Fundamentals of Mercury Oxidation in Flue Gas

Technical Annual Report

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ABSTRACT

The objective of this project is to understand the importance of and the contribution of gas-phase and solid-phase coal constituents in the mercury oxidation reactions. The project involves two experimental scales and a modeling effort. The team is comprised of University of Utah, Reaction Engineering International, and University of Connecticut. The objective is to determine the experimental parameters of importance in the homogeneous and heterogeneous oxidation reactions; validate models; and, improve existing models. Parameters to be studied include HCl, NO_x, and SO₂ concentrations, ash constituents, and temperature.

This report summarizes Year 1 results for the experimental and modeling tasks. Experiments in the drop tube are just beginning and a new, speciated mercury analyzer is up and running. A preliminary assessment has been made for the drop tube experiments using the existing model of gas-phase kinetics.

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INTRODUCTION

The objective of this project is to understand the importance and contribution of gas-phase and solid-phase constituents in the reactions of mercury oxidation. Included in the investigation are the effects of chlorine concentrations, NO_x concentration, SO₂ concentration, and reactions with ash constituents. A wet flue gas desulfurization system can remove most of the oxidized gaseous mercury in a coal-fired power plant. In addition, oxidized mercury is more likely to adsorb on fly ash, and, hence, removed by the particulate control device, or to be adsorbed by activated carbon. This removal uses existing equipment and requires no additives, making it a low-cost option. However, elemental mercury cannot be removed effectively using these methods. By understanding the important mechanisms in mercury oxidation, a greater fraction of the Hg could be captured using “back end” technology.

The project team includes the University of Utah, Reaction Engineering International, and the University of Connecticut. The team will collaborate on an experimental and modeling effort that will involve determination of experimental parameters, validation of the model, and improvement of existing models. Two stages of experiments will be performed: drop tube and a U-Furnace. Gas- and particle-phase constituents will be doped to determine the importance of specific parameters, such as HCl, NO_x, SO₂, and ash constituents.

Three tasks are envisioned:

Task 1.0 – Experimental Investigation of Mercury Chemistry

The University of Utah will perform natural gas and coal combustion experiments in both a drop tube furnace (Phase 1) and a facility with realistic time/temperature histories (Phase 2). The experiments will utilize “doped” constituents to investigate the importance of these constituents in the mercury oxidation mechanism. Both gas (HCl, NO_x, and SO₂) and solid (e.g. iron, calcium) constituents will be investigated.

Task 2.0 – Model Validation

REI and UConn will use existing versions of mercury oxidation models in the flue gas to guide the experimental design, predicting ranges of process parameters, e.g. temperature, chlorine concentration, and nitrogen oxide concentration, which would produce measurable changes in mercury speciation. UConn will focus on mechanism development; REI will focus on modeling and interpretation of experiments. The experimental data will be used to validate the gas-phase oxidation model (and improve it, if needed). The data will also clearly identify the effects of heterogeneous oxidation, as distinct from homogeneous oxidation. This information will be used to validate and improve heterogeneous models for mercury oxidation on fly ash.

Task 3.0 – Evaluation of Control Strategies

The effectiveness of mercury control strategies varies depending on the speciation of mercury in the flue gas. As a result of the experimental and model validation activities, we will be better able to predict the speciation of mercury in flue gas for a wide range of coal types and conditions. We will use this information to recommend modifications to existing control strategies or to suggest new control strategies, if they arise.

The project is on schedule as outlined in the proposal. The proposal stated that Year 1 accomplishments were to prepare the experimental facility and procure materials for the Phase 1 studies with natural gas and “doped” gases. This has been accomplished as described below. A mercury analyzer has been purchased and is expected to arrive the end of August (details on the analyzer are below). In the mean time, the existing Buck analyzer has been used to verify the experimental system and a mass balance has closed. The interaction between modeling and experimental results has also been accomplished. Using the temperature distribution of the drop tube, predictions of gas-phase conversion have been completed and will “feed back” to the experimental studies.

