

Bench-scale Kinetics Study of Mercury Reactions in FGD Liquors

Semiannual Technical Progress Report

October 1, 2005 – March 31, 2006

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ABSTRACT

This document summarizes progress on Cooperative Agreement DE-FC26-04NT42314, “Kinetics Study of Mercury Reactions in FGD Liquors,” during the time-period October 1, 2005 through March 31, 2006. The project is being co-funded by the U.S. DOE National Energy Technology Laboratory and EPRI. URS Group is the prime contractor.

The objective of the project is to determine the mechanisms and kinetics of the aqueous reactions of mercury absorbed by wet flue gas desulfurization (FGD) systems, and develop a kinetics model to predict mercury reactions in wet FGD systems. The model will be used to determine optimum wet FGD design and operating conditions to maximize mercury capture in wet FGD systems and to ensure that mercury leaves the system in the byproduct solids rather than in blow down liquor.

A series of bench-top, liquid-phase reactor tests are being conducted and mercury species concentrations measured by UV/visible light spectroscopy to determine reactant and byproduct concentrations over time. Other measurement methods, such as atomic absorption, are being used to measure concentrations of species that cannot be measured by UV/visible light spectroscopy.

These data are being used to develop an empirically adjusted, theoretically based kinetics model to predict mercury species reactions in wet FGD systems. The model will be verified in tests conducted with a bench-scale wet FGD system, where both gas-phase and liquid-phase mercury concentrations will be measured to determine if the model accurately predicts the tendency for mercury re-emissions and the phase in which mercury is found in the FGD byproducts. The model will be run over a wide range of potential wet FGD design and operating conditions to determine conditions that maximize mercury capture, minimize mercury re-emissions, and/or ensure that mercury captured leaves the system in the byproduct solids rather than in blow down liquor.

This is the third reporting period for the subject Cooperative Agreement. During this period, reaction kinetics measurements have been conducted using several measurement techniques, including using a UV/visible light spectrometer to track liquid-phase species concentrations and atomic absorption analyses of reaction liquor samples to measure elemental mercury release rates. Work during this period has focused on the effects of a chloro-mercuric sulfite complex on re-emissions reaction mechanisms and kinetics over a wide range of FGD operating conditions. The data collected are continually used to update an initial form of the kinetics model. Reactions involving the chloro-mercuric sulfite complex have been added to the model. Although no bench-scale wet FGD tests have yet been conducted, modifications to the bench-scale wet FGD apparatus are underway, and a preliminary test matrix has been developed.

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INTRODUCTION

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A series of bench-top, liquid-phase reactor tests are being conducted and mercury species concentrations measured by UV/visible light spectroscopy to determine reactant and byproduct concentrations over time. Other measurement methods, such as atomic absorption, are being used to measure concentrations of species that cannot be measured by UV/visible light spectroscopy, such as elemental mercury as it is released from the liquid phase due to re-emission reactions. These data are being used to develop an empirically adjusted, theoretically based kinetics model to predict mercury species reactions in wet FGD systems. The model will be verified in tests conducted with a bench-scale wet FGD system, where both gas-phase and liquid-phase mercury concentrations will be measured to determine if the model accurately predicts the tendency for mercury re-emissions and the phase in which mercury is found in the FGD byproducts.

The model will be run over a wide range of potential wet FGD design and operating conditions to determine conditions that maximize mercury capture, minimize mercury re-emissions, and/or ensure that mercury captured leaves the system in the byproduct solids rather than in blow down liquor.

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The remainder of this report is divided into five sections: an Executive Summary followed by a section that describes Experimental procedures, then sections for Results and Discussion, Conclusions, and References.

EXECUTIVE SUMMARY

Summary of Progress

The current reporting period, October 1, 2005 through March 31, 2006, is the third technical progress reporting period for the project. During this period, reaction kinetics measurements have been conducted using several measurement techniques, including using a UV/visible light spectrometer to track liquid-phase species concentrations and atomic absorption analyses of reaction liquor samples to measure elemental mercury release rates. Work during this period has focused on the effects of a chloro-mercuric sulfite complex on re-emissions reaction mechanisms and kinetics over a wide range of FGD operating conditions. The data collected are continually used to update an initial form of the kinetics model. Reactions involving the chloro-mercuric sulfite complex have been added to the model. Although no bench-scale wet FGD tests have yet been conducted, modifications to the bench-scale wet FGD apparatus are underway, and a preliminary test matrix has been developed.

Problems Encountered

There were no significant problems encountered during the reporting period.

Plans for Next Reporting Period

During the next reporting period (April 1, 2006 through September 30, 2006, the Task 2 reaction kinetics tests will be completed, and these data will be used to complete an empirically adjusted, theoretically based kinetics model to predict mercury species reactions in wet FGD systems. Task 3 will also be conducted, wherein the model will be verified in tests conducted with a bench-scale wet FGD system. Both gas-phase and liquid-phase mercury concentrations will be measured to determine if the model accurately predicts the tendency for mercury re-emissions and the phase in which mercury is found in the FGD byproducts. The model will be used to identify additives that could be used to reduce mercury re-emissions levels from wet FGD systems. These additives will also be investigated in the bench-scale wet FGD systems.

Prospects for Future Progress

The final reporting period, October 1 through December 31, 2006, will be used to complete any remaining Task 3 bench-scale model verification tests. The only additional project efforts will be related to reporting, including preparation and submittal of the fourth semi-annual technical progress report and the project final report.

EXPERIMENTAL

Task 2: Kinetic Data Gathering and Initial Model Development

This project is collecting kinetic data under conditions specific to wet FGD systems. Kinetic measurements include liquors containing chloride and thiosulfate, both of which may form strong complexes with Hg^{+2} . Chloride is known to form a series of complexes with Hg^{+2} . Thiosulfate may complex and/or reduce Hg^{+2} . Effects of other major species in FGD liquors, such as sulfate and nitrate ions, will also be determined. Another important variable is pH, which affects both the distribution of sulfite species and the kinetics.

In addition to chemical species effects, the effects of temperature and ionic strength on kinetics are being determined. Temperature is always important for chemical kinetics. While the project is concentrating on the normal FGD temperature range (50-55°C), higher and lower temperatures will be investigated. This will improve the accuracy of activation energy values used in the model and ensure that the model results apply to FGD that operate at other temperatures (e.g., on lignite-fired plants that have a high flue gas saturation temperature).

Ionic strength is related to the total concentration of dissolved, ionic species in the liquor. Determining ionic strength effects is often helpful for determining reaction mechanisms and for modeling. The rate of reaction in a solution can be increased, decreased, or unchanged with increasing ionic strength, depending on whether the reactants in a rate-determining reaction step have the same or an opposite charge, or if one reactant is uncharged. Ionic strength dependence is normally determined by measuring rate constants as a function of added electrolyte concentration, using non-complexing electrolytes such as sodium perchlorate (NaClO_4).

The key Hg-sulfite species have intense absorption peaks in the UV range and thus can be monitored as a function of time by taking periodic spectral measurements. Current instrumentation allows rapid gathering of complete UV/Vis spectra (nominally 50 spectra per second) or monitoring light absorbance at up to six wavelengths simultaneously, whichever is desired. This greatly enhances the ability to obtain both pathway information (by following multiple peaks in the spectra) and better kinetics data for construction of a meaningful model.

This has been done initially for model systems containing only a few species. As more information is obtained, it should be possible to extend these spectral methods to monitoring FGD solutions in the bench-scale FGD system, as described later in this section, and thus correlate the model results with liquid systems where good measurements of Hg absorption and re-emission are possible. This will prove especially valuable for evaluating additives intended to reduce re-emission of Hg^0 .

The experimental apparatus for following aqueous reactants at low concentrations consists of a stirred spectrophotometric cell housed in a special cell holder which provides precise temperature control, stirring, inert gas flow as required, and fiber optic hookups to a UV/Vis light source and a CCD spectrometer. The spectrometer and cell holder are computer controlled, enabling precise control and rapid sampling. Figure 1 is a photograph of the bench-top spectrophotometric equipment.

