



*Charlene R. Crocker
Principal Investigator*

INVESTIGATION OF MERCURY AND CARBON-BASED SORBENT REACTION MECHANISMS

Key Personnel: Charlene Crocker (EERC), Edwin Olson (EERC), Steve Benson (EERC), Jason Laumb (EERC), Jill Mackenzie (EERC), Blaise Mibeck (EERC).

Project Description

The EERC has developed a fundamental research consortium that focused on improving the mercury capture efficiency of carbon-based sorbents in flue gases typical of firing lignite and other low-chlorine, low-sulfur fuels through a better understanding of mercury–sorbent reaction mechanisms. Based on health and emissions data, EPA has decided to regulate mercury from utility power plants. Power plants burning lignite and subbituminous coals have demonstrated significantly higher mercury emission percentages than those burning bituminous coals.

Activated carbon injection upstream of pollution control devices such as a fabric filter (FF) (baghouse) or electrostatic precipitator (ESP) is the most mature technology available for mercury control. The projected annual cost for activated carbon adsorption of Hg in a duct injection system is significant. Carbon-to-mercury weight ratios of 3000–18,000 (lb carbon injected/lb Hg in flue gas) have been estimated to achieve 90% Hg removal from a coal combustion flue gas containing $10 \mu\text{g}/\text{Nm}^3$ of Hg (1). Many potential mercury sorbents have been evaluated (2). For activated carbons to be successful, they must effectively sorb both Hg^0 and Hg^{2+} . The evaluations have demonstrated that the chemical speciation of mercury in the flue gas controls its capture and ultimate environmental fate. The capture and retention of mercury on carbon-based sorbents are dependent upon the particle size, chemical and physical characteristics of the sorbent surface, and flue gas composition. These factors have had a major impact on the effectiveness of mercury control using activated carbon sorbents. However, the physicochemical basis for these impacts is not understood. More efficient carbon-based sorbents are needed to lower the carbon-to-mercury weight ratios used, thus reducing cost. The project is aimed at developing better sorbents to control mercury emissions in subbituminous- and lignite coal-fired power plants equipped with an FF, ESPs, and wet and dry scrubbers through investigation of surface reaction mechanisms by which carbon sorbents oxidize and capture mercury. The research plan examines flue gas–mercury interactions on carbon sorbents, sorbent surface chemistry, effects of surface modifications to the carbon structure on kinetics and capture, and evaluation of the efficiency of activated carbons prepared with surface modifications in low-chlorine fuel combustion applications. It is anticipated that the results of this research will enhance understanding of mercury–sorbent interactions in flue gas conditions typical of western subbituminous and lignite coal combustion resulting in recommendations for improvements in activated carbon sorbent effectiveness.

Goal

The goal of this EERC program is to improve the mercury capture efficiency of carbon-based sorbents through a better understanding of mercury–sorbent reaction mechanisms. The research will involve a fundamental investigation of physicochemical surface characteristics of sorbents exposed to flue gas that contains mercury vapors.

The objectives of the project include the following: 1) determining the role of HCl in promoting the oxidation of elemental mercury, 2) determining the role of the carbon structure in providing active sites for oxidation of mercury and SO₂ and the subsequent binding of the oxidation products, and 3) evaluating sorbents prepared from coal-based materials provided by project partners.

Rationale

Activated carbon injection is the most mature technology of the sorbent injection technologies available for mercury control. For activated carbons to be successful, they must effectively sorb Hg⁰ and Hg²⁺. Testing has demonstrated that the chemical speciation of mercury in the flue gas, to a large degree, determines its capture mechanism and ultimate environmental fate. The capture and retention of mercury on carbon-based sorbents are dependent upon the particle size, chemical and physical characteristics of the sorbent surface, and the flue gas composition. These factors have had a major impact on the effectiveness of mercury control using activated carbon sorbents.

Poor capture results have been associated with low-acid-gas-containing flue gas and the high proportion of elemental mercury in the flue gas stream. In bench-scale sorption tests, the amount of HCl in the flue gas has a significant effect on the initial Hg⁰ capture kinetics on carbon-based sorbents, where higher levels (50 ppm HCl) eliminate the induction period. Pretreatment of the sorbent with aqueous HCl has the same effect in bench-scale testing (3), but pilot-scale testing using stored samples of the pretreated sorbent failed to demonstrate an improved sorption capacity. The effect of storage time and conditions on the mercury capture efficiency of activated carbon sorbents has yet to be determined.

