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 both experimental and modeling efforts. The team is comprised of the University of Utah, Reaction Engineering International, and the 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, NOx, and SO_2 concentrations, ash constituents, and temperature.

This report summarizes Year 3 results for the experimental and modeling tasks. Experiments have been completed on the effects of chlorine. However, the experiments with sulfur dioxide and NO, in the presence of water, suggest that the wet-chemistry analysis system, namely the impingers, is possibly giving erroneous results. Future work will investigate this further and determine the role of reactions in the impingers on the oxidation results. The solid-phase experiments have not been completed and it is anticipated that only preliminary work will be accomplished during this study.

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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, NOx concentration, SO_2 concentration, and reactions with ash constituents. A wet flue gas desulphurization 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, be removed by the particulate control device, or 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.

Three tasks were envisioned:

Task 1.0 – Experimental Investigation of Mercury Chemistry
The University of Utah will perform natural gas and coal combustion experiments in both a mercury reactor (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, NOx, 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.

Previous results have focused on developing an experimental system which is reliable and without bias for gas-phase mechanism validation. These studies have included understanding the effects of the reactor and sampling system. Further work was done on the effects of sulfur dioxide and NO which have led us to believe that some of the observed oxidation occurred within the impingers, not the reaction system. Future work will focus on verification of the wet-chemistry system with the hope of determining the role of the impinger chemistry in our results, which could be extended to the work of others. In addition, dispersed-phase experiments will be run on coal ash constituents, including iron and calcium. Unburned carbon may also be a candidate once other major constituent heterogeneous interactions are understood.

EXPERIMENTAL

Mercury Reactor Furnace and Mercury Analyzer

The mercury reactor used in this study has been detailed in previous reports and in Fry, et al. (2006). The reactor has been fitted with a natural gas, premixed burner. In these experiments all reactants are introduced through the burner and pass through the flame.

A sample of flue gas is withdrawn from the bottom of the reactor and enters the sample-conditioning system, designed by Southern Research Institute (SRI). In this system the sample gas is pulled in two streams directly from the last section of the quartz reaction tube into a set of conditioning impingers. One stream is bubbled through a solution of stannous chloride to reduce oxidized mercury species to elemental mercury. The stream then contacts a solution of sodium hydroxide to remove acid gases. This stream represents the total mercury concentration in the reactor. The second stream is first treated with a solution of potassium chloride to remove oxidized mercury species and then is also treated in a caustic solution for acid gas removal. This stream is representative of the elemental mercury concentration in the reactor. Oxidized mercury species are represented by the difference between total and elemental mercury concentrations. Water is removed from the sample gas by a chiller and then each stream is intermittently sent to the analyzer by a valve box connected to the analyzer. Analysis is performed using a Tekran 2537A mercury vapor analyzer. The system, previously reported, is shown in Figure 1.

