

**Title: OXIDATION OF MERCURY IN PRODUCTS OF COAL COMBUSTION**

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### ABSTRACT

#### OBJECTIVE

A program of catalyst development, catalyst evaluation, and chemical kinetic analysis is being conducted by the University of Alabama at Birmingham (UAB), Southern Research Institute (Southern Research), Clark Atlanta University (CAU), Gas Technology Institute (GTI), and Southern Company Services. Southern Research and UAB are performing experiments in the Catalyst Test Facility and Combustion Research Facility at Southern Research. CAU and GTI are developing new catalyst formulations. UAB and Southern Research are developing reaction mechanisms to describe catalyst performance. Southern Company Services is providing guidance and advice from the electric utility perspective. The objective is to maximize conversion of mercury from the elemental state to water-soluble mercuric chloride during selective catalytic reduction (SCR) of NO while maintaining good NO reduction performance and minimizing oxidation of SO<sub>2</sub> to SO<sub>3</sub>. The work is intended to meet research needs identified in the review of mercury oxidation catalysts by Presto and Granite (*Environ. Sci. Technol.* 40, 2006, 5601).

#### ACCOMPLISHMENTS TO DATE

Measurements of catalyst performance with respect to mercury oxidation, NO<sub>x</sub> reduction, and SO<sub>2</sub> oxidation have been performed in the Southern Research Institute's Catalyst Test Facility using three commercial catalysts and a new formulation based on vanadium pentoxide from the Gas Technology Institute. In parallel to this work, a major effort has been directed toward measurement and simulation of the oxidation and absorption of mercury by unburned carbon and the synergistic effect of CaO in ash on removal of mercury from coal-derived flue gas at both laboratory and pilot scale.

A three-step mechanism describing dissociative adsorption and desorption of HCl on unburned carbon, dissociative adsorption of HgCl<sub>2</sub> on unburned carbon, and adsorption/reaction of HgCl with CaO in ash reproduced the principal features of a set of 15 measurements of mercury adsorption by fly ash and unburned carbon in the Southern Research Institute's pilot-scale Combustion Research Facility. The fuels were Eastern U.S. bituminous coals and blends of the bituminous coals with Powder River Basin coal. The mechanism, with pre-exponential factors and activation energies in the rate coefficients adjusted to fit the measurements, explains the dependence of mercury adsorption on temperature, residence time, unburned carbon concentration, and the ratio of CaO to unburned carbon.

Combination of the adsorption mechanism with six additional reactions describing the homogeneous and heterogeneous reactions between mercury and chlorine species was not successful in describing the distribution of mercury between the elemental and oxidized forms. Oxidation, in the model, was too sensitive to the unburned carbon concentration. Work on resolution of this problem continues.

Implementation of the Tennessee Valley Authority's dry, high temperature mercury reduction system (Meischen et al., *J. A&WMA* 54, **2004**, 60) for determination of total mercury, greatly improved the quality of mercury measurements at the outlet from the reactor in the Catalyst Test Facility, in which conditions are chosen to simulate those in SCR. Along with the improvement in data quality, there was a marked reduction in the time required to identify steady-state conditions and a higher probability of success in each test run.

Measurements of the mercury species distribution (oxidized or elemental) at the outlet from a 286-mm-long, 6 mm x 6 mm square cell monolithic SCR catalyst were conducted using the TVA mercury reduction system for determination of total mercury. In the absence of NH<sub>3</sub>, a steep rise in the fraction of oxidized mercury with increasing HCl volume fraction was observed in the range from 1 to 2 ppmv HCl, followed by a slow increase in the extent of mercury oxidation toward 100% with further increase in HCl to 100 ppmv. This is in contrast with the model calculations of the process in the presence of NH<sub>3</sub> by Niksa and Fujiwara (*J. A&WMA* 55, **2005**, 1866), who predicted a gradual increase in the extent of mercury oxidation over the range of HCl from 0 to 175 ppmv. The addition of NH<sub>3</sub> in the presence of 1 ppmv HCl resulted, at low NH<sub>3</sub>/NO ratio, in a gradual decrease in mercury oxidation followed by a steep decline in oxidation over the range of NH<sub>3</sub>/NO from 0.95 to 1.15, consistent with the predictions of Niksa and Fujiwara (2005) and Senior (*J. A&WMA* 56, **2006**, 23). The measurements in the presence and complete absence of NH<sub>3</sub> will be used to determine rate and equilibrium constants describing the Hg-HCl-NO-NH<sub>3</sub>-catalyst interactions.

A slight tendency for increased SO<sub>2</sub> oxidation to SO<sub>3</sub> with increasing HCl was observed over the range from 1 to 100 ppmv HCl, in the absence of NH<sub>3</sub>. Additional measurements are needed to establish whether or not there is a connection between HCl concentration and SO<sub>3</sub> formation, and the influence of NH<sub>3</sub>.

#### **FUTURE WORK**

Measurements to be made include the effects of NH<sub>3</sub>/NO ratio on mercury oxidation at very low HCl levels (1-2 ppmv), the effects of NH<sub>3</sub>/NO ratio and HCl on SO<sub>2</sub> conversion to SO<sub>3</sub>, and the effects of CO on both mercury and SO<sub>2</sub> oxidation. A mechanism for mercury oxidation in catalyst channels will be implemented in Chemkin (Reaction Design), building on the models developed by Niksa and Fujiwara (2005) and Senior (2006).

#### **LIST OF PAPERS**

Bhopatkar, N. S., Prediction of Mercury Speciation in Coal-Combustion Systems, M.S. Thesis, Department of Mechanical Engineering, University of Alabama at Birmingham, 2006.

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Gale, T. K., Bhopatkar, N. S., and Ban, H., Kinetics of Ca-C Synergism during Mercury Adsorption on Fly Ash in Coal-Fired Power Stations, Air Quality V Conference, Arlington, VA, September 18-21, 2005.

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#### **STUDENTS**

Neelesh S. Bhopatkar (M.S., 2006) and Giang Tong (Ph.D. candidate)