

Bench-scale Kinetics Study of Mercury Reactions in FGD Liquors

Semiannual Technical Progress Report

April 1, 2006 – September 30, 2006

Prepared by:

Gary M. Blythe
David W. DeBerry, PhD

October 2006

Cooperative Agreement No: DE-FC26-04NT42314

**URS Corporation
9400 Amberglen Boulevard
Austin, Texas 78729**

Prepared for:

Sara Pletcher

National Energy Technology Laboratory
U.S. Department of Energy
3610 Collins Ferry Road
Morgantown, West Virginia 26507

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

ABSTRACT

This document summarizes progress on Cooperative Agreement DE-FC26-04NT42314, “Kinetics Study of Mercury Reactions in FGD Liquors,” during the time-period April 1, 2006 through September 30, 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. In addition, new methods for operating and controlling bench scale FGD experiments have been developed and several of these runs have been completed.

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 fourth 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. A number of modifications to the bench-scale wet FGD apparatus, a preliminary test matrix has been developed, and 23 bench-scale wet FGD tests have been conducted

TABLE OF CONTENTS

	Page
Disclaimer	iii
Abstract	iv
Introduction	6
Executive Summary	7
Summary of Progress	7
Problems Encountered	7
Plans for Next Reporting Period	7
Prospects for Future Progress	7
Experimental	8
Task 2: Kinetic Data Gathering and Initial Model Development.....	8
Task 3: Model Refinement, Bench-scale Validation and Additive Testing	10
Results and Discussion	15
Task 2: Kinetic Data Gathering and Model Development	15
Kinetics Model Results	26
Task 3: Model Refinement, Bench-scale Validation and Additive Testing	27
Conclusion	34
References	36

INTRODUCTION

This document summarizes progress on Cooperative Agreement DE-FC26-04NT42314, “Kinetics Study of Mercury Reactions in FGD Liquors,” during the time-period April 1, 2006 through September 30, 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, 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 is being verified in tests conducted with a bench-scale wet FGD system, where both gas-phase and liquid-phase mercury concentrations are being 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 fourth 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. In addition, new methods for operating and controlling bench scale FGD experiments have been developed and a number of these runs have been completed. This report presents and discusses these project results.

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, April 1, 2006 through September 30, 2006, is the fourth 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. In addition, new methods for operating and controlling bench scale FGD experiments have been developed and a number of these runs have been completed.

Problems Encountered

There were no significant problems encountered during the reporting period.

Plans for Next Reporting Period

During the next reporting period (October 1, 2006 through March 31, 2007), 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 characterize 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, April 1 through August 31, 2007, 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 fifth semi-annual technical progress report and the project final report.

EXPERIMENTAL

Task 2: Kinetic Data Gathering and Initial Model Development

This project has focused on obtaining kinetic data under conditions common to wet FGD systems in such a way that effects of individual composition and physical variables can be determined. SO₂-derived species such as the various forms of "sulfite" are important since this is the main source of reductant for converting oxidized mercury to elemental mercury. Kinetic measurements have been done for solutions containing chloride and thiosulfate, both of which may form strong complexes with Hg⁺². Another important variable is pH, which affects both the distribution of sulfite species and the kinetics of many reactions. Most of the testing has been conducted with sulfite and chloride added as sodium salts, to avoid potential interferences from complexes that calcium and magnesium ions can form with these species. However, the effects of other major species in FGD liquors, such as magnesium, calcium, sulfate and NO_x-derived species, will also be determined, as will the possible catalytic effects of particulate matter. In addition to chemical species effects, the effects of temperature and ionic strength on kinetics are being measured. Most of the work has been done in the normal FGD temperature range (50-55°C), but activation energies are measured or estimated as necessary for modeling.

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 (NaClO₄).

Prior research has shown that 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 (up to 50 spectra per second) or monitoring light absorbance at up to six wavelengths simultaneously as desired. This greatly enhances the ability to obtain both pathway information (by following multiple peaks in the spectra) and 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 Hg⁰.

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.

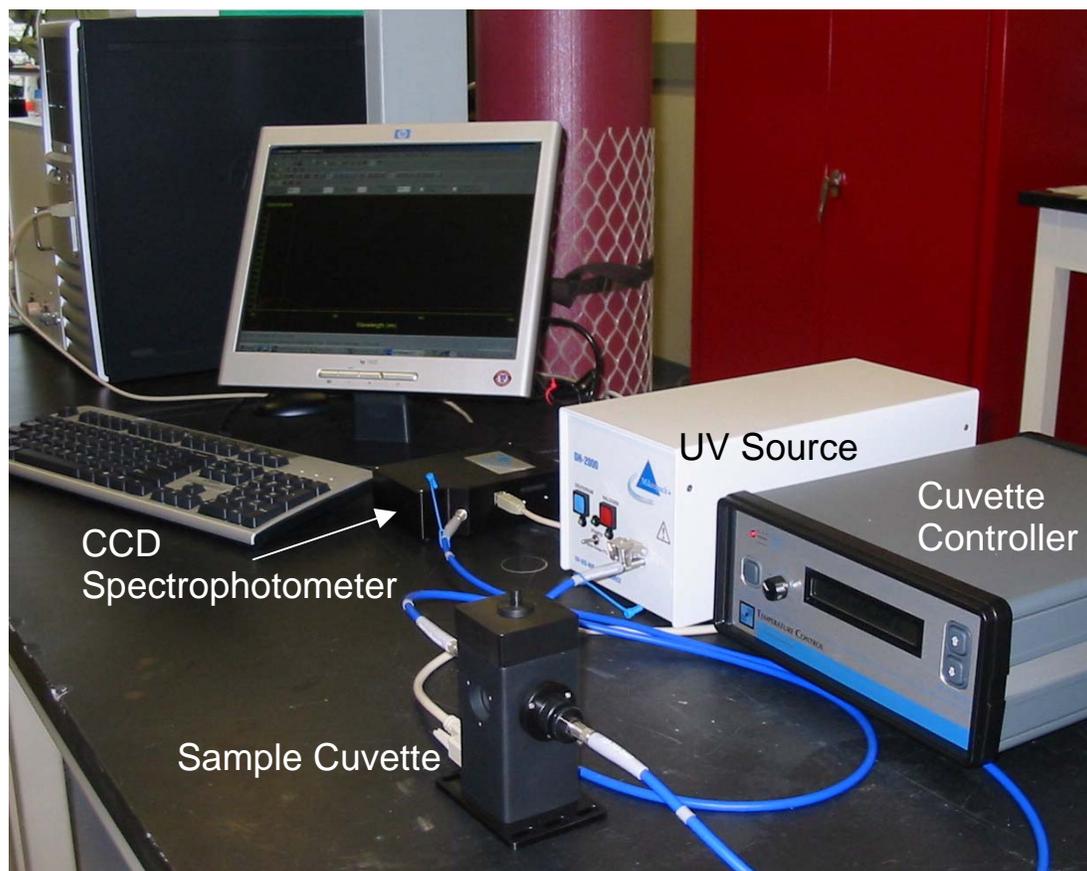


Figure 1. Photo of UV/Vis Spectrometer and Cell Holder Apparatus

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 obtained for background subtraction purposes, then a small amount of sulfite solution is injected into the stirred spectrophotometric cell to start the reaction (typically 20-50 microliter [μL] using a microliter pipetter). This addition results in the abrupt appearance of a peak in the 230-235 nm region due to formation of mercuric disulfite, the predominant aqueous complex formed between mercury ion and sulfite ion. The decay of this peak is then monitored by continuing to take spectra for up to several hours.

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, tests have been done which measure the evolution of Hg^0 from solution both by making gas phase Hg measurements on the outlet gas and measuring the amount of total mercury remaining in a continuously sparged solution. The test apparatus for this procedure 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, SO_2 , and presaturated with water is passed through this solution at a constant rate, typically 1.0 L/min. The SO_2 concentration in the gas and pH are chosen to give the desired SO_2 (sulfite species) concentration in the liquid.

The sparged reaction vessel is submerged in a water bath temperature controlled to $\pm 0.1^{\circ}\text{C}$. To start the reaction a solution containing mercuric ion is injected into the sparged solution via a hypodermic syringe and septum. 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) as a function of time using computer controlled data acquisition. Alternatively, for slow reaction rate conditions the liquid phase is periodically sampled and the preserved solutions analyzed for mercury by FIMS (cold vapor atomic absorption).

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

The kinetics data described above are being used to develop an empirically adjusted, theoretically based kinetics model to predict mercury species reactions in wet FGD systems. The model are being verified in tests conducted with a bench-scale wet FGD system, where both gas-phase and liquid-phase mercury concentrations are being 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 being used in the Task 3 bench-scale wet FGD simulation testing.

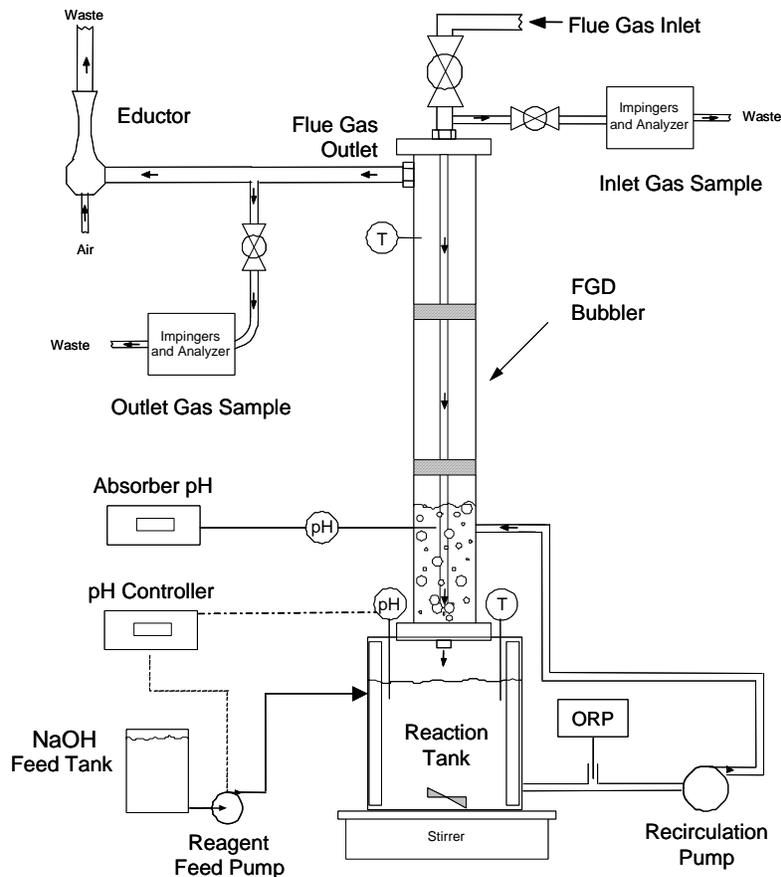


Figure 2. Bench-scale FGD Apparatus

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 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.

