

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

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1. ABSTRACT

Rationale and Objectives

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.

Accomplishments During the Current Period of Performance

A process model has been completed that describe homogeneous reactions of mercury species in a batch system. A total of 107 reactions involving 30 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. Density functional theory calculations were performed using B3LYP/6-31G(d) for all atoms except for Hg which used the SBKJC effective core potential. Geometry optimization was run at different multiplicities to determine the minimum energy of the model systems, followed by frequency calculations to verify that the energy was at a minimum. Binding energies were calculated for Hg and different flue gas components on a carbon black zigzag and armchair edge model. Equilibrium constants were obtained, and an equilibrium model accounting for homogeneous and heterogeneous reactions on carbon black is currently being developed for a batch and column system. Calculations will be performed to evaluate kinetic constants to be used for the process model.

In order to investigate a possible “pressure gap” in understanding molecular adsorption, we have compared the behavior of carbon materials exposed to simple molecules under high vacuum conditions (e.g. $\sim 10^{-6}$ Torr) and conditions closer to ambient (e.g. 10 Torr). While experiments under vacuum conditions allow us to ensure sample cleanliness, they typically require dosing at low temperatures. Exposure at higher pressures, e.g. 10 Torr, allows us to investigate dosing under ambient conditions or even higher temperatures, albeit with less certitude as to possible surface contamination. It is evident that dosing of simple molecules (butane, acetone, ethanol,...) at 10 Torr and 300 K, leads to the population of high energy binding sites in a variety of carbonaceous materials (carbon black, carbon nanotubes,). These high energy sites appear to be populated by activated adsorption, i.e. multiple adsorption attempts/collisions at “high” (ambient) temperature are required for molecules to access these sites. The molecules captured by activated adsorption are released by heating over a broad temperature range that stretches from 400 to 700 K. This suggests that studies at both high and low vacuum conditions are needed to completely characterize carbon materials.

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. Carbon black was used to simulate unburned carbon in fly ash. Mercury uptake tests revealed that LOI, surface area, and particle size of fly ash samples all had positive effects on mercury oxidation and adsorption, and unburned carbon was the most important fly ash component influencing mercury speciation. The importance of the interaction between flue gas and carbon surface on mercury uptake was also revealed in experiments with different flue gas composition. NO_2 and HCl promoted mercury oxidation and adsorption on carbon black, while SO_2 seemed to inhibit both mercury oxidation and adsorption.

Current efforts are directed towards the construction and testing of an entrained-flow reactor where the kinetics of mercury oxidation/adsorption can be tested under the conditions that resemble those in the flu gas duct.

2. LIST OF PUBLISHED JOURNAL ARTICLES, COMPLETED PRESENTATIONS AND STUDENTS RECEIVING SUPPORT FROM THE GRANT

Conference Presentations

1. Kazachkin, D.V., Nishimura, Y., Dementev, N.N., Irle, S., Morokuma, K., Vidic, R.D. and Borguet, E. "Interaction of simple molecules with carbon nanotubes", Proceedings of the 236th American Chemical Society National Meeting, August 17-21, 2008, Philadelphia, PA.
2. Chen, X., Bhardwaj, R., Monnell, J.D., Flora, J.R.V., Borguet, E. and Vidic, R.D. "Impact of fly ash composition and flue gas components on mercury speciation" Proceedings of the 235th American Chemical Society National Meeting, April 6-10, 2008, New Orleans, LA.
3. Zhu, H., Flora, J.R.V., Borguet, E. and Vidic, R.D. "Quantum modeling of Hg adsorption on carbon surfaces in the presence of HCl, NO₂ or SO₂" Proceedings of the 235th American Chemical Society National Meeting, April 6-10, 2008, New Orleans, LA.
4. Kazachkin, D.V., Nishimura, Y., Dementev, N.N., Irle, S., Morokuma, K., Vidic, R.D. and Borguet, E. "The interaction of simple molecules with CNT" 235th American Chemical Society National Meeting, April 6-10, 2008, New Orleans, LA.
5. 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.
6. Bhardwaj, R., Chen, X. and Vidic, R.D. "Mercury oxidation catalyzed by carbonaceous surfaces: Impact of surface area and water vapor" Proceedings of the 2007 AIChE Annual Meeting, November 4-9, 2007, Salt Lake City, UT.
7. Chen, X., 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.
8. 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.

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