

Bench-scale Kinetics Study of Mercury Reactions in FGD Liquors

Semiannual Technical Progress Report

October 1, 2004 – March 31, 2005

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April 2005

Cooperative Agreement No: DE-FC26-04NT42314

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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, 2004 through March 31, 2005. 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 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 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 first reporting period for the subject Cooperative Agreement. During this period, the project kickoff meeting was held and a project Test Plan was prepared. Reaction kinetics measurements have been conducted using several measurement techniques, primarily with the UV/visible light spectrometer, but also using atomic absorption. These data have been used to develop an initial form of the kinetics model. No bench-scale wet FGD tests have been conducted yet. This report presents and discusses project results to date.

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INTRODUCTION

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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, 2004 through March 31, 2005, is the first technical progress reporting period for the project. During this period, the project kickoff meeting was held and a project Test Plan was prepared. Reaction kinetics measurements have been conducted as part of Task 2 of the project. Several measurement techniques have been employed, primarily with the UV/visible light spectrometer, but also using atomic absorption. These data have been used to develop an initial form of the kinetics model. No bench-scale wet FGD tests have been conducted yet.

Problems Encountered

There were no significant problems encountered during the reporting period.

Plans for Next Reporting Period

During the next reporting period (April 1 through September 30, 2005), reaction kinetics testing will continue as part of Task 2. The only scheduled deliverable during the reporting period is this semiannual report, which is due by April 30. Also during the period, a presentation of project results to date will be made at the July 2005 NETL Contractors' Meeting in Pittsburgh.

Prospects for Future Progress

The next project period of performance will be the final reporting period. During this period, the Task 2 reaction kinetics tests will be completed, and these data will be used to develop an empirically adjusted, theoretically based kinetics model to predict mercury species reactions in wet FGD systems. Task 3 will 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.

The only additional project efforts will be related to reporting, including preparation and submittal of the second and third semi-annual technical progress reports, 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 will be 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.

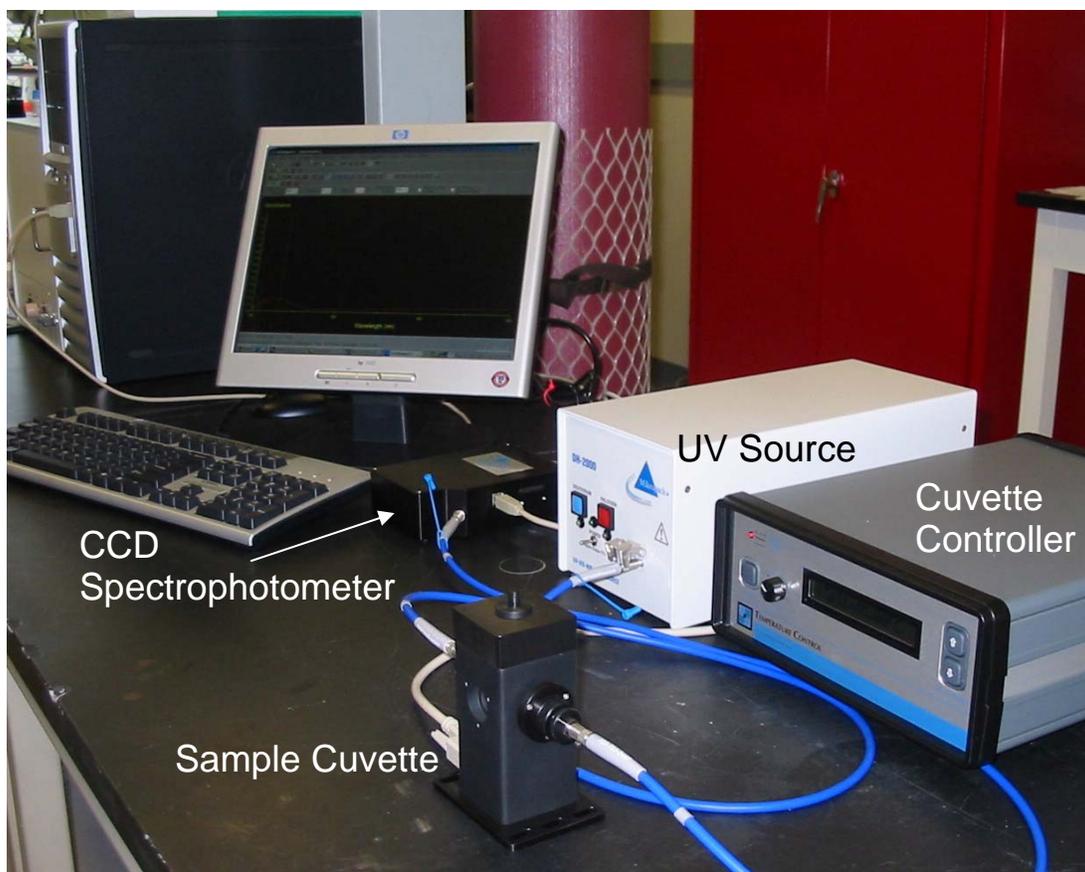


Figure 1. Photo of UV/Vis Spectrometer and Cell Holder Apparatus

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 will 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.

As an additional check on reaction product formation rates, in some experiments samples will be removed periodically from the reaction vessel and analyzed for sulfate by ion chromatography.

To improve the sensitivity of these measurements, such tests will be run under conditions where there is initially no sulfate present.

The possible involvement of mercurous (Hg^+) compounds will also be investigated. Some of these species have UV spectra, which could prove useful to identifying them and determining their fate. This is particularly important when chloride is present, since mercurous chloride (Hg_2Cl_2) is much less soluble than HgCl_2 . The possible formation of Hg-containing solids, particularly reduced sulfur compounds such as mercuric sulfite (HgS), will be investigated by examination of spent reaction liquids, material balance, and reactions run under conditions that could favor their formation.

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 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.

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.