Most activated carbon mercury control research has been performed in fixed-bed reactors that simulate relatively long-residence-time (gas–solid contact times of minutes or hours) mercury capture by an FF cake (4). However, it is important to increase the reactivity of the sorbents for short-residence-time (seconds) in-flight capture of Hg⁰ because most of the coal-burning boilers in the United States employ cold-side ESPs for controlling particulate matter emissions. More efficient carbon-based sorbents are required to enable lower carbon-to-mercury weight ratios to be used, thus reducing the operating costs of carbon injection.

Researchers at the EERC and elsewhere are striving to attain a more thorough understanding of mercury species reactions on activated carbon surfaces in order to produce more efficient sorbents. Mercury-reactive surface functional groups thought to have an impact on mercury capture include acidic carboxyl, lactone, hydroxyl, and carbonyl functionalities or alkaline pyrone and chromene functionalities (3, 5–7). Functional groups containing inorganic elements such as bromine, chlorine, or sulfur are also possibilities (8–10). Although halogen- and sulfur-bearing surface functional groups are not well characterized, the beneficial role of halogens and sulfur in capturing mercury species on activated carbons is well established (3, 11). Recently, Laumb and others (12) and Benson and others (13) have characterized sorbents exposed to flue gas and elemental mercury, and the results indicate that the key surface components that impact the oxidation and retention of mercury on the surface of the carbon result from the chemisorption of the chlorine and sulfur species from the flue gas. The chlorine species react to

form organically associated chlorine on the surface, and it appears that the organically associated chlorine on the carbon is the key site responsible for bonding with the Hg^{2+} species.

Olson and others (14) have developed an experimentally based model of the chemical mechanism of mercury oxidation and binding that offers more detail on the nature of the bonding site and its interaction with flue gases and mercury. This model, shown in Figure 1, uses the concept of zigzag carbene structures recently proposed by Radovic and Brockrath (15). It is hypothesized that the mechanism involves the reaction with HCl to form stable carbenium ion intermediates (16). These intermediate species can then promote oxidation of elemental mercury and create sites for bonding. The exact mechanism of reaction is currently not well understood. A detailed understanding of these mechanisms will provide information for the development of more effective and lower-cost sorbents.

A zigzag-edge carbene site comprises the basic binding site for which the various acid-gas components and Hg^{2+} compete. Figure 2 provides more details of the role of chlorine. The conversion of carbene to carbenium ion by HCl and other acids generates an oxidation site and is consistent with the promotion effect of acids on mercury oxidation. The mechanistic model shows Hg^0 oxidation by the carbenium ion to the organomercury intermediate and subsequent oxidation by NO_2 to the bound Hg^{2+} species. Ultimately, the refined model will have the potential to be used to describe flue gas-activated carbon interaction behavior and predict capture efficiency. In addition, knowledge developed from this model will be useful for stabilizing Hg^{2+} on the sorbent and promoting the kinetics of mercury capture.