EXPERIMENTAL

Drop Tube Furnace Modifications

The Phase I experiments will utilize the Drop Tube Furnace with several modifications. To oxidize mercury in a matrix of combustion products the Drop Tube Furnace at the University of Utah has been fit with a natural gas burner. Avoiding the adsorption of mercury and any interference with mercury speciation required that this burner be constructed of quartz glass, which has no known influence on or affinity for mercury. The burner was designed to operate at a burn rate of approximately 1000 BTU/hr producing 6 SLPM of combustion gas. Reactant nozzles for air, natural gas, oxidizing agents and mercury were incorporated into its design.

The addition of flame to the Drop Tube Furnace required significant modifications to the furnace control system as well. Opto 22 was the chosen control program. First, a flame detection system was installed. This system uses a UV detector to monitor the status of the flame in the burner. If the flame is extinguished, the control system shuts off the flow of natural gas to eliminate the possibility of uncontrolled ignition. Second, an ignition system was added. This system allows computer controlled ignition of the burner. Third, a monitoring system was added to the cooling water system on the furnace. This system facilitated the development of a control scheme that allows the furnace to be left hot overnight, eliminating several hours of unproductive heating and cooling each day of experimentation. Flow of reactants to the burner is controlled by mass flow controllers. Each of these controllers has been calibrated for their flow medium and this information has been incorporated into the control scheme. Each of these systems has been fully tested and proven to be effective.

A natural-gas flame in the Drop Tube Furnace introduces water into the gas matrix. This introduction is necessary to accurately represent combustion reaction conditions, but complicates gas analysis. To remove water before combustion gas enters the analytical equipment, a Perma Pure Dryer, with heating and control equipment, was installed at the exit of the furnace. This system requires consideration of pressure drop vs. flow of gas through the dryer. To avoid elevated pressures in the furnace, pressure control equipment has been installed.

Figure 1 illustrates the complete system as modified. Each module is identified in the figure and a “blow up” of the burner is also illustrated.

Figure 1. Schematic of Drop Tube

Buck Analyzer Calibrations

Previous mercury investigation at the University of Utah has been performed using a Buck 400A analyzer. This simple device consists only of an atomic adsorption cell and data output displays. It is capable of detecting elemental mercury only. For initial experimentation in the current project this analyzer will be used. Calibration curves were produced using a VICI Metronics mercury permeation tube and a nitrogen carrier gas. These curves were later validated by generating calibration gas with the PS Analytical Mercury Vapor Calibrator. We are now confident that we can use this instrument to detect elemental mercury accurately with known error.

Mass Balance

After completion of all necessary modifications it was desired to demonstrate that the drop tube furnace can be used for mercury experimentation. This was accomplished in steps. First, experiments were completed using a known amount of mercury having the system cold and hot. Finally, at nominal flame operating conditions, a known amount of mercury was introduced into the flame. The exhaust gas was dried and the dry exit gas was analyzed for mercury content using the Buck 400A analyzer. This analysis, coupled with flow measurements into and out of the furnace, represents a mercury material balance. As illustrated by the following figure, Figure 2, this material balance demonstrates that we can confidently perform mercury experimentation in the reactor.

Figure 2. Calibration of Drop-Tube Furnace System

Mercury Analyzer Assessment

Analysis of mercury species in combustion flue gas is a task that is significantly limited by current technology. Elemental mercury is typically detected using Cold Vapor Atomic Adsorption (CVAA) or Cold Vapor Atomic Fluorescence Spectrometry (CVAFS). These analytical methods are effective for elemental mercury, but have no ability to detect or differentiate between oxidized mercury species. For this reason oxidized mercury species must be chemically reduced to the elemental form for detection. Chemical reduction can be performed using lab analysis methods such as Ontario Hydro or any number of commercially developed systems. This approach allows for quantification of elemental mercury and total mercury. The amount of oxidized and particulate bound species must be arrived at by difference.

Mercury analyzers capable of speciation are a product of fairly young technology and understanding. There are several commercially available systems that were of interest to us after our initial investigation. Each of these systems had distinct advantages and disadvantages that were of importance in our selection of analytical equipment. Of particular interest to us at the time of our investigation was the advent of new technology allowing for mercury speciation without the use of cumbersome wet chemical reagents. In these systems, reduction of oxidized mercury species for measurement is accomplished using proprietary dry chemicals that are automatically regenerated within the system. It is speculated that these dry chemical systems will simplify analytical mercury measurement significantly.