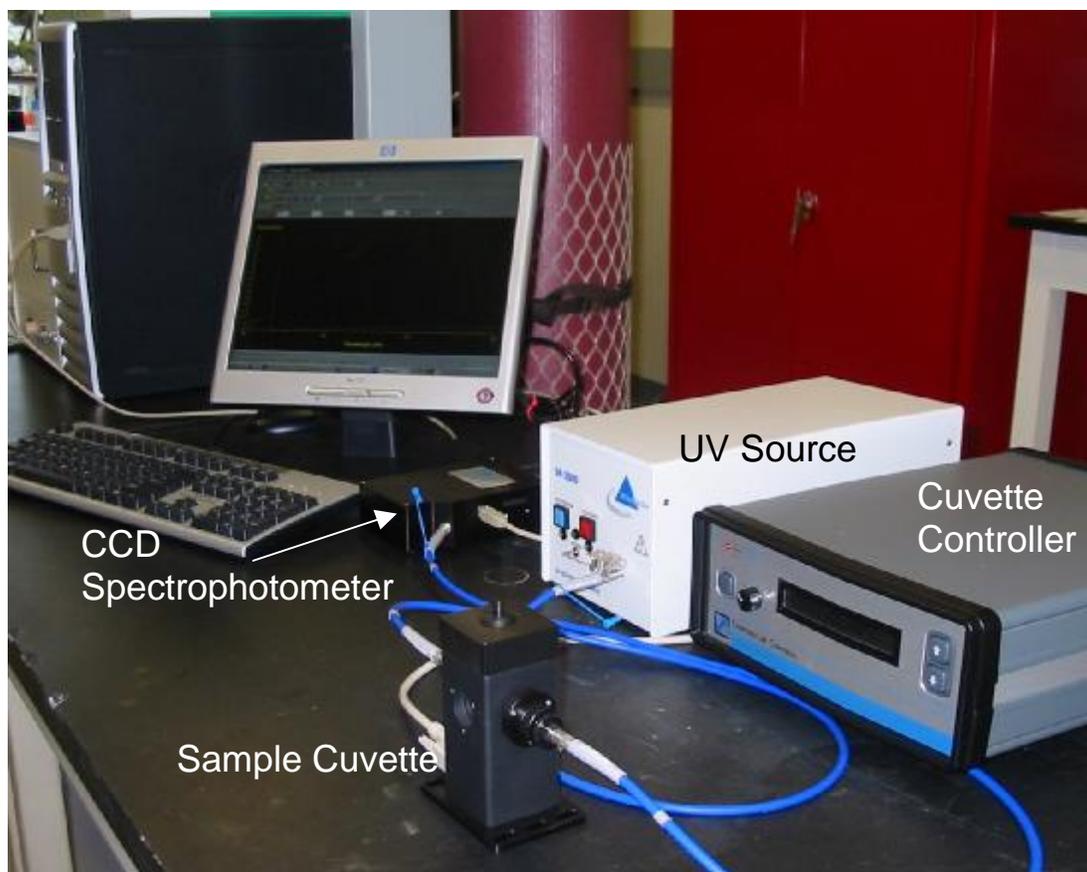


Figure 1. Photo of UV/Vis Spectrometer and Cell Holder Apparatus

The spectrophotometric system used for kinetics measurements is built around an Ocean Optics HR2000 high-resolution miniature fiber optic spectrometer, which includes a Sony ILX511 linear CCD array detector. The spectrometer interfaces to the main computer. It is capable of providing full spectrum scans into memory every 13 milliseconds and has an integration time variable from 3 milliseconds to 65 seconds. The high resolution of the optical bench of this spectrometer is provided by an expanded 1-inch diameter, 4-inch focal length (f/4) design in a symmetrical crossed Czerny-Turner optical design.

The optical system uses an Ocean Optics DT-1000 deuterium tungsten halogen light source, which combines the continuous spectrum of a deuterium UV light source and a tungsten halogen Vis/shortwave near-infrared light source into a single optical path. The combined-spectrum light source produces a stable output from ~200-1100 nm. The output is coupled to a fiber optic for transmission to the cuvette (measurement cell) holder.

This kinetics work uses a Quantum Northwest TLC 50F™ fiber optic temperature-controlled cuvette holder in conjunction with the spectrometer and light source. The computer-controlled cuvette holder provides precise temperature control of the 1-cm cuvette reaction vessel, built-in magnetic stirring, a dry gas purge to limit condensation or exclude oxygen from the cuvette, and optical slits for control of the illuminated volume.

The package includes a Quantum Northwest TC 101 microprocessor-controlled temperature controller and is calibrated against a NIST-traceable thermometer. It uses a Peltier device for temperature control and is capable of maintaining the cuvette temperature at -40 to $+105^{\circ}\text{C}$ $\pm 0.02^{\circ}\text{C}$.

Since the reactions studied thus far have been fairly slow, a simple but effective manual mixing method has been used to obtain kinetics data. Typically 2.00 mL of solution containing mercuric perchlorate and a pH buffer is placed in the spectrophotometric cell and temperature equilibrated in the cuvette holder. Continuous acquisition of spectra is initiated, typically taking a complete spectrum every five seconds. About 10 spectra are thus obtained for background subtraction purposes, and then a small amount of sulfite solution (typically 20-50 μL using a microliter pipetter) is injected into the stirred spectrophotometric cell to start the reaction. This addition results in the abrupt appearance of a peak in the 230-235 nm region due to mercuric disulfite. The decay of this peak is then monitored by continuing to take spectra for up to several hours.

The spectrophotometric zero of absorbance is set before the run using pure water at the same temperature as the reaction and is checked after the timed run. When chloride is used it is added directly to the spectrophotometric cell before the sulfite, using microliter amounts of a concentrated sodium chloride (NaCl) solution. The pH buffers used are based on chloroacetic acid for pH 3.0 and acetic acid for higher pH, all at the 0.01 M level and adjusted to the desired pH using sodium hydroxide (NaOH) solution. The pH of the solution after the run is also checked using a pH probe inserted into the spectrophotometric cell. A relatively low buffer concentration is used to minimize secondary effects on the kinetics. Initial checks at pH 3 did not indicate any spurious buffer effects.

In unraveling complex chemical kinetics, it is important to measure as many of the participating chemical species as possible, including both reactants and products. Therefore, some tests also measure the production of Hg^0 in solutions similar to those used for the UV/Vis spectrometer measurements, primarily by conducting gas phase Hg measurements. This will augment the results available for model fitting and will help determine if the Hg-SO₂ species actually exists and to further characterize it.

The test apparatus for following the formation of Hg^0 consists of a reaction vessel (sparger) charged with an aqueous solution containing a buffer for pH control and other chemical species, such as chloride, as desired. A gas stream containing nitrogen, SO₂, and presaturated with water is passed through this solution at a constant rate, typically 1.0 L/min. The SO₂ concentration in the gas and pH are chosen to give the desired SO₂ concentration in the liquid. The sparged reaction vessel is submerged in a water bath temperature controlled to $\pm 0.1^{\circ}\text{C}$. When steady state is reached, a solution containing mercuric ion is injected into the sparged solution via a hypodermic syringe and septum at "t = 0." This starts the reaction and elemental mercury sparged from the reaction vessel is measured using a UV gas cell spectrophotometer and a 254 nm mercury lamp (an atomic absorption analyzer). These measurements are done at regular time intervals using a computer controlled data acquisition system.

Task 3: Model Refinement, Bench-scale Validation and Additive Testing

The kinetics data described above will be used to develop an empirically adjusted, theoretically based kinetics model to predict mercury species reactions in wet FGD systems. The model will be verified in tests conducted with a bench-scale wet FGD system, where both gas-phase and liquid-phase mercury concentrations will be measured to determine if the model accurately predicts the tendency for mercury re-emissions and the phase in which mercury is found in the FGD byproducts. The model will be used to identify additives that could be used to reduce mercury re-emissions levels from wet FGD systems. These additives will also be investigated in the bench-scale wet FGD systems.

Prior to beginning this project, an existing bench-scale wet scrubber was modified to add a new absorber vessel with an integral reaction tank, a magnetic agitator drive for the reaction tank to allow the tank to be tightly sealed, and a venturi eductor to allow scrubber operation at negative gauge pressures. Figure 2 illustrates the revised 1-cfm (28-l/min) bench-scale scrubber to be used in the Task 3 bench-scale wet FGD simulation testing.

Simulated flue gas is mixed from a variety of compressed gases using calibrated rotameters. Figure 3 shows the simulation gas mixing apparatus. The dry simulation gas typically contains SO₂, NO_x, HCl, CO₂, oxygen, and nitrogen. Moisture is added to the simulation gas by feeding the oxygen, CO₂, 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.

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 (HgCl₂) crystals maintained at an elevated temperature. For these runs the simulation gas will be spiked only with oxidized mercury from HgCl₂ crystals. In actual practice, the oxidized mercury source produces a small amount of elemental mercury in the simulation gas; about 5% the total mercury in the flue gas entering 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.