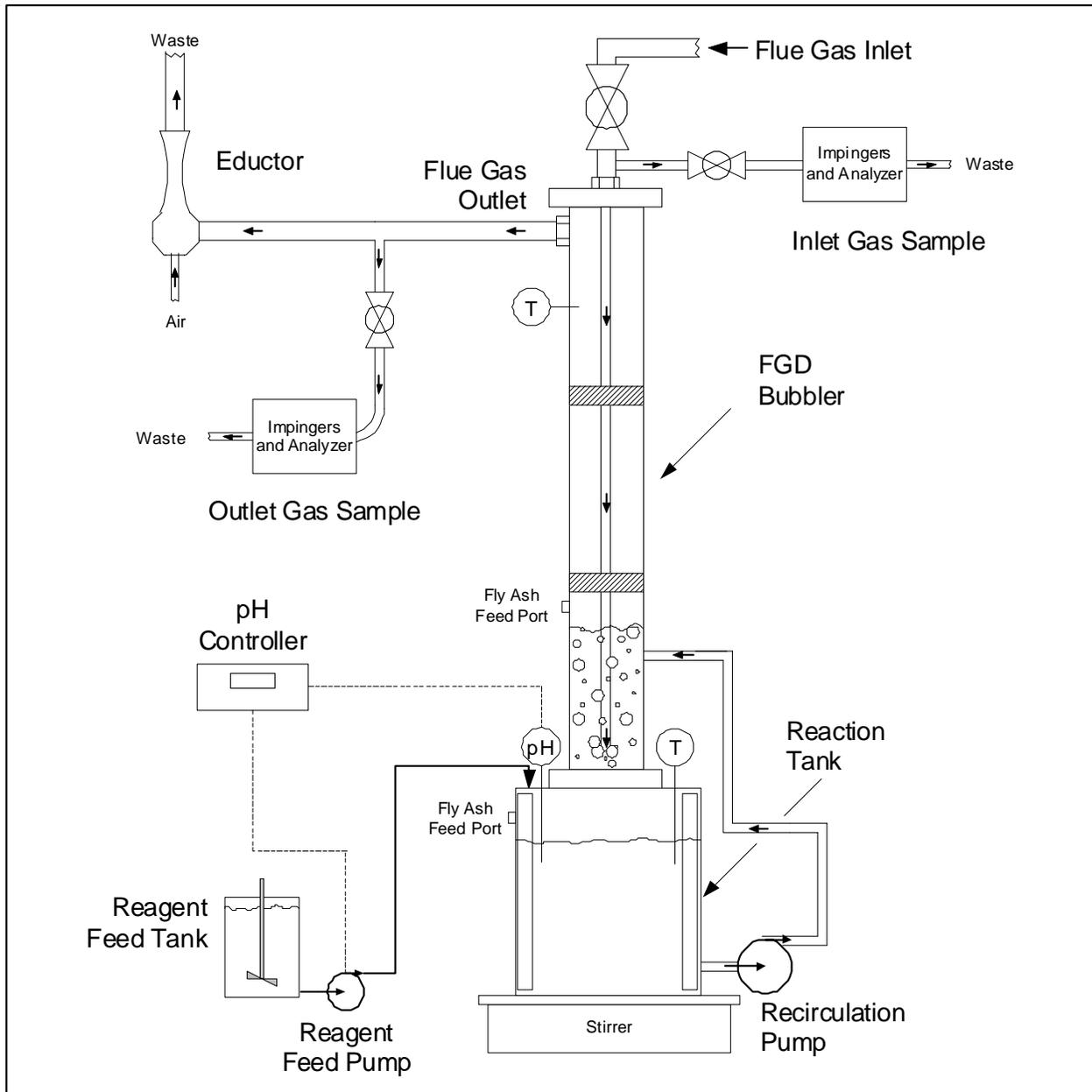


Figure 2. Bench-scale FGD Apparatus

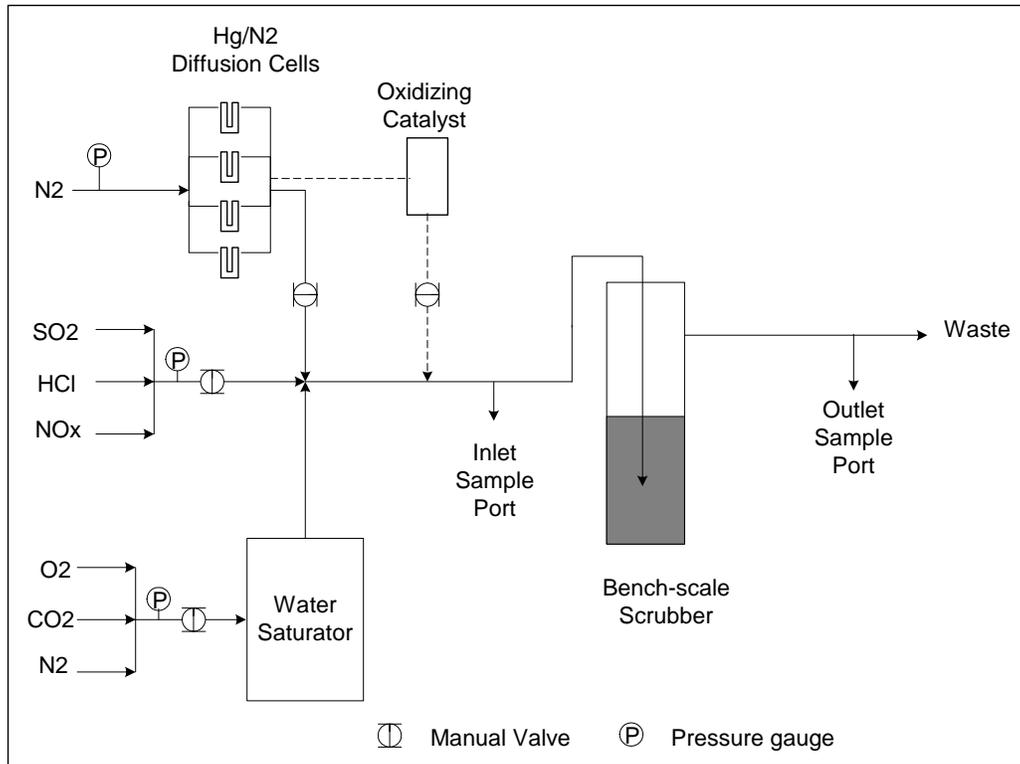


Figure 3. Bench-scale Simulation Gas Mixing Apparatus

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.