Our comparison of commercially available mercury analyzers is summarized in Table 1.

Table 1. Commercial Mercury CEM Details

	P S Analytical	Ecochem	Nippon	Tekran
Detection	Atomic Fluorescence	Atomic Absorption @ 253.7 nm	Atomic Absorption @ 253.7 nm	Atomic Fluorescence
Species Separation	Wet Chemistry	Thermal Catalyst	Dry Catalyst	Dry Catalyst
Stream Purification	Wet Chemistry / Gold Amalgamation	Gold Amalgamation	Dry Chemistry	Dry Chemistry / Gold Amalgamation
Min Sample Rate	0.1 l/min	2 l/min	0.5 l/min	0.5 l/min
Cost	\$80,000	\$90,000	\$57,000	\$95,000
Resolution (Minimum)	0.01 $\mu\text{g}/\text{m}^3$	NA	0.5 $\mu\text{g}/\text{m}^3$	0.01 $\mu\text{g}/\text{m}^3$
Advantages	AF Detector = Great Resolution Most Flexible Unit Huge Database (PS Analytical)	True Continuous Monitoring Dry Separation	True Continuous Monitoring Dry Chemical (No Reagents) Recommended by Jeff Ryan (EPA)	AF Detector, 0.01 $\mu\text{g}/\text{m}^3$ Resolution Good Reproduction of Ontario Hydro Advanced QA/QC (Calibration) Computer Control Dry Chemical (No Reagents) Industry Accepted Recommended by Sharon Sjostrom
Disadvantages	Steep Learning Curve Operation Is Labor Intensive	AA Detector = Poor Resolution Poor Half Life of Catalyst Accuracy Questionable - Jeff Ryan	AA Detector = Poor Resolution Validation Data? Technical People are in Japan	2.5 min Sample Time Price Tag

Significant investigation into the Nippon and Tekran dry chemical systems was conducted. While this type of analytical system promises to drastically simplify speciated mercury measurements, there are several disadvantages to our pursuit of these systems. Some of the major disadvantages are due to the infancy of the technology. There is a significant lack of data validating the accuracy and limitations of dry chemical systems. There is no indication of longevity and maintenance cost of these systems. It is also advantageous for us to completely understand the operation of analytical systems used for research in order to project their limitations. This was not possible with these proprietary systems. For these reasons it was decided that we would not purchase a dry chemical system at this time.

We have speculated that it is very desirable to have an analytical system that incorporates CVAFS detection. This type of detection results in a much higher resolution that is desirable in a research setting. This constraint limited analyzer choice to either a PS Analytical system or a Tekran Analyzer with an aftermarket conditioning and reduction system on the front end. Upon recommendation of Connie Senior of Reaction Engineering International (REI) we investigated the possibility of using a Tekran Analyzer coupled with a sampling and conditioning system designed and built by Randy Merritt of Southern Research Institute (SRI) in conjunction with Sharon Sjostrom of ADA Environmental Systems (ADAES). This system is very attractive for several reasons. The most significant of these is the advanced quality assurance and control that is possible using SRI's spike and recovery system (Gail, et al. 2003). Another very attractive aspect of the SRI system is that the system and its operation is completely understood. Because this system is not commercially available it was fabricated by SRI and then delivered, set up and tested by Randy Merritt at the University of Utah.

The major pieces of equipment for the SRI speciating mercury analyzer are:

1. Tekran Model 2537A Mercury Vapor Analyzer (Low Dead Volume Version)
2. Tekran 4-Port Synchronization Sampler
3. PS Analytical Model 10.534 Mercury Vapor Calibrator
4. Apogee Scientific QGIS Inertial Probe

As stated above, University of Utah has contracted with SRI to construct a mercury sampling and conditioning system. All of the equipment and supplies was purchased by the University of Utah. Each of the parts was shipped to SRI with the exception of the Tekran Model 2537A Analyzer and the PS Analytical Model 10.534 Calibrator which were shipped directly to the University of Utah. SRI agreed to fabricate the conditioning system and make all of the necessary modifications to the sampling probe. Simultaneous to the SRI fabrication, the University of Utah received the Tekran and PS Analytical equipment, became familiar with their operation and verified that the analyzer and the calibration unit agreed on mercury concentrations. Randy Merritt will deliver the conditioning and sampling systems to the University of Utah at the end of August. At this time these systems will be coupled to the Tekran Analyzer and the PS Analytical Calibration unit and Randy will spend a week at the University of Utah instructing on the proper use of the complete System. Details are shown in Figure 3.

