (12 h for 32-h tests)		0.420	0.402			
t = 24 h		0.383	0.389			
t = 32 h			0.443			
Sulfite DF (t = 0 h)		0.03	0.56			
Sulfite DF (t = 6 h)	mM	0.10	0.50	<0.015	0.025	1.624
Sulfite DF (t = 10 h) (12-h for 32-h tests)		0.11	2.35	<0.015	0.028	
Sulfite DF (t = 24 h)		0.51	4.66			
Sulfite DF (t = 32 h)			0.33			

Test Length	**Units**	**32 hour**	**32 hour**	**10 hour**	**10 hour**	**6 hour**
Run #		**23**	**23B**	**24**	**25**	**26b**
Date		**12/2/2009**		**4/13/2010**	**4/14/2010**	**6/28/2010**
Wt% Solids						
t = 0 h					6.81	
t = 6 h		8.35	9.29	7.20	6.96	
t = 10 h (12 h for 32-h tests)		10.35	8.56	7.07	7.26	
t = 24 h		10.19	8.58			
t = 25 h						
t = 26 h			9.22			
t = 27 h			9.40			
t = 28 h			7.95			
t = 29 h			8.04			
t = 30 h			8.17			
t = 31 h			8.00			
t = 32 h			7.82			
Hg/Fe mass ratio in solids	ug Hg/g Fe					
t = 3 h		-	-			
t = 6 h		79	284	12	4	
t = 10 h (12 h for 32-h tests)		39	126	11	3	
t = 24 h		27	100			
t = 32 h			107			
Fe/Hg mass ratio in solids	g Fe/gHg					
t = 3 h		-	-			
t = 6 h		12675	3522	82603	229960	
t = 10 h (12 h for 32-h tests)		25853	7918	95181	318133	
t = 24 h		37361	9965			
t = 32 h			9364			
Iron Mass Balance						
ppm Fe at t=0		3766	3965			
ppm Fe at t=12 h		3824	3859			
ppm Fe at t=24 h		3763				
ppm Fe at t=32 h						
ppm Fe avg		3784	3912			
Initial FeSO4 wt [g]		1439.1	720.5			
Final FeSO4 wt [g]		683.5	216.3			
FeSO4 added [g]		755.6	504.2			
g Fe added		2.86	1.97			
Fe in slurry liquor if all Fe had remained in liquid		583569	448313			
Sample time		~24h	~32h			
Solids wt%	wt%	10.19	7.82			
g solids		499.31	344.08			
g Fe in solids		1.91	0.78			
g Fe in solids removed for sampling		0.19	0.46			
Rough Fe recovery		**73%**	**63%**			

Test Length	**Units**	**6 hour**	**6 hour**	**6 hour**	**6 hour**	**6 hour**
Run #		**27**	**28**	**29**	**30**	**31**
Date		**8/31/2010**	**9/1/2010**	**9/16/2010**	**9/17/2010**	**9/21/2010**
Test		Nat LS, Anhydrite, 5 mM Cl	Nat LS, Anhydrite, 5 mM Cl, 0.5 M Br	Nat LS, Synth. Gypsum, 5 mM Cl	Nat LS, Synth. Gypsum, 100 mM Cl	Nat LS, Synth. Gypsum, 100 mM Cl, 0.5 M Br
Test Matrix Variables:						
pH (Default is 5.5)						
pH control		5 wt% natural limestone slurry	5 wt% natural limestone slurry	5 wt% natural limestone slurry	5 wt% natural limestone slurry	5 wt% natural limestone slurry
LS source		Conemaugh	Conemaugh	Conemaugh	Conemaugh	Conemaugh
Gypsum solids - $CaSO_4$ -2 H_2O (s)	wt%	8 (anhyd.)	8 (anhyd.)	8	8	8
Bromide (NaBr)	M	0	0.5	0	0	0.5
Chloride (NaCl)	M	0.005	0.005	0.005	0.100	0.10
ORP range	mV	130-180	90-110	140-200	90-125	80-100
ORP notes	-		125-140 during last hour		two excursions to 160	a few excursions to higher ORP (160)
Absorber pH	-	3.6 with low excursions	~3.5	4.3 with a few low excursions	4.2 with two low excursions	3.7 with low excursions
Liquid-phase TOC	mg/L					
t = 0 (combustion method)	mg/L					
t = 6 h (persulfate method)	mg/L					2 (1 mg/L DL)
t = 6 h (combustion method)	mg/L					ND (0.5 mg/L DL)
Liquor Hg						
t = 0 h	ug/L	<1.041	<0.510	<0.6	<0.6	1.190
t = 3 h	ug/L	<1.044	<0.508	<0.6	<0.6	7.550
t = 6 h	ug/L	<1.043	<0.509	<0.6	<0.6	9.14
t = 10 h (12 h for 32-h tests)	ug/L					
t = 24 h	ug/L					
t = 32 h	ug/L					

Test Length	**Units**	**6 hour**	**6 hour**	**6 hour**	**6 hour**	**6 hour**
Run #		**27**	**28**	**29**	**30**	**31**
Date		**8/31/2010**	**9/1/2010**	**9/16/2010**	**9/17/2010**	**9/21/2010**
Liquor Fe						
t = 0 h	mg/L	<0.041	<0.037	<0.436	<0.456	<0.488
t = 3 h	mg/L			<0.386	<0.644	<0.480
t = 6 h	mg/L	<0.031	<0.038	<0.391	<0.457	<0.459
t = 10 h (12 h for 32-h tests)	mg/L	<0.038	<0.062			
t = 24 h	mg/L					
t = 32 h	mg/L					
Solid Hg						
t = 0 h	ug/g	<0.019	<0.023	<0.031	<0.028	<0.052
t = 3 h	ug/g	0.141	0.147	0.2425	0.276	0.152
t = 6 h	ug/g	0.293	0.292	0.5185	0.3745	0.341
t = 10 h (12 h for 32-h tests)	ug/g					
t = 24 h	ug/g					
t = 32 h	ug/g					
Solid Fe						
t = 0	ug/g	390	35			
t = 3 h	ug/g			507	595	
t = 6 h	ug/g	1,265	998			851
t = 10 h (12 h for 32-h tests)	ug/g	1,832	1,505			
t = 24 h	ug/g					
t = 32 h	ug/g					
Chloride DF	M					
t = 0 h						
t = 6 h		0.0055	0.0061	0.006	0.086	0.087
t = 10 h (12 h for 32-h tests)						
t = 24 h						
t = 32 h						
Bromide	M					
t = 0 h						
t = 6 h			0.383			0.414
t = 10 h (12 h for 32-h tests)						
t = 24 h						
t = 32 h						
Sulfite DF (t = 0 h)						
Sulfite DF (t = 6 h)	mM	<0.03	0.150	0.03	0.41	<0.2
Sulfite DF (t = 10 h) (12-h for 32-h tests)						
Sulfite DF (t = 24 h)						
Sulfite DF (t = 32 h)						

Test Length	**Units**	**6 hour**	**6 hour**	**6 hour**	**6 hour**	**6 hour**
Run #		**27**	**28**	**29**	**30**	**31**
Date		**8/31/2010**	**9/1/2010**	**9/16/2010**	**9/17/2010**	**9/21/2010**
Wt% Solids	wt%					
t = 0 h						
t = 6 h		8.34	8.61	6.76	8.02	7.52
t = 10 h (12 h for 32-h tests)						
t = 24 h						
t = 25 h						
t = 26 h						
t = 27 h						
t = 28 h						
t = 29 h						
t = 30 h						
t = 31 h						
t = 32 h						

