TITLE: **MERCURY SPECIATION IN COAL-FIRED POWER PLANT FLUE GAS - EXPERIMENTAL STUDIES AND MODEL DEVELOPMENT**

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1. OBJECTIVE

The overall goal of the proposed project is to obtain a fundamental understanding of the catalytic reactions that are promoted by solid surfaces present in coal combustion systems and to develop a mathematical model that will describe key phenomena responsible for the fate of mercury in coal-combustion systems. This objective will be accomplished through carefully combining laboratory studies under ultra high vacuum conditions and under realistic process conditions using simulated flue gas with mathematical modeling efforts. Modeling studies will be used to facilitate understanding of key aspects of the proposed reactions and aid experimental work to reach maximum understanding of these complex processes. Laboratory-scale studies under ultra high vacuum conditions will be performed at Temple University to understand the fundamental aspects of chemical reactions that are catalyzed by solid surfaces in coal-combustion gases and that can not be elucidated in more complex and less sensitive systems at atmospheric pressures. The reactions to be studied include those between flue gas constituents and solid surfaces present in the fly ash and their impact on mercury speciation. The impact of these reactions on mercury speciation will then be tested under more realistic process conditions in the entrained-flow reactor at the University of Pittsburgh to obtain necessary kinetic data for the comprehensive mathematical model describing the fate of mercury in coal-combustion systems. The mathematical model developed by the University of South Carolina will be calibrated against laboratory data and its practical utility will be tested against pilot- and full-scale data available in the literature.

2. ACCOMPLISHMENTS TO DATE

A process model has been completed that describe homogeneous reactions of mercury species in a batch system. The model accounted for interactions between the following species: Hg, HgCl, Cl, $HgCl_2$, HOCl, OH, HCl, H, H_2, O, H_2O, ClO, O_2, HO_2, H_2O_2, Cl_2, N_2, NO, NO_2, HNO, HONO, NO_3, ClO_2, N_2O, CO, CO_2, HCO, ClCO, HgO, O_3. A total of 107 reactions involving the species, including reactions with a third body, were included in the model using Xu et al. (2003) as a basis for the kinetic constants. A subsequent batch and column model accounting for the adsorption/desorption kinetics and heterogeneous reactions of compounds on

a surface has been completed. A framework for parameterizing the sorption kinetics and surface reactions on a model carbon surface is being investigated using quantum chemical modeling.

The interaction of flue gas components (e.g., water, carbon dioxide, etc.) with carbon black and single wall carbon nanotubes (SWCNT) was investigated by temperature programmed desorption (TPD) and Fourier Transform Infrared Spectroscopy (FTIR). Oxygen functionalities are present on these materials, and their concentration can be increased as a result of oxidative processes (e.g purification protocols for SWCNT). Oxygen containing groups were removed from carbon black and SWCNT by annealing to high temperatures (>500 K). The effect of oxygen functionalities on water adsorption was investigated. Water desorbs at similar temperatures from carbon black and from carbon nanotubes (~160-170 K), suggesting non-specific interaction of water with surfaces of carbonaceous materials. Removal of oxygen functionalities reduces water uptake kinetics for carbon black and SWCNT samples, suggesting an increase of hydrophobicity for non-functionalized materials. Both water content and presence of oxygen functionalities is known to influence interaction of mercury with carbon materials.

To model the functionalization that occurs on fly ash particulates, a variety of chemical groups were grafted to carbon materials. Oxygen functionalities were successfully introduced by *ex situ* treatment of carbon black with nitric acid at ambient temperature. Complex oxygen-sulfur-chlorine functionalities were introduced to SWCNT by *ex situ* treatment with thionyl chloride ($SOCl_2$). The functionalized carbons will be tested for mercury uptake and oxidation effectiveness.

Six fly ashes samples and one carbon black sample (Cabot Black Pearl 460) were analyzed for surface area (BET), morphological characteristics (SEM), loss on ignition and chemical composition (XPS) and were tested for their ability to oxidize/adsorb mercury under simulated flue gas conditions. In addition, the effect of fly ash composition was investigated by conducting tests with pure components, such as alumina (Al_2O_3), silica (SiO_2), calcium oxide (CaO), magnesium oxide (MgO), manganese dioxide (MnO_2), ferric oxide (Fe_2O_3), magnetite (Fe_3O_4), rutile (TiO_2), anatase (TiO_2), and carbon black. At 140 °C, carbon black and Fe_2O_3 showed oxidation rates as high as 19.4% and 41.0% after 4 hours of exposure. Other tested components Al_2O_3, MgO, CaO, TiO_2 (anatase), MnO_2 showed no oxidation or adsorption at 140°C. SiO_2 showed slight affinity to oxidize elemental mercury under the conditions used in this test. However, all the oxidation of mercury was accompanied by adsorption of mercury. The four fly ash samples already tested showed the ability to oxidize and adsorb mercury. Surface area and LOI were found to have positive correlations with both adsorption and oxidation.

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Publications:

1. Kazachkin, D.V., Feng, X., Kwon, S., Dementev, N.N., Vidic, R.D. and Borguet, E. "Interaction of acetone with single wall carbon nanotubes: FTIR and TPD study" ACS Middle Atlantic Regional Meeting, Collegeville, PA, May 16 - 18, 2007.
2. Chen, X., Monnell, J., Borguet, E., Flora, J.R.V. and Vidic, R.D. "Impact of Fly Ash on Mercury Speciation in Flue Gas" Paper No. 487 VBCRLF, 100th AWMA Annual Conference and Exhibition, Pittsburgh, PA, June 26-29, 2007.