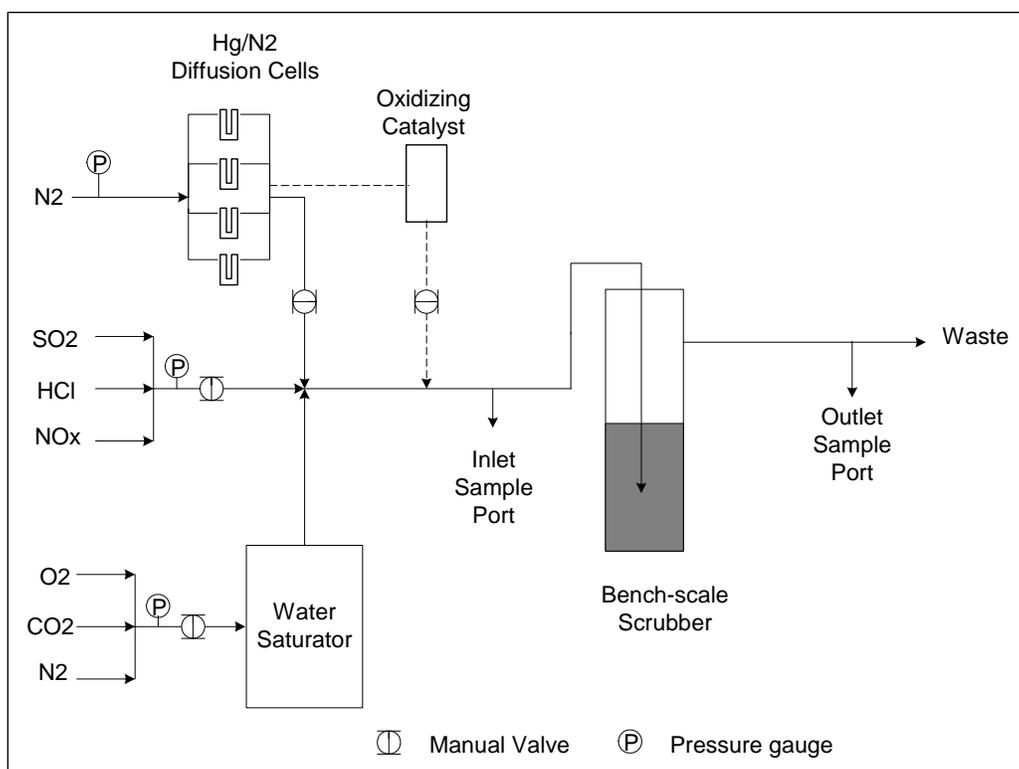


Figure 3. Bench-scale Simulation Gas Mixing Apparatus

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. For these runs the simulation gas will be spiked only with oxidized mercury from HgCl_2 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.

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. H_2O [1 kPa] gas pressure drop) and high slurry levels can be used to simulate a high-energy venturi scrubber (e.g., 15 in. H_2O [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. Solution from the reaction tank is pumped into the contactor to maintain solution level in the bubbler and to establish the desired liquid-to-gas ratio (L/G); spent solution returns to the reaction tank by gravity flow. For the clear liquid tests, sodium hydroxide solution 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 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 are made using two mercury semi-continuous emissions monitors (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.

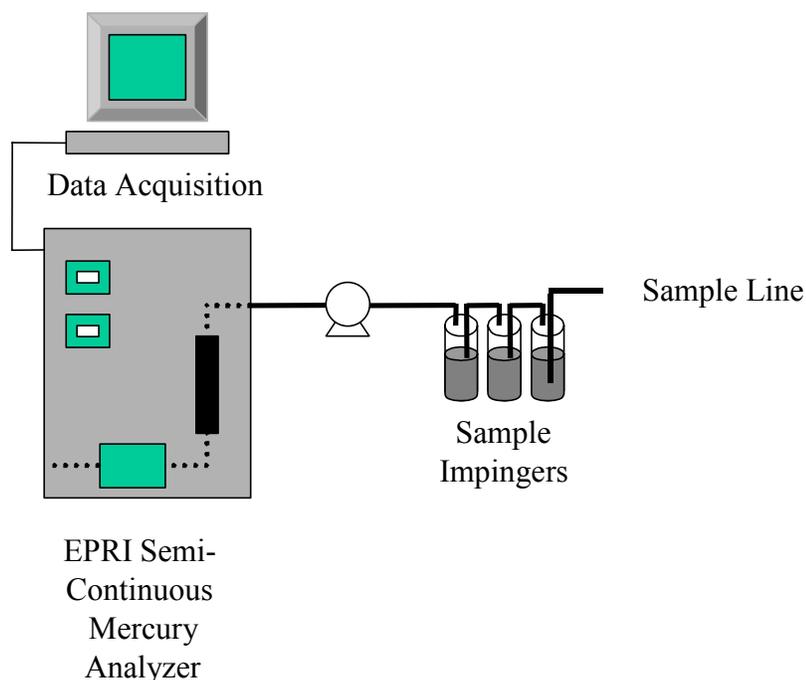


Figure 4. Schematic of Mercury SCEM

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 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.

SO₂ detection tubes are also 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.

Several modifications have been made to provide real time sulfite monitoring and control and meet other particular needs of the current program, as described in the Results and Discussion section.

RESULTS AND DISCUSSION

This section provides details of technical results for the current reporting period, April 1, 2006 through September 30, 2006. Technical results are presented from both the Task 2 reaction kinetics/modeling work and the Task 3 Bench-scale FGD unit investigations.

Task 2: Kinetic Data Gathering and Model Development

Overview of Previous Results

Results were initially obtained using the simplest representative chemical systems (mercuric ions and sulfite) and spectrophotometric measurement procedures. We then proceeded to more complicated chemical systems with addition of chloride and other chemical species.^{1,2} More recent results have been obtained following the reaction by measuring gas phase evolution of mercury from sparged solutions,³ or periodic analysis of the reaction solution for liquid phase mercury. Some of these previous results are repeated here for continuity.

"Raw" spectrophotometric results are shown in terms of absorbance (proportional to concentration of absorbing species) as a function of time. In all cases a 1.00 cm path length cell was used and for the simplest case (starting with only oxidized mercury and sulfite), the primary species absorbing near 230 nm is mercuric disulfite [$\text{Hg}(\text{SO}_3)_2^{-2}$], which has an absorptivity of $3.0 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$.⁴ For this case an absorbance of 1.0 corresponds to approximately $3.3 \times 10^{-5} \text{ M}$ $\text{Hg}(\text{SO}_3)_2^{-2}$. A decrease in absorbance thus corresponds to the disappearance of this species to form elemental mercury, as given by the following overall reaction:

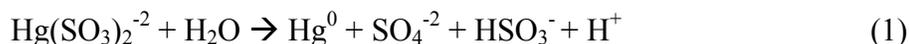


Figure 5 shows an example of absorbance (at 233 nm) vs. time results for the formation and decay of $\text{Hg}(\text{SO}_3)_2^{-2}$ on mixing 40 micromolar (μM) total Hg^{+2} with 0.23 mM total sulfite at pH 3.0 and 45°C. The inset in the figure shows the type of spectra used to generate the plot in Figure 5, although the inset data were obtained under slightly different conditions of 0.18 mM total sulfite. The wavelength used for the absorbance curve was selected by inspection of the peaks for each run. The peaks occasionally varied over a range of several nm during the run.

The effect of pH on the absorbance profiles is shown in Figure 6 for solutions without chloride at 55 °C and initially containing 1.0 mM sulfite and 40 μM Hg^{+2} . As shown, the rate of mercuric complex decomposition slows considerably in going from pH 3.0 to pH 3.9, and even more when the pH is adjusted to 4.9. The lower pH values in the figure represent the pH a droplet might achieve as it falls through an FGD absorber rather than a bulk reaction tank slurry pH, which would be in the range of pH 5 to 7.