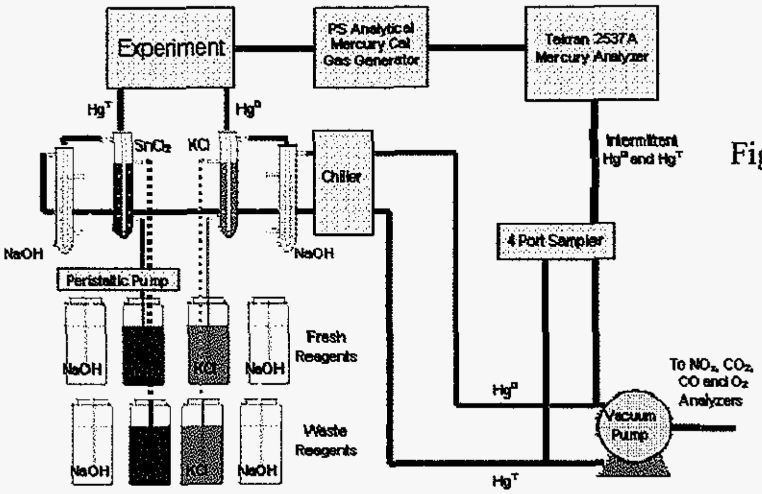

Figure 1. Mercury Analysis System

Experimental Results – NO and SO_2

Experiments were conducted with the addition of NO and SO_2 into the burner. Pure NO was provided to the system by a lecture bottle using a 0 – 6 ml/min rotameter flow tube and a high resolution valve. NO concentrations in the flue gas were measured using a California Analytical Instruments, Model ZRF CO / NO analyzer. SO_2 concentrations were controlled by injecting a standard of SO_2 in air.

The NO concentration generated by the quartz glass burner while operated at nominal conditions was 36 ppmv, dry. NO concentrations of 100, 250 and 500 ppmv, dry were produced upon the addition of NO to the burner. Cl_2 was injected into the burner to produce reactor chlorine concentrations (as Cl) of 0 – 600 ppmv. The oxidation curves (i.e., percent mercury oxidized versus input chlorine) generated from this set of experiments are presented in Figure 2. In addition, modeling of the experimental conditions was performed and model results are also presented for comparison in Figure 2. The experimental data show that, at a Cl concentration of 200 ppmv and 500 ppmv NO the oxidation is 28.2%, denoting a reduction in oxidation at these conditions of 44%. This result is similar to that found by Sterling, et al. (2004). They reported a 30% decrease in homogeneous mercury oxidation with the introduction of 300 ppmv NO and essentially no effect when 100 ppmv NO was introduced at all chlorine concentrations. The model predicted essentially no effect of NO on mercury oxidation at all NO and chlorine concentrations.

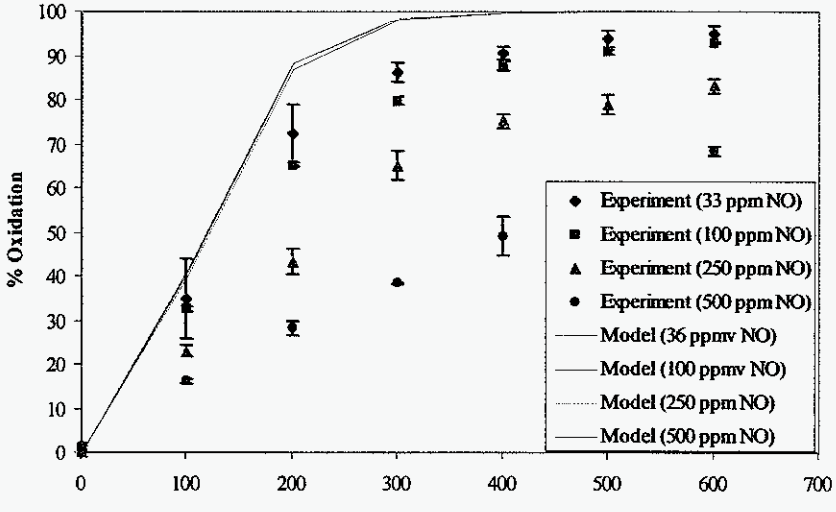

Figure 2. Experiment vs. Model Effects of NO on Mercury Oxidation

SO_2 was introduced into the quartz burner from the SO_2 calibration gas standard in air using a Brooks 5850E mass flow controller. For this set of experiments the concentration of SO_2 was not measured, but was calculated by mass balance. The SO_2 concentration in the reactor was set at 300 ppmv and the chlorine concentration (as atomic Cl) was varied from 0 to 600 ppmv.

Mercury oxidation for each of these conditions was measured and is presented in Figure 3. The data for mercury oxidation with no SO_2 are presented for comparison.

