Title:	**Analysis of Bromine-Mercury Reactions in Flue Gas**

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Objectives

At flame temperatures, mercury exists entirely in its elemental form (Hg^o). In the absence of halogens, mercury tends to remain in the elemental form as the combustion gases cool. Elemental mercury is difficult to remove from exhaust gases. Oxidized forms of mercury, such as $HgCl_2$, HgBrCl, and $HgBr_2$, are more easily captured using existing air pollution control equipment. They are also more readily adsorbed by carbon-based sorbents. There is considerable experimental evidence that the oxidation of mercury in combustion systems can be achieved by the direct injection of bromine-containing compounds. The data show that bromine is more effective than chlorine at oxidizing Hg^o. The objectives of this project are (1) to understand the fundamental chemistry of bromine and mercury that leads to the oxidized forms, HgBrCl and $HgBr_2$, and (2) to be able to predict the extent of oxidation for industrial applications.

Accomplishments to Date

A review of the literature on mechanisms and models for bromine-mercury reactions has been completed. This has included equilibrium thermodynamics, bromine chemistry in combustion systems, bromine-mercury reactions, atmospheric chemistry of mercury and bromine, and full-scale test results on bromine injection and brominated activated carbons. The full-scale data show that Br is effective at oxidizing Hg. Brominated activated carbons can capture Hg, even in hot-side ESP applications, although their performance declines at high SO_3 concentrations.

Thermodynamic calculations and preliminary kinetic calculations show that HBr is unstable relative to HCl, and that significant concentrations of Br and Br_2 are available to react with mercury at temperatures below 900K. A preliminary set of elementary reactions for chlorine, bromine, and mercury species in coal flue gas has been assembled. Modeling results with this set do not suggest that the addition of bromine enhances homogeneous mercury oxidation. This finding does not agree with full-scale data involving bromine addition. This may be because heterogeneous and homogeneous oxidation are possible in the full-scale systems.

Experiments are in progress to examine homogeneous oxidation by bromine. In preparation for these experiments, the sample conditioning system that is part of the mercury analysis process has been modified to include sodium thiosulfate ($Na_2S_2O_3$) in the impinger that is filled with an aqueous solution of KCl. The experiments that were conducted without the thiosulfate show that molecular chlorine (Cl_2) is reacting with the water in the KCl impinger to form hydrogen hypochlorite:

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

Similar chemistry is expected with Br_2. The hypochlorite readily oxidizes elemental mercury to give high apparent levels of mercury oxidation. The addition of sodium thiosulfate ($Na_2S_2O_3$) prevents the formation of hypochlorite. Additional experiments show that SO_2, NO, and $Na_2S_2O_3$ do not reduce Hg^{++} to Hg^0 in the KCl solution.

Future Work

The project will investigate bromine-mercury chemistry in experiments conducted in a bench-scale, natural gas-fired, flow reactor. An improved understanding of the fundamental chemistry will allow optimization of the bromine injection process to enhance the formation of $HgBr_2$. Mixed systems in which the formation of $HgCl_2$, HgBrCl, and $HgBr_2$ are possible will also be examined. Key parameters that will be considered include the temperature profile in the reaction zone, the concentrations of NO_x, SO_2, moisture, and surface to volume ratio (m^2/m^3) in the reactor. Fixed-bed studies will be included to examine the effects of coal fly ash. A model of the oxidation process will be developed. CHEMKIN 4.0 will be used to examine practical application of various injection schemes under a variety of boiler conditions.

List of Conference Presentations

Gas-Phase Reactions of Mercury and Halogens in Combustion Environments. C. Senior, A. Fry, C. Montgomery, A. Sarofim, J. Wendt, G. Silcox, J. Lighty, J. Bozzelli. A&WMA 100th Annual Conference and Exhibition. Pittsburgh, PA. June 26-28, 2007.

Mechanisms and Models for Hg Oxidation Reactions. G. Silcox, A. Fry, J. Lighty, C. Senior. Mercury, Trace Metals, and Fine Particulates – Issues and Solutions, Topic-Oriented Technical Meeting 28, American Flame Research Committee/International Flame Research Foundation. University of Utah. March 13-14, 2006.

Students Supported Under this Grant

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