Test Length	**Units**	**6 hour**	**6 hour**	**6 hour**	**6 hour**	**6 hour**
Run #		**32**	**33**	**34**	**35**	**36**
Date		**10/13/2010**	**10/14/2010**	**10/22/2010**	**12/20/2010**	**12/21/2010**
Test		Test 31 Repeat Nat LS, Synth. Gypsum, 100 mM Cl, 0.5 M Br	Nat LS, Synth. Gypsum, 0.5 M Cl, 0.5 M Br	Nat LS, Synth. Gypsum, 1.0 M Cl, 1.0 M Br	Nat LS, Synth. Gypsum, 0.1 M Cl, 150 mV ORP (max ORP)	Nat LS, Synth. Gypsum, 0.5 M Cl, 150 mV ORP (max ORP)
Test Matrix Variables:						
pH (Default is 5.5)						
pH control		5 wt% natural limestone slurry	5 wt% natural limestone slurry	5 wt% natural limestone slurry	5 wt% natural limestone slurry	10 wt% natural limestone slurry
LS source		Conemaugh	Conemaugh	Conemaugh	Conemaugh	Conemaugh
ORP setpoint (Target)	mV				150	150
Gypsum solids - $CaSO_4$ -2 H_2O (s)	wt%	8	8	8	8	8
Bromide (NaBr)	M	0.5	0.5	1.0	0.0	0.0
Chloride (NaCl)	M	0.10	0.5	1.0	0.1	0.5
ORP range	mV	100-125	125-160	100-125		
ORP notes	-			brief excursion to 200	maximum possible is 150 mV (originally targeted >=200 mV)	
Absorber pH	-	5.2	5.2	4.9		
Liquid-phase TOC	mg/L					
t = 0 (combustion method)	mg/L				1	1
t = 6 h (persulfate method)	mg/L					
t = 6 h (combustion method)	mg/L				2	1
Solid-phase TOC						
t = 0 h	%				<0.05	<0.05
t = 0 h (low-DL method)						
t = 6 h	%				0.06	<0.05
t = 6 h (low-DL method)						0.05

Test Length	**Units**	**6 hour**	**6 hour**	**6 hour**	**6 hour**	**6 hour**
Run #		**32**	**33**	**34**	**35**	**36**
Date		**10/13/2010**	**10/14/2010**	**10/22/2010**	**12/20/2010**	**12/21/2010**
Liquor Hg						
t = 0 h	ug/L	0.91	0.75	0.18	<0.306	<0.305
t = 3 h	ug/L	6.66	7.04	3.65	0.58	
t = 6 h	ug/L	6.63	10.23	7.21	0.45	0.60
t = 10 h (12 h for 32-h tests)	ug/L					12.00 (8-hour, 200 mV))
t = 24 h	ug/L					
t = 32 h	ug/L					
Liquor Fe						
t = 0 h	mg/L	<0.460	0.71	1.40		possible
t = 3 h	mg/L	<0.474	0.61	1.68		possible
t = 6 h	mg/L	<0.676	0.68	2.28		possible
t = 10 h (12 h for 32-h tests)	mg/L					
t = 24 h	mg/L					
t = 32 h	mg/L					
Liquor Mn						
t = 0 h	mg/L				0.365	0.283
t = 3 h	mg/L					
t = 6 h	mg/L				0.879	3.009
Solid Hg						
t = 0 h	ug/g	<0.03	<0.03	0.132	<0.025	<0.022
t = 3 h	ug/g	0.146	0.103	0.263	0.140	
t = 6 h	ug/g	0.359	0.205	0.402	0.271	0.364
t = 10 h (12 h for 32-h tests)	ug/g					
t = 24 h	ug/g					
t = 32 h	ug/g					
Solid Fe						
t = 0	ug/g					
t = 3 h	ug/g					
t = 6 h	ug/g	721				
t = 10 h (12 h for 32-h tests)	ug/g					
t = 24 h	ug/g					
t = 32 h	ug/g					
Chloride DF	M					
t = 0 h						
t = 6 h		0.091	0.383		0.09	0.46
t = 10 h (12 h for 32-h tests)						
t = 24 h						
t = 32 h						

Test Length	**Units**	**6 hour**	**6 hour**	**6 hour**	**6 hour**	**6 hour**
Run #		**32**	**33**	**34**	**35**	**36**
Date		**10/13/2010**	**10/14/2010**	**10/22/2010**	**12/20/2010**	**12/21/2010**
Bromide	M					
t = 0 h						
t = 6 h		0.436	0.398	0.773		
t = 10 h (12 h for 32-h tests)						
t = 24 h						
t = 32 h						
Sulfite DF (t = 0 h)						
Sulfite DF (t = 6 h)	mM	<0.3	<0.2		<0.037	0.02
Sulfite DF (t = 10 h) (12-h for 32-h tests)						
Sulfite DF (t = 24 h)						
Sulfite DF (t = 32 h)						
Sulfate (t = 6 h)	ppmw				4451	5537
Dithionate (t = 6 h)				<4	1.4	13.1
Persulfate (t = 6 h)				<2	12.0	8.1
Wt% Solids	wt%					
t = 0 h						
t = 6 h					7.59%	8.53%
t = 10 h (12 h for 32-h tests)						
t = 24 h						
t = 25 h						
t = 26 h						
t = 27 h						
t = 28 h						
t = 29 h						
t = 30 h						
t = 31 h						
t = 32 h						

Test Length	**Units**	**6 hour**	**6 hour**	**6 hour**	**6 hour**	**6 hour**
Run #		**37**	**38**	**39**	**40**	**41**
Date		**1/10/2011**	**1/13/2011**	**1/14/2011**	**1/18/2011**	**1/19/2011**
Test		Nat LS, Synth. Gypsum, 35 ppm Mn, 100 mV ORP	Nat LS, Synth. Gypsum, 35 ppm Mn, 300 mV ORP	Nat LS, Synth. Gypsum, 35 ppm Mn, 1000 ppmw Citric Acid, 100 mV ORP	Nat LS, Synth. Gypsum, 35 ppm Mn, 0.5 M Cl, 300 mV ORP	Nat LS, Synth. Gypsum, 35 ppm Mn, 0.25 M Br, 300 mV ORP
Test Matrix Variables:						
pH (Default is 5.5)						
pH control		10 wt% natural limestone slurry	10 wt% natural limestone slurry	10 wt% natural limestone slurry	10 wt% natural limestone slurry	10 wt% natural limestone slurry
LS source		Conemaugh	Conemaugh	Conemaugh	Conemaugh	Conemaugh
ORP setpoint (Target)	mV	100	300	Target was 300 mV, but actual was <100	300	300
Gypsum solids - $CaSO_4$ -2 H_2O (s)	wt%	8	8	8	8	8
Mn SO4	ppm as Mn	35	35	35	35	35
Bromide (NaBr)	M	0.0	0.0	0.0	0.0	0.25
Chloride (NaCl)	M	0.1	0.1	0.1	0.5	0.1
Liquid-phase TOC	mg/L					
t = 0 (combustion method)	mg/L	2	1	322	1	1
t = 6 h (persulfate method)	mg/L					
t = 6 h (combustion method)	mg/L	3	4	319	2	1
Solid-phase TOC						
t = 0 h	%	<0.05	<0.05	<0.05	<0.05	<0.05
t = 0 h (low-DL method)						
t = 6 h	%	0.06	<0.05	0.13	<0.05	0.05
t = 6 h (low-DL method)		0.07	0.04		0.06	
Liquor Hg						
t = 0 h	ug/L	<0.306	0.35	<0.308	0.74	0.69
t = 3 h	ug/L	<0.307	15.51	0.55	15.59	0.87
t = 6 h	ug/L	<0.307	4.17	2.20	42.75	1.52
t = 10 h (12 h for 32-h tests)	ug/L					
t = 24 h	ug/L					
t = 32 h	ug/L					