The introduction of 300 ppmv SO_2 results in a 68% reduction of mercury oxidation. Sterling and co-workers (2004) reported a reduction in mercury oxidation of 44% with a concentration of SO_2 at 400 ppmv and an initial Cl_2 concentration of 250 ppmv (or 500 ppmv of total chlorine as Cl). The impact of SO_2 in the current investigation is significantly greater. The model was again used to predict the effects of SO_2 on mercury oxidation for the conditions of interest. Results from this modeling effort are presented in the figure for comparison to the experimental results. The model predicts that SO_2 affects the concentrations of certain free radical species that promote oxidation of elemental mercury by chlorine compounds. Through this interaction a reduction in oxidation is observed, but much less than that shown in the experimental results.

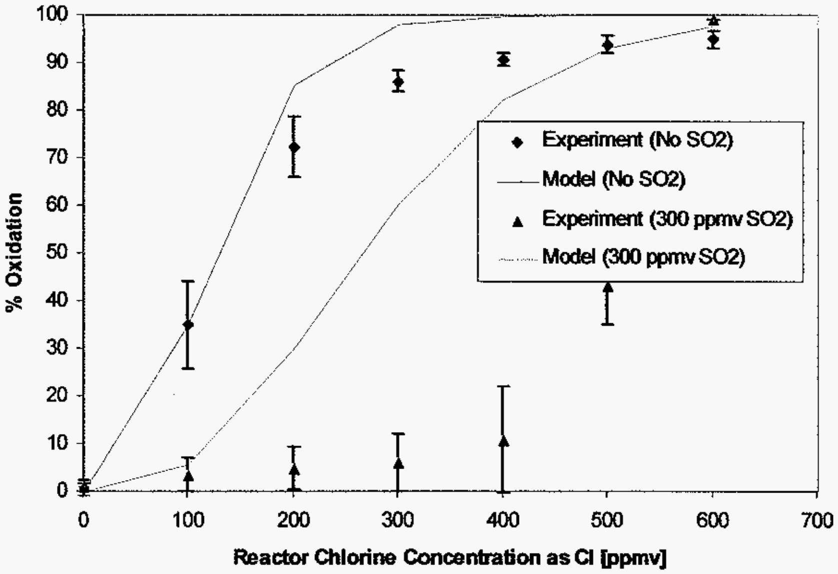

Figure 3. Experiment vs. Model Effects of SO_2 on Mercury Oxidation

We were surprised to see the difference between the data and the model, given that previous model predictions were quite close to the experimental results. Before looking at the model and detailed kinetics, we wanted to confirm the experimental findings. To do this, we started by directly injecting the NO and SO_2 in the impingers to ensure that we did not have any effects within the impinger system.

For these experiments, the reactor was operated with a chlorine concentration of 200 ppmv (with reactor chlorine as Cl), producing mercury oxidation of nearly 80%. Elemental mercury measurements were taken with a modified conditioning system. In this case, the conditioning system was modified to inject NO and SO_2 directly one the KCl impinger. The $SnCl_2$ solution was removed from the conditioning system and replaced by a second solution of 10% KCl, resulting in two redundant measurements of elemental mercury. Therefore, the impingers should be measuring the amount of elemental mercury in the system without regard to the total mercury.

The data for NO are shown in Figure 4. In this case, the NO was injected into the system and then turned off. Initially, the amount of injected elemental mercury is analyzed as the total amount of mercury in both impingers ("Control" being a KCl impinger and "NO" being a KCl impinger with NO injected into it). Initially, the two flows were not equal, resulting in a difference between the two systems (see 10:19:12 to 11:31:12). As this was adjusted, the two measurements were equal. As NO was injected into the KCl impinger, there was an increase in the measured concentration of elemental mercury, an apparent reduction in mercury oxidation. This was representative of 28.6% oxidation for the conditions of 200 ppmv Cl and 500 ppmv NO. Once the NO was removed, elemental mercury concentration went back to the concentrations of the "Control" case, indicating about 80% oxidation.