The following is a list of tasks required for the completion of the speciating mercury analyzer, including dates of completion.

1. Contract in place with SRI (04/06/04)
2. Required equipment, material and supplies ordered and shipped to the proper destination (05/10/04)
3. Fabrication of the sampling and conditioning system completed (07/06/04)
4. Verification of the operation of the Tekran Analyzer and the PS Analytical Calibration unit completed (07/30/04)
5. Delivery and setup of the sampling and conditioning system (08/23/04)

Figure 3. Mercury Analysis System

MODELING CHEMISTRY IN MERCURY FLUE GAS

Comparison of gas-phase mechanisms

Before beginning the validation of models, a comparison was made of two gas-phase mechanisms for mercury and chlorine chemistry. The first mechanism uses chlorine chemistry developed by Bozzelli and mercury rate constants published by Niksa et al. (2001); this is called REI. The second mechanism uses chlorine chemistry originally developed by Dryer and co-workers, updated Hg chemistry and SO₂ and NO_x chemistry as developed by Helble and co-workers (Qiu, et al., 2003); this is called the UConn mechanism. Since the original REI mechanism did not have NO_x and SO₂ chemistry, the UConn chemical mechanisms for NO_x and SO₂ were incorporated for the comparison calculations. Two benchmark cases were used to compare computational schemes:

I. 1600 K => 400 K using an exponential temperature decrease (~5000 K/s), then isothermal at 400 K for 4 seconds.

II. 1600 K => 400 K in 4 seconds using an exponential temperature decrease (~300 K/s).

Both cases cool the gas from 1600 K to 400 K in 4 seconds. Case I has a high cooling rate, while Case II has a lower cooling rate. The cooling rate in Case I is typical of quenching in a sample probe, while that in Case II is typical of the average cooling rate in a boiler (although a boiler would have regions of higher cooling rates). Table 1 gives the bulk gas composition used in these calculations.

Table 2. Composition for benchmark cases.

CO ₂ , vol%	9.0
H ₂ O, vol%	16.5
O ₂ , vol%	1.9
N ₂ , vol%	72.5
SO ₂ , ppm	700
HCl, ppm	260
Hg, ppb	6.18

First, consider the low cooling rate benchmark case, which goes from 1600 K to 400 K in 4 seconds (-300 K/s). Both the UConn and REI mechanisms produce a comparable amount of Cl₂ (0.17-0.18 ppm) at the end of 4 seconds, although REI's mechanism produces about 10% more (Figure 4). The concentrations of Cl and Cl₂ are nearly the same for both mechanisms after 2 seconds, but HOCl is markedly higher in the REI mechanism. The final Cl concentration at 400 K is about 0.15 ppm in the REI mechanism and about 0.05 ppm in the UConn mechanism.

Figure 4. Chlorine species in the 300 K/s benchmark case

In terms of mercury behavior, both mechanisms begin to oxidize mercury at temperatures below 900 K; this is manifested by increases in HgCl and HgCl₂ initially (Figure 5). In the REI mechanism, all the elemental mercury is consumed by 650 K. In contrast, the UConn mechanism results in only 30% conversion and about half of that conversion takes place below 650 K. Below 650 K, the UConn mechanism predicts a sharp increase in HgCl, which might be from the Hg + Cl₂ reaction rate increasing as the Cl₂ concentration increases. The conclusion from this case is that the REI mechanism produced more Cl, Cl₂ and HOCl than the UConn mechanism. The differences were not that great, however, at a cooling rate of ~300 K/s. This does not entirely explain the differences in Hg⁰ oxidation between the mechanisms, however, since the Cl atom concentrations predicted by the two mechanisms are comparable from 2.5 to 3 seconds, when the REI mechanism predicts a sharp increase in HgCl and HgCl₂ that is not predicted by the UConn mechanism.