Test Length	**Units**	**6 hour**	**6 hour**	**6 hour**	**6 hour**	**6 hour**
Run #		**37**	**38**	**39**	**40**	**41**
Date		**1/10/2011**	**1/13/2011**	**1/14/2011**	**1/18/2011**	**1/19/2011**
Liquor Mn						
t = 0 h	mg/L	34.665	19.079	35.21	26.242	32.222
t = 3 h	mg/L			37.27		33.27
t = 6 h	mg/L	38.164	0.082	37.478	0.184	34.933
Solid Hg						
t = 0 h	ug/g	<0.022	<0.024	<0.025	<0.024	0.018
t = 3 h	ug/g	0.161	0.117	0.354	0.189	0.283
t = 6 h	ug/g	0.311	0.598	1.984	0.314	0.544
t = 10 h (12 h for 32-h tests)	ug/g					
t = 24 h	ug/g					
t = 32 h	ug/g					
Solid Fe						
t = 0	ug/g					
t = 3 h	ug/g			335	705	645
t = 6 h	ug/g					
t = 10 h (12 h for 32-h tests)	ug/g					
t = 24 h	ug/g					
t = 32 h	ug/g					
Solid Mn						
t = 0	ug/g					
t = 3 h	ug/g			16.9	358	21
t = 6 h	ug/g					
Chloride DF	M					
t = 0 h						
t = 6 h		0.11	0.11	0.10	0.49	0.10
t = 10 h (12 h for 32-h tests)						
t = 24 h						
t = 32 h						
Bromide	M					
t = 0 h						
t = 6 h						0.248
t = 10 h (12 h for 32-h tests)						
t = 24 h						
t = 32 h						
Sulfite DF (t = 0 h)						
Sulfite DF (t = 6 h)	mM	0.17	<0.037	7.57	<0.025	<0.25
Sulfite DF (t = 10 h) (12-h for 32-h tests)						
Sulfite DF (t = 24 h)						

Test Length	**Units**	**6 hour**	**6 hour**	**6 hour**	**6 hour**	**6 hour**
Run #		**37**	**38**	**39**	**40**	**41**
Date		**1/10/2011**	**1/13/2011**	**1/14/2011**	**1/18/2011**	**1/19/2011**
Sulfite DF (t = 32 h)						
Sulfate (t = 6 h)	ppmw	5130	5051	4377	5484	5390
Dithionate (t = 6 h)		10.8	73.7	2.2	29.6	0.9
Persulfate (t = 6 h)		3.0	79.1	<2	32.5	1.0
Wt% Solids	wt%					
t = 0 h						
t = 6 h		7.75%	8.74%	1.54%	8.78%	8.71%
t = 10 h (12 h for 32-h tests)						
t = 24 h						
t = 25 h						
t = 26 h						
t = 27 h						
t = 28 h						
t = 29 h						
t = 30 h						
t = 31 h						
t = 32 h						

Test Length	**Units**	**6 hour**	**6 hour**	**6 hour**	**6 hour**	**6 hour**
Run #		**42**	**43**	**44**	**45**	**46**
Date		**1/20/2011**	**1/21/2011**	**1/25/2010**	**1/26/2011**	**1/27/2011**
Test		Reagent LS, Synth. Gypsum, 35 ppm Mn actual, 100 mV ORP, 2 ppm Humic Acid	Reagent LS, Synth. Gypsum, 35 ppm Mn actual, 100 mV ORP, 20 ppm Humic Acid	Natural LS, Synth Gypsum, 150 mV ORP, 1000 ppm DBA	Reagent LS, Synth Gypsum, 150 mV ORP, 1000 ppm DBA	Reagent LS, Synth. Gypsum, 35 Mn, 300 mV ORP, 20 ppm Humic Acid
Test Matrix Variables:						
pH (Default is 5.5)						
pH control		Reagent CaCO3	Reagent CaCO3	10 wt% natural limestone slurry	Reagent CaCO3	Reagent CaCO3
LS source		-	-	Conemaugh		-
ORP setpoint (Target)	mV	100	100	100 (original target), adjusted to 150	100 (original target), adjusted to 150	300
Gypsum solids - $CaSO_4$ -2 H_2O (s)	wt%	8	8	8	8	8
Mn SO4	ppm as Mn	0.01 initial target (35 ppm actually used)	0.01 initial target (35 ppm actually used)	0.01 mM	0.01 mM	35
Bromide (NaBr)	M	0.0	0.0	0.0	0.0	0.0
Chloride (NaCl)	M	0.1	0.1	0.1	0.1	0.1
Humic Acid	ppmw	2.0	20.0			20.0
DBA	ppmw			1000.0	1000.0	
Liquid-phase TOC	mg/L					
t = 0 (combustion method)	mg/L	<1	2	445	438	3
t = 6 h (persulfate method)	mg/L					
t = 6 h (combustion method)	mg/L	1	2	458	458	25
Solid-phase TOC						
t = 0 h	%	<0.05	<0.05	<0.05	<0.05	<0.05
t = 0 h (low-DL method)				0.02		0.01
t = 6 h	%	<0.05	<0.05	<0.05	<0.05	<0.05
t = 6 h (low-DL method)		0.01	0.01	0.05		0.01

Test Length	Units	6 hour	6 hour	6 hour	6 hour	6 hour
Run #		**42**	**43**	**44**	**45**	**46**
Date		**1/20/2011**	**1/21/2011**	**1/25/2010**	**1/26/2011**	**1/27/2011**
Liquor Hg						
t = 0 h	ug/L	<0.311	<0.510	0.76	<0.510	<0.509
t = 3 h	ug/L	17.55	24.74	31.49	22.64	19.01
t = 6 h	ug/L	43.62	53.05	38.59	48.09	39.52
t = 10 h (12 h for 32-h tests)	ug/L					
t = 24 h	ug/L					
t = 32 h	ug/L					
Liquor Mn						
t = 0 h	mg/L	34.116	32.365	1.465	0.838	31.95
t = 3 h	mg/L	32.24	34.61	4.07	0.91	17.30
t = 6 h	mg/L	32.489	34.744	5.236	0.896	10.379
Solid Hg						
t = 0 h	ug/g	<0.024	<0.024	<0.024	<0.024	<0.024
t = 3 h	ug/g	0.045	0.054	<0.025	<0.025	0.040
t = 6 h	ug/g	0.067	0.101	0.087	<0.024	0.071
t = 10 h (12 h for 32-h tests)	ug/g					
t = 24 h	ug/g					
t = 32 h	ug/g					
Solid Fe						
t = 0	ug/g					
t = 3 h	ug/g	77	77	449		
t = 6 h	ug/g					
t = 10 h (12 h for 32-h tests)	ug/g					
t = 24 h	ug/g					
t = 32 h	ug/g					
Solid Mn						
t = 0	ug/g					
t = 3 h	ug/g	11	16	18	16	187
t = 6 h	ug/g					
Chloride DF	M					
t = 0 h						
t = 6 h		0.10	0.10	0.11	0.10	0.10
t = 10 h (12 h for 32-h tests)						
t = 24 h						
t = 32 h						