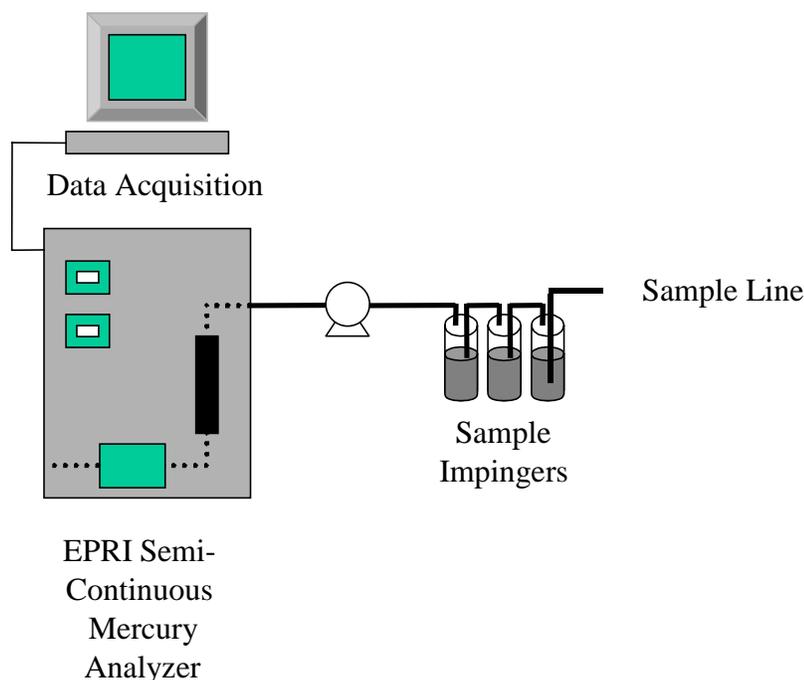


Figure 4. Schematic of Mercury SCEM

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.¹ 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.

For some tests, the UV/visible spectrophotometer described earlier in this section will be used in conjunction with the bench-scale wet FGD system to monitor the FGD reaction tank liquor for concentrations of mercury-sulfite complexes. For these tests a slipstream of slurry from the reaction tank or from the absorber effluent slurry will be filtered in line and pumped through the sample cuvette for the UV/visible spectrophotometer, then returned to the reaction tank.

RESULTS AND DISCUSSION

This section provides details of technical results for the current reporting period, October 1, 2004 through March 31, 2005. The technical results presented are from the Task 2 reaction kinetics investigations.

Task 2: Kinetic Data Gathering and Initial Model Development

A partial matrix of spectrophotometric kinetics runs was completed during this first reporting period. There is considerable work still to be done, and few of the existing runs have been replicated. Therefore, in that sense these results should be considered "preliminary," although they do appear to be of interest and pertinent to solution of the problem at hand. High quality data are just now being collected from experiments measuring the production of elemental mercury from the sparged reactor, as described in the previous section, so only a few of those results are presented here.

"Raw" spectrophotometric results are shown in terms of absorbance as a function of time. Since in all cases a 1.00 cm path length cell was used and the absorptivity of the primary species absorbing near 230 nm ($\text{Hg}(\text{SO}_3)_2^{-2}$) is $3.0 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$, then an absorbance of 1.0 corresponds to approximately $3.3 \times 10^{-5} \text{ M Hg}(\text{SO}_3)_2^{-2}$. The decrease in absorbance thus corresponds to the disappearance of this species as given by the overall reaction:

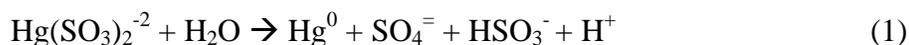


Figure 5 shows an example of absorbance (at 233 nm) vs. time results for the formation and decay of $\text{Hg}(\text{SO}_3)_2^{-2}$ on mixing 0.040 millimolar (mM) total Hg^{+2} with 0.23 mM total sulfite at pH 3.0 and 45°C. The inset in the figure illustrates the type of spectra used to generate the 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 generally varied only over a short range of 230-234 nm during the run.

The effect of pH on reaction 1 is shown in Figure 6 for solutions without chloride at 55 °C and initially containing 1.0 mM sulfite and 40 microM 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.

