

**TITLE:** FLY ASH CATALYZED MERCURY OXIDATION  
CHLORINATION REACTIONS

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**PERFORMANCE**

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**OBJECTIVES:**

The main goal of this study is to investigate the mechanism of surface-assisted mercury transformation reactions in the combustor cool zone. To achieve this goal, we will investigate the interaction between  $\text{Hg}^0(\text{g})$  and fly ash particles under various post-combustion reaction conditions. Role of fly ash composition (metal constituents, carbon and calcium) on mercury transformation reactions will be investigated and impact of  $\text{CO}$ ,  $\text{SO}_2$ ,  $\text{NO}/\text{NO}_2$  and  $\text{HCl}$  concentration on mercury transformation reactions will also be determined.

**ACCOMPLISHMENTS TO DATE:**

For this study we used ten coal fly ashes and eight model fly ashes to understand mercury transformation in the post-combustion zone. The model fly ashes (with and without inert matrix silica) were designed to investigate the impact of various fly ash components like carbon, iron and calcium on mercury transformation reactions. All these fly ashes were characterized for surface area, metal, and carbon content. Using these fly ash samples as fixed bed, mercury oxidation/chlorination reactions were investigated at 200, 300 and 400°C. These experiments were conducted using an  $\text{O}_2$  (4%) –  $\text{N}_2$  mix as a reaction gas. Other reactants ( $\text{HCl}$ ,  $\text{HBr}$ ,  $\text{SO}_2$ , and  $\text{H}_2\text{O}$ ) were added as needed to the reactor gas using syringe pumps. The reaction time was one hour for all experiments. The reactor exit gas was sampled for oxidized and elemental mercury using a modified Ontario-hydro method. After each experiment, fly ash particles were also analyzed for mercury. The results show that because of different composition fly ashes from different plants have different catalytic activities with respect to mercury oxidation. It was also observed that catalytic properties of fly ash do not change over time as fly ashes collected at different

times (from the same plant) gave similar results. The results suggest that carbon content of fly ash is important for mercury oxidation at lower temperatures (200 -300°C) but as the temperature increases to 300°C and higher the iron (oxide) content of fly ash becomes more important parameter for mercury oxidation. However, not all iron oxides are active in mercury transformation it is only the gamma iron oxide that shows high activity towards mercury adsorption and oxidation. The experiment with model fly ashes containing calcium showed that calcium is only active in adsorbing HCl or HgCl<sub>2</sub> and has no impact on Hg<sup>0</sup> or HgO adsorption and reactions.

It was observed that addition of HCl enhances mercury oxidation. The yields of oxidized mercury are higher under the conditions where there is a high probability of Hg<sup>0</sup> and HCl adsorbing in a close vicinity of each other. The addition of water enhanced yields of particulate mercury because water creates oxygen complexes on surface that are active adsorption sites for Hg<sup>0</sup>. It was observed that addition of SO<sub>2</sub> helps adsorption of elemental mercury but reduces yields of oxidized mercury. From our results we can deduce that in absence of SO<sub>2</sub>, HCl and mercury get adsorbed on surface and then react and some of the HgCl<sub>2</sub> is desorbed depending on HCl and mercury concentration and time of contact. However, when SO<sub>2</sub> is introduced it competes with HCl for carbon sites and gradually replaces surface Cl. This decrease in surface chlorine leads to decrease in surface HgCl<sub>2</sub> and ultimately lowers the yield of HgCl<sub>2</sub> in effluent gas. The presence of SO<sub>2</sub> does help mercury adsorption by formation of Hg-S-surface complexes but these Hg-S complexes are more strongly bonded to surface than the Hg-Cl complexes. This is the reason for increase in ash-mercury yields.

#### **FUTURE WORK:**

In the next quarter we plan to determine the impact of bromine on mercury transformation reactions. Our initial experiments with HBr (66 ppm) show that HBr can enhance mercury oxidation but to lesser extent than HCl. We will further explore role of bromine by conducting some experiments with 10ppm of Br<sub>2</sub> because our thermochemical calculations and literature data suggest that due to weak H-Br bond the bromine is most likely present as Br radical or Br<sub>2</sub> in the post-combustion zone. Both Br radical and Br<sub>2</sub> are more potent oxidizing agents than HBr. This set of experiments will test this hypothesis.

#### **LIST OF PAPER PUBLISHED, U.S. PATENT/PATENT APPLICATION(S), CONFERENCE PRESENTATION, AWARDS RECEIVED AS A RESULT OF SUPPORTED RESEARCH:**

P. Varanasi and S. S. Sidhu, "Mercury transformation reactions on Coal and model fly ashes," **The 10<sup>th</sup> International Congress on Combustion By-Products and their Health Effects**, Ischia, Italy, June 2007.

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