Test Length	**Units**	**6 hour**	**6 hour**	**6 hour**	**6 hour**	**6 hour**
Run #		**42**	**43**	**44**	**45**	**46**
Date		**1/20/2011**	**1/21/2011**	**1/25/2010**	**1/26/2011**	**1/27/2011**
Sulfite DF (t = 0 h)						
Sulfite DF (t = 6 h)	mM	0.13	0.27	1.37	3.81	<0.037
Sulfite DF (t = 10 h) (12-h for 32-h tests)						
Sulfite DF (t = 24 h)						
Sulfite DF (t = 32 h)						
Sulfate (t = 6 h)	ppmw	4685	4980	4467	4016	4393
Dithionate (t = 6 h)		11.0	4.4	42.0	44.7	27.6
Persulfate (t = 6 h)		1.3	1.0	<3	<2	10.5
DBA Components (t = 6 h)						
Succinic	ppm			158	148	
Glutaric	ppm			730	713	
Adipic	ppm			133	119	
Wt% Solids	wt%					
t = 0 h						
t = 6 h		8.44%	9.29%	8.66%	8.84%	
t = 10 h (12 h for 32-h tests)						
t = 24 h						
t = 25 h						
t = 26 h						
t = 27 h						
t = 28 h						
t = 29 h						
t = 30 h						
t = 31 h						
t = 32 h						

Test Length	**Units**	**6 hour**	**6 hour**	**6 hour**	**6 hour**	**6 hour**
Run #		**47**	**48**	**49**	**50**	**51**
Date		**2/22/2011**	**2/23/2011**	**3/2/2011**	**3/3/2011**	**3/10/2011**
Test		Nat LS, Synth. Gypsum, 35 ppm Mn, 300 mV ORP (Test 38 Repeat)	BAKED Nat LS, Synth. Gypsum, 35 ppm Mn, 150 mV ORP	Natural LS, Synth Gypsum, 35 ppm Mn, 200 mV ORP, 1000 ppm DBA, 1000 ppbw Se4	Natural LS, Synth Gypsum, 35 ppm Mn, 300 mV ORP, 1000 ppm DBA, 1000 ppb Se4	Natural LS, Synth Gypsum, 35 ppm Mn, 150 mV ORP, 1000 ppm DBA, 1000 ppb Se4
Test Matrix Variables:						
pH (Default is 5.5)						
pH control		10 wt% natural limestone slurry	10 wt% natural limestone slurry	10 wt% natural limestone slurry	10 wt% natural limestone slurry	10 wt% natural limestone slurry
LS source		Conemaugh	Conemaugh - BAKED @ 500 C	Conemaugh	Conemaugh	Conemaugh
ORP setpoint (Target)	mV	300	150	200	300	150
Gypsum solids - $CaSO_4$ -2 H_2O (s)	wt%	8	8	8	8	8
Mn SO4	ppm as Mn	35	35	35	35	35
Bromide (NaBr)	M	0.0	0.0	0.0	0.0	0.0
Chloride (NaCl)	M	0.1	0.1	0.1	0.1	0.1
DBA	ppmw			1000	1000	1000
Acetic Acid	ppmw					
Selenite (sodium selenite)	ppbw as Se			1000 (pp billion)	1000 (pp billion)	1000 (pp billion)
Liquid-phase TOC	mg/L					
t = 0 (combustion method)	mg/L	1	1			
t = 6 h (persulfate method)	mg/L					
t = 6 h (combustion method)	mg/L	1	1	520	601	634
Solid-phase TOC						
t = 0 h	%	<0.05	<0.05			
t = 0 h (low-DL method)						
t = 6 h	%	<0.05	<0.05			
t = 6 h (low-DL method)						

Test Length	**Units**	**6 hour**	**6 hour**	**6 hour**	**6 hour**	**6 hour**
Run #		**47**	**48**	**49**	**50**	**51**
Date		**2/22/2011**	**2/23/2011**	**3/2/2011**	**3/3/2011**	**3/10/2011**
Liquor Hg						
t = 0 h	ug/L	<0.503	<0.306	<0.508	<0.510	<0.643
t = 3 h	ug/L	10.97	0.40	<0.509 (4 h)	3.16	<0.641 @ 3h <0.643@ 4h
t = 6 h	ug/L	14.95	0.75	<0.508	8.72	<0.643
t = 10 h (12 h for 32-h tests)	ug/L					
t = 24 h	ug/L					
t = 32 h	ug/L					
Liquor Mn						
t = 0 h	mg/L	32.31	29.63	32.75	31.39	33.70
t = 3 h	mg/L	0.34	29.07	35.65 (4 h)	30.05	40.35 (4 h)
t = 6 h	mg/L	0.02	28.75	36.29	14.53	42.68
Solid Hg						
t = 0 h	ug/g	<0.025	<0.025	<0.025	<0.025	<0.026
t = 3 h	ug/g	0.075	0.166	0.402 (4 h)	0.341	0.359 @ 4h
t = 6 h	ug/g	0.252	0.317	0.616	0.633	0.571
t = 10 h (12 h for 32-h tests)	ug/g					
t = 24 h	ug/g					
t = 32 h	ug/g					
Solid Fe						
t = 0	ug/g	128	162	162	257	295
t = 3 h	ug/g	319	505	406	519	633
t = 6 h	ug/g	487	817	580	711	792
t = 10 h (12 h for 32-h tests)	ug/g					
t = 24 h	ug/g					
t = 32 h	ug/g					
Solid Mn						
t = 0	ug/g	56	15	12	49	15
t = 3 h	ug/g	301	22	16	57	23
t = 6 h	ug/g	217	25	16	109	22
Chloride DF	M					
t = 0 h						0.11
t = 6 h		0.10	0.08	0.09	0.11	0.11
t = 10 h (12 h for 32-h tests)						
t = 24 h						
t = 32 h						

Test Length	**Units**	**6 hour**	**6 hour**	**6 hour**	**6 hour**	**6 hour**
Run #		**47**	**48**	**49**	**50**	**51**
Date		**2/22/2011**	**2/23/2011**	**3/2/2011**	**3/3/2011**	**3/10/2011**
Sulfate (t = 6 h)	ppmw	4541	4290	4262	4471	4193
Dithionate (t = 6 h)		118.3	17.2	13.9	60.8	
Persulfate (t = 6 h)		79.5	5.9	2.0	15.0	
DBA Components (t = 0 h)						
Succinic	ppm			220	244	
Glutaric	ppm			659	720	
Adipic	ppm			174	211	
DBA Components (t = 6 h)						
Succinic	ppm			225	262	
Glutaric	ppm			659	758	
Adipic	ppm			181	213	
Wt% Solids	wt%					
t = 0 h						
t = 6 h		8.11%	7.68%	8.29%	9.47%	
t = 10 h (12 h for 32-h tests)						
t = 24 h						
t = 25 h						
t = 26 h						
t = 27 h						
t = 28 h						
t = 29 h						
t = 30 h						
t = 31 h						
t = 32 h						