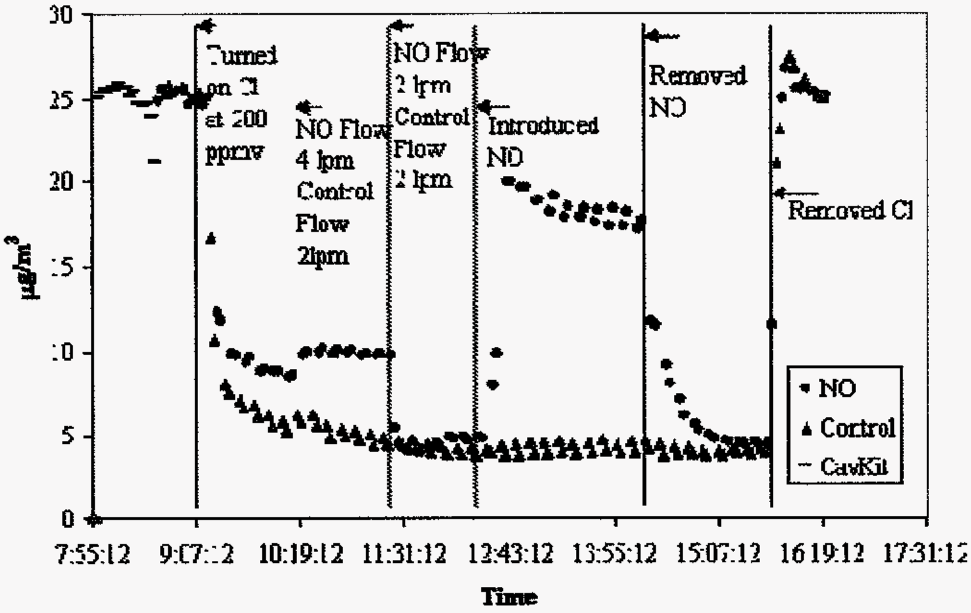

Figure 4. Effects of Injecting NO into KCl Impinger

Identical experiments were performed to elucidate the effects of injecting pure SO_2 into the KCl impinger. The reactor was operated with a Cl concentration of 200 ppmv, again providing mercury oxidation of nearly 80%. SO_2 was injected into the impinger at the valve settings found to produce a concentration of 300 ppmv in the KCl impinger. Data from this experiment are presented in Figure 5. Mercury measurements for the sample stream with the SO_2 injection are labeled "SO_2" and the standard sample stream is again labeled "Control". In this experiment the two sample streams were not reporting exactly the same value of elemental mercury. This is most likely a result of residual SO_2 in the impinger from the previous SO_2 mass balance experiment. At the point when 300 ppmv SO_2 was introduced into the "SO_2" impinger all of the mercury in the system was reported as elemental in this stream. When the SO_2 was removed, the amount oxidized mercury went back to 80%.