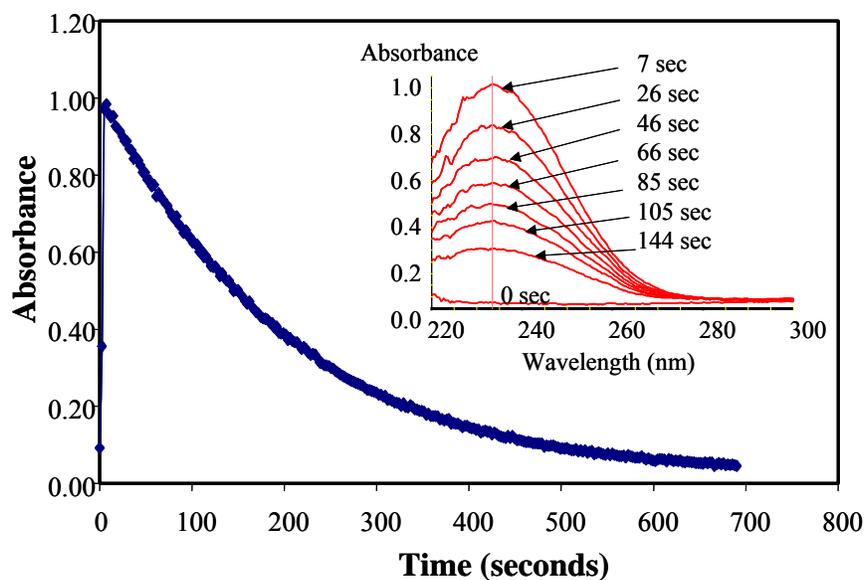


Figure 5. Experimental Absorbance and Spectra Data for Mercury Disulfite

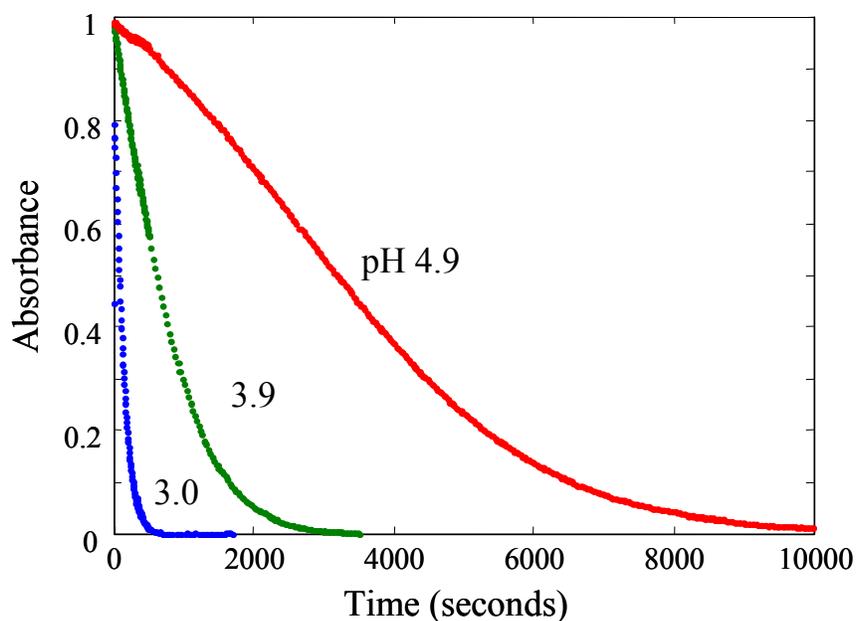


Figure 6. Effect of pH on Rate Curves (no chloride; 55 °C; 1.0 mM sulfite; 40 μM Hg^{+2})

In the pH 4.9 case, the shape of the absorbance - time curve starts to deviate significantly from what one would expect from a simple first order reaction, which should produce more of an asymptotic decay similar to the plot in Figure 5. However, for the purposes of comparing results from run to run to quantify variable effects, an "observed" rate constant, k_{obs} , has been calculated for each assuming a simple first order reaction. This is obtained from a least squares fit of the experimental data using the equation:

$$\ln A_t = \ln A_0 - k_{\text{obs}} t \quad (2)$$

A good fit to this equation is obtained only for the more "ideal" results, but even for conditions where the fit was poorer it is useful to use this value for comparison purposes. As an example, a plot of $\log k_{\text{obs}}$ versus pH has a slope of about -0.76, suggesting that the rate is close to being inversely proportional to hydrogen ion concentration in the absence of chloride and other complexing agents.

The effect of sulfite on the reaction profiles is shown in Figure 7 for solutions without chloride, at pH 3.9 and 55 °C and initially containing 40 μM Hg^{+2} . The lowest sulfite concentration gives the fastest reaction rate, followed by the intermediate sulfite concentration, with the highest sulfite showing both a very slow decomposition rate and considerable departure from ideal first order behavior. A log-log plot for k_{obs} and sulfite concentration gives a reaction order of -1.18, suggesting that the reduction rate is inversely proportional to sulfite concentration at these conditions.

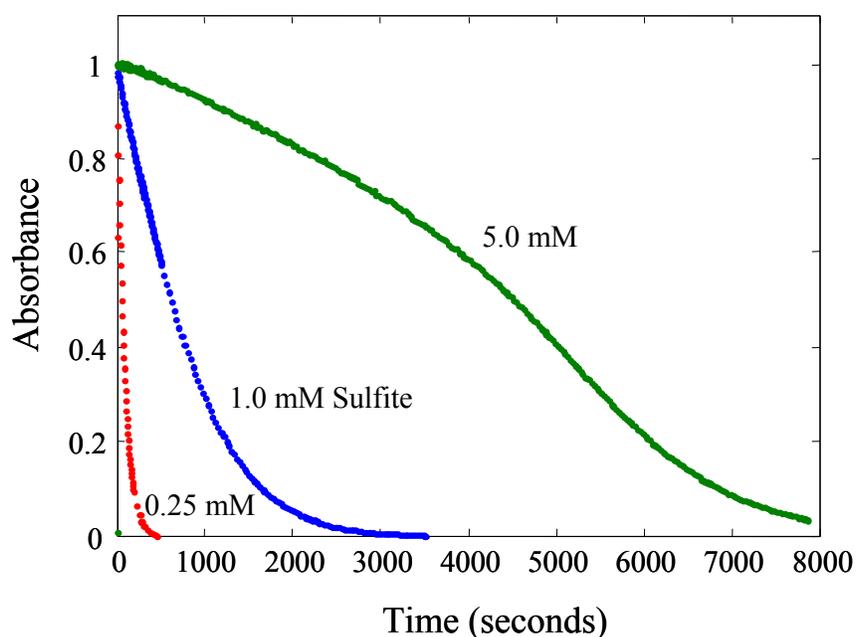


Figure 7. Effect of Sulfite on Rate Curves (no chloride; 55 °C; pH 3.9; 40 μM Hg^{+2})

Runs have been done from 45 °C to 55 °C at pH 3.0, in the absence of chloride, with initially 1.0 mM sulfite and 40 μM Hg^{+2} . The results for an Arrhenius plot using k_{obs} gives an activation energy of 39.2 kcal/gmole, close to the literature value of 39.7 kcal/gmole.⁴ This is a high activation energy, which tends to make the reduction of Hg^{+2} by sulfite quite sensitive to temperature.

Addition of low concentrations of chloride produces quite different time profiles. Figure 8 shows the effects of starting the reaction with 10 mM chloride. The lower initial absorbance indicates that the apparent initial concentration of $\text{Hg}(\text{SO}_3)_2^{-2}$ is lowered (or more likely the UV absorbing species is changed, see below) when chloride is present, and there is a major difference in the rate of disappearance of the absorbing species. The value of k_{obs} for the run without chloride is about 20 times that of the run with chloride.

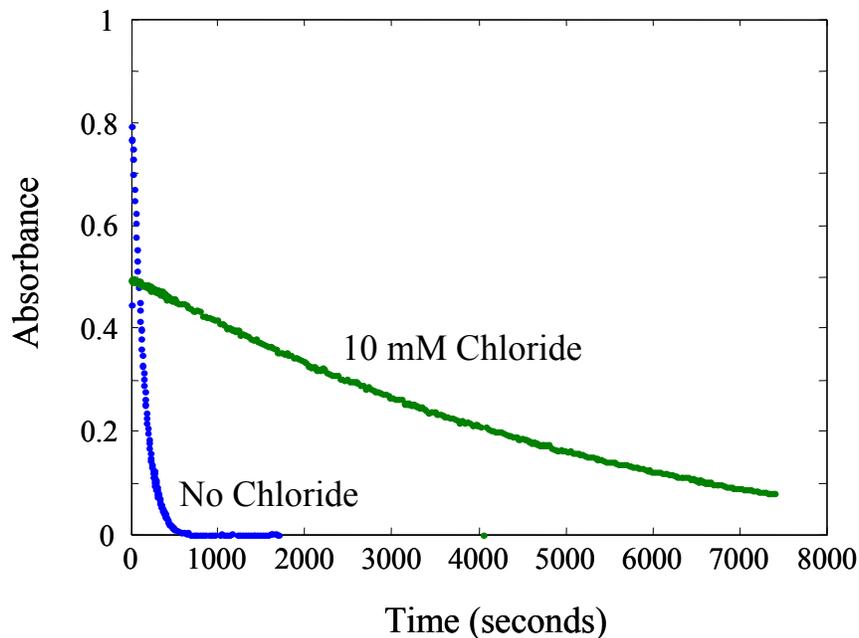


Figure 8. Effect of Chloride on Rate Curve (pH 3.0, 55 °C, 1.0 mM sulfite, 40 μM Hg^{+2})

The drastic change in rate can also be observed with a different order of reagent mixing. Figure 9 shows a run that was started without any chloride present. Chloride was injected about 70 seconds into the run, resulting in the sharp drop in absorbance noted in the figure, and the change to the much slower disappearance noted at later times. The run was continued for over 7500 seconds, and the k_{obs} calculated from data obtained after chloride injection was within 25% of the value found when the run was done with chloride initially present.