Figure 5. Mercury species in the 300 K/s benchmark case

The most important reactions in the REI mechanism are shown in Figure 6, which shows the calculated forward rate constants. For this case, the oxidation of elemental mercury proceeds fairly directly via: $\text{Hg} + \text{Cl} \Rightarrow \text{HgCl} + \text{Cl} \Rightarrow \text{HgCl}_2$. The $\text{Hg} + \text{Cl}_2$ reaction is the only other one that is significant. The $\text{Hg} + \text{HOCl}$ reaction is not significant.

Figure 6. Forward rate constants for 300 K/s case from REI mechanism.

The major route to oxidation is by Cl atoms. The concentrations of Cl_2 and Cl are sensitive to the cooling rate. In a flame system, we need to better understand the radical pool and its effect on Cl atoms. Experiments without flames, as discussed below, pose problems for modeling because it is difficult to quantify the production of radicals; walls may play a role.

Review of experimental datasets

Six data sets were reviewed (Table 3). As part of this review, we examined the consistency of the experimental data from one experiment to another and how well the gas-phase models predicted the reported experimental results.

Ghoishi (1998) used a heated quartz tube and simulated flue gas mixtures. The amount of mercury oxidation was measured in the flue gas. A description of the sampling system and cooling rate is given by Edwards, et al. (2001). Hall (1991) used similar experimental conditions and compositions. Table 4 compares the simulated flue gas mixtures used by Ghorishi and Hall. Figure 7 compares the observed mercury oxidation from the two studies.

Hall observed oxidation of mercury by HCl, without water, even at a temperature of 573 K. Ghorishi observed oxidation of mercury by HCl at a temperature of 773 K, although the oxidation was lower than that observed by Hall. In Ghorishi's experiments, O_2 was low (2%) compared to Hall's experiment (10%). In terms of the Cl/Hg ratio, Hall's experiment with 300 ppm HCl is comparable to Ghorishi's experiment with 200 ppm HCl. The difference between the two sets of experimental results is large and puzzling. Heterogeneous oxidation may play a role.

Figure 7. Comparison of Ghorishi's and Hall's data for 100 and 200 ppm initial HCl.

Sliger's quartz reactor experiments varied the water concentration from 0% to 14% and thus can be compared to Hall's experiments. The peak temperature in Sliger's quartz furnace was approximately 1200 K, similar to Hall's. Sliger's 0% water result is consistent with Hall's data with 300 ppm HCl (Figure 8) and Sliger's 10% water result is consistent with Widmer's data, although the Widmer experiment with 300 ppm HCl had a lower Cl/Hg ratio than the Sliger experiment with 274 ppm HCl.

When the peak temperature in the experiment was above 1100-1200 K, there appeared to be good agreement among experiments from different laboratories with similar gas compositions. At temperatures below about 1000 K, however, there is not always good agreement from one experiment to another, as illustrated in Figure 8, the comparison of Hall's and Ghorishi's data without water.

The water content of the simulated flue gas affects mercury oxidation, as illustrated by data from Sliger's quartz reactor experiments in Figure 9, in which the mercury oxidation (peak temperature circa 1200 K) is shown as a function of water content for two different concentrations of HCl. The presence of water reduces the oxidation of mercury.

Table 3. Laboratory datasets.

