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.

Experiments are in progress in a 300 W, natural gas-fired, quartz-lined reactor to examine homogeneous oxidation by bromine as a function of concentration (0-40 ppm as HBr), quench rate (440 and 210 K/s), NO concentration (30 and 500 ppm), SO_2 concentration, and reactor surface area. The completed experiments show a linear dependence on bromine concentration up to about 25 ppm. For the high quench rate at 20 ppm, the extent of mercury oxidation is 50 % while for the low quench condition it is 85 %. Increasing the concentration of NO from 30 to 500 ppm has little effect on oxidation.

The effect of tripling the interior, quartz surface area of the reactor from 1000 cm^2 to 3000 cm^2 is a modest increase in oxidation although the scatter in the data prevents a firm conclusion. We increased the surface area by inserting a bundle of thin-walled quartz tubes. The insert decreases the reactor residence time by about 5 %.

Future Work

Future experimental work will focus on the effects of SO_2 on homogeneous oxidation and on heterogeneous oxidation on fly ash and activated carbon. A fixed-bed reactor will be used for the heterogeneous reactions. The kinetics of homogeneous oxidation of mercury by chlorine and bromine are still an active area of research. Future work will proceed in several steps: (1) a sensitivity study with the existing rate constants will be used to identity the most important reactions involving halogens and elemental mercury, (2) the reduced set of reactions will be fit to the bench-scale data to obtain improved rate constants, and (3) CHEMKIN 4.0 will be used to examine practical application of various injection schemes under a variety of boiler conditions.

List of Papers Published

Cauch, Brydger, Silcox, Geoffrey D., Lighty, JoAnn S., Wendt, Jost O. L., Fry, Andrew, and Senior, Constance L., Confounding Effects of Aqueous-Phase Impinger Chemistry on Apparent Oxidation of Mercury in Flue Gases, *Environ. Sci. Technol.*, **42**, 7, 2594 - 2599 (2008).

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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