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

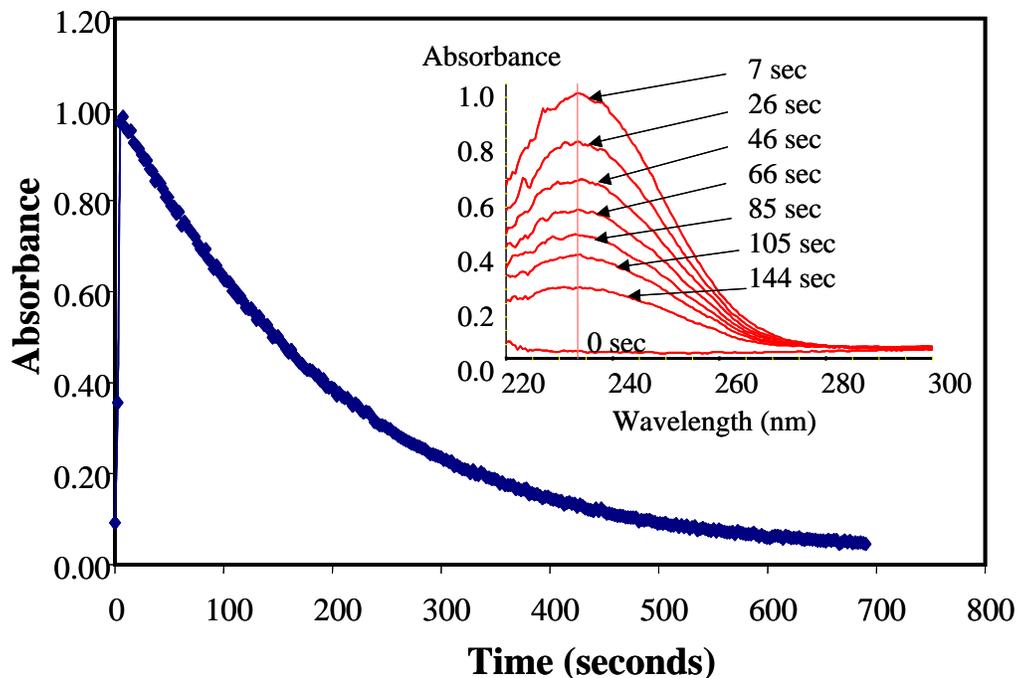


Figure 5. Experimental Absorbance and Spectra Data for Mercury Disulfite

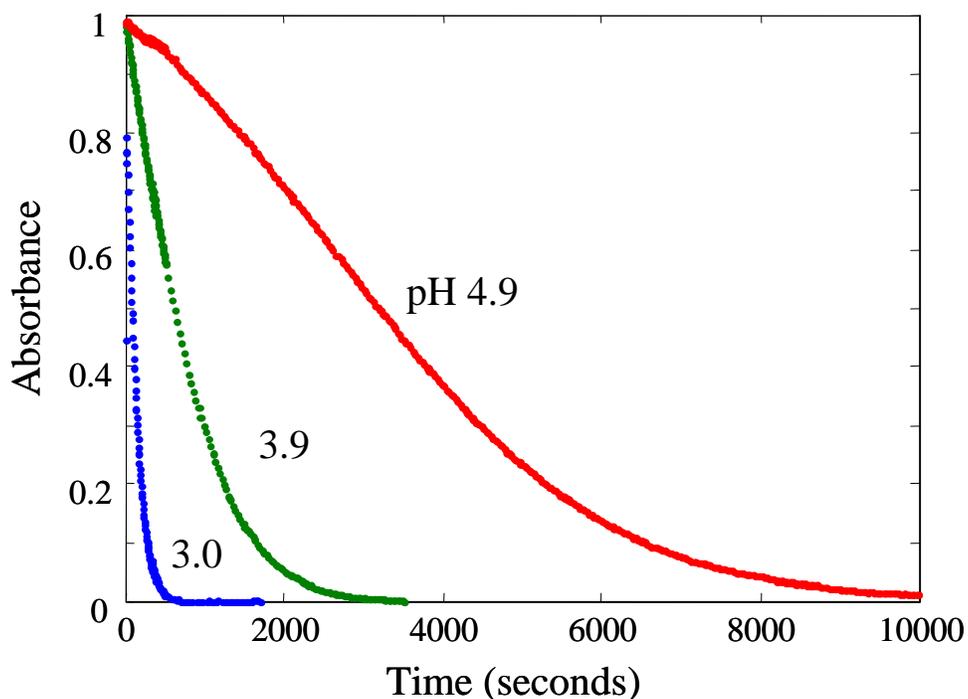


Figure 6. Effect of pH on Rate Curves (no chloride; 55 °C; 1.0 mM sulfite; 40 microM Hg^{+2})

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 near pH 3 and without chloride, 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 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 under these conditions.

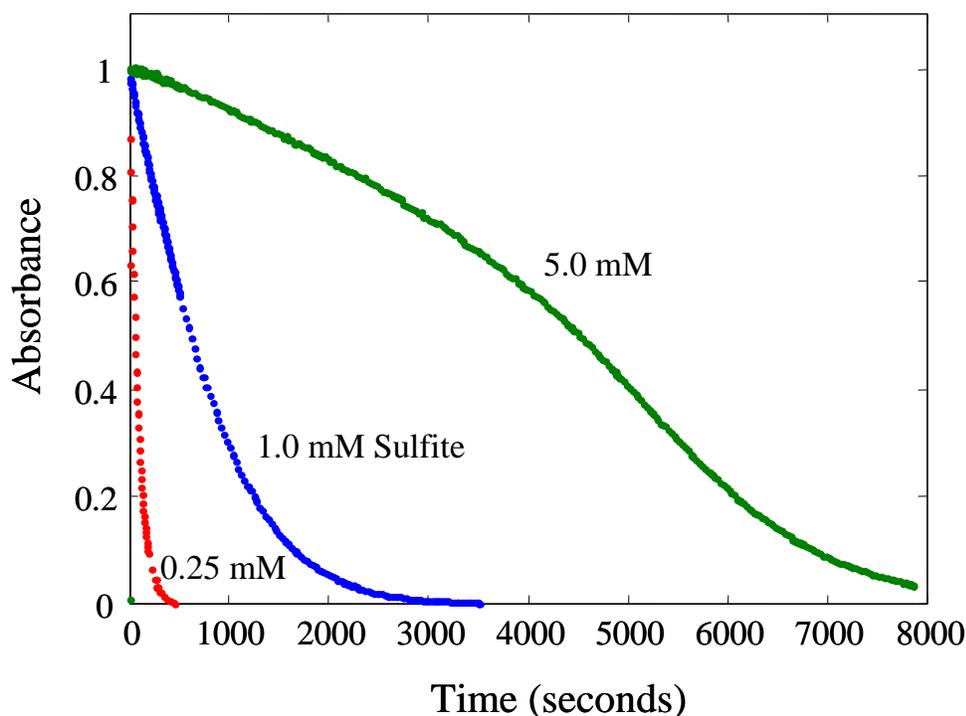


Figure 7. Effect of Sulfite on Rate Curves (no chloride; 55 °C; pH 3.9; 40 μM Hg^{+2})

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} is shown in Figure 8. The results are somewhat scattered at this stage of testing, possibly from using the "ideal" k_{obs} approximation. However, the slope of the curve gives an activation energy of 39.2 kcal/gmole, close to the literature value of 39.7 kcal/gmole.² This is a high activation energy which tends to make the reduction of Hg^{+2} by sulfite quite sensitive to temperature.