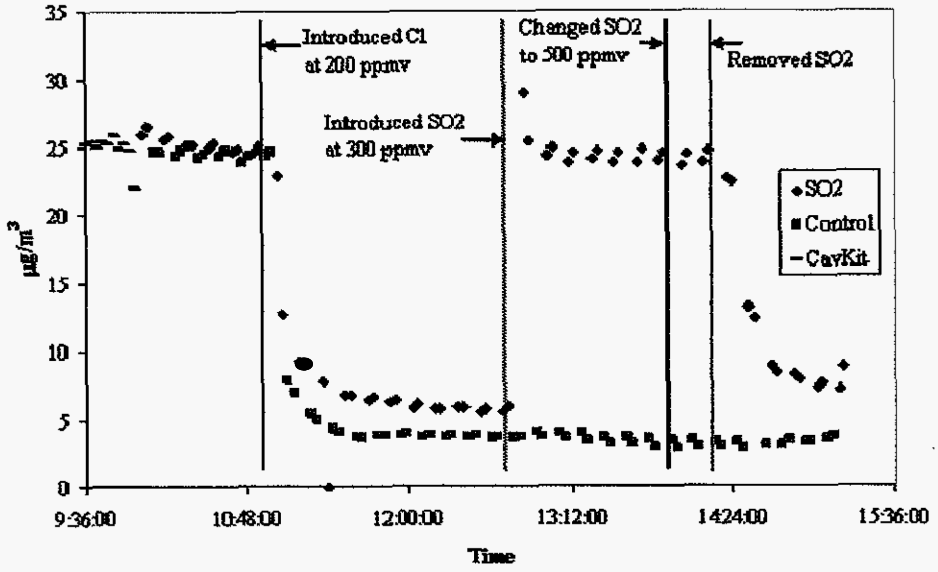

Figure 5. Effects of Injecting SO_2 into KCl Impinger

For conditions of 200 ppmv Cl and 500 ppmv NO, oxidation of 28.6% was observed when the NO was injected directly into the impinger and 28.2% when NO was injected into the flame. These data indicate that all of the reduction in mercury oxidation was occurring in the KCl impinger, relative to the amount of oxidation in the experiments with chlorine only. Model results confirm that these observed effects of NO are not occurring in the reactor due to gas-phase reactions. Impinger experiments also show that 300 ppmv SO_2 in the KCl impinger reduced all oxidized mercury to elemental. Similar results were found when the SO_2 was injected into the burner.

These results have led us to question the role of the KCl impinger. In the absence of NO and SO_2, it appears as though HOCl is being formed in the KCl impinger, via the reaction:

$$Cl_2 + 2H_2O = HOCl + H_3O^+ + Cl^-$$

The HOCl in turn oxidizes the elemental mercury; hence the appearance of oxidation without the NO and SO_2 additions, but limited oxidation under those conditions. The work of (Linak et al. 2001) from EPA indicates that these interactions could be limited by the addition of sodium thiosulfate. Presently, we are studying these reactions to determine the issue with regard to the wet sampling system. As yet, no conclusions have been drawn, especially in light of the model predictions matching the experimental data in the absence of NO and SO_2. Consistent with our experiments, good agreement between the model and experimental data from UConn was also demonstrated previously by Qiu et al.

Experimental Results – Oxygen

Previous mercury oxidation experiments were performed at a measured O_2 concentration of 0.88% exceeding the expected value of 0.46%. To compare data collected at different O_2 concentrations and to infer oxidation behavior at O_2 concentrations representative of coal combustion flue gas, experiments and model predictions were performed. Experiments spanned a range of O_2 concentrations from 0 to 3% with one fuel rich experiment. These data are presented in Figure 6 and show little or no dependence of oxidation on O_2 concentration at concentrations above zero.

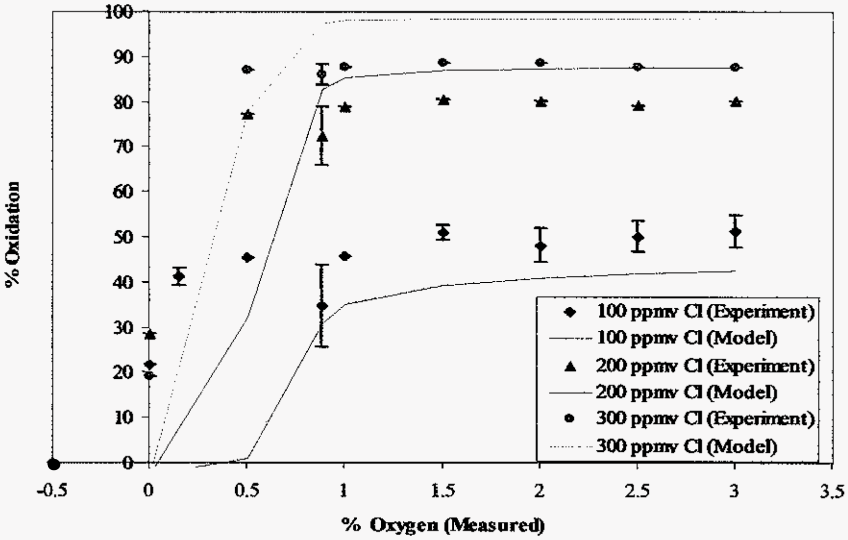

Figure 6. Experimental Effects of Oxygen Concentration on Mercury Oxidation and Model Predictions

