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

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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.

ACCOMPLISHMENTS TO DATE

- We have completed the design of a vacuum chamber that is used to study mercury reactions on solid surfaces. Sample mount that provides for both heating and cooling in vacuum and the optical access to the sample over a range of angles (normal to grazing incidence) was custom-made by the machine shop and installed in the chamber.

- We are currently studying the interactions of typical gases (e.g. H_2O, SO_2, NO, NO_2, CO, CO_2, ...) that are present in thermoelectric power plant flue stream with carbon black as a model surface for unburned carbon in fly ash using temperature programmed desorption.
- We have received and installed a new instrument from PSA Analytical (Sir Galahad), which is capable of detecting both elemental and oxidized mercury species at low concentration with its atomic fluorescence detector. We have successfully calibrated the instrument and obtained some expertise in its use.
- We have purchased mass flow controllers (MFCs) required for the assembly of the system for producing simulated flue gas that will be used in fixed-bed and entrained flow reactor studies. These MFCs are now calibrated to ensure proper composition and flow rate of the simulated flue gas.
- We have initiated a detailed design of the entrained flow reactor and fly-ash dosing system.
- We have obtained some expertise in performing quantum mechanical calculations to assist in estimating kinetic parameters of mercury reactions in the bulk. Using Gaussian software, we optimized the geometry of the mercury species with different reactants and products using built-in basis sets. We calculated the frequencies of these compounds and the corresponding heat of reaction. Our results were verified through comparison with other work published in the literature.

FUTURE WORK

- Experimental evaluation of the catalytic properties of carbonaceous surface for mercury oxidation under UHV conditions using Fourier Transform Infrared (FTIR) studies
- Assembly of the fixed-bed reactor with simulated flue gas.
- Procurement of fly ash samples and inorganic oxides to be tested in the fixed bed and entrained flow reactor. Fly ash samples will first be tested for their ability to catalyze mercury oxidation in a fixed bed reactor.
- We are currently exploring approaches to obtain the transition state structure and the activation energy. The reaction rate constants will be estimated from the activation energy at temperatures representative of conditions in coal-fired power plants. We will explore semi-empirical methods and compare results to *ab initio* calculations. These semi-empirical methods will then be used to estimate reaction kinetics on surfaces. These kinetic constants will be used for a process model to predict the fate of mercury in the flue gases of coal fired power plants.