

TITLE: REDUCTION OF INHERENT MERCURY EMISSIONS IN PC COMBUSTION **DATE:** May 1997

PI: John C. Kramlich
kramlich@u.washington.edu
(206) 543-5538
FAX (206) 685-8047

STUDENTS: Rebecca N. Sliger, Ph.D. Candidate; and David J. Going, MS Student

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

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I. ABSTRACT

OBJECTIVE: At present, mercury emission compliance presents one of the major potential challenges to the electric utility industry raised by the Clean Air Act Amendments. Simple ways of controlling emissions have not been identified. The variability in retention of mercury by ash in field data suggests that means exist to reduce inherent mercury emissions, if the factors controlling the variability can be identified and controlled. Key steps appear to include the oxidation of elemental mercury to Hg⁺⁺, generally producing the slightly less volatile HgCl₂. Some forms of the oxidized mercury appear to have a capacity to form complexes with certain types of fly ash aerosols. The principal thrust of the 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 that promote inherent capture.

WORK DONE AND CONCLUSIONS:

The entrained flow coal reactor was modified to provide an isothermal environment with T=200-1000°C and one second residence time. An air-assist atomizer was added into the flame zone to atomize a dilute mercuric acetate solution into the flame. The high temperature of the flame provides for vaporization of the mercury and reduction into Hg⁰. A sonic air staging lance partway through the furnace adds sufficient dilution air to reduce the furnace gas temperature to the target level. Hydrochloric acid is added to the furnace gases along with this dilution air. The relatively low surface/volume ratio of the furnace is designed to prevent surface reactions, particularly the reduction of oxidized mercury noted on convective surfaces at lower temperatures. For this reason, dilution cooling of the flame gases to the target temperatures was preferred over the use of high surface area convective cooling.

A modified version of the Method 29 multimetals train was assembled and tested. Since mercury was the only metal targeted in the present experiments, the procedure for the initial impinger bank was simplified. Also, since the initial test series focused only on mercury reactions in the gas phase, some of the equipment and procedures associated with determining the particulate catch were eliminated. Mercury is determined by cold vapor atomic absorption after it is released from the digested catch solution by reduction.

Testing has examined the factors controlling gas-phase mercury oxidation to determine the reaction order with both Hg and Cl. At present, we are continuing tests which focus on the role of free radicals as promoters of the oxidation process. The conditions have focused on the burnout step as applied to reburning for NO_x control. At

these high temperatures, however, the Hg will generally remain in elemental form. Thus, the test matrix generally extends to lower air addition temperatures than is usually common in reburning practice.

Some tentative results suggest a direct role of certain metals present in coal ash in directly catalyzing Hg oxidation. This may provide an additional role for the metals beyond the potential complexing behavior mentioned above. This is to be explored following the homogeneous testing.

A kinetic model of the high-temperature oxidation process involving elementary reactions has been assembled and tested. The model makes use of a literature mechanism for the behavior of the HCl/Cl/Cl₂ system to establish the population of Cl-atoms as a function of temperature. A literature value of the rate constant for the second-order reaction of Cl-atoms with Hg⁰ is used. (Hg+Cl=HgCl, HgCl+HCl= HgCl₂+H). The resulting behavior closely replicates the literature results of Hall et al. for MSW conditions, indicating the principal homogeneous oxidation pathway is driven by free radical chemistry rather than low-temperature chemistry. This also explains the anomaly in the Hall data in which conversion to Hg⁺⁺ increases at the highest temperatures examined, which contradicts the trends predicted by equilibrium analysis. The need for Cl-atoms as a driving force indicates that the reaction will only be favored at higher temperatures where equilibrium chlorine atom concentrations are significant.

SIGNIFICANCE TO FOSSIL ENERGY PROGRAM: The results of DOE- and EPRI-sponsored field testing show that organic emissions are generally insignificant. Likewise, most toxic metals are collected to greater than 90% concentrations in modern particulate control devices. The principal exceptions are Hg, Se, U-238, and Pb-210. The mercury and selenium are the least well controlled, with the Hg presenting the greatest environmental risk. Thus, Hg presents one of the greater possible challenges to coal-based power production arising out of the Clean Air Act Amendments. While Hg is well-controlled in spray dryer systems using activated carbon additives, not all sources are equipped with this equipment. The variability noted in the field data suggests that mechanisms promoting Hg retention onto fly ash exist. The current project is directed towards identifying the steps that control this process and suggesting means of promoting retention in full-scale systems without undue cost or system modification.

PLANS FOR THE COMING YEAR:

- Complete free radical oxidation testing.
- Perform a limited matrix examining catalytic effects.
- Complete model development, including secondary reactions and reverse steps.

II. HIGHLIGHT ACCOMPLISHMENTS

- Furnace modified to provide an isothermal time/temperature environment with a low surface/volume ratio to prevent catalytic reactions.
- Modified Method 29 Multimetals train set up and tested.
- Elementary studies on Hg oxidation as a function of basic parameters completed.
- Free radical-promoted oxidation of Hg investigated.
- Potential low-temperature catalytic oxidation path noted.
- Kinetic free-radical model developed that replicates literature trends.

III. ARTICLES AND PRESENTATION

Two papers are presently in preparation.