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INVESTIGATION OF MERCURY AND CARBON-BASED SORBENT REACTION MECHANISMS

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Project Description

Based on health and emission 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 (ACI) upstream of pollution control devices such as fabric filters (FFs) (baghouses) or electrostatic precipitators (ESPs) 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.

The EERC has developed a fundamental research consortium 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. Since halogens such as chlorine play a critical role in promoting the reactivity of activated carbon sorbents, this work focused on chlorine as an enhancement to the carbon surface. The approach involved examining lignite flue gas-mercury interactions on carbon sorbents pretreated with various chlorination techniques, evaluating surface chemistry analytical techniques, and preparing activated carbon from sponsor-provided lignite coals.

Goal

The goal was to improve the mercury capture efficiency of carbon-based sorbents through a better understanding of mercury-sorbent reaction mechanisms. The research involved a fundamental investigation of physicochemical surface characteristics of sorbents exposed to flue gas that contains mercury vapors.

The objectives of the project included 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 $S O_2$ and the subsequent binding of the oxidation products, and 3) evaluating sorbents prepared from coal-based materials provided by project partners.

Rationale

During the pilot-scale lignite and utility-scale Fort Union coal tests using ESP and ESP-FF particulate controls, maximum mercury removal efficiencies for ACI ranged from 45% to 75% and 85%, respectively, with 7–25 lb/Macf carbon injection concentration required. Conversely, mercury removal efficiency was never >70%, regardless of the ACI rate into the Powder River Basin subbituminous coal combustion flue gas. This limitation is probably caused by the small amount of acidic flue gas constituents, such as HCl, that promote mercury-AC sorption. Testing conducted at a Fort Union lignite-fired power plant equipped with a spray dryer baghouse indicated that conventional ACI ineffectively controlled mercury (1). The results indicate poor control efficiency for injection of Norit DARCO[®] FGD in a spray dryer baghouse system (2). The poor performance is the result of the low-acid flue gas and the high proportion of elemental mercury (Hg⁰) in the flue gas stream. The iodine-impregnated activated carbon showed approximately 90% control.

Researchers at the EERC and elsewhere are striving to attain a more thorough understanding of mercury species reactions on AC surfaces in order to produce more efficient sorbents. There has been speculation that acidic or alkaline oxygen-containing functional groups could be responsible for or could mediate the capture of mercury on AC. A thorough study of the effects of acidic and alkaline oxygen-containing groups on mercury capture was published by Ghorishi and others (3). His group found no correlation between mercury removal and oxygenated functional groups. Although halogen- and sulfur-bearing surface functional groups are not well characterized, the beneficial role of halogens and sulfur in capturing mercury species on ACs is well established (3, 4). Recently, Laumb and others (5) and Benson and others (6) characterized sorbents exposed to flue gas and Hg⁰, 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 for reaction with elemental mercury.

Olson and others (7) developed a 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 uses the concept of zigzag carbene structures recently proposed by Radovic and Bockrath (8). A zigzag-edged carbene site is a basic binding site for which the various acid-gas components and the Hg(II) compete, including the HCl, which is important in promoting the oxidation of Hg⁰. This mechanism appears to involve the reaction with HCl to form stable carbenium ion intermediates. Figure 1 provides more details of the role of the chlorine adduct to the carbon. 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 Hg⁰ oxidation by the carbenium ion to the organomercury intermediate and subsequent oxidation by NO₂ to the bound Hg(II) species. A detailed understanding of these mechanisms will help us develop more effective and lower-cost sorbents. Ultimately, the refined model will have the potential to be used to describe flue gas-AC interaction and to predict capture efficiency. In addition, knowledge developed from this model will be useful for stabilizing Hg(II) on the sorbent and promoting the kinetics of mercury capture. A better understanding of the interactions and effects of flue gas constituents and conditions will result in an improved mechanistic model and the development of more effective sorbents for mercury capture and control.