Name	Experiment	Comments on Experimental Data	References
<u>Ghorishi</u>	Flow tube, HCl, no water, 2% O ₂	Oxidation is much lower than Hall's data (no water). O ₂ is low (2%) compared to Hall (10%).	S. B. Ghorishi, Fundamentals of Mercury Speciation and Control in Coal-Fired Boilers, EPA-600/R-98-014, February 1998; J.R. Edwards, R.K. Srivastava, J.D., Kilgroe, "A Study of Gas-Phase Mercury Speciation Using Detailed Chemical Kinetics," J. Air & Waste Manage. Assoc. 51:869-977, 2001.
<u>Sliger (1)</u>	Flow tube, effect of water and HCl, 11% O ₂	Oxidation consistent with Hall (no water)=> nearly complete at ~1200 K. Water inhibits oxidation.	R.N. Sliger, J.C. Kramlich, N.M. Marinov, "Towards the development of a chemical kinetic model for the homogeneous oxidation of mercury by chlorine species," Fuel Process. Technol. 65-66: 423-438 (2000); R.N. Sliger, Ph.D. Thesis, University of Washington.
<u>Widmer</u>	Flow tube, high HCl, 10% O ₂ , effect of initial temperature	300 ppm results consistent with Sliger at 8% O ₂ . High oxidation at temperatures <900 K	J.A. Gaspar, N.C. Widmer, J.A. Cole, W.R., Seeker, "Study of mercury speciation in a simulated municipal waste incinerator flue gas," in Proceedings of the 1997 International Conference on Incineration and Thermal Treatment Technologies, Oakland, CA, May 12-16, 1997.; J.R. Edwards, R.K. Srivastava, J.D., Kilgroe, "A Study of Gas-Phase Mercury Speciation Using Detailed Chemical Kinetics," J. Air & Waste Manage. Assoc. 51:869-977, 2001.
<u>Hall</u>	Flow tube, HCl, no water, 10% O ₂ , effect of temperature	High oxidation (>50%) for all temperatures except 573 K.	B. Hall, P. Schager, O. Lindquist, "Chemical Reactions of Mercury in Combustion Flue Gases," Water, Air, Soil Poll. 56:3-14 (1991).
<u>UConn</u>	CH ₄ flame, HCl or Cl ₂ added after flame; low cooling rate, ~100 ppm NO	Conversion (ϕ =0.9) lower than Sliger (ϕ ~0.8); effect of O ₂ or cooling rate?	Qiu, J., Sterling, R.O., Helble, J.J. Development of an Improved Model for Determining the Effects of SO ₂ on Homogeneous Mercury Oxidation, presented at the 28th International Technical Conference on Coal Utilization & Fuel Systems, Clearwater, FL, March 10-13, 2003
<u>Sliger (2)</u>	Nat. gas flame, HCl added after flame, high cooling rate, 25 ppm NO	Experimental data: Lower oxidation observed in tunnel furnace than in quartz furnace. Why? <ul style="list-style-type: none"> - Higher O₂ in quartz furnace - 25 ppm NO in tunnel furnace - wall effects in quartz furnace - radicals from flame 	R.N. Sliger, J.C. Kramlich, N.M. Marinov, "Towards the development of a chemical kinetic model for the homogeneous oxidation of mercury by chlorine species," Fuel Process. Technol. 65-66: 423-438 (2000); R.N. Sliger, Ph.D. Thesis, University of Washington.

Table 4. Comparison of gas compositions used in experiments with simulated flue gas.

		Ghorishi	Hall	Widmer	Sliger
N2	vol%	93.0%	90.0%	72.0%	balance
O2	vol%	2.0%	10.0%	10.0%	11.0%
CO2	vol%	5.0%	0.0%	10.0%	0.0%
H2O	vol%	0.0%,	0.0%	8.0%	0-14%
HCl	ppm	50-200	100-300	300, 3000	39, 274
Hg	ppm	0.04	0.12	0.37	0.10
Cl/Hg ratio		1250-5000	800-2500	800-8000	390-2700

Figure 8. Comparison of quartz reactor data with and without water present.

Figure 9. Mercury oxidation as a function of water content of gas: data from Sliger's quartz furnace experiments.

The experiments at UConn and Sliger's tunnel furnace both used natural gas (or methane) flames instead of simulated flue gas mixtures. In the tunnel furnace experiments, mercury was added to the flame (as mercury nitrate solution) and HCl was added downstream of the flame where the gas temperature was approximately 1200 K. In the UConn experiments, HCl and mercury (and, in some cases, NO and SO₂) were added downstream of the flame at a temperature of about 1350 K. The tunnel furnace flue gas has 24 ppm of NO_x and the UConn baseline condition (equivalence ratio = 0.9) had about 125 ppm NO_x. Sliger's tunnel furnace had a nominal mercury concentration of 53 µg/Nm³, while the UConn experiments had 45-50 µg/Nm³.

Figure 10 compares the flame experimental data with the quartz reactor (simulated flue gas) data of Sliger (274 ppm HCl) and Widmer (300 ppm HCl). The quartz reactor data of Sliger and Widmer (peak temperatures of 1227 K and 1142 K, respectively) produced *higher* oxidation of Hg⁰ than the flame experiments even though the quartz reactor experiments had *lower* Cl/Hg ratios than the flame experiments. This may be due to the concentration profiles of Cl generated from the flame as opposed to generated from dissociation of HCl in the quartz reactor experiments.