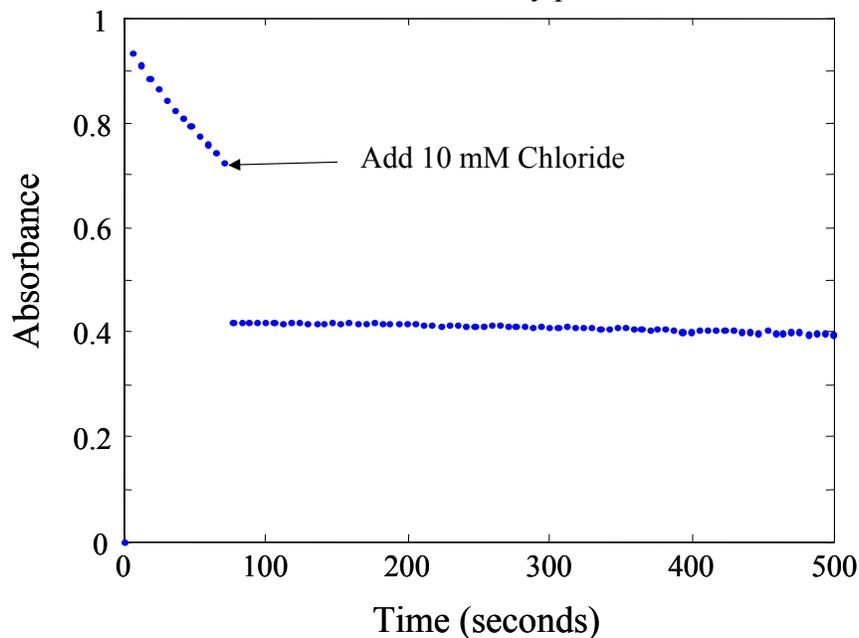


Figure 9. Effect of Adding Chloride After Start of Run (1.0 mM sulfite, 55 °C, 40 μM Hg^{+2} , pH 3.0)

Further examination of the complete spectra from this run showed that there was a small but definite shift of about 4-5 nm in the spectral peak wavelength when the chloride was added. This shift was essentially completed during the 5 seconds that elapsed between spectrum acquisition. This same difference in spectral peak wavelength is noted in the individual runs done with and without chloride addition. The peak values occur at approximately 232 nm with chloride and 237 nm without chloride. This behavior suggested the formation of a different complex than the mercuric disulfite $[\text{Hg}(\text{SO}_3)_2^{-2}]$ complex formed in the absence of chloride.

Inspection of analytical chemistry literature showed that mixed chloride-sulfite mercuric complexes have been suspected in analytical methods for SO_2 that use tetrachloromercurate as an absorbent. Dasgupta and DeCesare assigned a spectral peak similar to the one we observed to the complex ClHgSO_3^- , but did not investigate it in detail.⁵ We have been able to "titrate" sulfite into a solution of mercuric ion with a low concentration of chloride present. This was done at a low temperature of 10 °C to minimize mercury reduction. The absorbance increases rapidly as sulfite is added up to about 0.04 mM sulfite, which is equal to the original concentration of mercuric ion, then changes much more slowly with further increases in sulfite concentration.

This is consistent with the formation of a 1:1 complex between a chlorinated Hg^{+2} species and SO_3^{-2} , rather than the 2:1 complex between Hg^{+2} and SO_3^{-2} to form mercuric disulfite. Even more complicated behavior is seen as the concentration of chloride is increased. Considerable effort has been required to unravel the 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:



According to our current model, the $\text{Cl}_2\text{HgSO}_3^{-2}$ does not decompose (or decomposes at a negligible rate).

Chloride also has a substantial effect on the pH dependence of the reaction. 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 plot of $\log(k_{\text{obs}})$ versus pH, which is relatively flat for the 10 mM chloride case (a slope of only -0.21), as shown in Figure 10.

Although much progress has been made, it is difficult to interpret and determine all of the necessary information for modeling based on spectrophotometric results alone. Therefore, other approaches such as the "mercury stripping" tests and tests with simultaneous redox potential, spectrophotometric, and pH monitoring were used to supplement spectrophotometric results.

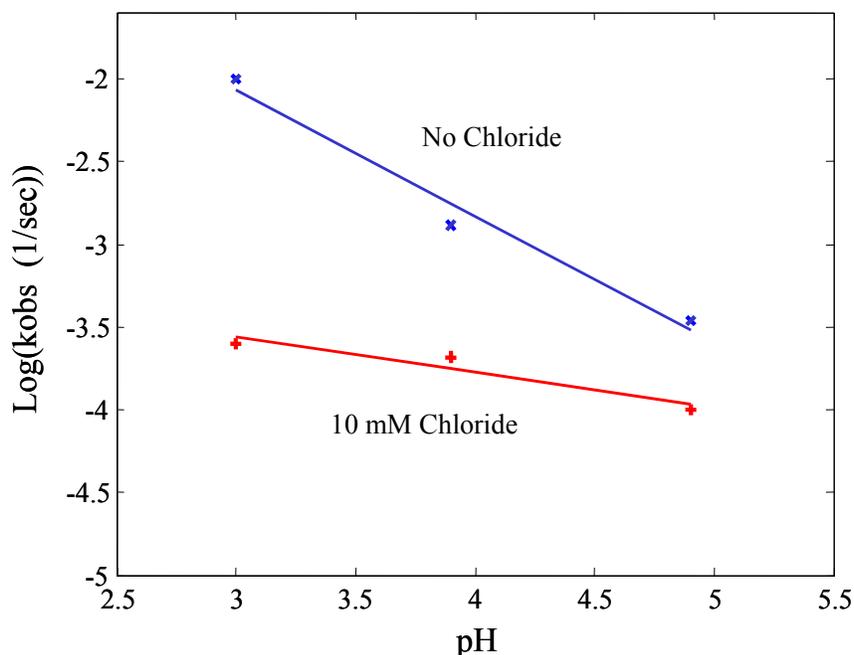


Figure 10. pH Dependence of k_{obs} with and without 0.01 M Chloride (55°C, 1.0 mM sulfite, 40 μM Hg^{+2})

The elemental mercury stripping rate method measures the amount of gas phase elemental mercury produced by the reactions as a function of time. In one mode the apparatus can measure gas phase mercury concentrations directly in a continuous manner, without having to use gold amalgamation in semi-continuous measurements. The gas phase Hg^0 is measured directly in a 17.5 cm flow tube using a 254 nm mercury lamp source and photomultiplier detector. The absorptivity of gas phase Hg^0 was taken as $4.1 \times 10^6 \text{ L}/(\text{gmole cm})$.⁶ This approach provides a direct measurement and much shorter time between measurements which is good for fast reaction conditions, but is subject to long term drift and is difficult to apply at low mercury concentrations. Therefore we use liquid phase mercury measurements for very slow reaction conditions.

Typical results obtained with this equipment are shown in Figure 11 for three different levels of Hg^{+2} injected at $t = 0$. These runs were done at 55 °C with 124 ppm SO_2 , balance N_2 in the gas passing through the absorber. This corresponds with a sulfite level of 1.3 mM and pH of 3.1.

As shown in Figure 11, elemental mercury starts to evolve at once, reaches a peak, and then shows a decline similar in shape to the spectrophotometric decay curves of the mercuric sulfite complex that have been shown previously. Values of the "observed" rate constant, k_{obs} , were calculated from the slope of the natural log of absorbance versus time in the absorbance decay region of the figure. For these three runs the k_{obs} was essentially the same, $2.0 \pm 0.15 \times 10^{-3} \text{ sec}^{-1}$, as would be expected for a reaction that is first order in dissolved Hg^{+2} overall. This is also in very good agreement with the k_{obs} calculated from the corresponding spectrophotometric experiment, $3 \times 10^{-3} \text{ sec}^{-1}$ (which would be expected to be somewhat higher since it was done at lower sulfite concentration, 1.0 mM vs. 1.3 mM).

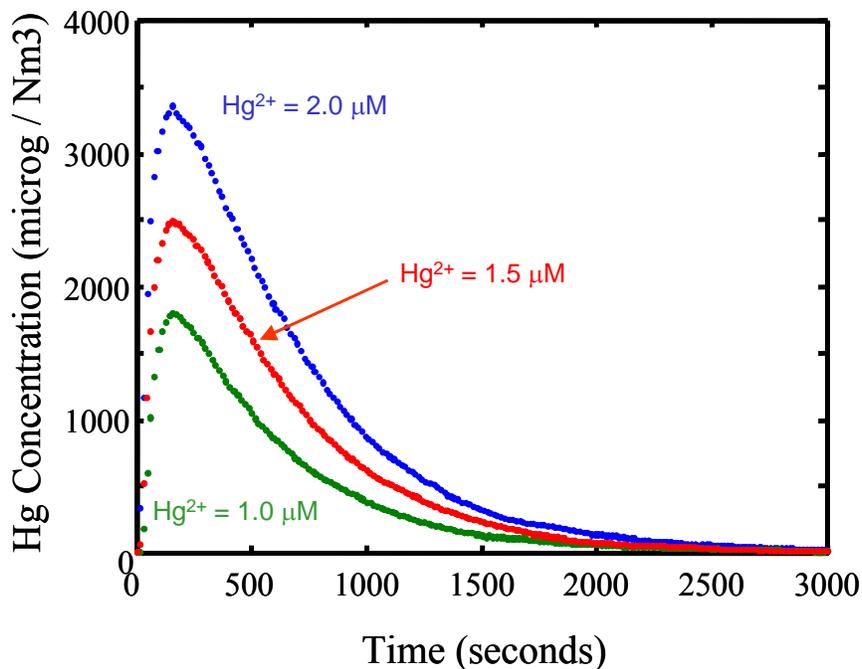


Figure 11. Hg^0 Stripping Kinetics Results for Addition of 1.0, 1.5, and 2.0 μM Hg^{2+} to Solution Containing 1.3 mM Sulfite at pH 3.1, with 124 ppm SO_2 in Gas Phase at 55 °C

The effect of adding 10 mM chloride on re-emission kinetics is shown in Figure 12. As expected from the spectrophotometric work, both the amount of Hg emitted and the rate of emissions is lowered drastically. The average k_{obs} from three stripping runs is $1.7 \pm 0.7 \times 10^{-4} \text{ sec}^{-1}$ and is again in good agreement with the spectrophotometric value of about $2 \times 10^{-4} \text{ sec}^{-1}$.