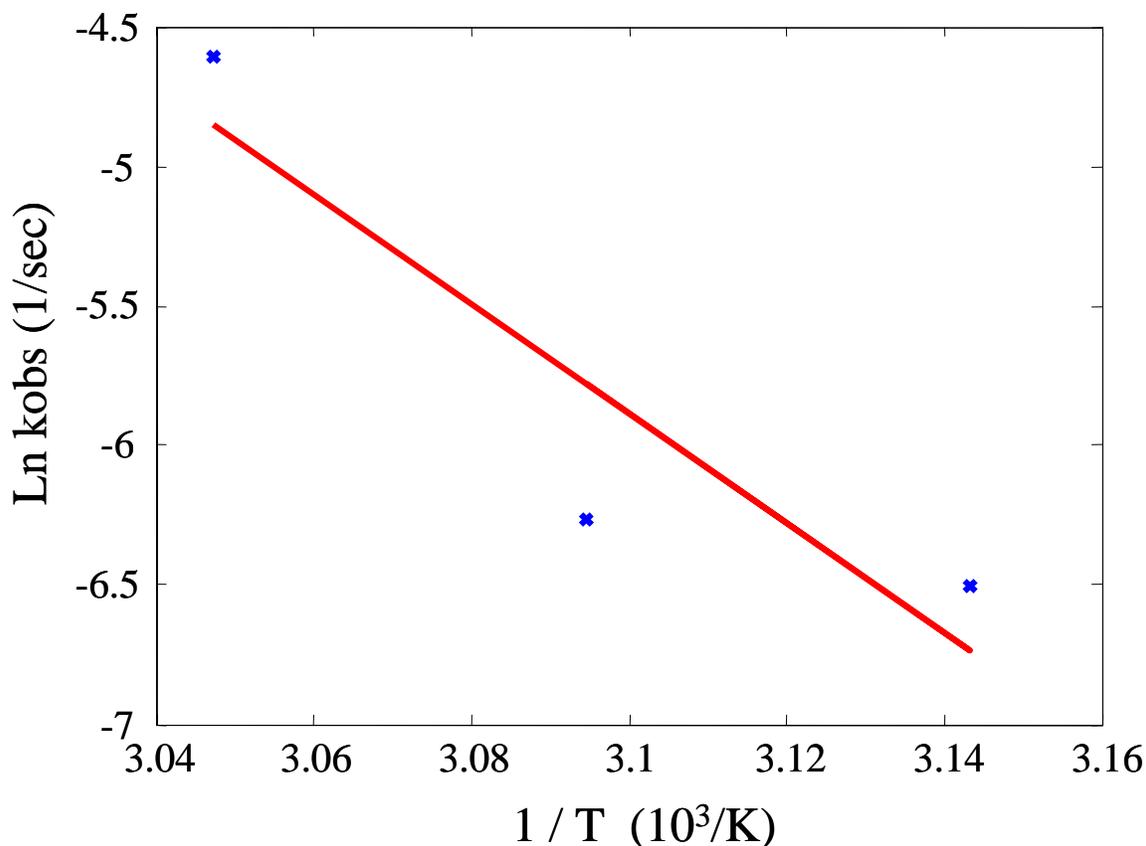


Figure 8. Effect of Temperature on k_{obs} (no chloride, pH 3.0, 1.0 mM sulfite, 40 μM Hg^{+2})

Drastically different results are obtained on addition of low concentrations of chloride. Figure 9 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 lower when chloride is present, but the major difference is on the rate of disappearance of the complex. The value of k_{obs} for the run without chloride is 40 times that of the run with chloride.

The drastic change in rate can also be observed with a different order of reagent mixing. Figure 10 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.

Chloride also has a substantial effect on the pH dependence of the reaction. As shown in Figure 11, the initial absorbances change with pH when chloride is present, but the slopes of the curves are much closer to being the same with chloride. 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 12.

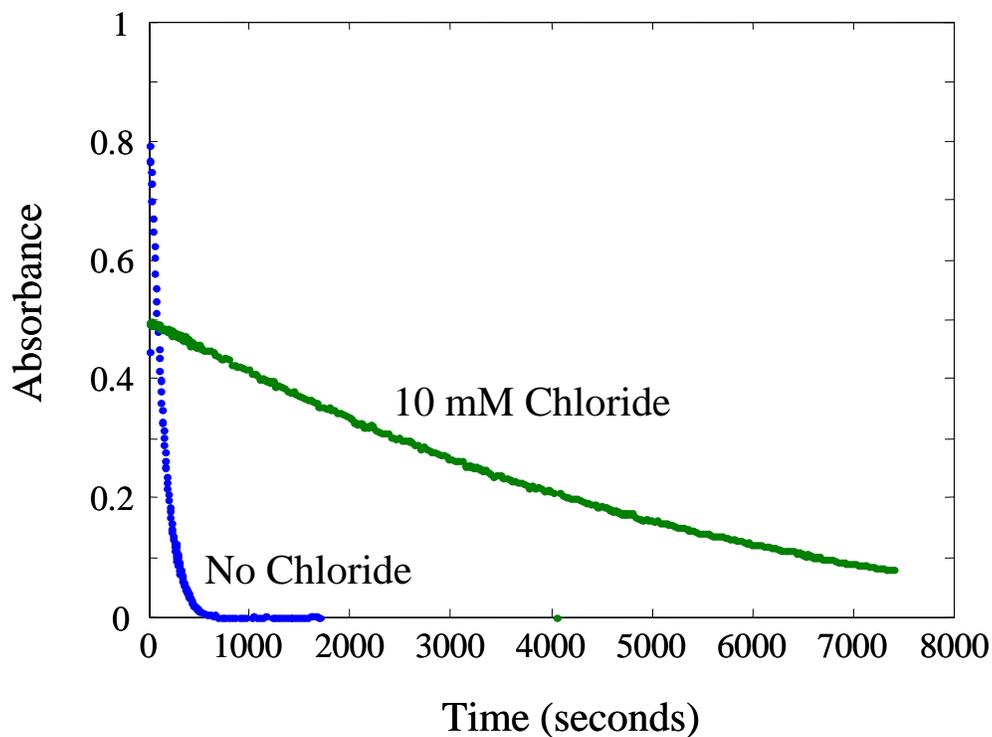


Figure 9. Effect of Chloride on Rate Curve (pH 3.0, 55 °C, 1.0 mM sulfite, 40 microM Hg⁺²)