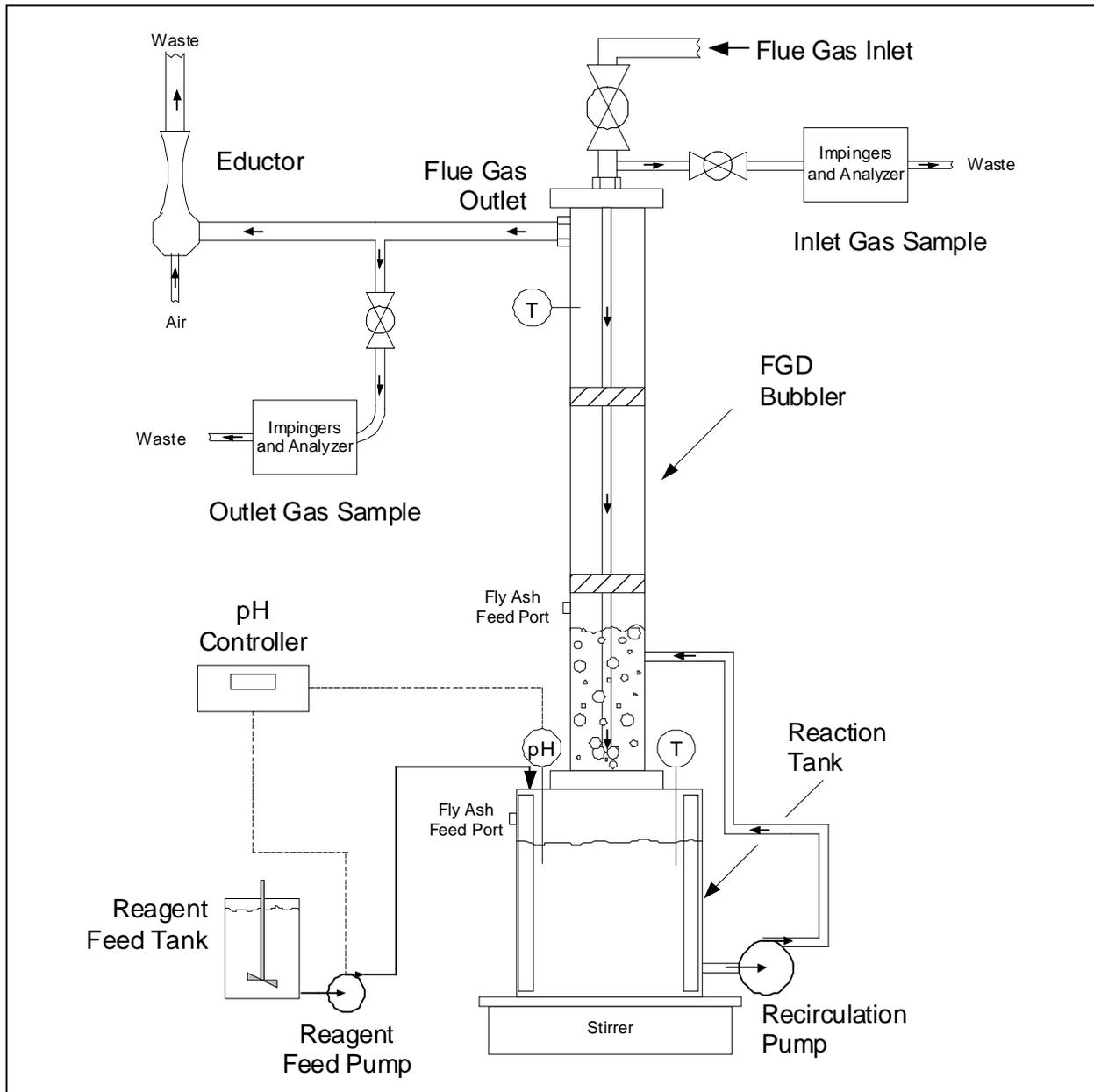


Figure 2. Bench-scale FGD Apparatus

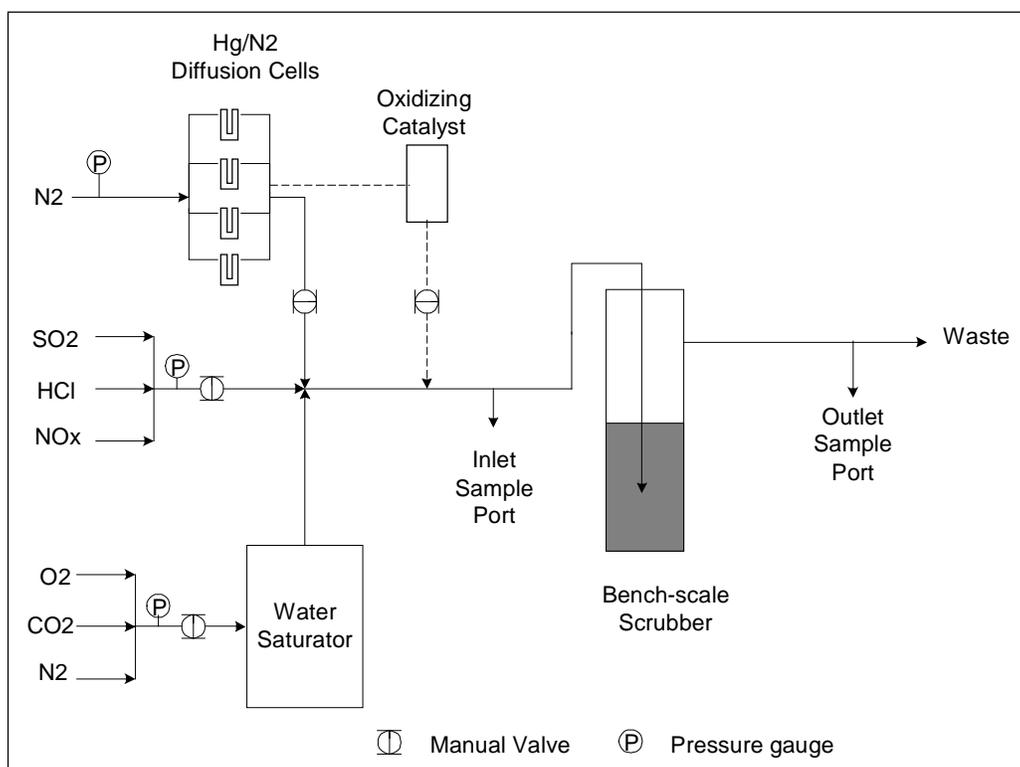


Figure 3. Bench-scale Simulation Gas Mixing Apparatus

The wet scrubber uses a “bubbler” type gas contactor. Low slurry levels in the bubbler simulate conventional spray or tray contactors (e.g., 4 in. H₂O [1 kPa] gas pressure drop) and high slurry levels can be used to simulate a high-energy venturi scrubber (e.g., 15 in. H₂O [3.7 kPa] gas pressure drop). However, the normal motive force for the flow through the scrubber is the pressure of the simulation gases, so the scrubber outlet pressure is slightly positive. A venturi eductor is available to be added to the scrubber outlet gas path, so that, if desired, the scrubber outlet can be operated at negative gauge pressures.

A stirred reaction tank is situated directly below and integrally mounted to the gas contactor. Slurry from the reaction tank is pumped into the contactor to maintain slurry level in the bubbler and to establish the desired liquid-to-gas ratio (L/G); spent slurry returns to the reaction tank by gravity flow. Lime or limestone reagent slurry is added to the reaction tank as needed to control pH at the set point value. A pH controller cycles the reagent makeup pump as needed. The bench-scale apparatus is heat traced, insulated and is controlled to typical full-scale wet scrubber temperatures.

The bench-scale scrubber can be operated in a continuous mode, with fresh water makeup to maintain a set weight percent solids level in the reaction tank and slurry blow down to maintain slurry level in the reaction tank. However, for this project, the runs will typically be 10 to 14 hours in duration each, and the slurry weight percent solids level and the reaction tank slurry level will be allowed to increase during the run. The slurry weight percent solids levels will typically range from 4% to 10% during these runs. Slurry will be removed for sample collection

or when necessary to lower the reaction tank slurry level, and wt% solids will be monitored visually and by gravimetric measurements.

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 are either teflon or quartz components.

Mercury measurements will be made using a mercury semi-continuous emissions monitor (SCEM) developed for EPRI, as illustrated in Figure 4. In the analyzer, flue gas is pulled 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.