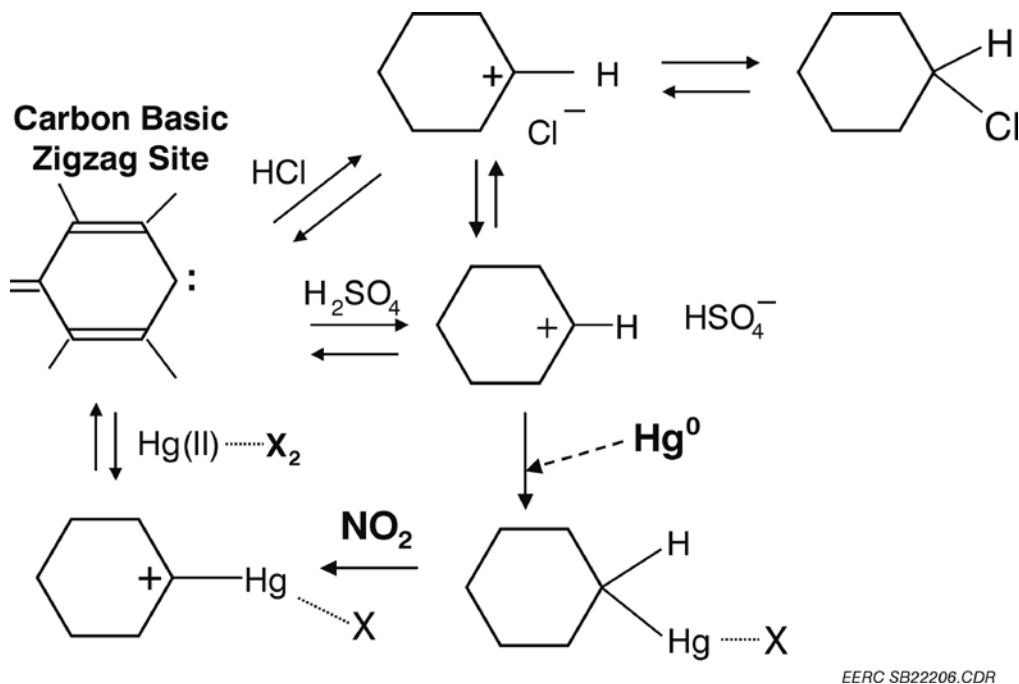


Figure 1. Oxidation site model for AC—the role of hydrochlorination in generating carbenium oxidant (9).

Approach

The overall approach to this research consisted 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

Work Plan

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

Task 1.1 – Hydrochlorination Effects on Sorbent Kinetics

The nature of the sorbent–Cl bond(s) was investigated for several hydrochlorinated (aqueous, gas, alternative compounds) carbon-based 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 had 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 was intended to provide insight into the oxidizing interactions of the carbon surface with Hg^0 and other flue gas constituents. Halogen-impregnated sorbents were loaded to various stages of capacity with Hg^0 using the bench-scale screening test apparatus. The loaded sorbents underwent 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 were compared to previously collected data. The research focused on two areas:

1. The effects of various chlorine impregnation techniques were investigated. The performance of aqueous, gas-phase, and alternative halogenating agents (SOCl_2 , for example) were compared.
2. The influence of HCl and other acids on the NO_2 -assisted oxidation of SO_2 to SO_3 was 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 were determined and correlated with mercury oxidation. The possibility of an induction period for sulfur(VI) formation at low-flue gas HCl concentration was investigated. The rate of sulfur(VI) formation was determined by ion chromatography.

Task 1.2 – Evaluation of Surface Chemistry

This effort attempted to use several analytical techniques to identify correlations between the kinetics of mercury oxidation and capacity for virgin or modified (e.g., impregnated) sorbents and various structural parameters. Test procedures included temperature-programmed desorption, Raman spectroscopy, and x-ray fine structure (XAFS) spectroscopy. Temperature-programmed desorption may identify phase transitions during the heating of lignite coals that may be related to the subsequent formation of graphene-edge structures in the AC prepared from the coal and may thereby affect the ability of the AC to oxidize and bind elemental mercury. 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 was investigated as a potential distinguishing tool. XAFS has the capability to detect mercury present in various compounds and on sorbent surfaces. It can distinguish different types of bonding.

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 focused on conditions that pertain to surface modifications that could alter the properties of the carbonaceous material. The effectiveness of a halide-based surface modification was determined.

