REDUCTION OF INHERENT MERCURY EMISSIONS IN PC COMBUSTION

Semi-annual Report

Reporting Period: 01/01/1998 through 06/30/1998

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Report Issue Date: 08/19/1998
DE-FG22-95PC95216--06

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Abstract

Mercury emission compliance is one of the major potential challenges raised by the 1990 Clean Air Act Amendments. Simple ways of controlling emissions have not been identified. The variability in the field data suggests that inherent mercury emissions may be reduced if the source of this inherent capture can be identified and controlled. The key mechanisms appear to involve the oxidation of the mercury to Hg^{++} , generally producing the more reactive HgCl_2 , followed by its capture by certain components of the fly ash or char. This research focuses on identifying the rate-limiting steps associated with the oxidation step.

Work in this reporting period focused on the development and application of a kinetics model to the oxidation data developed in the present program and literature data under MSW conditions. The results indicate that the pathway $\text{Hg} + \text{Cl} = \text{HgCl}$ followed by $\text{HgCl} + \text{HCl} = \text{HgCl}_2 + \text{H}$ predominates over $\text{Hg} + \text{Cl}_2$ under high-temperature conditions. This primarily occurs because Cl_2 concentrations are too low under the present conditions to contribute significantly.

Introduction and Objectives

The 1990 Clean Air Act Amendments presented a major challenge for the utility industry. The legislation requires that the U.S. Environmental Protection Agency set emission standards for the 189 compounds or compound families identified in the act as air toxics. Evaluations by EPRI have identified 37 of these species as concerns in power generation (Feldman et al., 1993). These include toxic organics, HCl, HF, and trace metals. Metals frequently mentioned include: arsenic, barium, beryllium, cadmium, chromium, cobalt, copper, lead, manganese, mercury, molybdenum, nickel, selenium and vanadium. The organic compounds considered include formaldehyde, various aromatic hydrocarbons, and chlorine-substituted dioxins and furans.

The EPA initially addressed the problem of estimating emissions through literature values of emission factors (Radian, 1989). The major weaknesses of this approach include the broad range of trace element content in coal, the wide variety of boiler design and operating conditions, and the variable performance of pollution control equipment, assuming any exists (Chow and Torrens, 1994). In response to this perceived weakness in the emission database, EPRI and DOE have performed comprehensive studies of power plant emissions. Although ongoing, critical trends have emerged from these data that provide direction.

First, the emissions of toxic organic compounds have generally been below detection limits. This is a consequence of high combustion temperatures sustained over long periods of time. In addition, chlorine levels are usually so low in coals that it becomes difficult to synthesize the toxic chlorinated dioxin congeners. Finally, the presence of SO₂ from the fuel-sulfur has been shown to interfere with the downstream dioxin formation process. In any case, toxic organic emissions are not perceived to be a major problem.

Measurements on the trace metals listed above generally show that over 90% of the initial elements present in the coal are collected with the bottom ash or the fly ash. These metal compounds have low volatility and condense out onto the existing fly ash, where they are collected by the fabric filter or the electrostatic precipitator (Chow and Torrens, 1994; Devito et al., 1994). However, the removal efficiencies do show considerable variability.

Only mercury and selenium generally show low removal efficiencies and correspondingly high emission factors. This is attributed to the high volatility of these elements in both their combined and uncombined forms. Rather than condensing onto fly ash particles, these species tend to stay in vapor phase, pass through the particulate control systems, and become emissions. The data show, however, wide variation in the emission indices of these two elements. Some forms of mercury (e.g., Hg⁺⁺) appear to be less volatile than the element, and show a greater tendency to collect on the fly ash. The processes governing inherent mercury capture are not well understood. The reason for this wide variability in emissions is not well understood (Chow and Torrens, 1994). This is a concern because mercury and selenium appear to be the only two elements, beyond the traditional pollutants, that may become air toxic compliance problems for the utility industry. In recognition of this, there has already been substantial work on identifying ways of reducing emissions.

A recent environmental assessment of the power plant mercury problem helps to focus concerns (Fthenakis et al., 1995). They find that U.S. power plants contribute about 1% of the world's Hg burden, the bulk being natural volcanic emissions. The lifetime of elemental Hg in the atmosphere is around 0.5-1.5 years, and that for oxidized Hg is of the order of hours. Elemental emissions are essentially dispersed world wide before deposition, and they thus do not represent a significant increase upon the natural

deposition. Oxidized Hg, however, will deposit in a footprint downstream of the power plant, leading to a potentially significant increase in local Hg. This suggests a dilemma in which furnace generation of elemental Hg (which is difficult to capture) may not significantly affect the environment, while furnace generation of oxidized Hg (which is easier to capture) may lead to more local degradation. At issue is whether the increased capture for the oxidized Hg offsets the inherently more concentrated deposition pattern.