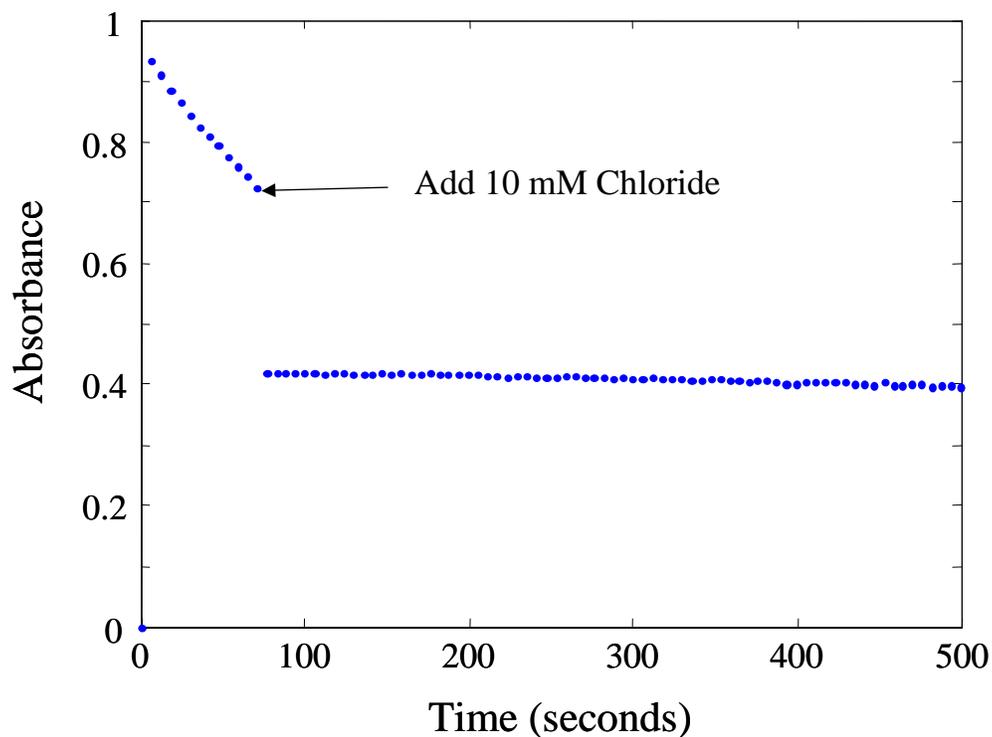


Figure 10. Effect of Adding Chloride After Start of Run (1.0 mM sulfite, 55 °C, 40 microM Hg⁺², pH 3.0)

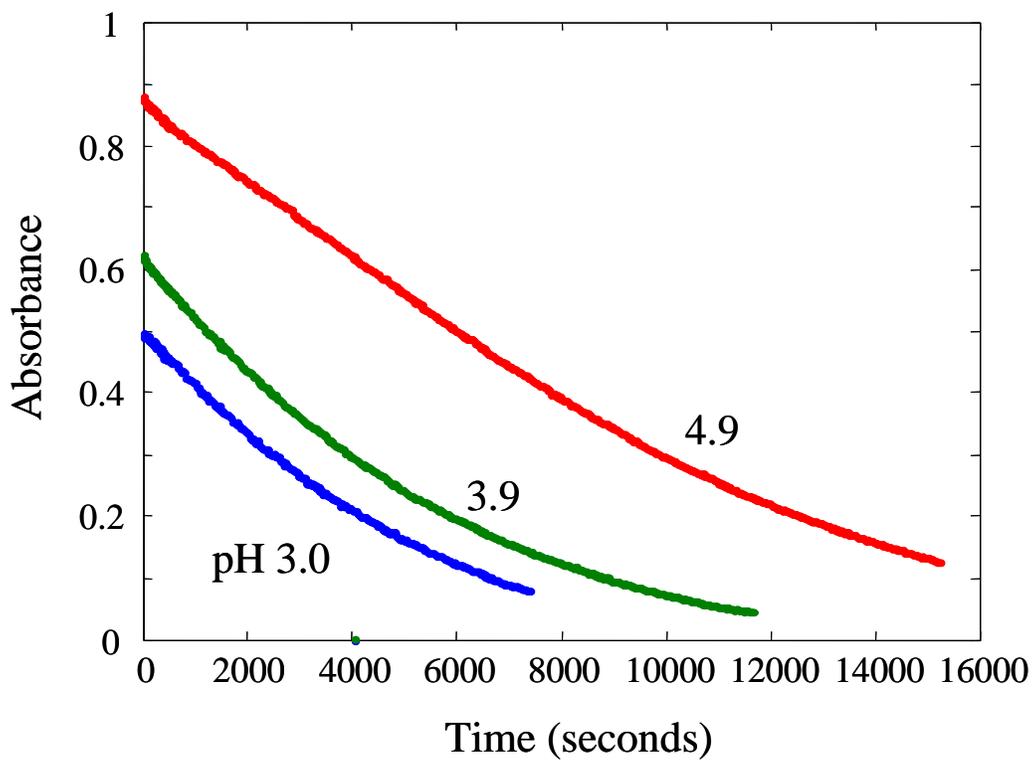


Figure 11. Effect of 10 mM Chloride at Different pH Values (55 °C, 1.0 mM sulfite, 40 $\mu\text{M Hg}^{+2}$)