Task 3 – Evaluation of Activated Carbons

Currently, most carbon sorbent development activities have concentrated on a commercially available AC—DARCO[®] FGD. Under this task, four ACs were prepared from coals provided by project partners. ACs were prepared in the 2.5-in.-diameter fixed-bed furnace and the 6-in.-diameter rotary kiln system. The ACs were evaluated for Hg^0 sorption using the bench-scale test apparatus.

Progress

In previous years, the research in this project focused on examining the role of HCl in promoting the oxidation of elemental mercury on the carbon surface, the mechanism of SO_2 oxidation as a competing reaction on the carbon surface, and the evaluation of AC produced from Fort Union lignite coals (Tasks 1 and 3). The commercially available DARCO FGD was the starting material for all tests

under Task 1. Aliquots of DARCO FGD were pretreated with various levels of chlorine as gaseous Cl_2 and HCl and as aqueous HCl and then exposed to simulated low-acid flue gas containing a nominal $10 \mu\text{g}/\text{m}^3$ Hg. The prepared samples were analyzed using XPS. The mechanism of SO_2 oxidation was examined using untreated and Cl_2 -treated DARCO FGD exposed to simulated flue gas containing various concentrations of NO_2 for several time periods. The exposed samples were leached, and soluble SO_4^{2-} was measured using ion chromatography. The Task 3 evaluation of Fort Union-derived ACs involved the production and subsequent bench-scale mercury screening of AC prepared from four coals supplied by project sponsors.

The resulting observations of this work were as follows:

- Inorganic chlorine on the surface is rapidly lost.
- For the Cl_2 - 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.
- The addition of Cl_2 to the carbon prior to flue gas exposure appears to facilitate SO_2 oxidation.
- The promotion effect of Cl_2 on the oxidation of SO_2 is consistent with the promotion effect on the oxidation of mercury. This inference suggests that the carbon catalysis mechanisms are similar.
- ACs 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 AC produced than the characteristics of the starting materials did.
- Chlorine pretreatment of ACs 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.

The effort this year focused on an examination of other analytical techniques that elucidate the surface of the carbon (Raman and XAFS spectroscopy) and the effectiveness of surface modification.

Raman Spectra of Halogenated Carbons

Raman spectra of carbon materials feature a pair of spectral lines at 1575 cm^{-1} (G-band) and 1360 cm^{-1} (D-band) corresponding, respectively, to vibrations (E_{2g2}) in the regular graphene structure and structurally disordered graphites. The structure of a brominated AC was investigated using dispersive Raman spectroscopy (532 nm). The brominated carbon was chosen because of previous Raman studies available in the literature, and the fact that brominated carbons are currently used in mercury control (e.g. NORIT DARCO HG-LH, Sorbent Technologies' B-PAC). The results show that the polybromide charge transfer complexes that formed in the graphitic carbon fibers do not occur in the brominated ACs. Bands corresponding to the C–Br vibrations also were not seen at the expected wave numbers.

There does not appear to be any way to get definitive structural information on the nature of the carbon bromine bonds in brominated carbons. Infrared spectra collected from chlorinated carbon samples in an earlier project showed similar lack of C–Cl bonding information. Of great interest is the finding that polybromine anions are not present in the brominated ACs, whereas their bands predominate in the carbon fiber spectra. The structural difference in the corresponding carbons is that the carbon fibers consist of highly laminar sheets into which the halogen anions can intercolate, whereas ACs comprise large amounts of edge structures that could be more reactive toward forming carbon–halogen bonds. Either structure could be reactive toward Hg; however, further research is needed to elucidate this structure–reactivity question.

XAFS Spectroscopy

XAFS was also examined intensely in a related project funded by SaskPower, the North Dakota Industrial Commission and the U.S. Department of Energy. The results of that work are being compiled and presented separately in a report entitled “Investigation of Mercury and Carbon-Based Sorbent Reaction Mechanisms – Comparison of Surface Analysis Techniques.”

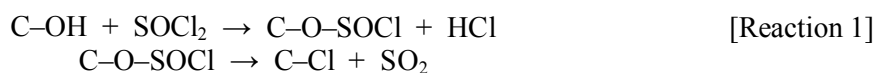
In a side-by-side comparison of XPS and XAFS analyses of ACs pretreated with chlorine and exposed to simulated flue gas for varying lengths of time (similar to the experimental matrix described in Table 1), the XAFS analysis confirmed the XPS data showing the reduction in chlorine on the sorbent surface over time with exposure to low-acid simulated flue gas. Both techniques indicated an increase in sulfur at the sorbent surface exclusively as S(VI).