Ideas for post-flame mercury control have centered around existing air pollution control devices, or relatively simple modifications of these that improve their specific mercury performance. Much of this work was originally done to control toxic metals from MSW incineration, and it is now being reevaluated for the lower metals content of coal. One example is the hydrated lime spray dryer for SO₂ control. The mercury removal of an unmodified spray dryer system is of the order of only 30-50%, but the addition of activated carbon in the flue gas leads to greater than 90% removal in some tests (Gleiser and Felsvang, 1994); not all results have shown such high efficiency, however (Chow and Torrens, 1994). Wet scrubbers are relatively effective against Hg⁺⁺ due to their low operating temperatures (ca. 45°C), but still remove only 50-70% of elemental mercury (Meij, 1991). Dry sorbent injection has been tested at EPA (Gullett and Raghunathan, 1994).

At present, mercury emission compliance presents one of the major potential challenges raised by the Clean Air Act Amendments. Simple ways of controlling emissions have not been identified. The variability in the field data suggest that means exist to reduce inherent mercury emissions, if these can be identified and controlled. The key mechanisms appear to involve the oxidation of the mercury to Hg⁺⁺, generally producing the less volatile HgCl₂. A portion of this may condense on ash particles in time to be collected by cold-side particulate removal equipment.

This research focuses on identifying the rate-limiting steps associated with inherent mercury capture. Key areas are enhancement of mercury oxidation and providing a sufficient amount of an appropriate surface (e.g., ash aerosol) under the correct conditions to promote inherent capture.

Results and Discussion

The furnace is down-fired by a swirl-stabilized diffusion flame burner by natural gas. The nominal firing rate is 16.1 kW. A mercuric acetate solution is sprayed into the flame, where the temperature is sufficiently high to ensure that all mercury is reduced to elemental mercury. At the throat of the furnace, quench air is added to reduce the gas temperature to the desired level. The HCl is also introduced at this point. Auxiliary heaters are used to hold the reaction temperature fairly constant throughout the remainder of the furnace, up to the sampling point.

The analytical procedure follows EPA Method 29 with the exception that an uncooled quartz probe is used without a filter. This is acceptable since no particulate matter is present in the furnace. Problems reported by others regarding SO₂ and Cl₂ interferences on the speciation measurement are not expected to be a problem here due to the absence of these two species in the furnace gas. Details of the analytical procedure are presented in the third progress report.

Figure 1 shows the current data base generated in the furnace. In both the present data and the data of Hall et al. (1991), the yield of oxidized mercury is significantly above equilibrium at these high temperatures. Modeling by the present project suggests that this super-equilibrium conversion of elemental mercury to oxidized mercury at high temperatures is due to the presence of free radical chemistry involving the relatively simple radicals that are abundant under these conditions. The project experiments were modeled as a plug flow reactor.

Figure 1. Fraction oxidation of Hg as a function of temperature and HCl for a residence time of ~1 s.

Several reaction mechanisms were combined to develop the model. Elementary reactions for the H₂-CO-O₂ system were obtained from a basic combustion mechanism (Warnatz *et al.*, 1996), with the restriction that no carbon-based reactions would be used except those exclusively involving CO and CO₂. Reactions involving chlorine species were taken from a mechanism used to study chlorine inhibition of CO flames that was compiled by Chang, Karra and Senkan (1987). No reactions involving organic chlorine compounds were used.

The reactions involving the interaction between mercury and chlorine were partially obtained from a study by Horne *et al.* (1968). Horne directly measured the following rates for the formation of mercurous chloride or calomel (Hg_2Cl_2):

Reaction 2 is of little interest in this study, since typical operating temperatures are well above 382 °C, the decomposition temperature at which Hg_2Cl_2 dissociates into Hg and HgCl_2 . Also, since the concentration of HgCl is low (with mole fractions on the order of 10^{-15}), the probability of two HgCl molecules reacting is low. For these reasons, reaction 2 was not included in the mechanism. Reaction 1, however, is of interest since it is an initial step in the formation of HgCl_2 .

