

FY05-LI(51)-131

Investigation of Mercury and Carbon-Based Sorbent Reaction Mechanisms

Submitted by: Energy & Environmental Research Center

Principal Investigator: Charlene R. Crocker

PARTICIPANTS

<u>Sponsor</u>	<u>Cost Share</u>
CATM	\$50,000
DOE	\$46,870
EPRI	\$18,000
Coteau Properties	\$18,000
Westmoreland Coal	\$15,000
Westmoreland Coal (in-kind)	\$ 3,000
Falkirk Mining Co. (in-kind)	\$18,000
BNI Coal (in-kind)	\$18,000
NDIC	<u>\$54,000</u>
Total Cost	\$240,870

Project Schedule - 20 Months

Contract Date – 6/24/04

Start Date – 7/1/04

Completion Date – ~~1/31/06~~

Extension to – ~~5/31/06~~

Extension to – ~~11/30/06~~

Extension to – 9/30/07

Project Deliverables

Contract Signed: 6/24/04✓

Quarterly Reports:

10/31/04(✓);1/31/05(✓)

3/30/05(✓); 7/31/05(✓); 10/31/05(✓);

Final Report: ~~1/31/06(–)~~

~~5/31/06(–)~~

~~11/30/06(–)~~

9/30/07(✓)

OBJECTIVE / STATEMENT OF WORK:

Improve mercury capture efficiency of carbon sorbents through a better understanding of mercury-sorbent reaction mechanisms. Project will produce information to develop more effective and lower-cost sorbent to control elemental mercury emissions.

STATUS

July – Sept, 2004. Activities included defining the experimental test matrix, collecting and preparation of lignite samples and reactants.

Sept – Dec, 2004. A test matrix of char was treated with aqueous HCl, gaseous HCl and with gaseous Cl₂ to determine changes to the char surface structure. After exposure to a simulated flue gas, the sorbent surface was analyzed using XPS. Preliminary results indicate that the aqueous treated carbon was enriched in several minerals and oxygen. All three groups of test species showed an increase in chlorine concentration compared to the baseline levels.

Jan – Mar, 2005. Several carbon samples were pretreated using chlorine gas, hydrochloric gas and aqueous hydrochloric acid. Initial reactivity and capacity breakthrough tests were conducted. The chlorine treated carbon sample exhibited high initial activity (10% of inlet) but climbed rapidly to 17%; thus, no induction period was required to obtain good mercury capture and breakthrough after

33 minutes. The hydrochloric gas treated sample exhibited an initial mercury capture of 10% of inlet, and dropped to less than 5% of inlet and leveled out – a very small induction period that produced excellent mercury capture with breakthrough occurring at 30 minutes. The aqueous hydrochloric acid treated sample showed mediocre initial sorption at 28% of inlet and slowly increase to 23% of inlet, reflecting a long induction period that obtain poor mercury capture. None of the treated carbon samples exhibited superior performance.

April 1 – June 30, 2005. Activities this quarter focused on evaluation of activated carbons. Four different sources of lignite were tested for carbonation and activation. The various carbon/coal yield percentages were reported. One of the lignite carbons tested demonstrated very favorable mercury capture results when compared to the commercially available DARCO FGD.

July 1 – September 30, 2005. Activities this quarter focused on dissemination of results. A paper was prepared for presentation of results at the first International Conference on Carbon for Energy Storage and Environmental Protection in Orleans, France. The presentation was titled *Surface Chemistry of Pretreated Activated Carbon Sorbents Exposed to Mercury in Simulated Flue Gas*. A paper with the same title was prepared and submitted to the journal *Carbon*.

October 1 – December 31, 2005. Activities this quarter focused on determining whether the oxidation of SO₂ to S(VI) on a carbon surface is closely related to the oxidation of mercury on the same surface. It appears the addition of HCL to the carbon prior to flue gas exposure appears to facilitate SO₂ oxidation.

January 1 – March 31, 2006. Activities this quarter focused on Tasks 1 & 3. There was continued work on SO₂ oxidation rates and evaluation of activated carbons to identify phase transitions during heating of lignite.

Final Report (6/28/04 – 9/30/07). An investigation of chemical interaction at the surface of carbon-based sorbents used for mercury capture was conducted. The resulting observations of this work were as follows:

- In chlorine-pretreated sorbents, inorganic chlorine on the surface is rapidly lost during exposure to simulated flue gas.
- For the Cl₂- and HCl(aq)-treated samples, part of the chlorine in the sample is tightly fixed organochlorine and part is more easily displaced.
- For the HCl(g)-treated carbon, none of the chlorine in the sample is tightly fixed organochlorine.
- All three pretreatments improved initial mercury capture by eliminating the induction period in low-acid flue gas conditions.
- Based on the reactivity screening, the HCl(g)-pretreated sorbent was the most reactive at the outset. Likewise, the mercury breakthrough curve of the loading experiment suggests that the HCl(g)-pretreated sorbent has the best capacity.
- Another chlorine-based modification to the surface using SOCL resulted in good mercury capture similar to that of HCL and Cl₂ pretreatments. This rejects the hypothesis that oxygen functionality is important to mercury oxidation
- The most useful analytical techniques for examining inorganic interactions on the carbon surface were XPS and XAFS.
- Raman spectroscopy may be useful for investigating carbon-halide bonding on the carbon surface. This will require additional deconvolution of the broad spectral peaks. Currently, methods to accomplish this are not definitive.

- DSC-TGA was not a useful technique for distinguishing differences in the structural changes of coals during heating.
- Activated carbons prepared from several different lignite coals under the same conditions produced similar results for mercury control reactivity.
- Activation conditions had a greater effect on the quality of activated carbon produced than the characteristics of the starting materials did.
- Chlorine pretreatment of activated carbons produced from Fort Union lignites improved the mercury capture ability of the sorbents in the same sense as pretreatment of DARCO FGD; i.e., the induction period was eliminated.