Test Length	**Units**	**6 hour**
Run #		**52**
Date		**3/11/2011**
Test		Natural LS, Synth Gypsum, 35 ppm Mn, 300 mV ORP, 1000 ppm Acetic Acid, 1000 ppb Se4
Test Matrix Variables:		
pH (Default is 5.5)		
pH control		10 wt% natural limestone slurry
LS source		Conemaugh
ORP setpoint (Target)	mV	300
Gypsum solids - $CaSO_4$ -2 H_2O (s)	wt%	8
Mn SO4	ppm as Mn	35
Bromide (NaBr)	M	0.0
Chloride (NaCl)	M	0.1
Acetic Acid	ppmw	1000
Selenite (sodium selenite)	ppbw as Se	1000 (pp billion)
Liquid-phase TOC	mg/L	
t = 0 (combustion method)	mg/L	
t = 6 h (persulfate method)	mg/L	
t = 6 h (combustion method)	mg/L	398
Liquor Hg		
t = 0 h	ug/L	<0.646
t = 3 h	ug/L	2.680
t = 6 h	ug/L	10.07
t = 10 h (12 h for 32-h tests)	ug/L	
t = 24 h	ug/L	
t = 32 h	ug/L	
Liquor Mn		
t = 0 h	mg/L	30.66
t = 3 h	mg/L	25.76
t = 6 h	mg/L	8.23

Test Length	**Units**	**6 hour**
Run #		**52**
Date		**3/11/2011**
Solid Hg		
t = 0 h	ug/g	<0.028
t = 3 h	ug/g	0.314 @ 4h
t = 6 h	ug/g	0.480
t = 10 h (12 h for 32-h tests)	ug/g	
t = 24 h	ug/g	
t = 32 h	ug/g	
Solid Fe		
t = 0	ug/g	209
t = 3 h	ug/g	483
t = 6 h	ug/g	649
t = 10 h (12 h for 32-h tests)	ug/g	
t = 24 h	ug/g	
t = 32 h	ug/g	
Solid Mn		
t = 0	ug/g	50
t = 3 h	ug/g	121
t = 6 h	ug/g	125
Chloride DF	M	
t = 0 h		
t = 6 h		0.18
t = 10 h (12 h for 32-h tests)		
t = 24 h		
t = 32 h		
Sulfate (t = 6 h)	ppmw	1098
Dithionate (t = 6 h)		
Persulfate (t = 6 h)		
Wt% Solids	wt%	
t = 0 h		
t = 6 h		9.27%
t = 10 h (12 h for 32-h tests)		
t = 24 h		
t = 25 h		
t = 26 h		
t = 27 h		
t = 28 h		
t = 29 h		
t = 30 h		
t = 31 h		
t = 32 h		

Table A-3
Data for Tests 53 to 58

Test Date		**4/4/2011**	**4/5/2011**	**4/11/2011**	**4/12/2011**	**4/25/2011**	**4/26/2011**
Run #		**53**	**54**	**55**	**56**	**57**	**58**
Test		**Plant ORP**	**Low ORP**	**DBA at 230 mV (actual)**	**Iron Addition**	**High Iron Addition**	**Standard DBA at Variable pH**
Test length (hours)		6	6	8	6	6	6
Temperature	F	131	131	131	131	131	131
pH (reaction tank)	-	5.5	5.5	5.5	5.5	5.5	pH 5.5 first 3 hours, then decrease pH until SO2 removal = ~92% (try 5.2)
pH control		10wt% LS	10wt% LS	10wt% LS	10wt% LS	10wt% LS	10wt% LS
ORP	mV	450	Initial Target ~150 (adjust to <2 mM SO3--)	Variable ORP: 6 h @ 300 mV, then 2 h @ 450 mV ACTUAL = ~230 mV	200	200	200
Initial Solids Charge:		8 wt% scrubber solids	8 wt% scrubber solids	8 wt% scrubber solids	8 wt% scrubber solids	8 wt% scrubber solids	8 wt% scrubber solids
Constituents / Additives:							
Na_2SeO_3 (Se IV)	ppb as Se	2000	2000	2000	2000 ppbw as Se equiv, metered over time	2000 ppbw as Se equiv, metered over time	2000
DBA				2000			1000
FeCl3	ppmw				1500 ppmw as FeCl3 equiv, metered over time	3000 ppmw as FeCl3 equiv, metered over time	

Test Date		4/4/2011	4/5/2011	4/11/2011	4/12/2011	4/25/2011	4/26/2011
Run #		53	54	55	56	57	58
Test		Plant ORP	Low ORP	DBA at 230 mV (actual)	Iron Addition	High Iron Addition	Standard DBA at Variable pH
Liquor Hg							
t = 0 h	ug/L	157	70.3	144	113	2	101
t = 1.0 h	ug/L						98
t = 1.5 h	ug/L	155	55.7	124	129	118	111
t = 3 h	ug/L	182	34.9	108	140	97	86
t = 4.5 h	ug/L						47
t = 6 h	ug/L	173	11.4	71	74	45	108
Solid Hg							
t = 3 h	ug/g	0.234	0.930	0.588	0.313	-	0.90 (note t = 4.5 h)
t = 6 h	ug/g	0.366	1.277	1.000	1.134	1.49	0.55
Wet Sieve Solid Hg							
t = 0 h							
Fraction 1	ug/g					-	0.08
Fraction 2	ug/g					-	0.07
Fraction 3 (smallest)	ug/g					-	0.88
t = 6 h							
Fraction 1	ug/g					0.17	0.33
Fraction 2	ug/g					0.17	0.40
Fraction 3 (smallest)	ug/g					2.56	1.60
Liquor Fe							
t = 0 h	mg/L	0.23 (<DL)	-	0.30 (<DL)	-		
t = 3 h	mg/L	0.23 (<DL)	0.21 (<DL)	-	0.26 (<DL)		
t = 6 h	mg/L	0.22 (<DL)	0.20 (<DL)	0.28 (<DL)	0.30 (<DL)		
Solid Fe							
t = 3 h	ug/g	1692	1725 (M)	-	7115		
t = 6 h	ug/g	1709	1675	1160	12862		
Liquor Mn							
t = 0 h	mg/L	13.6	-	0.7	-		
t = 3 h	mg/L	4.4	15.1	-			
t = 6 h	mg/L	0.6	16.9	0.9	25.6		
Solid Mn							
t = 3 h	ug/g	109	79	-	181		
t = 6 h	ug/g	96	76	131	149		

Test Date		**4/4/2011**	**4/5/2011**	**4/11/2011**	**4/12/2011**	**4/25/2011**	**4/26/2011**
Run #		**53**	**54**	**55**	**56**	**57**	**58**
Test		**Plant ORP**	**Low ORP**	**DBA at 230 mV (actual)**	**Iron Addition**	**High Iron Addition**	**Standard DBA at Variable pH**
Sulfur Species at t = 0 h							
Sulfite (SO3)	ppm SO3	<2					
Sulfate (SO4)	ppm SO4	1119					
Dithionate (S2O6)	ppm S2O6						
Persulfate (S2O8)	ppm S2O9						
Sulfur Species at t = 6 h							
Sulfite (SO3)	mM SO3	<3	<1	<2	6.2		
Sulfate (SO4)	ppm SO4	1098	1133	1524	1134		
Dithionate (S2O6)	ppm S2O6	510	501				
Persulfate (S2O8)	ppm S2O9		3.8				
Chloride at t= 6h (*Host = 171 mM*)	mM	179	164	176	227		
Solids content at t = 6h	wt% solids	8.71	7.81	9.85	9.35		
Liquor TOC at t = 6 h	mg/L	9	8	1080	7	7	527
Solid TOC at t = 6 h	%	0.05	0.05	0.09	0.10	0.09	0.04