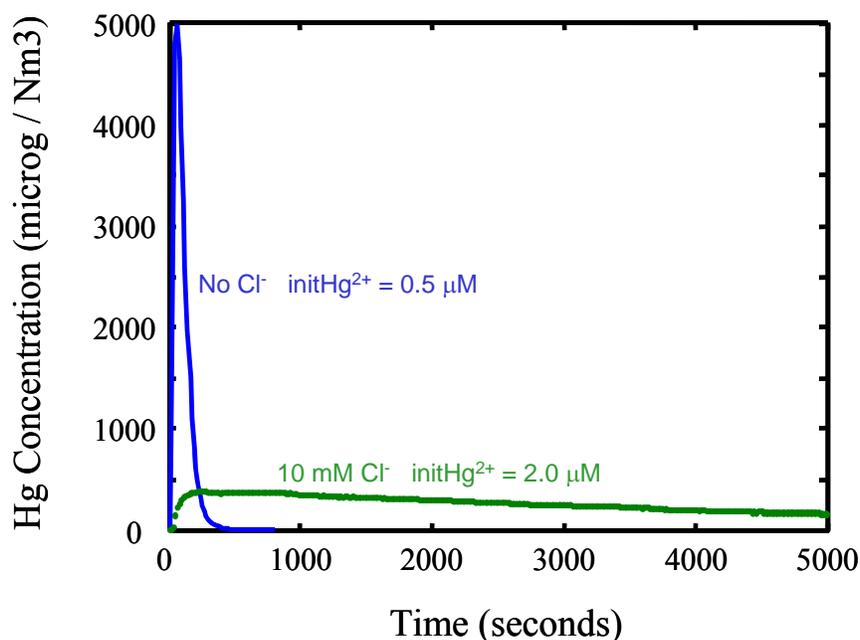


Figure 12. Re-emission Kinetics Results with and without 10 mM Chloride at 55 °C

A comparison of Hg emission kinetics for runs with 10 mM, 100 mM, and 250 mM chloride is shown in Figure 13. The 10 mM (~350 ppm) chloride run started with an injection of 2.0 μM Hg^{+2} . The 100 (~3500 ppm) and 250 mM (~8900 ppm) chloride runs used ten times the initial amount of mercury (20 μM Hg^{+2}), to produce measurable vapor phase Hg^0 concentrations.

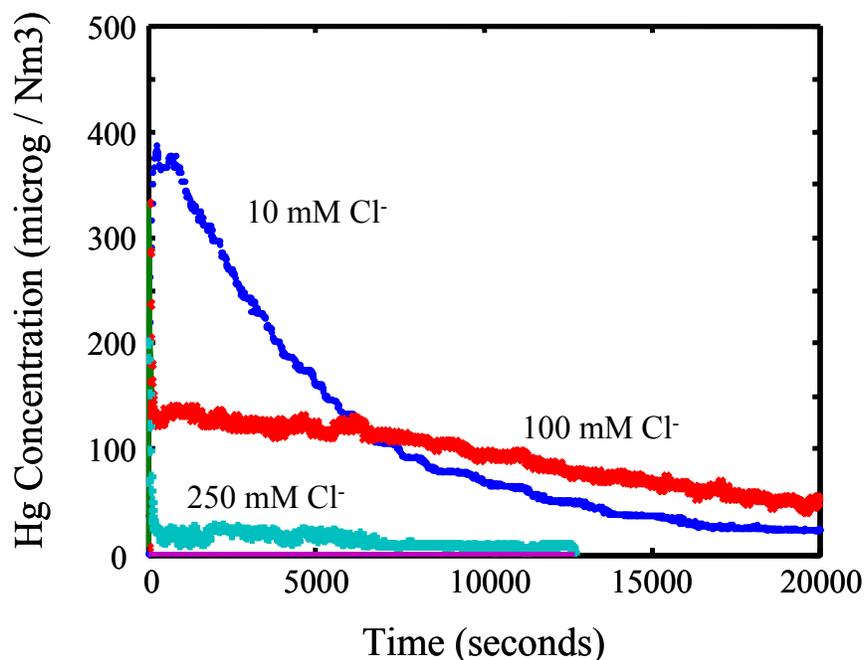


Figure 13. Stripping Kinetics Results with 10 mM, 100 mM and 250 mM Chloride at 55 °C

Again, the data in this figure show that each increasing level of chloride substantially decreases the overall amount and rate of evolution of Hg^0 from the solution. There is typically a "spike" of Hg^0 released at the start of the run. This may be associated with a spike in absorbance seen at the start of many of the high chloride spectrophotometric runs but more work is needed to establish a relationship.

The sorbent liquids from the initial set of stripping kinetics runs (done with gas phase mercury analysis) were analyzed for mercury after each run by cold vapor atomic absorption. Over 99.5% of the mercury was stripped out of the solution in the 0 and 10 mM chloride cases. For the 100 mM chloride case only 37 % of the added mercury was stripped and for the 250 mM chloride case less than 3 % was stripped after a total run duration of more than 50 hours. To put these chloride concentrations into the perspective of typical FGD liquor chloride concentrations, 10 mM (~350 ppm) would represent a very low FGD chloride ion concentration, while 100 mM (~3500 ppm) would represent a mid-range value for an FGD system with a moderate chloride purge rate. The highest value of 250 mM (~8900 ppm) is not atypically high for FGD systems with a lower chloride purge rate (e.g., systems that produce wallboard-grade gypsum), which can range up to 10 times that chloride concentration.

We have briefly looked at the effects of thiosulfate ion (present in inhibited oxidation FGD liquors) on mercury reduction using the gas phase stripping kinetics method. The mercuric-thiosulfate complexes are strong and have high UV absorbance, complicating spectrophotometric measurement even at low thiosulfate concentrations. Results of a stripping kinetics using 1.0

mM thiosulfate added to a 100 mM chloride solution are compared in Figure 14 to those obtained without thiosulfate but also with 100 mM chloride; both were spiked with 20 μM Hg^{+2} . Note that 1.0 mM of thiosulfate (~ 110 ppm) is a relatively low concentration compared to typical values in inhibited oxidation FGD liquors, where values of 10 to 30 mM are common.

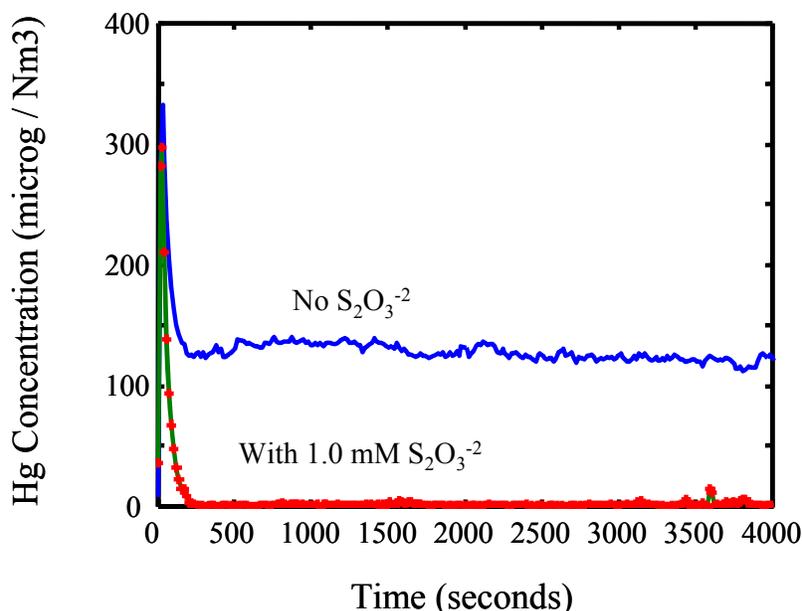


Figure 14. Effect of Adding 1.0 mM Thiosulfate to a 100 mM Chloride Solution on Hg^0 Stripping Kinetics

As can be seen, the initial sharp Hg^0 emission peak is very similar in the two cases. In the case without thiosulfate there follows a period of slowly declining evolution of Hg^0 . In the thiosulfate case, however, the Hg^0 evolution essentially goes to zero after the initial spike. Analysis of the thiosulfate solution for mercury concentration indicated that less than 10% of the original mercury had been stripped after over 21 hours. Less than 0.1% of the added mercury could be accounted for in the gas phase for this run. Thus, it appears that even low concentrations of thiosulfate inhibit Hg^0 evolution under these conditions, probably due to formation of mercuric-thiosulfate complexes which are stable and which block the more rapid reduction pathways involving chloromercuric sulfite complexes.

Another interesting example of effects of a strong complexing agent is shown in a run done with only 80 μM iodide (~ 10 ppm), which is compared to results with 80 μM of chloride (~ 3 ppm) under the same pH 3.0, 1.0 mM sulfite, and 55 $^{\circ}\text{C}$ conditions in Figure 15.

The response with 80 μM chloride is similar to and about as fast as without chloride, indicating that chloride cannot compete very well with sulfite in complexing (and reducing) mercuric ion at this low concentration. However, iodide, which is known to be a very strong complexing agent for mercuric ion, reduces the rate of reaction substantially. The k_{obs} for the run with 0.080 mM iodide is $1.3 \times 10^{-4} \text{ sec}^{-1}$, similar to but still somewhat slower than that obtained for the 10 mM chloride runs.