Horne gives an approximate second order rate constant (k_{1a}) for reaction 1 as between 0.9×10^{13} and 3×10^{13} cc/(mol • sec), with an error factor of up to but not exceeding a factor of three. This reaction rate constant was found to be independent of temperature over a narrow range. For this study, a rate constant of 3×10^{13} cc/(mol • sec) and an activation energy of zero were used. The backward reaction rate (k_{1b}) equals $2.5 \times 10^{15} \text{ T} \cdot \text{cc}^2 / (\text{gmol}^2 \cdot \text{sec} \cdot ^\circ \text{K})$.

No data on the mechanism or reaction rate for the conversion of HgCl to HgCl_2 (mercuric chloride) were readily available. Due to the low reactant concentrations, the contribution of the reaction:

to the overall HgCl_2 production was assumed to be insignificant compared to the production from the following reaction:

The rate constant for reaction 4 was estimated to be 1×10^{14} cc / (gmol • sec • °K), based on typical gas-kinetic collision-rate-constant values. Therefore, in summary, only equations 1 and 4 were used in the Mark II model for the Cl mechanism.

Alternatives to reaction 4 are also being considered (Cole, 1998). These include:

Rates for these reactions are being calculated from ab initio techniques at Lawrence Livermore National Laboratory as part of a collaboration under the present grant. These reactions will be evaluated in the model in the future.

Recently, two modifications have been made to the model. First is the addition of free radicals as reactants in the model. In the original model, complete combustion of methane and air was assumed to produce CO₂, H₂O, N₂ and O₂. This has been modified by assuming a full equilibrium distribution (H, HO₂, H₂, H₂O₂, O, OH, and CO) as the initial composition for the model. The second change to the model was the inclusion of the Cl₂-mechanism:

The reaction rate constant was calculated to be approximately $7.1 \times 10^{10} \text{ T}^{-1} \text{ cc}^2 / (\text{gmol}^2 \cdot \text{sec} \cdot ^\circ \text{K})$ based on data by Hall *et al.* (1991).

Figure 2 compares the experimental and Mark II model results for the 922 °C case. The largest discrepancy between the model and the experimental work is that the model does not predict the plateau seen in both Hall's data and the UW data. In the sets of experimental data, once a threshold value of hydrochloric acid was passed, higher hydrochloric acid concentrations did not lead to greater conversion from elemental to oxidized mercury. However, since the 453 ppm HCl point is the only data point which does not match the trend predicted by the model, repeating the experimental procedure for that data point may help to determine if this discrepancy is a result of modeling inaccuracies or experimental error.

By running the model with both the Cl and Cl₂ mechanisms for mercury oxidation and then with only the Cl-mechanism and only the Cl₂-mechanism, the relative importance of these mechanisms in the oxidation process became apparent. The Cl-mechanism provided all the mercury oxidation seen in the modeling. The Cl₂-mechanism was not a significant contributor. Future tests to confirm the importance of the Cl-mechanism are planned for future work.

Figure 2. Comparison of University of Washington experimental data at 922 °C with Hall data and computer models

Conclusions

The data are consistent with the high-temperature path for mercury oxidation being driven by Cl-atoms. The strong temperature dependence observed in both the present data and the data of Hall et al. (1991) appear because of the strong temperature dependence of Cl-atom oxidation. The superequilibrium oxidation appears to occur because of a slow reverse rate for the reaction $\text{HgCl} + \text{HCl} = \text{HgCl}_2 + \text{H}$. The Cl_2 mechanism is not indicated to be active at these conditions.

References

- Chow, W. and I. M. Torrens: Managing power plant trace substances emissions: An overview. *Proc. American Power Conference*, **Vol. 56-1**, p. 427 (1994).
- Cole, J.A.: Personal communication, August 18, 1998.
- Devito, M., L. Rosendale, V. Conrad, and B. Jackson: Trace elements in coals and their emissions. *Proc. American Power Conference*, **Vol. 56-1**, p. 438 (1994).
- Feldman, P. L., K. S. Kumar, and J. M. Quimby: *Power* **137(7)**, 48 (1993).
- Gleiser, R. and K. Felsvang: Mercury emission reduction using activated carbon with spray dryer flue gas desulfurization. *Proc. American Power Conference*, **Vol. 56-1**, p. 452 (1994).

Gullett, B. K., and K. Raghunathan: *Energy and Fuels* **8**, 1068 (1994).

Meij, R.: *Water, Air, and Soil Pollut.* **56**, 21 (1991).

Radian Corporation: *Estimating Air Toxics Emissions from Coal and Oil Combustion Sources*. EPA Report 450/2-89-001 (1989).