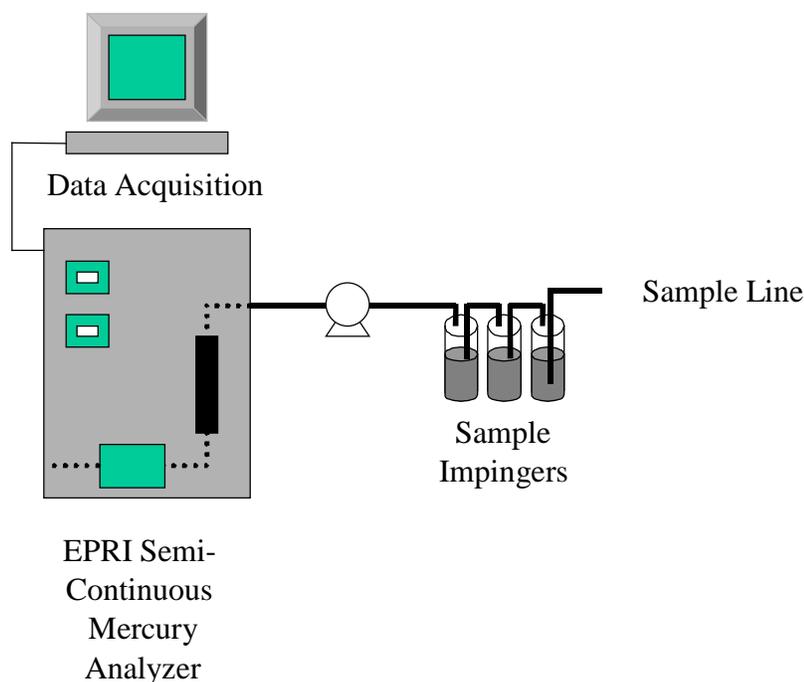


Figure 4. Schematic of Mercury SCEM

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. After passing through the SnCl_2 impinger, the gas flows through the Na_2CO_3 and NaOH solutions to remove acid gases, thus protecting the downstream, analytical gold surface. Gas exiting the impinger solutions flows through a gold amalgamation column where the mercury in the gas is adsorbed at less than 100°C . After adsorbing mercury onto the gold for a fixed period of time (typically 1 to 5 minutes), the mercury concentrated on the gold is thermally desorbed ($>700^\circ\text{C}$) from the column into nitrogen. The desorbed mercury is sent as a concentrated stream to a cold-vapor atomic absorption spectrophotometer (CVAAS) for analysis. 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 an impinger containing either tris(hydroxymethyl)aminomethane (Tris) or potassium chloride (KCl) solution. The Tris solution has been shown in other EPRI studies to capture oxidized mercury while allowing elemental mercury to pass through without being altered. KCl is used to collect oxidized mercury in the Ontario Hydro train. Mercury passing through the Tris or KCl solution to the gold is analyzed as described above and assumed to be elemental mercury only. The difference between the total mercury concentration (stannous chloride solution) and elemental mercury concentration (Tris or KCl solution) is assumed to be the oxidized mercury concentration.

Two analyzers will be used to semi-continuously monitor scrubber inlet and outlet gas mercury concentrations. The analyzers will be switched intermittently between sampling for elemental versus total mercury concentrations.

SO₂ detection tubes will also be used periodically during the testing, to quantify SO₂ removal across the bench-scale absorber. Overall SO₂ removal levels are typically 90% or greater. Aliquots of the scrubber liquor will be removed from the reaction tank periodically, and analyzed by iodometric titration to determine sulfite ion concentrations. For each test condition a set of slurry and preserved FGD liquor samples will be collected and analyzed to document the end-of-test scrubber chemistry conditions.

RESULTS AND DISCUSSION

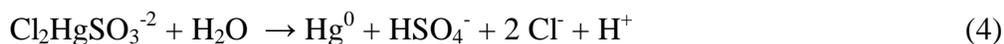
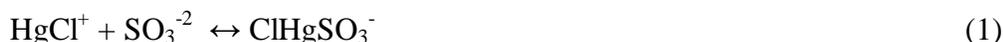
This section provides details of technical results for the current reporting period, April 1, 2005 through September 30, 2005. The technical results presented are from the Task 2 reaction kinetics investigations.

Task 2: Kinetic Data Gathering and Model Development

Overview of Previous Results

In the first semi-annual report for this project we showed how relatively low concentrations of chloride had a significant effect on the rate of mercuric ion reduction by sulfite, as determined from spectrophotometric test results.¹ Figure 9 of that report showed a smaller initial absorbance jump (believed to be due to the formation of mercuric disulfite [$\text{Hg}(\text{SO}_3)_2^{-2}$]) when sulfite was added to a solution containing chloride ion, compared to results for solutions with no chloride present. Figure 9 also showed a major slowing of the rate of decomposition of the mercuric disulfite complex (k_{obs} decreasing by a factor of 25 with chloride present) as indicated by the rate of decay of that absorbance.

Current project efforts are attempting to unravel the possible interplay between kinetics and equilibria of formation of multiple complexes of Hg^{+2} with Cl^- and SO_3^{-2} . For example, the kinetics may be affected by the formation of other mercury complexes containing both chloride and sulfite, along with their decomposition reactions as shown below:



Initial modeling and lab measurements to determine the formation constants of the complexes indicate that this may help fit the observed data to a kinetics model, although the formation of the dichloro complex ($\text{Cl}_2\text{HgSO}_3^{-2}$, reaction 3) is less favored than the formation of the monochloro complex (ClHgSO_3^- , reaction 1). At high chloride concentrations the chloromercuric complexes alone tend to dominate over the formation of mercuric sulfite and mercuric disulfite, and "shut down" the other reactions. However, it is difficult to interpret and determine all of the necessary information based on spectrophotometric results alone. Therefore, other approaches such as the mercury stripping tests described in previous technical progress reports and the "macro cell" described below are being used to supplement spectrophotometric results.

Chloride also has a substantial effect on the pH dependence of the reaction. As shown in Figure 5, the initial absorbance changes with pH when chloride is present, but the slopes of the curves are close to being the same. This is quantified by a log-log plot of k_{obs} and sulfite concentration, which has a slope of only -0.21 for the 10 mM chloride case as shown in Figure 6.

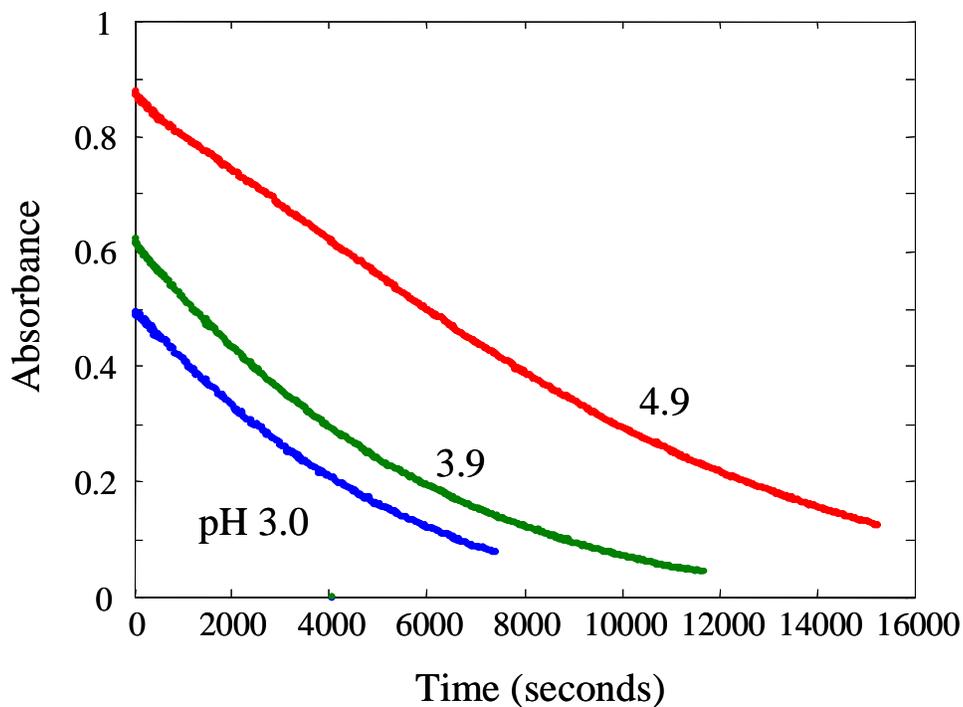


Figure 5. Effect of 10 mM Chloride at Different pH Values (55°C, 1.0 mM sulfite, 40 mM Hg²⁺)