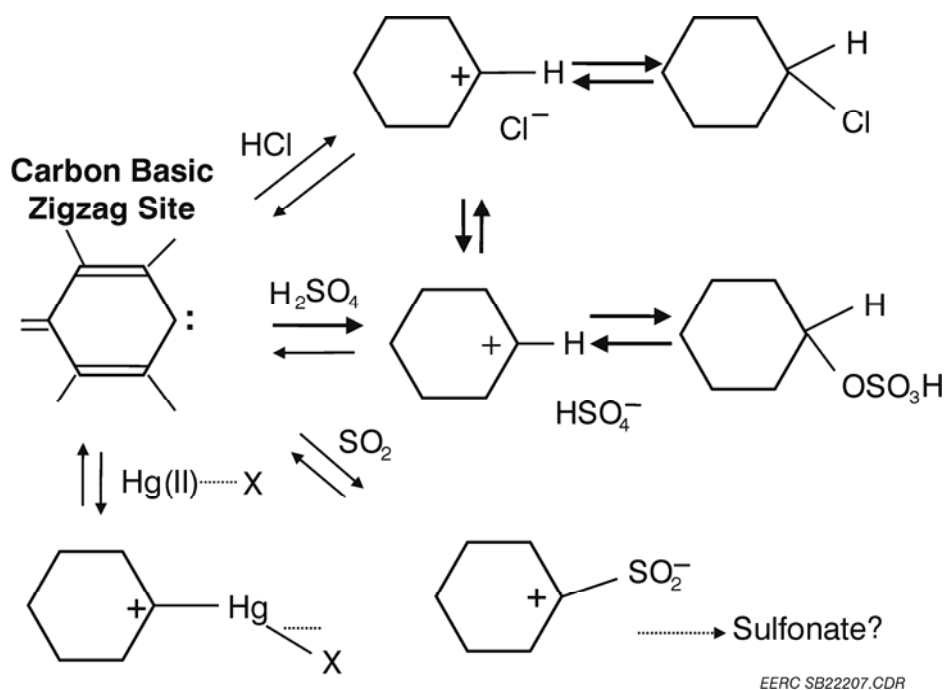


Figure 1. Binding site model for activated carbon.

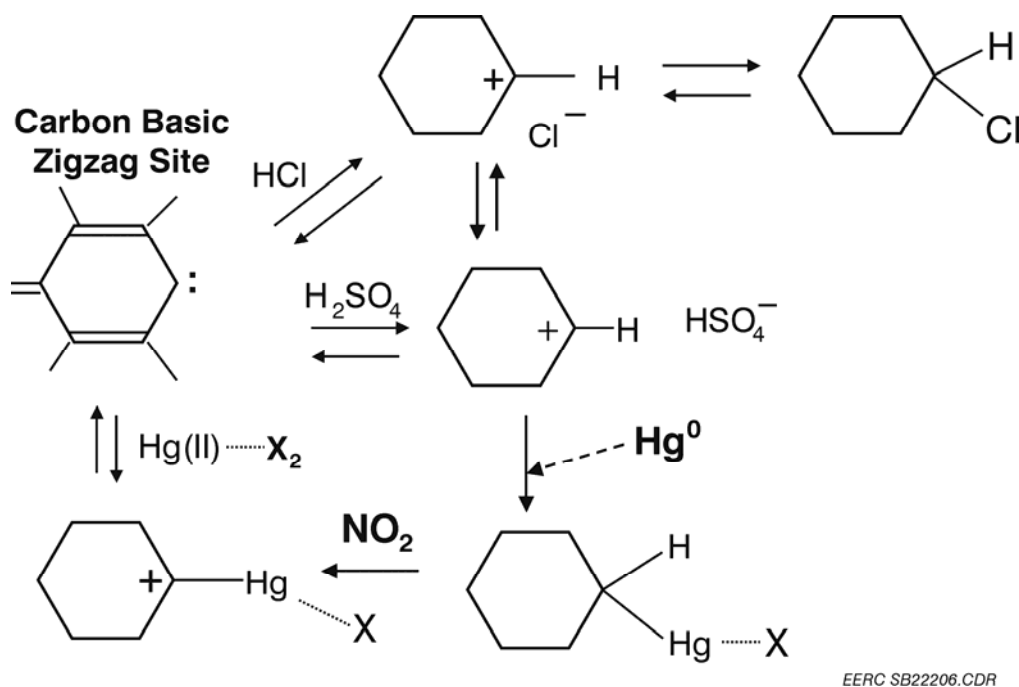


Figure 2. Oxidation site model for activated carbon—the role of hydrochlorination in generating carbenium oxidant (16).

Approach

Overall approach to this research consists of three tasks outlined as follows:

- Task 1 – Flue Gas–Mercury Interactions on the Carbon Sorbent
- Task 2 – Investigation of the Effects of Surface Modifications on Kinetics and Capture and Evaluation of Activated Carbons
- Task 3 – Evaluation of Activated Carbons

Task 1 Flue Gas–Mercury Interactions on the Carbon Sorbent

Task 1.1 – Hydrochlorination Effects on Sorbent Kinetics

In bench-scale sorption tests, the amount of HCl in the flue gas has a significant effect on the initial Hg^0 capture kinetics on carbon-based sorbents, where higher levels (50 ppm HCl) eliminate the induction period. A proposed mechanism for oxidation requires acid activation of the graphene-edge carbene site for oxidation to occur (6). Pretreatment of the sorbent with aqueous HCl has the same effect in bench-scale testing (7), but pilot-scale testing using stored samples of the pretreated sorbent failed to demonstrate an improved sorption capacity.