The advantage of the XPS over XAFS for chlorine and sulfur analysis is the semi-quantitative nature of the XPS technique over the qualitative XAFS technique. XPS, however, does not provide good information for mercury concentration or speciation on most carbon sorbents because of the low levels of mercury present and the spectral interference from silicon, ubiquitous in coal- and biomass-derived ACs. XAFS has the capability to detect mercury present in various compounds and on sorbent surfaces. It can distinguish different types of bonding, as was demonstrated for all three species of interest—chlorine, sulfur, and mercury. The issues to be overcome associated with its use are the effects of sample preparation and subsequent data collection and the overwhelming need for a broader range of spectral data for standard compounds and combinations of compounds that might be present in an AC sample. Overall, the technique is the most promising tool found thus far for understanding the reactions and bonding taking place on the surface of ACs for mercury control.

Surface Modification Effects on Kinetics

Treatment of DARCO FGD carbon with an alternative chlorinating reagent was attempted to determine if a reagent that facilitates addition of chlorine to carbon atoms via replacement of the oxygens on the carbon would affect the kinetics of oxidation of mercury on the carbon.

DARCO FGD AC was pretreated with thionyl chloride (SOCl₂) at 3 wt% and tested in the bench-scale screening apparatus under low-acid flue gas concentrations described earlier. The mercury concentration was a nominal 11 μg/m³. The sample was exposed to the point of mercury breakthrough. The intent was to attempt to reject the hypothesis that oxygen functionality is important to mercury capture, since oxy groups will have been converted to organochloro groups via Reaction 1.



The effect of the treatment in eliminating the induction period was clearly seen. The initial capture (reactivity) was 95% compared with the untreated FGD at about 75%. As is typical for treated carbons, the capture decreases gradually (slow breakthrough) and eventually crosses over the FGD curve.

Based on these results, the addition of halogen in the form of thionyl chloride improves the oxidation reactivity, similar to addition of halogen as HCl or Cl₂, by promoting formation of oxidation sites. Thus the hypothesis that oxygen functionality is important to mercury oxidation is rejected.

Quality Assurance/Quality Control (QA/QC)

Quality Objectives

Activities within this multi-client 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 were as follows:

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 were evaluated for accuracy, validity, and completeness.

Measurement/Data Acquisition

The EERC's Process Chemistry and Development Laboratory (PCDL) produced various sorbent-based samples to be screened for mercury control effectiveness. The Mercury Research Laboratory (MRL) at the EERC was responsible for conducting the bench-scale mercury-screening measurements. All EERC laboratories use documented methods for calibration and QC.

XPS analysis was performed at Evans Analytical Laboratory in Eden Prairie, Minnesota. The laboratory has established QA/QC protocols for instrument calibration and sample analysis.

Assessment and Validation

The compiled data were evaluated for accuracy, validity, and completeness. Method validation and evaluation of measurement accuracies are included as part of the MRL procedures. Instrument and mass flow calibration checks have been incorporated into bench-scale screening protocols to help interpret data and provide results within known confidence limits. Periodic analysis of a baseline sorbent provides assurance for consistent results. Where possible, results were based on independent collaborating measurements to ensure that valid conclusions are drawn.

Status

This project is 100% completed. There are still many remaining questions in the mechanism of carbon–mercury oxidation and binding. It is unlikely that all questions can be answered by the results of this project, but much has been learned about the state of the carbon surface.

Potential Applications and Benefits

Potential Users and Real-Life Applications

The industrial and governmental consortium members are 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.

Technology Transfer

The results were transferred to the consortium members through written reports. In addition, results were presented at a national meeting.

Technical and Economic Benefits

Results of this research could be used to improve mercury control technologies that will allow for economical control in coal-fired combustion systems.

Environmental and/or Health Benefits

Ultimately, this research could result in improved methods of mercury control, which are intended to protect the natural environment and humans by removing mercury from combustion stack gases before it can be released to the atmosphere.

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