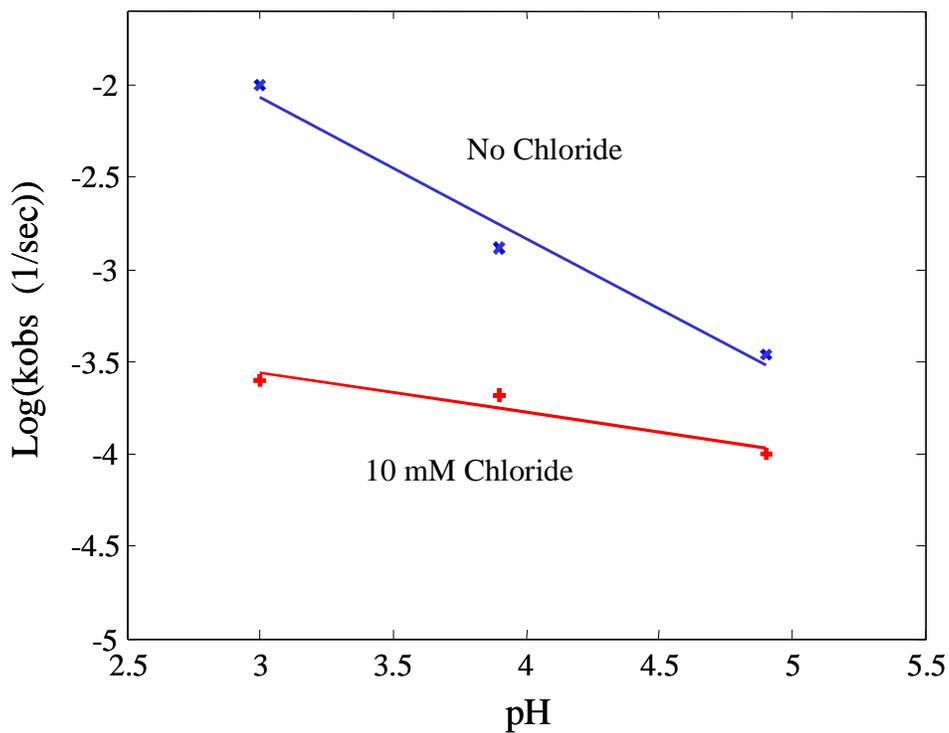


Figure 6. pH Dependence of k_{obs} with and without 0.01 M Chloride (55°C, 1.0 mM sulfite, 40 mM Hg²⁺)

Macro Cell Results

Recently a "macro cell" has been constructed and checked out as an experimental enhancement as well as check on some of the previous "micro" scale (2-mL reaction volume) UV absorbance results. This cell is designed to allow simultaneous and continuous measurement of UV absorbance, open circuit potential (OCP, or "redox potential"), pH, and temperature. In the previous micro cell, only UV absorbance and temperature could be monitored. The volume of this cell is large enough (100 mL) to allow periodic sampling during a run with subsequent measurement of sulfite/sulfate by ion chromatography. A photograph of the cell and ancillary equipment is shown in Figure 7.

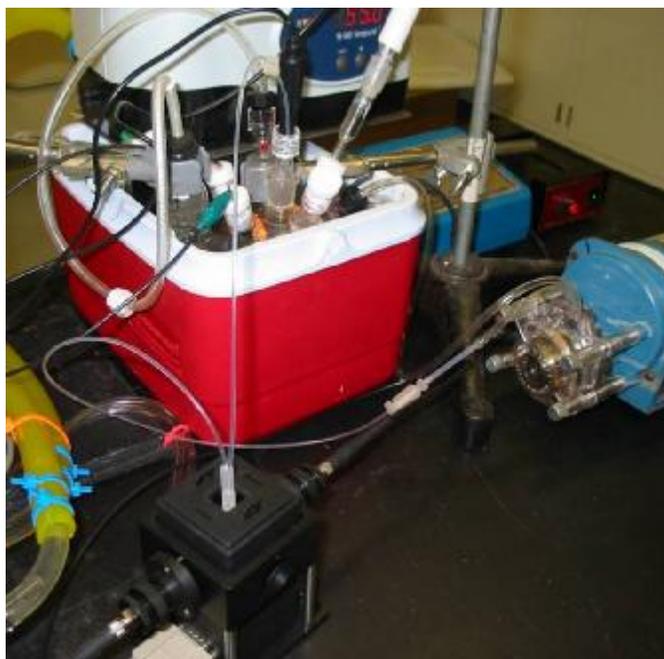


Figure 7. Multi-port Reaction Cell in Thermostatted Bath Showing Pumping to External Thermostatted Spectrophotometric Cell

Results from a macro-cell run starting with 10 mM chloride buffered to pH 4.0 with 20 mM acetate, adding first 40 μM Hg^{+2} and then 1.0 mM sulfite at 55°C, is shown in Figure 8. The absorbance time profile for this run agrees fairly well with that obtained for 12,000 seconds in the micro cell. The OCP changes show both the effect of adding the "oxidizing" mercuric ion (increase in OCP) and the sulfite (negative shift in OCP). The changes in OCP as the reaction proceeds are relative small and practically imperceptible at the scale of this figure. However, from several run results it appears that OCP changes due to the effects of mercuric complexes may be discernible. Generally, a slow increase in OCP can be seen at long times as sulfite is consumed (see the right side of Figure 8 below).

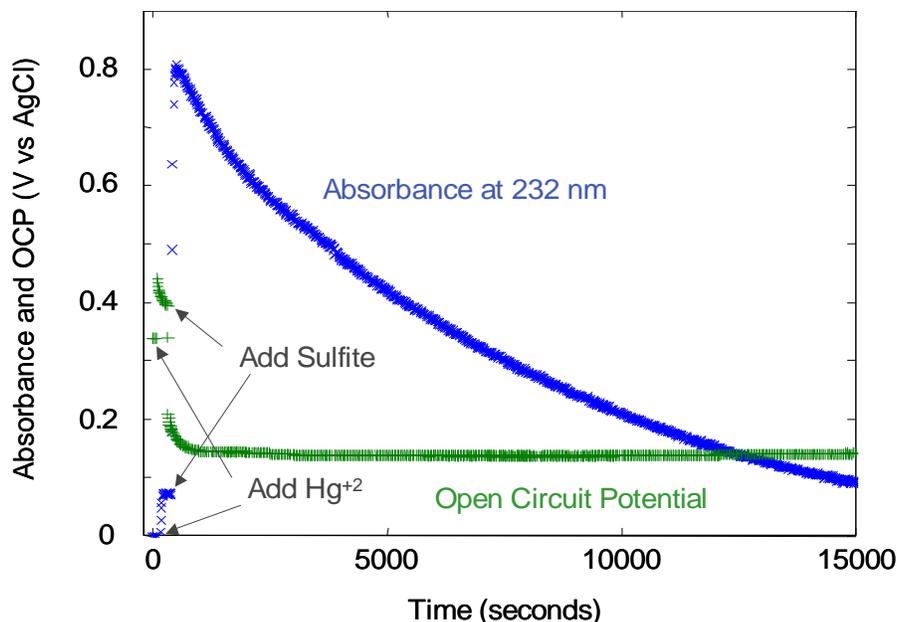


Figure 8. Absorbance and OCP on Addition of 40 mM Hg²⁺ and 1.0 mM Sulfite to Solution Containing 10 mM Chloride and 20 mM Acetate Buffer (55°C, pH 4.1)

Although the spectrophotometric results agree for this case, as noted in previous technical progress reports, some of the micro-cell results show abrupt variations during the run, particularly at higher chloride concentrations. These abrupt transitions have not yet been observed in the larger macro cell. A contributing factor may be pH excursions when sulfite is added to unbuffered solutions, which have been observed with the continuous pH monitoring that is possible with the macro cell. Checks of the pH in the micro cell after each run show it is usually near the starting pH (before sulfite addition). But this may be fortuitous and due to acidification that occurs on sulfite oxidation, which was observed to occur during the course of a run in the macro cell (see below). Buffers have been used for all runs above pH 3.5, but problems have been encountered with low pH buffers, as detailed in the previous technical progress report (see Figure 15 in that report).²

Another unexpected phenomenon observed in the macro-cell runs is the oxidation of sulfite that occurs noticeably over long run periods, even with careful initial purging and then blanketing of the reaction liquid with nitrogen. At long run times (10,000 to 15,000 seconds), about 50% of the initial 1.0 mM sulfite is oxidized to sulfate, as determined by ion chromatograph measurements. Possible causes of the unexpected oxidation, such as photo-oxidation or oxygen diffusion through cell tubing were investigated. At present the effect appears to be due to oxygen diffusion, since sulfite oxidation was not affected by turning off the light source, but it was eliminated when solution was not pumped to and from the spectrophotometric cuvette.