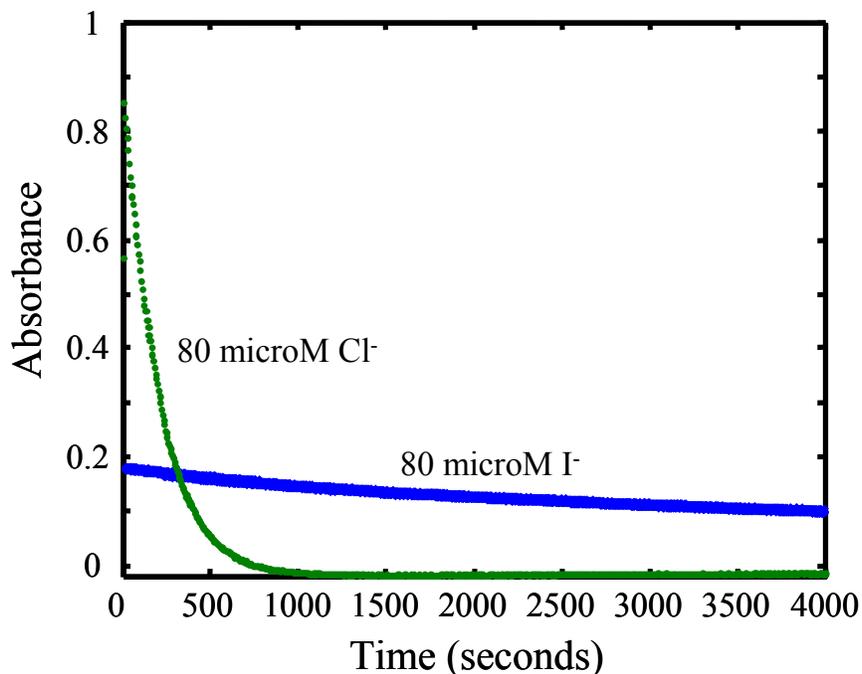


Figure 15. Comparison of Effects of 80 μM Iodide and 80 μM Chloride on Kinetics of Mercuric Ion Reduction

In another series of longer-term tests under slow reaction conditions, the Hg^0 stripping apparatus was 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. These runs employed 100 mM acetate buffer to obtain better pH stability for the long run times. This 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.

Some examples of individual run results obtained using this method are shown in Figure 16. 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.

Apparent first order rate constants, k_{obs} , were calculated for each run from the first order rate fits. Results obtained thus far are shown in Figure 17. Since there was some variation in pH during the high pH runs in particular, results are plotted for both the initial pH and final pH, joined by a horizontal line for clarity as needed. The lines and solid markers show results obtained from the kinetics model, basing the corresponding k 's on the rate of formation of Hg^0 predicted by the model.

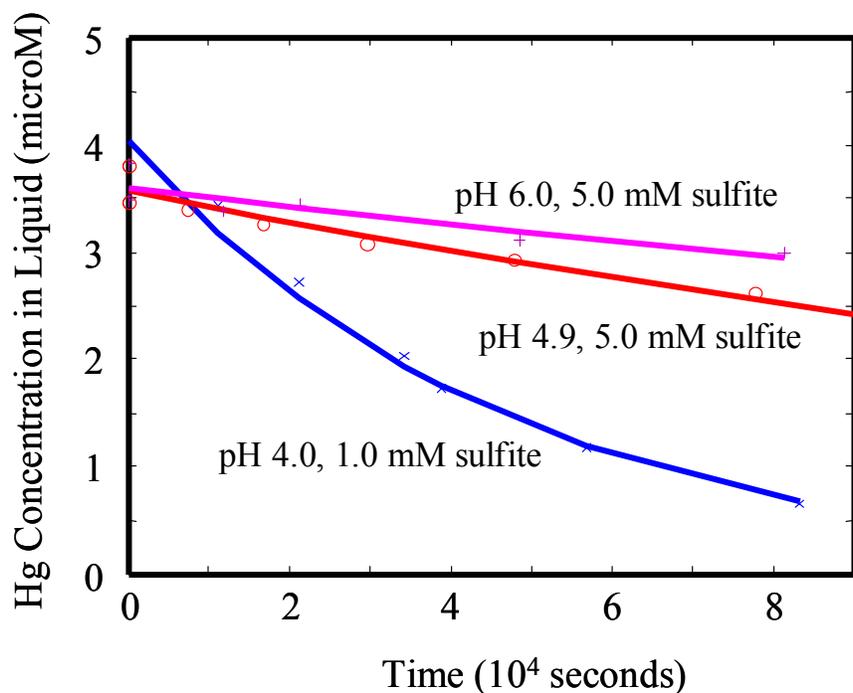


Figure 16. Amount of Mercury Remaining in Solutions of Compositions Shown, also Containing 100 mM NaCl and 100 mM Acetate Buffer, on Continuous Stripping with N₂-SO₂ Gas Mixture (Solution spiked with 4.0 μM Hg(ClO₄)₂ at t = 0)

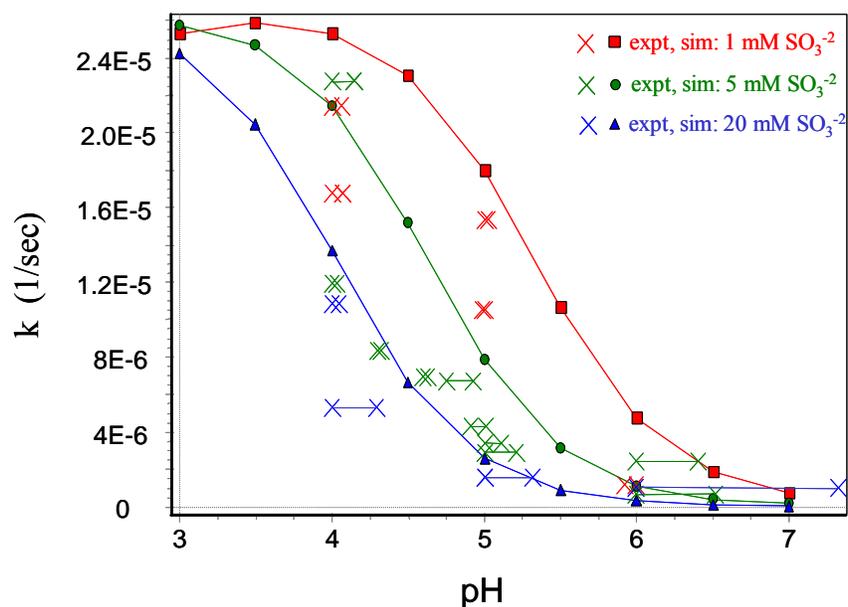


Figure 17. Observed and Model-Simulated Rate Constants for Reduction and Evolution of Mercury in 1.0, 5.0, and 20 mM Sodium Sulfite Solutions as a Function of pH. (Solutions contained 100 mM NaCl and 100 mM sodium acetate at 55 °C)

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 SO₂ 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 Results

As is the case for most "real world" reacting chemical systems, the reactions under investigation represent composites of several simpler reactions, and are not subject to analytic, single-reaction kinetic equation analysis. Therefore results are being incorporated into a chemical kinetics model that can numerically solve relatively large systems of chemical kinetics differential equations (representing on the order of 30 to 50 individual reactions). URS Corporation has developed kinetics modeling software that keeps a database of reactions and rate constants along with a database of reaction conditions such as initial concentrations and temperature. A driver program sends these inputs to a very efficient differential equation solver that produces a set of time-dependent concentrations for all species. Experimental data can be easily displayed alongside the calculated results.

This solver simultaneously solves the set of ordinary differential equations using a semi-implicit Runge-Kutta method with automatic interval-step-size adjustment. Given a set of reactions, the rate constants for the reactions, and the initial concentrations of reactants, the program produces concentration-time profiles for all chemical species in the reaction set. The model is developed by entering known or measured rate constants, then fine tuned by comparing experimental time-concentration profiles to the calculated profile and varying unknown or uncertain rate constants until a satisfactory match is obtained over a wide range of conditions of pH, temperature, and ionic strength.

Considerable progress has been made on adapting this general model to the present mercury re-emissions investigation. All of the pertinent reactions found in the Hg-sulfite kinetics literature have been added to the model. In addition, reactions which model mercuric ion-chloride equilibria have been added, although rate constants for most of these reactions are not available

and estimates are currently being used. Many of the temperature dependences of the individual rate constants are also unknown. However, relationships between the forward and back rate constants and the heats of reaction were used to obtain an internally consistent data set that allows the proper temperature dependence of the equilibrium constants to be maintained. A simplified schematic depiction of the current model reactions is shown in Figure 18.

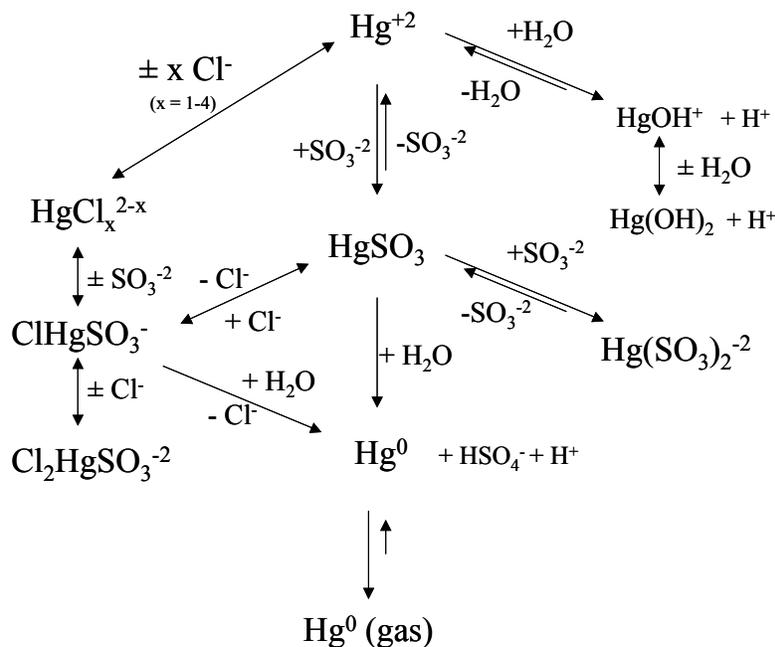


Figure 18. Schematic Diagram of Main Reaction Pathways in Current Kinetics Model

In most respects the kinetics model now adequately describes both the short-term spectrophotometric results and the long-term total mercury stripping results. The model implies that the mechanism of reduction proceeds primarily via the chloro-mercuric 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 chloro-mercuric sulfite complexes play a role, because without them the mercuric chloride complexes tend to shut down mercuric reduction completely at approximately the 100 mM (~3500 ppm) chloride level. As was shown in Figure 17, the model is predicting the basic trends seen experimentally for pH and sulfite effects. It is also showing fairly good numerical agreement with these and the chloride-dependence data.