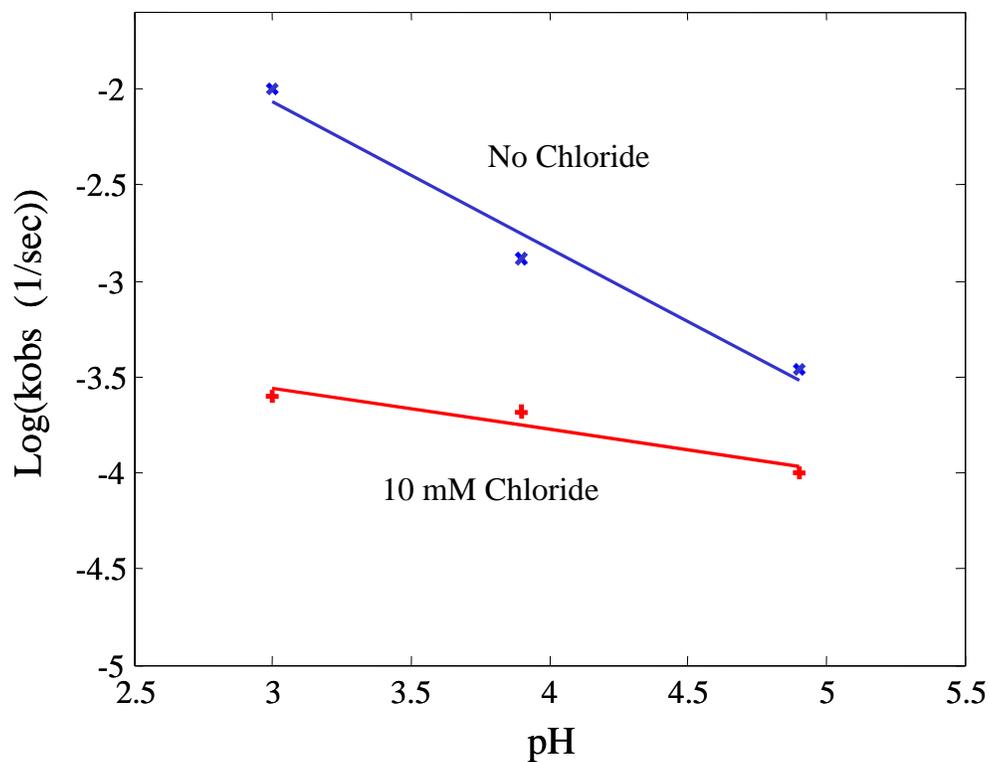


Figure 12. pH Dependence of k_{obs} with and without 0.01 M Chloride (55 °C, 1.0 mM sulfite, 40 microM Hg^{+2})

The present model predicts a slowing of the Hg^{+2} reduction rate when chloride is added, but does not predict the pH dependence. This may indicate a change in mechanism which is not taken into account in the model. This could involve, for example, the formation of a mixed complex of Hg^{+2} containing both chloride and sulfite. The model presently uses complexes containing chloride and sulfite separately, but not combined. Another possibility is that the reaction starts to go through mercurous intermediates instead of being the "concerted" (effectively two-electron-transfer) process proposed in the literature. Electron transfer reactions of mercurous/mercuric species have been added to the model to aid in investigating this possibility.

Initial results have been obtained using the kinetic method that measures the time evolution of gas phase elemental mercury produced by the reaction. Results are shown in Figure 13 for a run at 50 °C, which had an initial pH of 3.0 and was saturated with 184 ppm SO_2 in the gas phase. At "t = 0" in the graph, an aliquot of mercuric perchlorate was injected into the solution to give an initial liquid phase concentration of 0.5 microM Hg^{2+} . As shown, elemental mercury starts to be evolved at once, reaches a peak, and then shows a decline similar in shape to the spectrophotometric decay curves of the mercuric sulfite complex. After the run, the solution pH was 2.65 and the liquid contained 0.93 mM sulfite, reasonably close to the target of 1.0 mM.

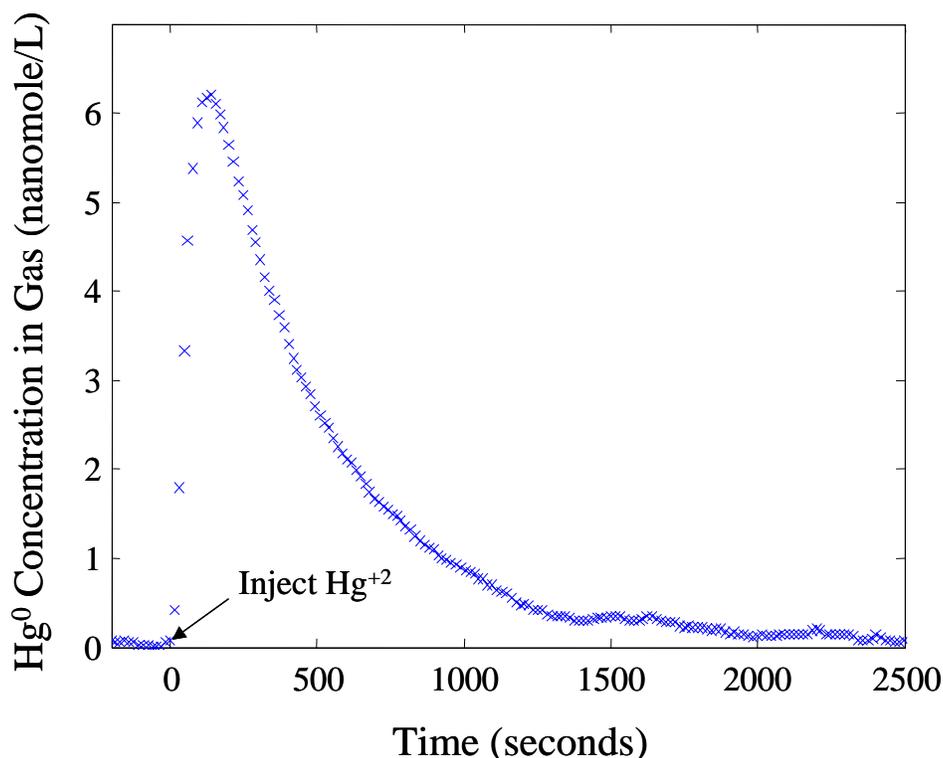


Figure 13. Evolution of Gas Phase Hg^0 from Reaction at 50 °C (initially at pH 3.0 and spiked with 0.5 microM Hg^{2+} ; 184 ppm SO_2 in gas; pH 2.65 and 0.93 mM sulfite in liquid after the run)

A mercury material balance for this run shows that 53 nanomoles of mercuric ion was injected, 4 nanomole was remaining in the liquid after the run, and 57 nanomole of Hg^0 was recovered from the gas phase based on integration of the data in Figure 5-10, giving an overall recovery of 116%. This appears to be good closure although efforts continue to tighten up the measurements to improve closure. Liquid phase mercury measurements for four other similar runs have all been lower than 2.2 nanomole, indicating that most of the mercury is "re-emitted" under these conditions.

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, as this project progresses, results such as those provided above will be interpreted and 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 all 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.