Longer-term Mercury Stripping Test Results

As described in previous technical progress reports, a “mercury stripping” apparatus has been used to supplement UV results to determine the rate at which elemental mercury is stripped from

reaction liquors as a result of the reduction of Hg^{+2} . Most of the previous stripping runs were conducted with cold-vapor atomic absorption measurement of elemental mercury in the gas phase above the solutions, to determine Hg^0 evolution rates. However, measurement of gas phase concentrations becomes less accurate for conditions where the reactions are quite slow and gas phase mercury concentrations are low, including many typical FGD process conditions. In the current series of longer-term tests, the apparatus has instead been operated in combination with periodic liquor sampling and cold-vapor atomic absorption measurement of oxidized mercury remaining in the liquid phase. Thus, the rate of Hg^0 evolution has been determined for these slower reaction rate conditions by determining the rate at which Hg concentrations drop in the reaction liquor.

For these stripping runs, the apparatus was modified to get better pre-saturation of the gas with water, to minimize water evaporation from the solutions. In addition, these runs employ 100 mM acetate buffer to obtain better pH stability for the long run times. The present set of runs was done to determine the effect of varying pH (4.0, 5.0, and 6.0) and sulfite concentration (1, 5, and 20 mM) at a fixed chloride value (100 mM) typical of FGD conditions, over a duration of 24 hours.

During this series of runs, problems were still encountered in maintaining a constant liquid volume in the reactor due to variations in temperature of the pre-saturator, the long duration of the runs and the high gas stripping rates used to insure complete stripping of elemental mercury as it is formed. To correct for these volume changes the initial and final volumes of liquid in the reactor were measured and each mercury concentration data point was corrected assuming the volume varied linearly with time over the duration of the experiment. Maintaining the pH and sulfite concentration of these solutions is difficult particularly at higher pH (6) and lower sulfite concentrations.

Some examples of individual run results obtained using this method are shown in Figure 9. All runs reported below were done using 100 mM sodium chloride and 100 mM sodium acetate at 55 °C. The inlet SO_2 concentration in the gas mixture was varied from approximately 1 ppm to 200 ppm to match the calculated equilibrium total sulfite value for the desired pH and sulfite concentration.

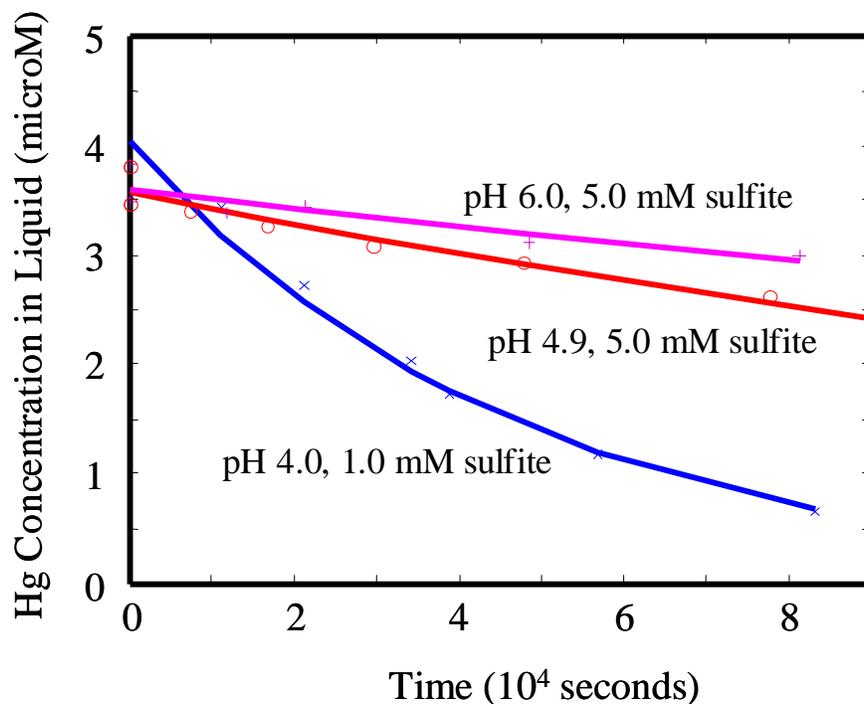


Figure 9. Amount of Mercury Remaining in Solutions of Compositions Shown, also Containing 100 mM NaCl and 100 mM Acetate Buffer, on Continuous Stripping with N₂-SO₂ Gas Mixture (Solution spiked with 4.0 mM Hg(ClO₄)₂ at t = 0)

Apparent rate constants, k_{obs} , were calculated for each run from the negative of the slope of a least squares fit of $\ln(C^0/C)$ versus time, where C^0 is the initial mercury concentration (nominally 4.0 micromolar) and C is the concentration of mercury measured at each sample time. All of the results obtained thus far are shown in below in Figures 10 through 12, where the results for each sulfite level have been separated out. The error bars shown on the figures represent the standard deviation of the points in each $\ln(C^0/C)$ versus time curve. Since there was some variation in pH during the runs, results are plotted for both the initial pH (symbol "x") and final pH (symbol "o") values. All three plots are drawn to the same scale to facilitate comparison. The solid lines are from a cubic fit and are only intended to aid visualization.

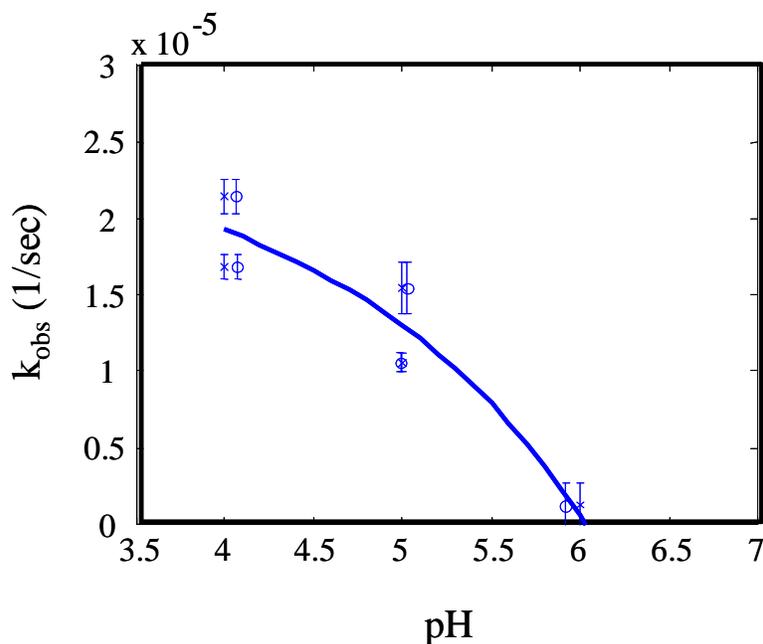


Figure 10. Observed Rate Constants for Reduction and Stripping of Mercury in 1.0 mM Sodium Sulfite Solutions as a Function of pH. (Solutions contained 100 mM NaCl and 100 mM sodium acetate at 55 °C).

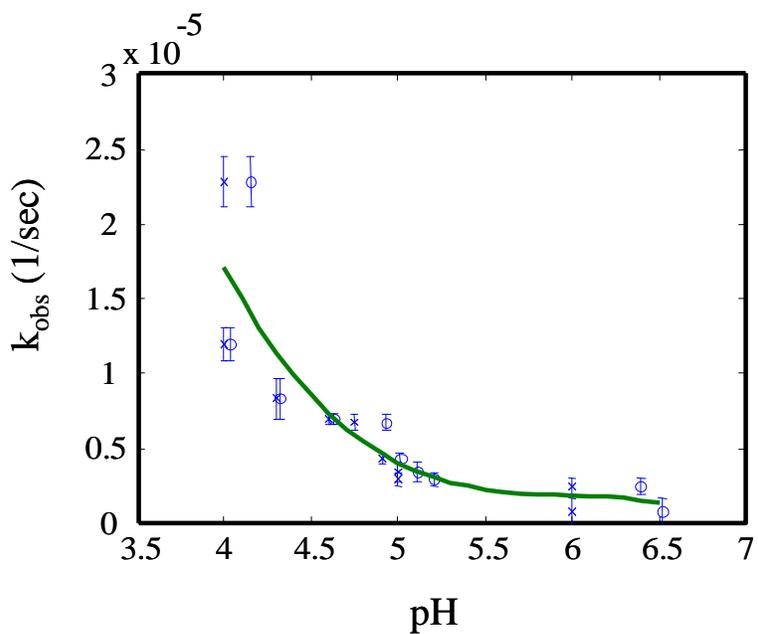


Figure 11. Observed Rate Constants for Reduction and Stripping of Mercury in 5.0 mM Sodium Sulfite Solutions as a Function of pH. (Solutions contained 100 mM NaCl and 100 mM sodium acetate at 55 °C).