The nature of the sorbent–Cl bond(s) will be investigated for several hydrochlorinated (aqueous, gas, alternative compounds) flue gas desulfurization (FGD) sorbents utilizing bench-scale mercury sorption testing with flue gas constituents at levels representative of firing lignite or other low-chlorine,

low-sulfur coals. Since previous test results have indicated that the low HCl level in the flue gas representative of lignite-fired combustion systems required a significant induction period before effective Hg^0 capture on carbon-based sorbents occurred, the investigation of pretreated sorbent will provide insight into the oxidizing interactions of the carbon surface with Hg^0 and other flue gas constituents. Halogen-impregnated sorbents will be loaded to various stages of capacity with Hg^0 using the bench-scale screening test apparatus. The loaded sorbents will undergo x-ray photoelectron spectroscopy (XPS) analysis, which determines the oxidation state and bonding associations of surface atoms present at detectable levels. The results of the following tests will be compared to previously collected data. The research will focus on two areas:

1. The effects of various chlorine impregnation techniques will be investigated. The performance of aqueous, gas-phase, and alternative halogenating agents (SOCl_2 , for example) will be compared.
2. The influence of HCl and other acids on the NO_2 -assisted oxidation of SO_2 to SO_3 will be evaluated to address the question of whether the SO_2 oxidation site is the same site that performs the Hg oxidation. The reaction kinetics for the various acids will be determined and correlated with mercury oxidation. The possibility of an induction period for sulfur(VI) formation at low flue gas HCl concentration will be investigated. The rate of sulfur(VI) formation will be determined by titration, ion-selective electrode, or ion chromatography.

Task 1.2 – Evaluation of Surface Chemistry

Surface chemistry plays a major role in mercury capture on sorbents, which has yet to be well defined. The development of a method to integrate various analytical techniques for the evaluation of oxidation and binding potential of sorbent surfaces will increase the understanding of surface interactions and provide an assessment tool for newly developed sorbents. This effort uses several analytical techniques to identify correlations between the kinetics of mercury oxidation and capacity on virgin or modified (e.g., impregnated) sorbents and various structural parameters. Test procedures include oxygen content, temperature-programmed desorption, Boehm titrations, base titrations, Raman spectroscopy, and electron paramagnetic resonance (EPR) spectroscopy. The oxygen content desorption with CO/CO_2 measurement will be used to evaluate potential correlations between activity of sorbent and CO/CO_2 evolution on heating which indicate oxygen binding on edge structure. The Boehm titration procedures determine oxygen functional groups at the surface. Titration of bases will elucidate the total basic sites and soft base sites on the carbon surface. Raman spectroscopy may detect some sulfur groups participating in surface oxidation and/or binding reactions. There is also a need to distinguish halide formations on the surface of sorbents exposed to flue gas. Raman spectroscopy will be investigated as a potential distinguishing tool. EPR indicates the presence of free radicals at the surface. These may be important intermediates in Hg^0 oxidation reactions. The exact number and variety of tests to be performed are dependent on the relevant data obtained from each test based on methods development research included in the task.

Task 2 – Investigation of the Effects of Surface Modifications on Kinetics and Capture and Evaluation of Activated Carbons

As there appears to be competition between mercury and SO_2 on the surface oxidation sites, it is important to identify activation conditions that improve selectivity of carbons for mercury and less selectivity for SO_2 . This task will focus on conditions that pertain to surface modifications that could alter the properties of the carbonaceous material. The effectiveness of two surface modifications will be

determined. XPS analyses and the suite of surface chemistry analyses will be used to determine the nature of modifications that improve mercury capture through halogenation or other means.