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

Overview of Progress

During the current reporting period, the bench-scale was modified to provide necessary controls and measurements for effective mercury re-emission testing, the apparatus and methods were checked out, and a series of runs was initiated. Modifications to the existing bench-scale wet

FGD apparatus were necessary because of the complex relationship between pH, sulfite concentration and chloride concentration on mercury re-emissions and in particular the need to set and control sulfite concentration.

Of the concentration variables, 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 makeup 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 was added to monitor the slurry liquor pH in the absorber.

In normal practice 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.

We initially tried to control the sulfite oxidation rate and thus the liquor sulfite concentration by varying the amount of oxygen fed to the bench-scale FGD inlet simulation gas. To minimize total gas flow variations as the oxygen concentration varied, the simulation gas oxygen content was changed to being introduced by pure O₂ rather than air as previously used. Since we did not (initially) have a real time sulfite analyzer, we tried using the oxidation-reduction potential (ORP) as a surrogate for controlling sulfite concentration. This was not successful because the ORP was not a reliable indicator of sulfite concentration or often even of the trend of sulfite concentration. In conducting these initial runs, however, we developed a spectrophotometric method, based on a literature method,⁷ to measure sulfite quickly. It was quite successful, enabling results to be obtained in only few minutes and requiring only a few milliliters of solution, instead of the rather large sample requirement and tedious nature of the usual iodimetric titration for sulfite concentration.

We used an oxidation catalyst (MnSO₄ at 0.01 mM loading) to try to stabilize the rate of sulfite oxidation, which is known to be highly dependent on the presence of catalytic materials. However, we still had a great deal of difficulty obtaining steady sulfite levels, apparently due to the highly variable rate of sulfite oxidation by oxygen. The oxidation rate seemed to vary from

very sluggish, producing high sulfite levels, switching to very fast as perhaps some critical intermediate concentration was obtained, forcing low sulfite concentrations. Thus extreme oscillations in sulfite were often obtained even with close manual monitoring and control of oxygen flow.

Therefore we decided to use hydrogen peroxide instead of oxygen for oxidizing sulfite. The reaction of sulfite with H_2O_2 is apparently quite fast and not subject to the temporal variations we observed with oxygen. We believe that the use of H_2O_2 is justified since it is a "natural product" of the reduction of oxygen to water in any case. The spectrophotometric method for sulfite was modified to make it a real time measurement by adding a flow-through spectrophotometric cell, peristaltic pumps for sampling and reagent addition, and a digital controller. The controller meters a dilute H_2O_2 solution to the reactor as dictated by the sulfite concentration. Stable sulfite concentrations can be maintained fairly consistently with this method.

Baseline conditions for this series of runs are given below:

Sorbent solution:

- Temperature 131 °F,
- 100 mM NaCl (varied in some runs),
- 10 mM Na_2SO_4 initially added,
- mM MnSO_4 ,
- 0.5 μM HgCl_2 injected as 0.5 mM HgCl_2 solution after steady conditions reached,
- M H_2O_2 solution added for sulfite control,
- M NaOH solution added for pH control.

Simulated flue gas:

- 15-25 $\mu\text{g}/\text{Nm}^3$ HgCl_2 (typically 0.5 $\mu\text{g}/\text{Nm}^3$ elemental measured),
- 12 % CO_2 ,
- 3 % O_2 ,
- 1000 ppm SO_2 ,
- 15 ppm HCl,
- No NO_x ,
- Balance nitrogen,
- 28 L/min nominal total flow.

Typically the solution is made up with all ingredients except HgCl_2 added, brought up to temperature in the reaction vessel, acid gases started, and MnSO_4 and Na_2SO_3 solutions added. Then "oxidized" mercury is admitted to the gas stream and its concentration determined by CVAA. The pH control is stabilized and when the system is at "steady-state" the injection of 0.5 μM HgCl_2 starts the main part of the run. Separate CVAA units are used to monitor the inlet Hg and the outlet Hg concentrations. In most cases a nearly constant difference between the inlet elemental Hg and the (higher) outlet elemental Hg is observed. Typically the runs show a 2 to 3 hour steady period over which the inlet and the outlet concentrations can be separately averaged and then subtracted to give what we term the "average re-emission" for the run:

$$\text{Average re-emission} = [\text{average elemental Hg in outlet}] - [\text{average elemental Hg in inlet}] \quad (7)$$

Figure 19 shows time profiles of mercury and sulfite for a typical run including preliminary setup and calibration, while Figure 20 shows an expanded scale for the steady period of main interest.

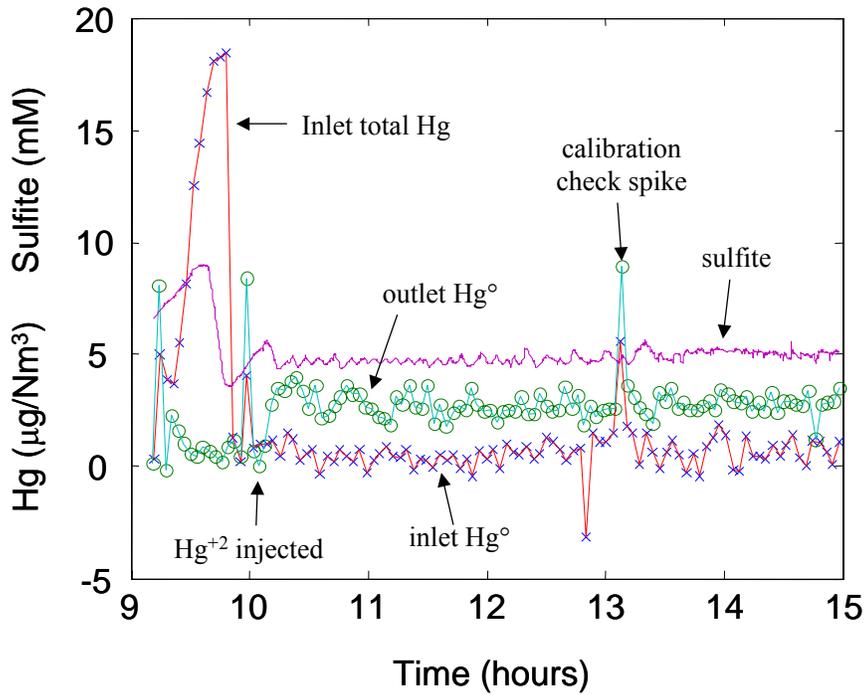


Figure 19. Time Profiles for a Typical Run Including Preliminary Setup and Calibration

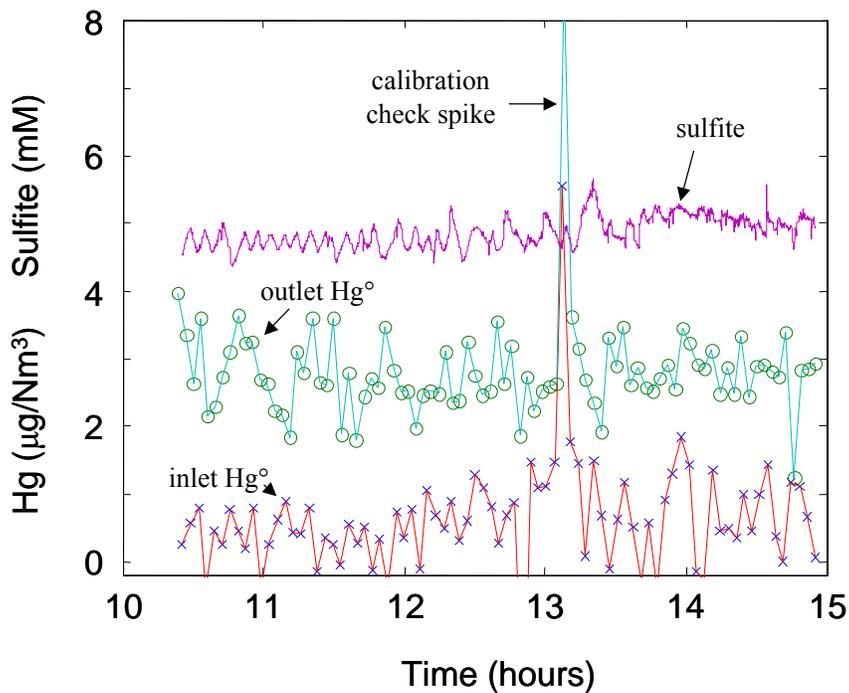


Figure 20. Example of Period for Which Re-emissions are Measured

Although the run series is far from complete and results should be considered tentative until it is complete, results to date are shown in Table 1.