Figure 10 Comparison of flame experiments (Sliger and UConn) with quartz reactor data (Sliger and Widmer).

Model Validation

After review of experimental data and investigation of two different kinetic mechanisms, the two models, REI and UConn, were compared against experimental data. Figures 11 and 12 compare the models against simulated flue gas data of Ghorishi and Sliger. In general, the REI model overpredicted mercury oxidation and the UConn model underpredicted mercury oxidation. From the comparison of the two models on the benchmark cases, it was apparent that the REI model had a tendency to predict more conversion because of differences in the rates of reaction of mercury with chlorine species and because the REI mechanism produced more Cl , Cl_2 and HOCl than the UConn mechanism.

Figure 11. Comparison of models with Ghorishi's simulated flue gas data (no water).

Figure 12. Comparison of models with Sliger's simulated flue gas data.

The simulated flue gas experimental data were problematic, however, as cases for validating gas phase models. Review of the data showed discrepancies among some experimental results with similar initial conditions, leading to speculation that heterogeneous chemistry might have played a role in some of these experiments, particularly at temperatures below 1000 K. Thus, the models should also be validated against the flame data. Sliger's tunnel furnace experiments and the UConn experiments produced similar conversion of mercury as a function of HCl content in the flue gas.

Figure 13 shows the comparison between the UConn model and Sliger's tunnel furnace data. The prediction of mercury oxidation as a function of HCl content is good, considering the scatter in the experimental data. Figure 14 shows the comparison between the UConn model and the UConn data for HCl addition, with and without added NO. The UConn model overpredicts the oxidation by HCl by 20-40%, except for one case. The REI model results are not shown here, since the REI model predicted complete oxidation even at low HCl concentrations.

Figure 13. Comparison of UConn model results with data from Sliger's tunnel furnace.

Based on a comparison between the models and the laboratory data, the general conclusion is that the UConn mechanism fits the data from two different flame experiments reasonably well (both the UConn experiments and Sliger's tunnel furnace).

The REI mechanism consistently predicts more oxidation than the UConn mechanism. When we look at the experimental data, the UConn mechanism predicts little or no oxidation for these two cases. The poor agreement between the UConn mechanism and simulated flue gas data, in the face of better agreement with the flame data, is disappointing. It suggests that perhaps it is futile to try to predict laboratory data in the absence of a flame (i.e., with simulated flue gases) because it is difficult to know the starting conditions. This is not a criticism of the mechanism so much

as of the difficulty of knowing what might influence the initial formation of free radicals in experiments without flames.

The UConn mechanism did a better job of predicting two different laboratory (flame) experiments than the REI mechanism. The differences between the two mechanisms seemed to be primarily in the mercury rates, with a secondary effect of the chlorine mechanism. (That is, the REI mechanism produces more Cl and HOCl at lower temperatures.) The general conclusions about the modeling results are that the model results are very sensitive to the initial temperature in non-flame systems, because this determines the Cl concentration.

Figure 14. Comparison of UConn model results with data from UConn flame experiments

RESULTS AND DISCUSSION

The first step in the project is to use the homogeneous model with the drop tube furnace results. Given that we have only recently obtained the analyzer system, the modeling results are the only results discussed below.

The drop tube furnace at the University of Utah was simulated based on the measured temperature profile in the furnace. Since the temperature cannot be measured in the methane flame itself, a temperature of 1900 K was assumed for the flame temperature (about 300 K less than the adiabatic flame temperature for a near-stoichiometric flame). The temperature profile was assumed to be linear from the burner to the heated zone within the furnace. Figure 15 shows the temperature profile as a function of distance from the burner. The linear region from 1900 K to circa 1370 K is assumed; the rest of the points are measured.

Figure 15. Temperature as a function of distance from burner in drop tube furnace

The total flow of combustion products in the furnace is 6.117 slpm. The equivalence ratio in the furnace for the baseline condition is 0.95, giving an O_2 concentration after the burner of 1.1 vol%. This gives a residence time in the furnace as shown in Figure 16. The flame was approximated as a plug flow reactor at 1900 K for 0.5 seconds.