MODELING

The majority of the homogenous Hg rate constants reported in the literature have been based on hard-sphere collision limits and/or empirical data-fitting procedures. Recently, rate constants developed using theoretical methods such as quantum chemistry and transition state theory have been reported (Wilcox et al. 2004). Wilcox et al. provide theoretical rate constant estimates for the following seven reactions:

$Hg + Cl + M = HgCl + M$ (1)
$Hg + Cl_2 = HgCl + Cl$ (2)
$Hg + HCl = HgCl + H$ (3)
$Hg + Cl_2 + M = HgCl_2 + M$ (4)
$HgCl + Cl + M = HgCl_2 + M$ (5)
$HgCl + HCl = HgCl_2 + H$ (6)
$HgCl + Cl_2 = HgCl_2 + Cl$ (7)

Although the reaction sequence above does not consider Hg oxidation mediated by HOCl, it clearly accounts for the major channel of Hg oxidation by Cl. The HOCl reactions are potentially as important as those of Cl_2 and HCl, which have been found to be less important than the Cl reaction. To evaluate these theoretical rate constants, the above Hg reaction sequence was coupled to the sub-models elucidating Cl, NO_x, and SO_x chemistry as assembled from literature by Helble and co-workers (Qiu et al. 2003) as part of the University of Connecticut (UConn) subcontract to this project. This overall reaction mechanism scheme is referred to as 'Wilcox Hg-UConn' mechanism.

Data from the Utah experimental system (Fry et al. 2005) were used to evaluate the model predictions of the Wilcox Hg-UConn mechanism. The predictions using the original UConn mechanism are also presented for comparison with those of Wilcox Hg reaction rates. A summary of the experimental conditions is presented in Table 1.

Table 1. Operating conditions for Univ. of UT experiments

Case	Quench (K/s)	Residence time (s)	Initial temperature (K)
I	Low (~220)	7	1120
II	High (~440)	~8	1060

The temperature profile for both these cases is reported in literature (Fry et al.) and is reproduced in Figure 7. In both the cases, the post-combustion flue gas temperature increased to approximately 1400K prior to the controlled quench. The system was modeled as a plug flow reactor (PFR) starting with an equilibrium composition calculated at 1100 K corresponding to the burner stoichiometry. The equilibrium predicted concentration of NO (38.2 ppmv) at this temperature also agreed well with the reported value of 38 ppmv. The remainder of the reported temperature profile was implemented without any modifications.

