REDUCTION OF INHERENT MERCURY EMISSIONS IN PC COMBUSTION

Semi-annual Technical Report

Report Period: 07/01/1997 through 12/31/1997

Authors: John C. Kramlich, Rebecca N. Sliger, David J. Going

Report Issue Date: 08/06/1999

DE-FG22-95PC95216

Department of Mechanical Engineering
Box 352600
University of Washington
Seattle, Washington 98195-2600

Disclaimer

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United State Government or any agency thereof.

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 of oxidation data as a function of temperature and HCl concentration. The temperature range was 800-1200 °C. The results show a lower level of oxidation than indicated by the earlier data of Hall et al. (1991). One possible reason for this discrepancy was the preheating of the HCl stream in the Hall experiment, leading to the partial decomposition of the HCl into reactive species. In the present experiments, the HCl was injected as a cold stream. The measured oxidation at these conditions was substantially above that predicted by equilibrium, indicating the dominance of finite rate chemistry. This is to be explored in subsequent work.

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 and the reason for the wide variation in emissions are 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 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 low concentration of these two

species in the furnace gas. Details of the analytical procedure are presented in the third progress report.

The principal experimental difficulty has been uneven mercury feed rates to the furnace. This has been traced to uncontrolled precipitation of the mercuric acetate solution used to feed the reactor. This causes the presence of both soluble and insoluble suspended mercury in the solution used in the syringe drive, resulting in mercury gradients in the solution and uneven feeding concentrations. This will be addressed by acidifying the mercury solution with nitric acid.

A test series has been initiated exploring the influence of both HCl concentration and temperature on the extent of oxidation. The results, shown in Figure 1, suggest an increasing extent of oxidation with temperature. Another comparison is shown in Figure 2, in which the present data (at 922°C) is contrasted with the data of Hall et al. (1991) at 900°C. In both cases, no oxidation is noted without hydrochloric acid. However, once a threshold value of hydrochloric acid is passed, higher hydrochloric acid concentrations do not lead to greater conversion from elemental to oxidized mercury. Consistent with Hall's data, higher temperatures tend to promote higher conversions.

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

Figure 2 Comparison of experimental data at 922 °C and Hall data (1991) at 900 °C

There are important differences, however, between Hall's data and the present results. While the general trend of the relationship between temperature, hydrochloric acid concentration and mercury speciation is consistent, the Hall data suggests significantly higher mercury oxidation than the University of Washington data. A probable reason for this discrepancy was identified from the model. In the modeling, the principal process generating HgCl_2 is the reaction sequence:

In the UW experiment, the HCl is injected cold, with an initial Cl-atom concentration of zero. The Cl-atom concentration builds over time from reactions between the HCl and the radical pool, *e.g.*,

In the Hall *et al.* experiment, both the Hg and HCl streams are preheated for a considerable time before being mixed at the start of the reactor test section. This leads to a significant Cl-atom generation before the start of the test section. This causes the Hall *et al.* experiment to appear more reactive than the UW experiment if both are modeled with identical initial conditions. Hence, the Hall *et al.* experiment shows higher conversions at comparable conditions.

We are presently analyzing the present data set with a kinetic model. This will be reported in the subsequent progress report.

Conclusions

The data indicate a high-temperature path for mercury oxidation. However, the present experiment shows lower oxidation than indicated by the data of Hall et al. (1991) for comparable conditions. It is suggested that the preheating of the HCl stream in the Hall experiment led to a partial decomposition of the HCl into reactive intermediates (Cl or Cl₂), causing the experiment to appear to be more “reactive”.

References

- Chow, W. and I. M. Torrens: Managing power plant trace substances emissions: An overview. *Proc. American Power Conference*, **Vol. 56-1**, 427 (1994).
- Devito, M., L. Rosendale, V. Conrad, and B. Jackson: Trace elements in coals and their emissions. *Proc. American Power Conference*, **Vol. 56-1**, 438 (1994).
- Feldman, P. L., K. S. Kumar, and J. M. Quimby: *Power* **137(7)**, 48 (1993).
- Fthenakis, V. M., *et al*, “An assessment of mercury emissions and health risks from a coal-fired power plant”, *Journal of Hazardous Materials*. **44**, 267-283 (1995).
- 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).
- Hall, B., Schager P., Lindquist, O., “Chemical Reactions of Mercury in Combustion Flue Gases”, *Water, Air and Soil Pollution*. **56**, 3-4 (1991).
- 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).