Title: FUNDAMENTALS OF MERCURY OXIDATION IN FLUE GAS

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Objective

On March 15, 2005, EPA announced the final regulations for mercury emissions from coal-fired power plants. The regulations embrace a cap-and-trade approach, which favors the use of combinations of existing air pollution control equipment ("co-benefits"). To effectively satisfy the new regulations and remove mercury from flue gas, an adequate fundamental understanding of the system chemistry is required. The objective of this project is to understand the importance of gas- and solid-phase constituents in mercury oxidation reaction chemistry. The effects of chlorine, nitrogen oxide, sulfur dioxide and ash particles on mercury oxidation are being studied. These oxidation reactions are believed to be important because oxidized mercury is effectively removed by wet flue gas desulfurization systems at no additional cost to plant operation.

Accomplishments To Date

At the University of Utah, the mercury analysis equipment, designed and constructed by Southern Research Institute, has been tested and proven to be effective. Mercury analysis has been performed on a 5 MMBtu/hr coal-fired boiler and mercury concentrations and speciation varied with changes in boiler operation as expected. Introduced mercury spikes were also recovered adequately. The mercury sampling and conditioning system were modified to analyze mercury during gas phase experimentation in a natural gas-fired, quartz-line, drop-tube furnace. Mercury mass balances were performed in the drop tube furnace and discrepancies between calculated mercury concentration and measured mercury concentrations were never greater than 13% with mercury concentrations ranging from 50 to 500 $\mu g/m^3$. Mercury was recovered within 2 % of the calculated concentration at concentrations representative of typical coal combustion (25 $\mu g/m^3$).

Mercury oxidation reactions with chlorine have been conducted in the drop tube furnace. Comparison between data generated and modeling results by REI suggest that oxidation reactions are being inhibited. A possible cause for inhibition is the scavenging of chlorine radicals by the quartz walls of the reactor. Surface scavenging in the reactor was studied by varying quench rate and surface area in the quench section of the reactor. Manipulation of quench rate was not possible in the original drop tube due to internal cooling within the graphite heating element. To eliminate this problem a new drop-tube reactor was constructed. Oxidation reactions in this new furnace have been conducted using quench rates of -440 K/s and -210K/s. Observed oxidation was 50 % greater at 300 ppmv chlorine for the high quench experiments. This result is explained by chlorine radical chemistry suggested by Procaccini et al. (2000). Quartz surface area in the quench section was varied from 1000 cm^2 to 3000 cm^2. The increase in surface area reduced oxidation by 70% at a chlorine concentration of 300 ppmv using the high quench rate, suggesting that surfaces have an effect on chlorine chemistry and in turn mercury oxidation.

The effect of SO_2 on mercury oxidation with chlorine was also investigated. Sulfur dioxide drastically slowed the rate of mercury oxidation by reacting with chlorine radicals. Sulfur dioxide concentrations of 300 ppmv resulted in no oxidation with reactor chlorine concentrations of 300 ppmv. With no SO_2 these same reactor conditions produced almost 70% oxidation.

At the University of Connecticut, the flue gas temperature profile for the entrained flow reactor, at equivalence ratios of 0.9 and 0.98. (from post-flame to sampling system), has been obtained. A thermodynamic data file for all pertinent chemical species primarily from NIST-JANAF, CHEMKIN database has also been assembled. The mercury homogeneous model was revised by including mercury reactions from Niksa, et al. (2001) and Qui, et al. (2003) and supporting sub-mechanisms. The total number of reactions is 168. This revised model matched the baseline case simulations by Niksa, et al (2001). Additional modeling results for the effect of SO_2, under different time/temperature history were also obtained to evaluate the model. These will be compared with experimental results obtained at the University of Utah.

References

- Qiu, J., Helble, J.J., Sterling, R., "Kinetic Modeling Of Cl-Containing Species Transformations And Their Effects On Mercury Oxidation Under Simulated Coal Combustion Conditions", Presented at the 12th International Conference on Coal Science, Cairns, Australia, Nov (2003)
- Niksa, S., Helble, J.J., Fujiwara, N., "Kinetic Modeling of Homogeneous Mercury Oxidation: The Importance of NO and H_2O in Predicting Oxidation in Coal-Derived Systems", Environmental Science & Technology 35 (2001) 3701-3706
- Procaccini, C., et al. "Presence of Chlorine Radicals and Formation of Molecular Chlorine in the Post-Flame Region of Chlorocarbon Combustion," Environmental Science and Technology, 34, 4565-4570 (2000).

Future Work

Planned work for subsequent periods of this project is detailed as follows:

- Continued investigation and publication of the effects of quartz surfaces on mercury oxidation with chlorine.
- Experimental investigation of the effects of NO_x, SO_2 on gas-phase mercury reactions with chlorine in the new drop-tube furnace.
- Experimental investigation of mercury oxidation reactions with oxygen and bromine
- Comparison of drop-tube oxidation data and results from REI Mercury oxidation model.
- Identification of the effects of fly ash particles, particularly unburned carbon, on mercury oxidation in the entrained-flow reactor at the University of Connecticut.
- Update of the REI Mercury Oxidation Model with new heterogeneous oxidation mechanisms generated by the University of Connecticut entrained flow experimentation and literature data.
- Coal combustion experimentation for model validation.
- Feasible mercury control schemes evaluated using the REI Oxidation Model and U Furnace experimentation.

List of Paper Published/Conference Presentations

- "Fundamentals of Mercury Oxidation in Flue Gas," Andrew R. Fry, JoAnn S. Lighty, Geoffrey D. Silcox, poster at the 18th Annual ACERC Technical Conference, 2004.
- "Fundamental Homogeneous Reactions of Mercury in Coal Fired Utility Boilers," Andrew R. Fry, JoAnn S. Lighty, Geoffrey D. Silcox, 30th International Technical Conference on Coal Utilization & Fuel Systems, April 2005.

Students Supported Under this Grant

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