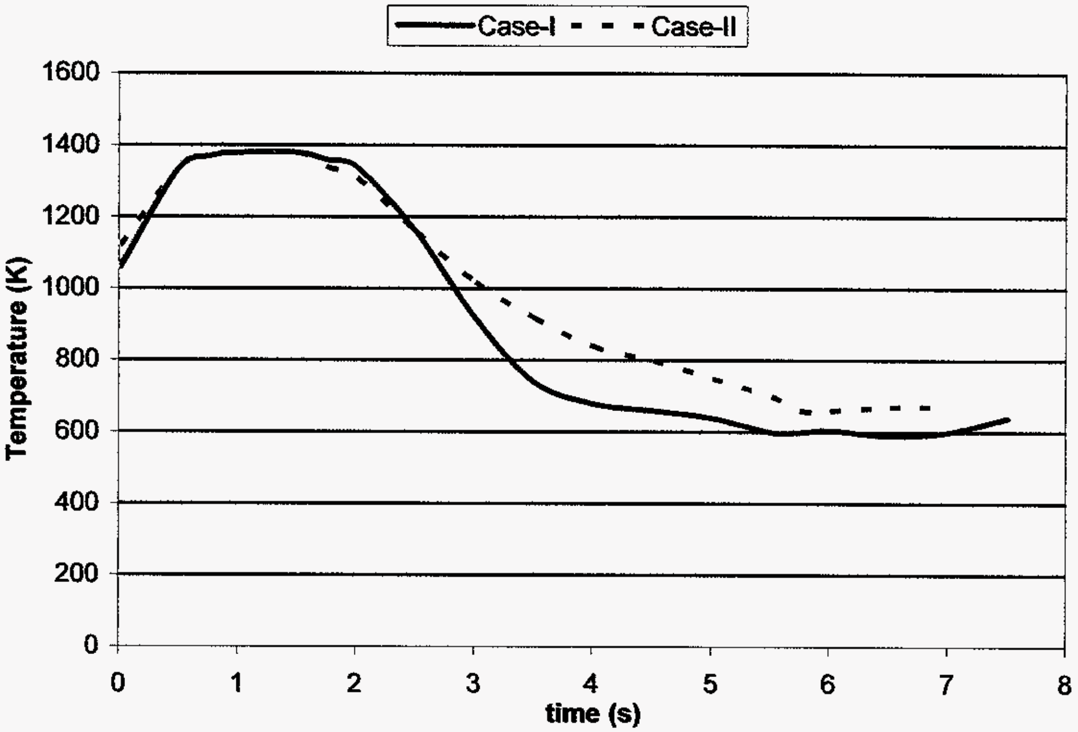

Figure 7: Temperature profile reported by Fry et al. for the Univ. of UT system

The model predictions using the UConn and the Wilcox Hg-UConn mechanisms are compared against the experimental data in Figure 8. Recall that the difference in the two models is the Hg reaction scheme alone and the corresponding rate constants.

At quench rates of 220 K/s (Case-I), the UConn mechanism predicts Hg oxidation accurately over the entire range of chlorine concentrations, however, at faster quench rates of 440 K/s (Case-II), there is greater divergence from the data. The scatter is especially high at lower chlorine concentrations (< 400 ppmv). Both mechanisms predict greater oxidation at the higher quench rate, in agreement with the data. In fact, this is the only trend that is predicted by the Wilcox Hg-UConn mechanism. The most significant discrepancy with the theoretical reaction parameter set is that the predictions are insensitive to Cl concentration. For the two quench rates, the Wilcox Hg-UConn mechanism predicts on average 35 and 77% oxidation across 100-700 ppmv HCl suggesting that this scheme, in its present form, is inadequate to model the experimental system. One of the factors for the discrepancies in the Wilcox-derived reaction scheme could be the absence of any Hg interactions with HOCl, though such reactions are generally believed to have only a secondary influence in comparison to Cl/Cl_2.