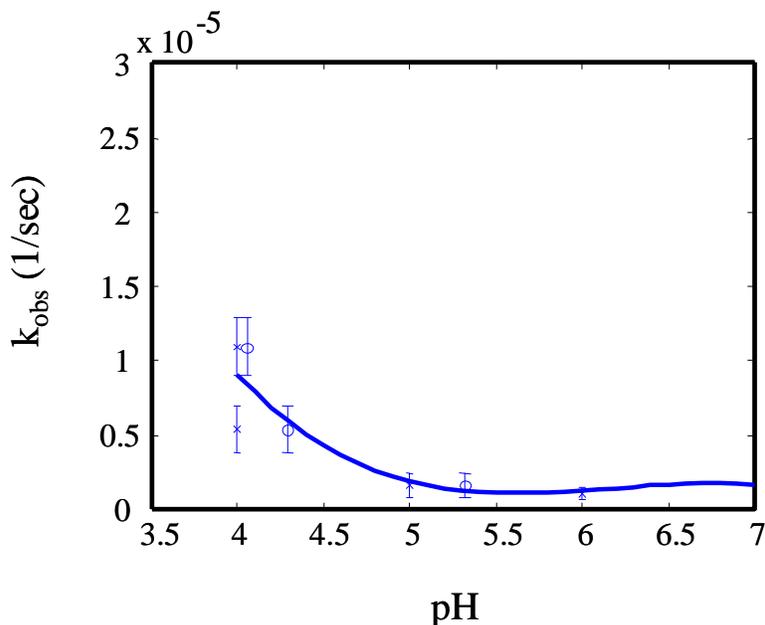


Figure 12. Observed Rate Constants for Reduction and Stripping of Mercury in 20 mM Sodium Sulfite Solutions as a Function of pH. (Solutions contained 100 mM NaCl and 100 mM sodium acetate at 55 °C).

These results show that the rate of reduction of oxidized mercury increases significantly (by a factor of about 10) as the pH decreases from about 5 to 6 down to pH 4 in the presence of 100 mM chloride. This is consistent with the results obtained at low chloride values using the spectrophotometric method. Although there is considerable scatter, the shape of the rate constant versus pH curve appears to depend on the sulfite concentration. In general, the rate decreases with increasing sulfite concentration, though the dependence seems to be more pronounced in the transition region between high and low pH. The behavior shown here could be particularly relevant to actual FGD systems since it would indicate that the fastest elemental mercury formation rates would occur in the absorber and could even vary with type of absorber, position in the absorber, or FGD chemistry.

As an example, in limestone reagent spray-tower absorbers, the absorber recycle slurry is fed to the spray nozzles at a pH value of about 5.5. As slurry droplets fall through the absorber, countercurrent to the flue gas flow, the droplets are exposed to inlet flue gas with a high inlet SO_2 concentration, and the droplet pH decreases significantly. Values of pH 3 or less are possible. However, in absorbers that operate with high liquid phase alkalinity, such as with magnesium-enhanced lime reagent or with dibasic acid additives, the pH drop can be much less significant. Similarly, absorber types other than open spray towers may have significantly different droplet pH profiles.

Kinetics Model Update

We have continued work on the kinetics model (see the previous semi-annual technical progress reports for a description of the model^{1,2}), using it to describe the results presented above as well

as previous spectrophotometric results. A good numerical fit has been obtained under some, but not all conditions. However, in spite of the need to improve the model fit at some conditions, the model implies that the mechanism of reduction proceeds primarily via the chloromercuric sulfite complexes in more acidic solutions. The chloride essentially provides a ceiling to limit the rate of reaction at low pH. The mechanism changes to primarily occur through the mercuric disulfite complex at higher pH. This change of mechanism could explain some of the "complex" behavior often observed in re-emission results. Even at higher pH the chloromercuric sulfite complexes play a role, because without them the mercuric chloride complexes tend to shut down mercuric reduction completely at approximately the 100 mM chloride level.

Task 3: Model Refinement, Bench-scale Validation and Additive Testing

Overview of Progress

During the current reporting period, the Task 3 bench-scale model validation effort was begun. To date, the efforts have focused on test planning and on preparing the existing bench-scale apparatus to support these tests. The draft test plan is discussed in the following subsection. Modifications to the existing bench-scale wet FGD apparatus have been determined to be necessary because of the complex relationship between pH, sulfite concentration and chloride concentration on mercury re-emissions.

Of these, chloride concentration is the most readily controlled. Since chloride is a highly soluble ion, it tends to cycle up in concentration in the FGD liquor over time in FGD systems that operate with a closed or nearly closed water loop, as do most wet FGD systems. Thus, most bench-scale wet FGD runs are conducted by spiking the reaction tank liquor to simulated steady-state chloride concentrations. The chloride absorbed into the liquor from HCl in the simulation gas has only a minor effect on liquor chloride concentrations, so the chloride concentration is predominantly controlled by the initial spiking level.

At a given set of inlet flue gas and FGD liquor dissolved species conditions, the liquor pH is controlled by reagent addition to the reaction tank. The pH of the reaction tank slurry liquor is continuously monitored and used to start and stop a reagent make up pump. However, for mercury re-emissions, it may be the pH of the slurry liquor in the absorber rather than in the reaction tank that is most important. Consequently, a second pH meter is being added to monitor the slurry liquor pH in the absorber. Testing will have to be conducted to determine whether the absorber pH can be controlled indirectly by controlling the reaction tank pH set point at an appropriate higher value, or whether the reagent addition scheme will need to be modified to use reagent makeup to the reaction tank to control the absorber pH directly.

The FGD liquor sulfite concentration is typically not controlled, except when operating in a limestone/forced oxidation mode where it is controlled to very low concentrations with the oxidation air rate. In natural or inhibited oxidation modes, the sulfite concentration is a function of the inlet flue gas SO₂ concentration, liquor pH, concentrations of other species in the FGD liquor, FGD solids surface area, and sulfite oxidation rates. For a given set of run conditions, the inlet SO₂ concentration, pH, concentrations of other species in the FGD liquor, and FGD solids surface area (if solids are to be present) will be set by test conditions. This leaves sulfite

oxidation rate as the sole remaining variable that can be used to control FGD liquor sulfite concentration. Therefore, the sulfite oxidation rate, and hence the liquor sulfite concentration will be controlled by varying the amount of oxygen in the bench-scale FGD inlet simulation gas. To minimize total simulation gas flow variations as the oxygen concentration varies, the simulation gas oxygen content will be made up as pure O₂ rather than air, as it has been made up previously. Since a continuous liquor sulfite analyzer is not available, oxidation-reduction potential (ORP) will be used as a surrogate for controlling sulfite concentration. Some trial and error will be required to develop the relationship between ORP and sulfite concentration for each run condition. Once established, a proportional/integral/derivative (PID) controller will be used to modulate the bench-scale scrubber simulation gas O₂ makeup flow rate to control the FGD liquor ORP. These modifications are currently underway.

Draft Test Plan

This subsection describes a series of bench scale runs to determine causes of mercury re-emissions from FGD absorbers and to check and calibrate the chemical kinetics model for predicting such emissions. The test series will initially concentrate on the effects of chloride concentration, sulfite concentration, and pH on Hg emissions from simulated FGD solutions. Based on lab runs and modeling, chloride is expected to have a dominant effect. For the first series of runs the liquor chloride concentration will be fixed at 100 mM (approximately 3500 ppm), which appears to be a "tipping point" concentration and is also fairly typical of many FGD systems. Following this series, higher and lower concentrations of chloride will be tested with somewhat smaller test matrices. Then the effects of other factors which could influence Hg emissions such as NO₂, thiosulfate, solids, inhibitors (TMT, EDTA), other "FGD" species (Mg⁺², etc), and gas/liquid interface conditions (including inlet SO₂ concentration and bubble height/area) will be tested under conditions selected from the first test matrix results.

Tests will be done using a "clear liquid" reagent to allow a better focus on key solution concentration effects without the complications of running with a slurry. Either concentrated solutions of sodium carbonate or sodium hydroxide will be to neutralize the absorbed SO₂ and thus control the pH. The following conditions are planned for the initial test matrix (following shakedown runs for working out control methods).