Task 3 – Evaluation of Activated Carbons

Task 3.1 – Evaluation of Activated Carbons

Currently, most carbon sorbent development activities have concentrated on a commercially available activated carbon—DARCO[®] FGD. Limited research suggests that activated carbons prepared from Fort Union lignites may have equal or improved capability to sorb the mercury present in combustion flue gas. All activated carbons tested to date initially exhibited poor sorption kinetics in low-Cl flue gas conditions. The important questions to be answered are which carbons can be activated by HCl or other treatments to achieve the highest Hg sorption rates and what conditions of activation will achieve optimum capture for each activated carbon. Under this task, four activated carbons will be prepared from coals provided by project partners. The extent of enhancing efforts will depend on the interests of the commercial partners. Activated carbons can be prepared in the 2.5-in.-diameter fixed-bed furnace and the 6-in.-diameter new rotary kiln system, providing information for process scale-up issues for charring and activated carbon preparation. The activated carbons will be evaluated for Hg⁰ sorption using the bench-scale test apparatus. The various coal-derived carbons may exhibit different capacities for Hg²⁺ versus Hg⁰ sorption because of different mineral content and functional groups. Sorption mechanisms are not the same for mercury in elemental versus the oxidized state. However, the option to evaluate sorbent performance for HgCl₂ is not included in the current budget.

Task 3.2 – Evaluation of Coal Characteristics

The final activity under this task is determination of the availability of materials possessing the most promising characteristics for producing effective activated carbons for mercury control. Coal-seam core data provided by commercial project partners will be examined and compared to the characteristics of the test coals to determine how representative the most promising coals are in the various seams of the Fort Union lignites.

Progress

Accomplishments of this ongoing project include a sponsor kickoff meeting and development of a test matrix for Task 1. The kickoff meeting participants included all project sponsors and several EERC personnel. The meeting focused on the introduction of the project, and the potential expansion to include XAFS (x-ray absorption fine structure) analyses as discussed in the kickoff meeting.

Task 1 – Flue Gas–Mercury Interactions on the Carbon Sorbent

A test matrix of sample preparation for XPS analysis was developed to begin to examine the nature of the sorbent–chlorine bonds and potential effects on mercury capture. DARCO FGD will be pretreated with 1%–2% chlorine using three application methods: aqueous HCl, gaseous HCl, and chlorine gas. Aliquots of the pretreated carbons will be exposed to low acid simulated flue gas (6% O₂, 12% CO₂, 15% H₂O, 580 ppm SO₂, 120 ppm NO, 6 ppm NO₂, and 1 ppm HCl) on the bench-scale apparatus. Exposure times will represent optimum capture of the sorbent and just before mercury breakthrough as noted in the table. All samples will be analyzed by XPS as the final step in the kinetic study. The test matrix is presented in Table 1.

Table 1. Task 1.1 Sample Matrix for Preparation of Pretreated Carbons for XPS Analysis

Test No.	Bench-Scale Exposure Level	DARCO FGD Pretreatment
T1-1 (baseline)	None	Aqueous HCl
T1-2	Initial maximum capture	Aqueous HCl
T1-3	Before Hg breakthrough	Aqueous HCl
T1-4 (baseline)	None	Gaseous HCl
T1-5	Initial maximum capture	Gaseous HCl
T1-6	Before Hg breakthrough	Gaseous HCl
T1-7 (baseline)	None	Gaseous Cl ₂
T1-8	Initial maximum capture	Gaseous Cl ₂
T1-9	Before Hg breakthrough	Gaseous Cl ₂

Problems with the bench-scale sorbent screening apparatus delayed the test schedule and precluded preparation of samples. The tentative sample loading date has been pushed to the week of December 13–17. We are investigating alternative methods of flue gas mercury loading of the samples to avoid future delays related to the bench-scale screening system.

Quality Assurance/Quality Control

Activities within this multiclient project are focused on improving the mercury capture efficiency of carbon-based sorbents through a better understanding of mercury–sorbent reaction mechanisms. Specific quality objectives of this project are:

1. The test and comparisons performed will produce sufficient data to show the effect of hydrochlorination on sorbent kinetics.
2. The project will provide enough additional data to evaluate the potential use of Fort Union lignite as a carbon sorbent source equal to DARCO FGD.

All support laboratories have established QA/QC protocols for instrument calibration and sample analysis. The compiled data will be evaluated for accuracy, validity, and completeness.

Status

This consortium-based research project is in the early stage. The research is scheduled to be completed in January 2006.

Potential Users/Technology Transfer

The industrial and governmental consortium members will be the immediate beneficiaries of this research. However, anyone interested in the capture and control of mercury in coal-fired flue gas, such as coal producers and energy generators, could benefit from the results of this research. The results will be transferred to the consortium members through regular sponsor meetings and written reports. In addition, results will be presented at a national meeting.