B
FULL-SCALE SYSTEM COAL AND ASH DATA

The following tables comprise Appendix B:

- Host site coal data
- Host site ash data

Table B-1
Host Site Coal Data

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

Table B-2
Host Site Ash Data

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

C
METALS DATA FOR FULL-SCALE AND PILOT-SCALE SYSTEMS

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

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

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

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

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

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

D
GAS-PHASE MERCURY DATA FOR PILOT SCRUBBER TESTS

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

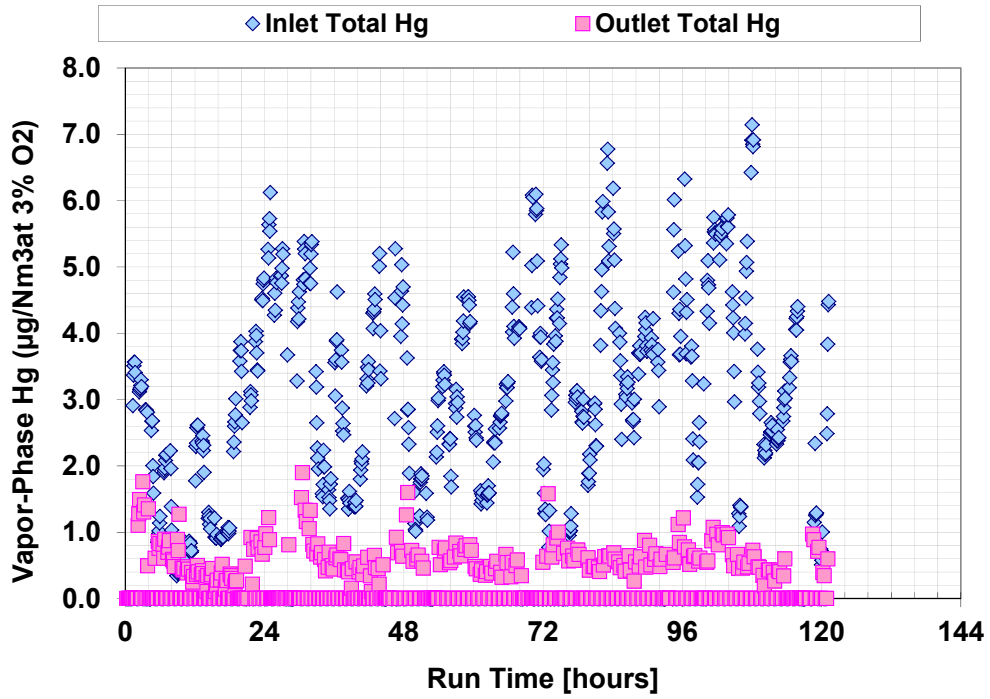

Figure D-1
Inlet and Outlet Flue Gas Total Mercury (Pilot Scrubber) for Low ORP Trial 2 (Natural Oxidation)

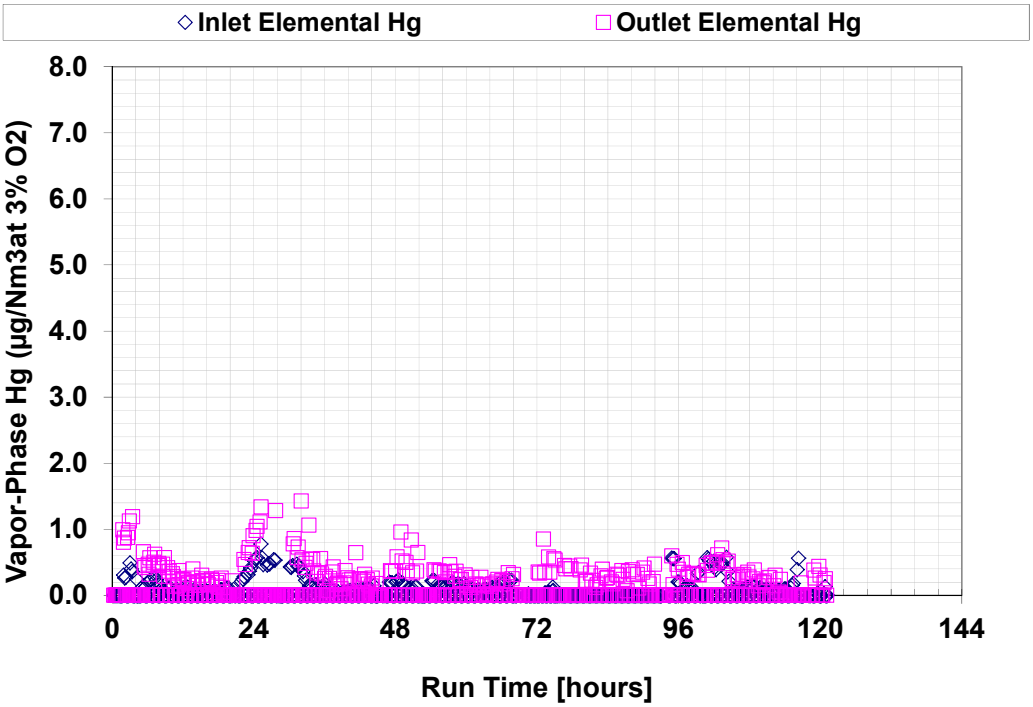

Figure D-2
Inlet and Outlet Flue Gas Elemental Mercury (Pilot Scrubber) for Low ORP Trial 2 (Natural Oxidation)

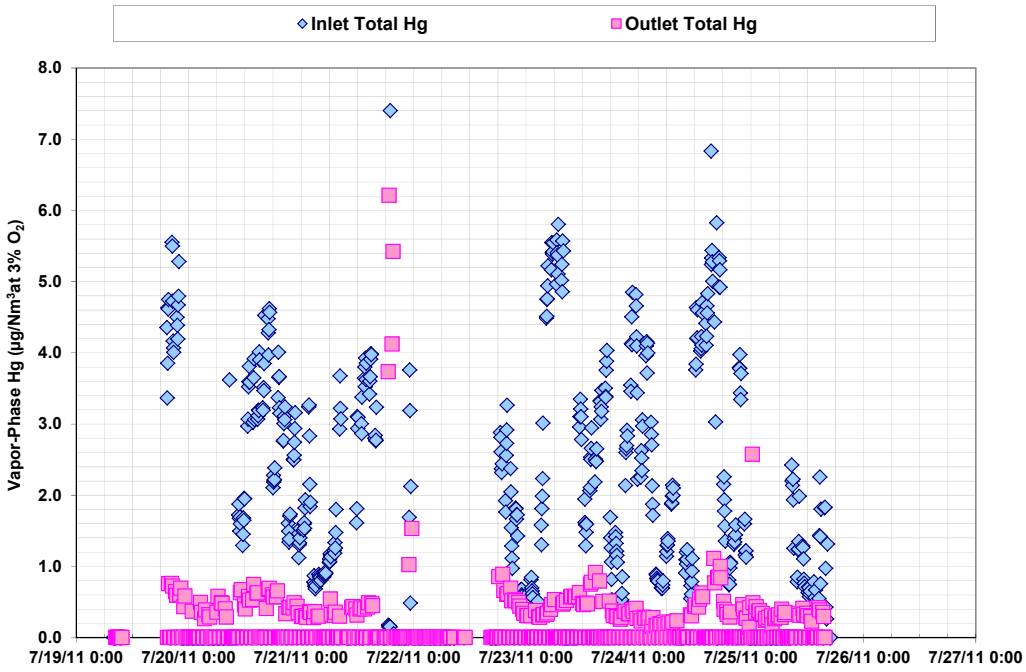

Figure D-3
Inlet and Outlet Flue Gas Total Mercury (Pilot Scrubber) for Ferric Chloride Test