Figure 16. Temperature as a function of residence time.

Assuming mercury concentrations of $20 \mu\text{g}/\text{m}^3$ or $150 \mu\text{g}/\text{m}^3$, an initial NO concentration of 20 ppm and a range of chlorine contents (as added HCl in the flue gas), the mercury oxidation in the furnace as a function of time was calculated using the homogeneous model discussed above; the results are shown in Figure 17. The Cl/Hg ratio affects the conversion. As in other experiments, the amount of conversions is predicted to increase with increasing HCl in the flue gas. The effect of HCl is more pronounced for this experimental set-up than for Sliger's or the UConn experimental set-up because of the relatively long residence time at temperatures below 600 K in the drop tube system. The other experiments previously cited did not have such a long residence time at relatively low temperature. Figure 18 shows that mercury oxidation begins during the quench at the end of the hot zone in the upper furnace at about 800 K and continues until the sampling point.

Figure 17. Predicted oxidation of elemental mercury in the drop tube reactor as a function of HCl and Hg contents.

Figure 18. Temperature and mole fraction of Hg^0 and HgCl_2 as a function of residence time for 1000 ppm HCl and $150 \mu\text{g}/\text{m}^3$.

CONCLUSIONS

The accomplishments during the first year have included:

- the purchase and verification of a speciated mercury sampling system
- determination of the temperature distribution through a modified drop tube furnace
- modeling of the furnace to begin the exchange between data results and modeling results

During this next year, we hope to complete the drop tube studies which include both homogeneous and heterogeneous validation of the model. In addition, we will begin to explore the needs of using the larger U-Furnace facility to begin coal-fired studies.

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REFERENCES

Edwards, J.R.; R.K. Srivastava; J.D., Kilgroe. "A Study of Gas-Phase Mercury Speciation Using Detailed Chemical Kinetics," J. Air & Waste Manage. Assoc. 51:869-977, 2001.

Gale, T. K., Merritt, R. L., Cushing, K. M., "Mercury Speciation as a Function of Flue Gas Chlorine Content and Composition in a 1 MW Semi-Industrial Scale Coal-Fired Facility", Combined Power Plant Air Pollutant Control Mega Symposium-2003, Washington D.C., (2003).

Gaspar, J.A.; N.C. Widmer; J.A. Cole; W.R., Seeker. "Study of mercury speciation in a simulated municipal waste incinerator flue gas," in Proceedings of the 1997 International Conference on Incineration and Thermal Treatment Technologies, Oakland, CA, May 12-16, 1997.

Ghorishi, S.G. Fundamentals of Mercury Speciation and Control in Coal-Fired Boilers, EPA-600/R-98-014, February 1998.

Hall, B.; P. Schager; O. Lindquist. "Chemical Reactions of Mercury in Combustion Flue Gases," Water, Air, Soil Poll. 56:3-14 (1991).

Kilgroe, J.D.; Sedman, C.B.; Srivastava, R.K.; Ryan, J.V.; Lee, C.W.; Thorneloe, S.A., 2001, Control of Mercury Emissions from Coal-Fired Electric Utility Boilers: Interim Report, U.S. Environmental Protection Agency, Office of Research and Development, National Risk Management Laboratory, Air Pollution Prevention and Control Division, EPA-600/R-01-109, December 2001.

Niksa, S.; J.J. Helble; N. Fujiwara. "Kinetic Modeling of Homogeneous Mercury Oxidation: The Importance of NO and H₂O in Predicting Oxidation in Coal-Derived Systems," Environmental Science and Technology 2001, 35(18), 3701 – 3706.

Qiu, J.; R.O. Sterling; J.J. Helble. "Development of an Improved Model for Determining the Effects of SO₂ on Homogeneous Mercury Oxidation," presented at the 28th International Technical Conference on Coal Utilization & Fuel Systems, Clearwater, FL, March 10-13, 2003

Sliger, R.N.; J.C. Kramlich; N.M. Marinov. "Towards the development of a chemical kinetic model for the homogeneous oxidation of mercury by chlorine species," Fuel Process. Technol. 65-66: 423-438 (2000).