References

1. Pavlish, J.H.; Holmes, M.J.; Benson, S.A.; Crocker, C.R.; Galbreath, K.C. Application of Sorbents for Mercury Control Technologies for Utilities Burning Lignite Coal. In *Proceedings of the Air Quality III: Mercury, Trace Elements, and Particulate Matter Conference; Special Issue of Fuel Process. Technol.* **2004**, 85 (6–7), 563–576.
 2. Center for Air Toxic Metals. *Final Report Series*; 1996–2002.
 3. Ghorishi, S.B.; Keeney, R.M.; Serre, S.D.; Gullett, B.K.; Jozewicz, W.S. Development of a Cl-Impregnated Carbon for Entrained-Flow Capture of Elemental Mercury. *Environ. Sci. Technol.* **2002**, 36, 4454–4459.
 4. Miller, S.J.; Dunham, G.E.; Olson, E.S. Controlling Mechanisms That Determine Mercury Sorbent Effectiveness. In *Proceedings of the Air & Waste Management Association 92nd Annual Meeting & Exhibition*; St. Louis, MO, June 20–24, 1999; Paper 99-898.
 5. Coughlin, R.W.; Ezra, F.S. *Environ. Sci. Technol.* **1968**, 2 (4), 291–297.
 6. Tessmer, C.H.; Vidic, R.K.; Uranowski, L.J. *Environ. Sci. Technol.* **1997**, 13 (7), 1872.
 7. Liu, W.; Vidic, R.D.; Brown, T.D. Optimization of Sulfur Impregnation Protocol for Fixed-Bed Application of Activated Carbon-Based Sorbents for Gas-Phase Mercury Removal. *Environ. Sci. Technol.* **1998**, 32, 531–538.
 8. Vidic, R.D.; McLaughlin, J.B. Uptake of Elemental Mercury Vapors by Activated Carbons. *J. Air Waste Manage. Assoc.* **1996**, 46, 241–250.
 9. Krishnan, S.V.; Gullett, B.K.; Jozewicz, W. Sorption of Elemental Mercury by Activated Carbon. *Environ. Sci. Technol.* **1994**, 28, 1506–1512.
 10. Nelson Jr., S.G. U.S. Patent 20040003716, 2004.
 11. Dunham, G.E.; Olson, E.S.; Miller, S.J. Impact of Flue Gas Constituents on Carbon Sorbents. In *Proceedings of the Air Quality II: Mercury, Trace Elements, and Particulate Matter Conference*; McLean, VA, Sept 19–21, 2000; Paper A4–3.
 12. Laumb, J.D.; Benson, S.A.; Olson, E.S. X-Ray Photoelectron Spectroscopy Analysis of Mercury Sorbent Surface Chemistry. In *Proceedings of the Air Quality IV: Mercury, Trace Elements, and Particulate Matter Conference*; Arlington, VA, Sept 22–23, 2003.
 13. Benson, S.A.; Olson, E.S.; Crocker, C.R.; Pavlish, J.P.; Holmes, M.J. Mercury Sorbent Testing in Simulated Low-Rank Coal Flue Gases. In *Proceedings of the 6th Electric Utilities Environmental Conference*; Jan 27–30, 2003.
 14. Olson, E.S.; Laumb, J.D.; Benson, S.A.; Dunham, G.E.; Sharma, R.K.; Mibeck, B.A.; Miller, S.J.; Holmes, M.J.; Pavlish, J.H. Chemical Mechanisms in Mercury Emissions Control Technologies. *J. Phys. IV France*, **2003**, 107.
 15. Radovic, L.R.; Bockrath, B. *Prepr. Pap.—Am. Chem. Soc., Div. Fuel Chem.* **2000**, 47 (4), 886.
-

16. Olson, E.S.; Laumb, J.D.; Benson, S.A.; Dunham, G.E.; Sharma, R.; Mibeck, B.A.; Crocker, C.R.; Miller, S.J.; Holmes, M.J.; Pavlish, J.P. The Mechanistic Model for Flue Gas–Mercury Interactions on Activated Carbons. In *Proceedings of the Air Quality IV: Mercury, Trace Elements, and Particulate Matter Conference*; Arlington, VA, Sept 22–24, 2003.
-