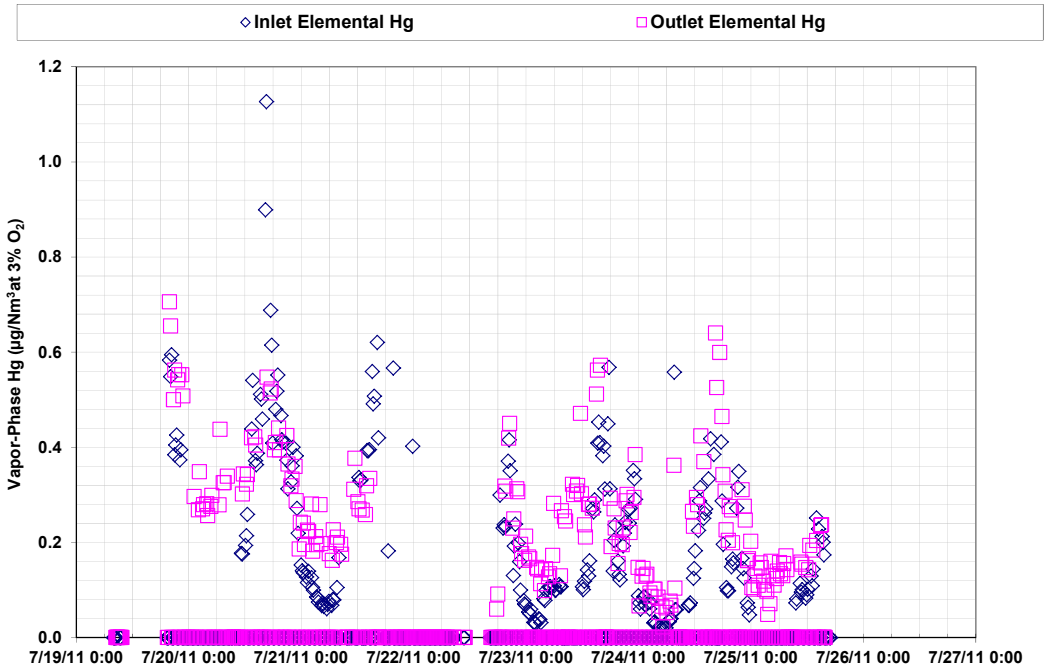

Figure D-4
Inlet and Outlet Flue Gas Elemental Mercury (Pilot Scrubber) for Ferric Chloride Test

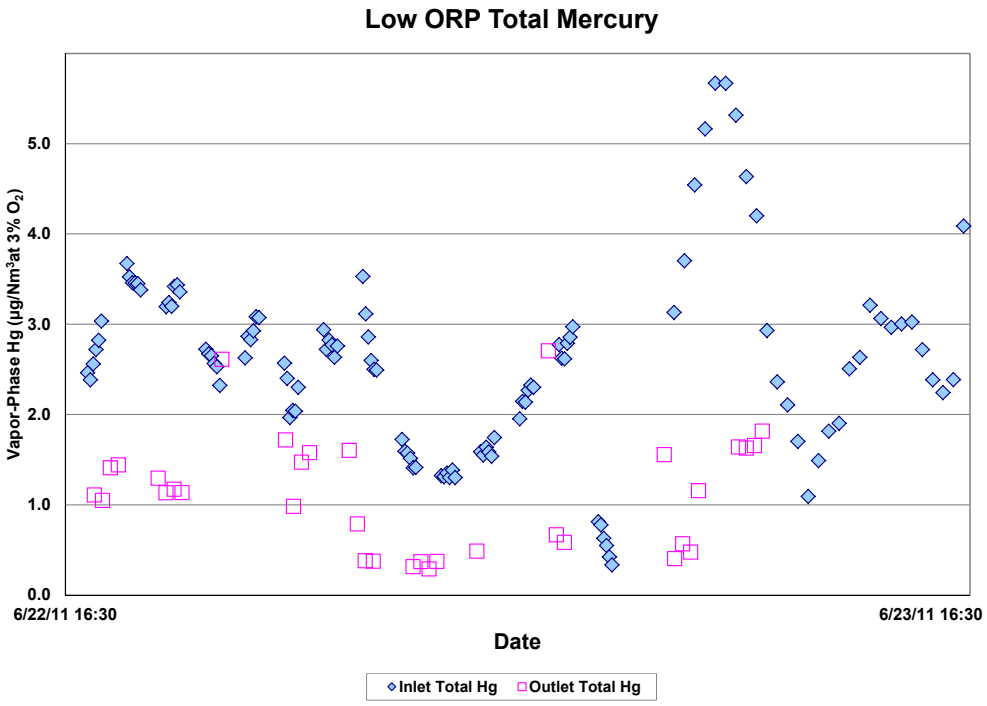

Figure D-5

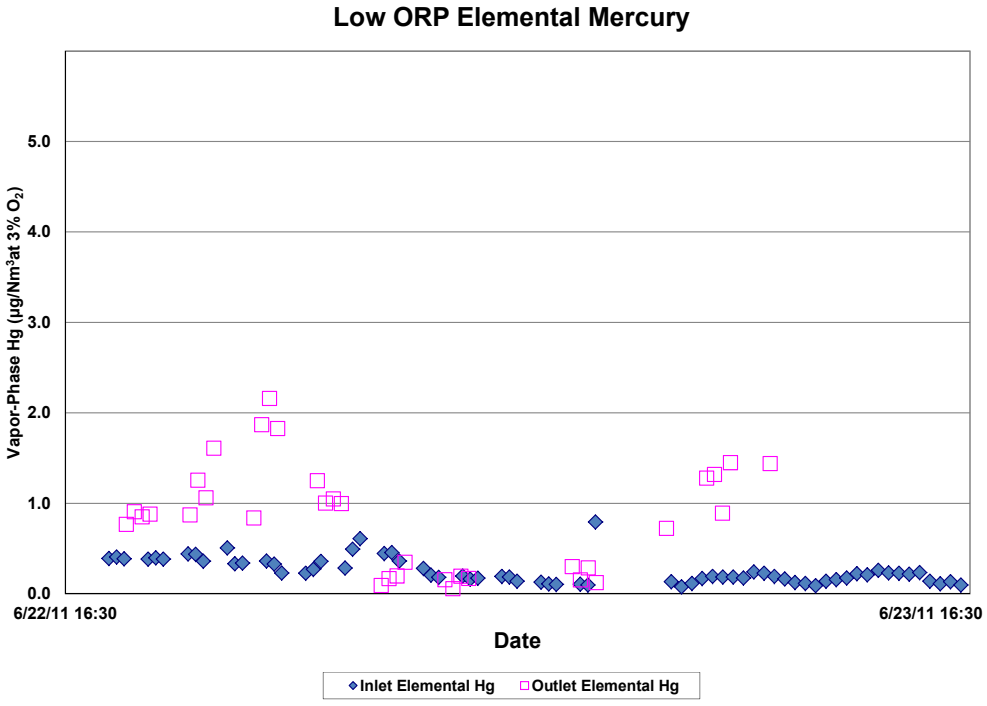

Figure D-6
Inlet and Outlet Flue Gas Elemental Mercury (Pilot Scrubber) for One-day Low ORP Trial 1

E

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

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

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

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

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

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

F

SUMMARY OF ENGINEERING AND ECONOMIC EVALUATION OF BROMIDE ADDITION TO AND RECOVERY FROM WET FGD SCRUBBERS

[Excerpt from May 2010 Progress Report]

Task 5: Engineering and Economic Evaluation

For the mercury control approach under development in this SBIR project, the mercury emission control economics are dominated by the cost of maintaining appropriate concentrations of Additive A in the scrubber liquor. Loss of additive in the FGD blowdown was determined to be cost prohibitive; therefore, a means of recovering the additive from the blowdown was determined to be key to the economic feasibility.