The current data set is shown in Table 1, where A is the pre-exponential factor (in units of gmole, L, and second) and E_{act} is the activation energy (kcal/gmole) in the Arrhenius equation, $k = A \exp(-E_{\text{act}}/RT)$ where R is 1.987 cal/(gmole-°K) and T is the absolute temperature in °K. This data set is currently under development and the values shown should be considered preliminary; some of the values are artificially set for modeling purposes.

**Table 1. Preliminary Reaction Set and Kinetics Parameters for Hg - SO₂ Reaction Model
(see text for symbol explanation and units)**

Reaction	A	E _{act}
H ₂ O → H ⁺ + OH ⁻	1.66E+03	9.85E+00
H ⁺ + OH ⁻ → H ₂ O	1.58E+12	3.00E+00
H ⁺ + SO ₃ ⁻² → HSO ₃ ⁻	1.58E+13	3.00E+00
HSO ₃ ⁻ → H ⁺ + SO ₃ ⁻²	7.34E+03	1.00E-01
H ⁺ + HSO ₃ ⁻ → H ₂ SO ₃	1.58E+13	3.00E+00
H ₂ SO ₃ → H ⁺ + HSO ₃ ⁻	8.60E+08	-8.60E-01
Hg ⁰ + HSO ₃ ⁻ + H ⁺ → HgSO ₂ + H ₂ O	1.00E+03	0.00E+00
HgSO ₂ + H ₂ O → Hg ⁰ + HSO ₃ ⁻ + H ⁺	1.00E+00	0.00E+00
HgSO ₃ + SO ₃ ⁻² → Hg(SO ₃) ⁻²	3.45E+09	3.00E+00
Hg(SO ₃) ₂ ⁻² → HgSO ₃ + SO ₃ ⁻²	2.22E+10	1.76E+01
HgSO ₃ + H ₂ O → Hg ⁰ + HSO ₄ ⁻ + H ⁺	7.29E+16	2.57E+01
Hg ⁺² + SO ₃ ⁻² → HgSO ₃	2.14E+15	1.00E+01
HgSO ₃ → Hg ⁺² + SO ₃ ⁻²	1.93E+07	1.72E+01
SO ₂ (gas) + H ₂ O → H ₂ SO ₃	1.00E+06	0.00E+00
Hg ⁰ → Hg(gas)	1.00E+06	0.00E+00
Hg(gas) → Hg ⁰	1.00E+00	0.00E+00
Hg ⁺² + Cl ⁻ → HgCl ⁺	1.31E+10	1.01E+01
HgCl ⁺ → Hg ⁺² + Cl ⁻	2.11E+07	1.55E+01
HgCl ⁺ + Cl ⁻ → HgCl ₂	8.57E+16	9.67E+00
HgCl ₂ → HgCl ⁺ + Cl ⁻	6.72E+15	1.69E+01
HgCl ₂ + Cl ⁻ → HgCl ₃ ⁻	1.01E+09	1.12E+01
HgCl ₃ ⁻ → HgCl ₂ + Cl ⁻	1.24E+01	0.00E+00
HgCl ₃ ⁻ + Cl ⁻ → HgCl ₄ ⁻²	4.00E+09	1.16E+01
HgCl ₄ ⁻² → HgCl ₃ ⁻ + Cl ⁻	1.46E+08	1.11E+01

Table 1 (continued)

Reaction	A	E _{act}
$\text{Hg}^{+2} + \text{H}_2\text{O} \rightarrow \text{HgOH}^+ + \text{H}^+$	1.53E+06	1.33E+01
$\text{HgOH}^+ + \text{H}^+ \rightarrow \text{Hg}^{+2} + \text{H}_2\text{O}$	2.04E+04	5.88E+00
$\text{HgOH}^+ + \text{H}_2\text{O} \rightarrow \text{Hg}(\text{OH})_2 + \text{H}^+$	1.92E+06	1.21E+01
$\text{Hg}(\text{OH})_2 + \text{H}^+ \rightarrow \text{HgOH}^+ + \text{H}_2\text{O}$	1.05E+07	9.58E+00
$\text{Hg}^{+2} + 2 \text{S}_2\text{O}_3^{-2} \rightarrow \text{Hg}(\text{S}_2\text{O}_3)_2$	2.00E+09	0.00E+00
$\text{Hg}(\text{S}_2\text{O}_3)_2 \rightarrow \text{Hg}^{+2} + 2 \text{S}_2\text{O}_3^{-2}$	1.00E-20	0.00E+00

CONCLUSION

Previous modeling results from this study and literature data suggest 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 has developed a series of chemical reactions between Hg^{+2} and sulfite ion that lead to re-emissions. Experimental methods have been developed using UV spectrophotometry to verify the presence of the proposed reaction intermediate species, and to track their changes in concentration as the reactions proceed.

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. The initial work described here has concentrated on the effects of initial reactant concentrations, temperature, pH, and chloride concentration. Investigations to date have primarily focused on the rate of disappearance of the mercuric disulfite complex, although the elemental mercury release monitoring method will soon be applied more extensively.

Initial results indicate that in the absence of chloride, the rate of Hg^{+2} reduction is approximately inversely proportional to pH and to sulfite concentration. The reaction is very sensitive to temperature. The presence of chloride, however, as is the case in wet FGD systems, drastically decreases the rate of reaction and causes suppression of the pH effects. This possibly indicates a change in mechanism when chloride is present. Further investigation of the effects of chloride on the rate dependences is needed. Other experimental methods may be needed to determine if chloride indeed changes the re-emission mechanism and for elucidating the new mechanism if this is so.

In several instances, the reaction rate curves deviate significantly from simple "first order" behavior. This is to be expected for a reaction which involves a number of individual steps instead of just one rate-controlling reaction. An existing chemical kinetics model has been adapted to the mercury-sulfite-chloride-thiosulfate system, and will take into account the simultaneous occurrence of a number of reaction steps. Additional experimental work is needed to develop the reaction rate constants and activation energy values needed for upwards of 30 chemical reactions that may participate in mercury re-emissions. Once fully developed, the model will also allow prediction of kinetics in low pH regions, such as the SO_2 gas-aqueous interface, which are difficult to investigate experimentally and that may not be simulated well in the existing bench-scale wet FGD absorber.

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