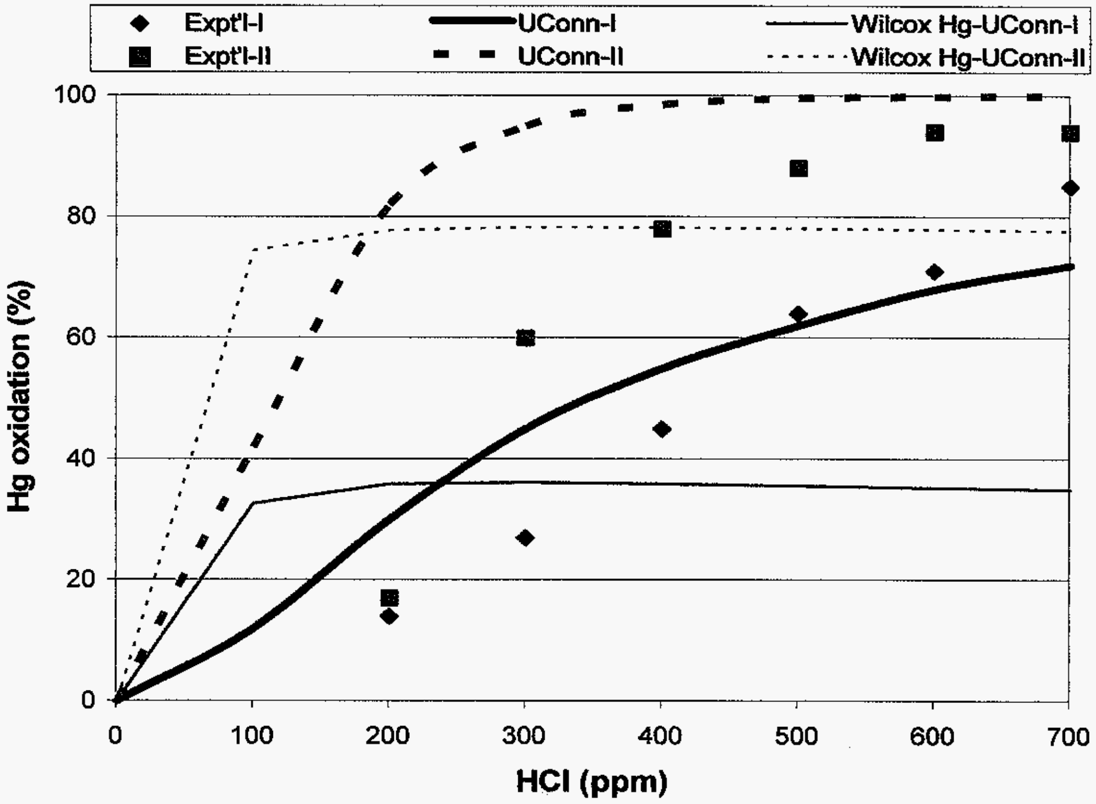

Figure 8: Comparison of model predictions (UConn and Wilcox Hg-UConn) with experimental data of Fry et al.

CONCLUSIONS

The accomplishments during the third year have included:

- Experimental runs investigating the role of NO and SO_2.
- Experiments and modeling regarding the role of oxygen.

During this next year, we will continue to investigate the effects of NO and SO_2 and their role in the impinger chemistry. If the oxidation is occurring in the impingers, adjustments to the model will be necessary since the predictions did match the data. In addition we will begin disperse phase experiments on coal constituents, namely iron and calcium.

PRESENTATIONS and PUBLICATIONS

A. Fry, B. Cauch, G. D. Silcox, J. S. Lighty, "Experimental evaluation of the effects of quench rate and quartz surface area on homogeneous mercury oxidation," accepted to the 31st International Symposium on Combustion, Heidelberg, Germany (2006).

A. Fry, J. Lighty, G. Silcox, and B. Cauch, "Experimental Study of Homogeneous Mercury Oxidation Reactions Designed to Facilitate Model Development and Mechanism Validation," International Conference on Air Quality, Arlington, VA, September 2005.

C. L. Senior, A. Fry, J. S. Lighty, G. D. Silcox, "Detailed kinetic modeling of homogeneous mercury oxidation reactions in a 1000 Btu/hr quartz furnace, presented at 22nd Annual International Pittsburgh Coal Conference, Pittsburgh, PA, September 2005.

ACKNOWLEDGEMENTS

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REFERENCES

Fry, A.R.; Lighty, J.S.; Silcox, G.D. 2005. *Proc. 30th International Technical Conf. on Coal Utilization & Fuel Systems*, April.

Linak W. P. et al., 2001. *J. Air & Waste Manage. Assoc.*, 51, p. 688.

Qiu, J.; Helble, J.J.; Sterling, R., 2003, *Proc. 12th International Conf. on Coal Sci.* Cairns, Australia, November.

Sterling, R. O.; Qiu, J.; Helble, J. J. 2004, 18th Annual ACERC Technical Conference, Provo, Ut, February 12.

Wilcox, J., 2004. "On the Path to Elucidating the Speciation of Mercury in the Flue Gases of Coal Combustion", PhD Thesis, University of Arizona.