In the previous reporting period, several additive recovery process concepts were screened, and the most promising additive recovery process concept was developed into a more detailed design basis, process flow diagram, and accompanying material and energy balance. Major process equipment for the mercury emission control technology was sized, materials of construction were determined, and purchased equipment costs were estimated. Capital and operating costs for the technology were estimated and converted into overall costs per pound of mercury emission controlled.

During the current reporting period, internal documentation of the engineering and economic evaluation was completed, and the economic calculations were refined slightly. Total mercury capture costs were estimated for 95%, 98%, and 100% additive recovery. While it is not possible to achieve quantitative, 100% recovery of the additive, the 100% recovery offers a best case scenario in which operating costs are minimized. If the 100% recovery case is not economically viable, then none of the lower recoveries would be viable either given the assumptions used for the evaluation. (For a given FGD blow down rate, the capital costs for the additive recovery system are assumed to be equal for the 95%, 98%, and 100% recovery cases.) The previous progress report presented results for 95% additive recovery only.

Results for four cases are presented below: two coals (a medium-sulfur, high-chloride coal and a high-sulfur, medium-chloride coal), each at two scrubber chloride concentrations. The maximum chloride concentration that a FGD scrubber can cycle up to is dictated by the materials of construction of the FGD system. Table 4 shows the mercury captured, gypsum produced, and FGD blowdown estimated for the four cases. Table 5 and Figure 3 show the estimated capital and operating costs for the additive recovery system and the total annual cost per pound of mercury captured. The target cost of mercury capture is <= $10,000/lb Hg. These results show that as the sulfur-to-chlorine ratio increases, use of the scrubber additive becomes more favorable. The ability to operate at higher scrubber chloride levels reduces required blow down rates, and is thus more favorable for scrubber additive use. For many FGD systems, 98% recovery of the additive from the FGD blowdown could achieve economic viability for this mercury control approach. A higher recovery is desirable, but 98% recovery would likely be sufficient.

The engineering and economic evaluation work summarized in this section has not been presented with substantive technical details due to the confidential nature of the additive itself. It is not possible to describe the process equipment in any detail without revealing the identity of the additive. The reader may contact Trimeric to request more details on the progress of the engineering and economic evaluation task.

Table 4. Cases for Engineering and Economic Evaluation

Coal type	-	Med S, High Cl Bituminous	High S, Med Cl Bituminous
Coal Composition			
Hg	ppmw	0.113	0.113
Cl	ppmw	1033	500
S	wt%	1.69	3.5
Heating value	Btu/lb	13,203	11,500

Hg captured	lb/yr	337		387	
Gypsum production	TPD	392		932	
Chloride concentration	M	0.28	0.10	0.28	0.10
	ppmw	10,000	3,545	10,000	3,545
FGD liquor blow down rate	gpm	77	217	41	119

Table 5. Updated Total Mercury Capture Costs

Coal type	-	Med S, High Cl Bituminous		High S, Med Cl Bituminous	
Chloride concentration	M	0.28	0.10	0.28	0.10
	ppmw	10,000	3,545	10,000	3,545
98% additive recovery	MM$/yr	2.63	6.26	1.82	3.91
	$/lb Hg	7,800	18,600	4,700	10,100
	$/ton gypsum	18.4	43.7	5.4	11.5
95% additive recovery	MM$/yr	3.59	8.72	2.64	5.61
	$/lb Hg	10,700	25,900	6,800	14,500
	$/ton gypsum	25.1	60.9	7.8	16.5

Note: An annual capital cost recovery factor of 0.14 was used.

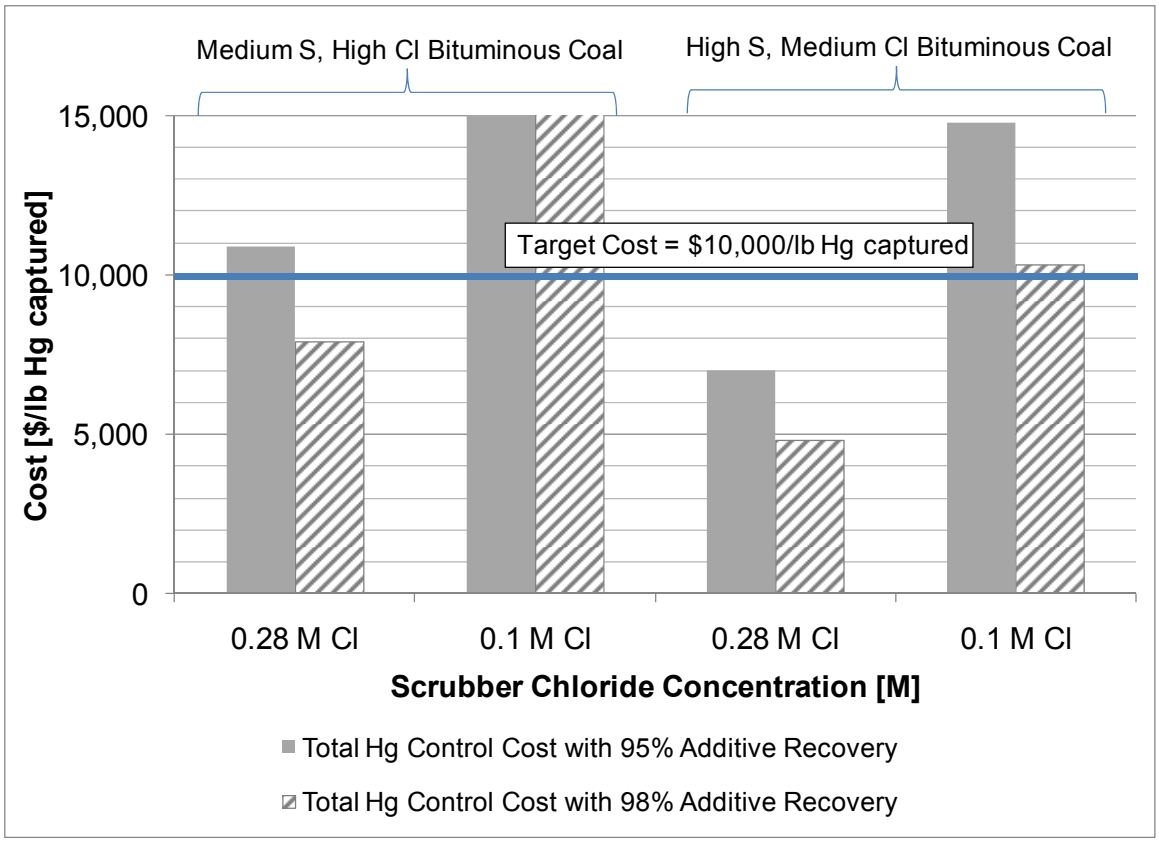

Figure 3. Updated Total Mercury Capture Costs