Table 1. Preliminary Results of Bench-scale Mercury Re-emission Tests

Run Number	Brief Descriptor	Target Conditions				Hg ⁰ Re-emitted (µg/Nm ³)	Notes, Issues
		pH	Sulfite (mM)	Chloride (mM)	Additive		
1	Base case - medium pH and sulfite, 100 mM Cl ⁻	5.0	5	100	none	1.60	this result lower than repeats
2	Lower pH than base case	4.0	5	100	none	4.60	
3	Higher pH than base case	6.0	5	100	none	1.40	
4	Lower sulfite than base case	5.0	1	100	none	5.80	
5	Lower pH, low sulfite	4.0	1	100	none	3.80	
6	Higher pH, low sulfite	6.0	1	100	none	3.40	
7	Higher sulfite than base case	5.0	20	100	none	2.00	
8	High sulfite, low pH	4.0	20	100	none	5.60	sulfite dropped during run, noisy; Hg out slowly decreased
9	High sulfite, high pH	6.0	20	100	none	0.65	had up to 40 mM short duration sulfite spikes
10	High chloride	5.0	20	250	none	0.91	
11	Low chloride	5.0	20	10	none	1.97	
12	With Mg ⁺² , high sulfite	5.0	20	100	144 mM Mg ⁺²	1.35	re-emit 0.73 overall; 1.35 for last part with new tris impinger
13	Repeat run 8	4.0	20	100	none	4.98	
14	Repeat run 5	4.0	1	100	none	4.22	
15	With Mg ⁺² , low sulfite	4.0	1	100	200 mM Mg ⁺²	7.93	
16	Repeat run 1	5.0	5	100	none	3.59	
17	With EDTA	5.0	5	100	1 mM Na ₂ EDTA	4.99	new Hg ⁺² stock; redox E ~50 mV
18	With TMT	5.0	5	100	0.15 mM TMT	0.30*	low ORP, strange outlet Hg ⁰ peaks - avg emit= 0.74; sulfite high
19	Repeat run 1	5.0	5	100	none	2.22	
20	With bromide instead of Cl ⁻	5.0	5	0	100 mM NaBr	0.69	
21	With lower TMT conc	5.0	5	100	0.01 mM TMT	Varied	with lower TMT conc; big initial Hg ⁰ peak
22	Low Cl ⁻ , medium sulfite	5.0	5	10	none	3.78	
23	Na diethyldithiocarbamate	5.0	5	100	0.15 mM DEDTC	0.68	early Hg peak may be due to transition from very high to lower sulfite

One of our initial points of focus is the sulfite concentration - pH - chloride dependence of the emissions. Some preliminary results shown in Figure 21 indicate that for the 5 mM and 20 mM sulfite cases the expected trend of rates increasing as pH is lowered is obtained. The 1 mM

sulfite case has higher emission rates than the higher sulfite concentrations at pH 5 and 6, as expected, but anomalous behavior is seen at pH 4. This particular combination of low pH and low sulfite is difficult to control and we intend to do additional testing in that region. There is also an uncertainty as to "which pH" to use for comparing experiment and modeling: in our apparatus, the pH of the absorber is typically 0.3 to 0.4 pH units lower than the pH of the reaction tank, which is the value which is controlled and reported here.

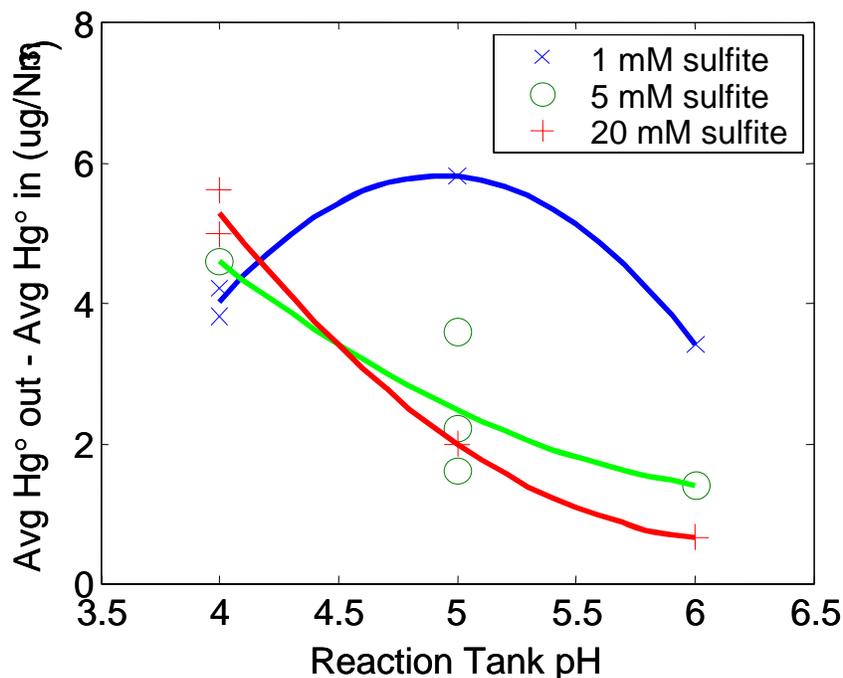


Figure 21. Bench-scale Re-emissions as a Function of pH

As shown Table 1, increasing the chloride concentration to 250 mM (Run 10) significantly reduces re-emission. Lowering the chloride to 10 mM produces somewhat higher re-emission. Replacing chloride with 100 mM bromide (Run 20) yields somewhat lower re-emission than 250 mM chloride. The effect of magnesium ion is complex and in accord with modeling, it appears that at high sulfite magnesium has little effect on re-emission (lowering it somewhat in Run 12) while at low sulfite it tends to increase re-emission (Run 15). This is probably due to the ion pairing of Mg^{+2} with SO_3^{-2} , which tends to lower the effective sulfite concentration, allowing the reduction of mercuric sulfite (chloride) complexes to speed up.

We have begun "surveying" the effects of potential inhibitor and have observed definite effects, although with a number of complications. Addition of 1 mM EDTA (ethylenediaminetetraacetate), a strong chelating agent for mercuric ion, caused an unexpected increase in re-emission (Run 17). EDTA had no apparent effect on the measured oxidation-reduction potential (ORP).

Addition of 0.15 mM TMT (trimercapto-s-triazine), on the other hand, produced very low (about $0.3 \mu\text{g}/\text{Nm}^3$) re-emissions over much of the run, but there was an initial peak emission of over $5 \mu\text{g}/\text{Nm}^3$ and an apparent increase starting about 3 hours into the run to give a small peak of about $3 \mu\text{g}/\text{Nm}^3$. At these levels, TMT appears to shift the ORP to more negative values (-10 to -20

mV) than we usually measure (~50 mV). When we used a lower concentration of TMT (0.01 mM) we observed a very large re-emission peak of about 32 $\mu\text{g}/\text{Nm}^3$ followed by a slow decay over several hours to nearly 0 $\mu\text{g}/\text{Nm}^3$. Obviously more experimental work is needed to characterize this potentially very useful additive. We have also started testing another inhibitor, sodium diethyldithiocarbamate, which appreciably lowers the re-emission rate to about 0.68 $\mu\text{g}/\text{Nm}^3$ without any "side effects" noticed thus far.

CONCLUSION

Experimental methods have been developed to use spectrophotometry to identify key reaction intermediate species and to track their changes in concentration as the reactions proceed to reduce mercuric species to elemental mercury. Separate but complementary methods of following the rate of evolution of mercury in the gas phase, and loss of mercury from the liquid phase have also been developed and applied. Using these methods, both the rate of disappearance of the mercuric sulfite and chlorosulfite complexes and the rate of formation of elemental mercury product can be monitored by independent means. This work is determining 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 addition, new methods for operating and controlling bench scale FGD experiments have been developed and several of these runs have been completed.

We have shown that even fairly low concentrations of chloride have a significant effect on the rate of mercuric ion reduction by sulfite. Evidence has been found for the formation of complexes of mercuric ion with both sulfite and up to two chloride ions. Each chloride ion attached to the mercury slows the decomposition of the mercuric chloride complex to elemental mercury by a very substantial amount. The key role played by the sulfite aqueous species (SO_3^{-2}) indicates that other solution components (such as magnesium and calcium) which ion pair with sulfite could also influence the kinetics of mercury reduction. Work is under way to define the potential effects of FGD cations.

Measurements of the rate of stripping of elemental mercury from solution as a function of time have been used to verify and extend the spectrophotometric results to high chloride and long reaction time conditions. 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.

The elemental mercury stripping apparatus 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. 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.

A chemical kinetics model has been developed to describe the aqueous mercury-sulfite-chloride-thiosulfate system and takes into account the simultaneous occurrence of a number of reaction steps. The model is predicting the basic trends seen experimentally for pH, sulfite, and chloride effects, and is giving fairly good numerical agreement with experimental data. It is being used to

design bench-scale experiments for testing as well as to predict kinetics in low pH regions, such as at the SO₂ gas-aqueous interface, which are difficult to investigate experimentally.

Bench-scale wet FGD tests are under way which will provide validation as well as additional data for extension of the model to a wide range of chemical conditions and additive treatments.

REFERENCES

1. Gary M. Blythe and David W. DeBerry, Ph.D. "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.
2. Gary M. Blythe and David W. DeBerry, Ph.D. "Bench-scale Kinetics Study of Mercury Reactions in FGD Liquors, Semiannual Technical Progress Report, April 1, 2005 – September 30, 2005," DOE/NETL Cooperative Agreement No: DE-FC26-04NT42314, October 2005.
3. Gary M. Blythe and David W. DeBerry, Ph.D. "Bench-scale Kinetics Study of Mercury Reactions in FGD Liquors, Semiannual Technical Progress Report, October 1, 2005 – March 31, 2006," DOE/NETL Cooperative Agreement No: DE-FC26-04NT42314, April 2006.
4. Van Loon, L. L.; Mader, E. A.; Scott, S. L., "Sulfite Stabilization and Reduction of the Aqueous Mercuric Ion: Kinetic Determination of Sequential Formation Constants," *J. Phys. Chem. A*, 105(13); 3190-3195 (2001).
5. Dasgupta, P. K., and K. B. DeCesare, "Stability of Sulfur Dioxide in Formaldehyde Absorber and its Anomalous Behavior in Tetrachloromercurate(II)," *Atmospheric Environment*, 16 (12), 2927 (1982).
6. Oda, C. E. and J. D. Ingle, Jr., "Continuous Flow Cold Vapor Atomic Absorption Determination of Mercury," *Anal. Chem.*, 53, 2030 (1981).
7. Scoggins, M. W., "Ultraviolet Spectrophotometric Determination of Sulfur Dioxide," *Analytical Chemistry* 42 (9), 1091 (1970).