Chloride: 100 mM as NaCl

Sulfite: 1.0, 5.0, and 20.0 mM as Na₂SO₃

pH: 4.0, 5.0, 6.0 (adjust starting pH with dilute H₂SO₄ or NaOH/Na₂CO₃)

Other solution components: 100 mM Na₂SO₄; 1.0 ppm MnSO₄; 0.1 microM HgCl₂

Temperature: 55.0 °C

Total simulation gas flow rate: 24 L/min at 25 °C and 1.0 atm

Solution volume: 5.0 L

Inlet SO₂ concentration: 1000 ppm

Inlet O₂ concentration: adjust as needed to maintain sulfite concentration

pH control/monitoring: control on reaction tank pH, also monitor absorber pH (may have to control absorber pH directly)

Redox potential: measure redox potential and use to control inlet O₂ at set point determined by sulfite measurement

The primary response to be measured is the outlet elemental mercury concentration in the gas stream. Close control of sulfite concentration is needed since it is a key variable. A relatively large amount of SO₂ is added to the liquor during a run, and, as described above, the only means of maintaining a steady sulfite concentration in a clear liquid system is by oxidation to sulfate.

The oxidation rate of sulfite is highly variable in the absence of any catalyst. This could make the sulfite control by oxidation very erratic. Therefore, a small "natural" amount of catalyst will be added to the simulation liquor to obtain a consistent sulfite oxidation rate. MnSO₄ at a 1.0 ppm level should be a good starting point for sulfite oxidation catalyst addition. This is within the range of manganese normally found in scrubber liquors. The literature indicates that when manganese is present, it does not make much difference what the iron concentration is (another sulfite oxidation catalyst), so iron concentrations will not be of concern. Iron is a much more common contaminant than manganese, and thus would be harder to control in the simulation liquor.

The sulfite oxidation rate is said to be proportional to the manganese level, so the manganese concentration in the liquor can be increased or decreased within reasonable limits to get in the right control region, if necessary. At least one preliminary run will be conducted where the sole objective will be to control pH and sulfite level by adjusting O₂ makeup rates while SO₂ is being absorbed from the inlet simulation gas.

The main overall reactions for SO₂ conversion are expected to be:



Using 24 LPM of simulation gas with a 1000 ppm inlet SO₂ concentration should consume about 150 mL of 2.0 M Na₂CO₃ solution (or the same amount of 4 M NaOH) in a five-hour run. This would add 60 mM of Na₂SO₄ to 5.0 L of scrubber solution. The run will start with sodium sulfate in solution so that the relative amount of salt and sulfate buildup during a run is not significant.

The following startup procedure is suggested, but can be adjusted as operating experience dictates.

- Make up 2.0 M Na_2CO_3 solution for pH control;
- Make up main starting solution with 100 mM NaCl, 100 mM Na_2SO_4 , 1.0 ppm MnSO_4 (add as liquid from a concentrate stock solution);
- Put solution in reaction tank and adjust to desired starting pH;
- Add 0.1 microM HgCl_2 (add as liquid from a concentrate stock solution);
- Start gas components flows, except SO_2 ;
- Start Hg measurements;
- Start pH controller;
- Start O_2 controller;
- Add sulfite to desired operating concentration (add as liquid from a concentrate stock solution). Note - may want to also add enough dilute H_2SO_4 to neutralize the sulfite at this point;
- Start SO_2 flow;
- Monitor/adjust controllers until they appear to be controlling correctly. This will include determining the redox potential corresponding to desired sulfite concentration and setting O_2 controller to hold this potential.

A spectrophotometric method will be used for frequent measurement of sulfite as needed, since it uses only a small volume of solution. Iodimetric titrations will be done for verification.

After this initial test matrix is completed and the results have been reviewed, a follow-on plan will be prepared and implemented. The follow-on plan may explore a wider range of FGD conditions, slurry rather than clear solution operation, the effects of additives, etc.

CONCLUSION

There is ample evidence that mercury re-emission reactions are limited by kinetics rather than equilibrium. Fundamental laboratory studies of the kinetics of mercury reactions in the aqueous phase are currently being conducted as part of this project. A review of the literature produced an initial series of chemical reactions between Hg^{+2} and sulfite ion that could lead to re-emissions, and additional pathways have been identified as described here. Experimental methods have been developed using UV spectrophotometry to identify reaction intermediate species, and to track their changes in concentration as the reactions proceed. A separate but complementary method of following the rate of evolution of mercury from the liquid phase has also been developed and applied.

Using these methods, both the rate of disappearance of the mercuric disulfite complex (a major pathway for Hg^{+2} reduction) and the rate of formation of elemental mercury product can be monitored. Work is in progress to define the effects of temperature, ionic strength, initial reactant concentrations, pH, chloride, thiosulfate, and other complexing agents on the rates of these reactions, and thus on the re-emission of Hg from FGD systems.

In a previous semi-annual report we showed how fairly low concentrations of chloride had a significant effect on the rate of mercuric ion reduction by sulfite.¹ In the next report, progress in explaining the effects of chloride ion on the kinetics was reported.² Evidence was found for the formation of at least one complex of mercuric ion with both sulfite and chloride. The chloride ion attached to the mercury apparently slows the decomposition of the complex by a very substantial amount. The monosulfite complex (HgSO_3) is thought to decompose much faster than the disulfite ($\text{Hg}(\text{SO}_3)_2^{-2}$) complex, which in turn decomposes much more rapidly than the complex containing chloride. The results become more complicated as the chloride concentration is increased from 30 to 1000 mM. At high chloride concentrations the chloromercuric complexes alone (without attached sulfite) tend to dominate (at least at low pH values) and shut down mercury reduction reactions.

However, it is difficult to interpret and determine all of the necessary information based on spectrophotometric results alone. Measurements of the rate of stripping of elemental mercury from solution as a function of time are being used to verify and extend the spectrophotometric results. In the absence of chloride, the Hg^0 stripping rate measurements confirm the first order disappearance of Hg^{+2} and equivalent rate constants are obtained for this case as well as at low chloride concentrations. At elevated chloride levels the Hg^0 stripping rate measurements show a sharp initial release of elemental mercury, but then very low rates of release are observed for extended times. These results have been verified by measurement of mercury retained in the liquor after each run and expanded by periodic liquid sampling as discussed below.

During the current reporting period, modifications have been made to both the spectrophotometric and the elemental mercury stripping apparatus, to enhance the information derived from this project. The spectrophotometric apparatus has been modified to a larger, "macro" cell size that allows continuous measurement of pH and open circuit potential (OCP) over time in the reaction liquors, and intermittent measurement of liquor sulfite and sulfite concentrations. These macro cell runs have not shown the same abrupt transitions in UV

absorbance that were seen in some of the previous “micro” cell results, particularly at high chloride concentrations. It is speculated that some of the abrupt transitions seen previously were due to transient pH and sulfite oxidation effects that could not be tracked versus time with the micro cell. These possible effects are currently under further investigation with the macro cell.

The elemental mercury stripping apparatus was modified to accommodate longer run times, which allow data to be collected over a wider range of conditions (e.g., pH 6) where mercury reduction rates are low. These results show that the rate of reduction of oxidized mercury increases by a factor of about 10 as the pH decreases from 5 to 6 down to pH 4, in the presence of 100 mM chloride. Although there is considerable scatter, the shape of the rate constant versus pH curve appears to depend on the sulfite concentration. In general, the rate decreases with increasing sulfite concentration, though the dependence seems to be more pronounced in the transition region between high and low pH. These results suggest that mercury re-emissions in full-scale wet FGD systems could be greatly influenced by factors such as slurry droplet pH drop, sulfite pick up, and sulfite oxidation within the absorber rather than reaction tank conditions.

An existing chemical kinetics model has been adapted to the mercury-sulfite-chloride-thiosulfate system and takes into account the simultaneous occurrence of a number of reaction steps. The model will be used to design bench-scale experiments for testing as well as for prediction of kinetics in low pH regions, such as at the SO₂ gas-aqueous interface, which are difficult to investigate experimentally.

Efforts have begun to conduct bench-scale wet FGD tests to validate reaction kinetics model predictions. An initial test matrix has been developed, and required modifications to the bench-scale FGD apparatus have been identified. The modifications are currently underway, and bench-scale testing will commence during the next reporting period.

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1. Gary M. Blythe and David W. DeBerry, PhD. "Bench-scale Kinetics Study of Mercury Reactions in FGD Liquors, Semiannual Technical Progress Report, October 1, 2004 – March 31, 2005," DOE/NETL Cooperative Agreement No: DE-FC26-04NT42314, April 2005.
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