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INVESTIGATION OF MERCURY AND CARBON-BASED SORBENT REACTION MECHANISMS

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Project Description

The EERC has developed a fundamental research consortium that is 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 a 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 the 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 a 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.

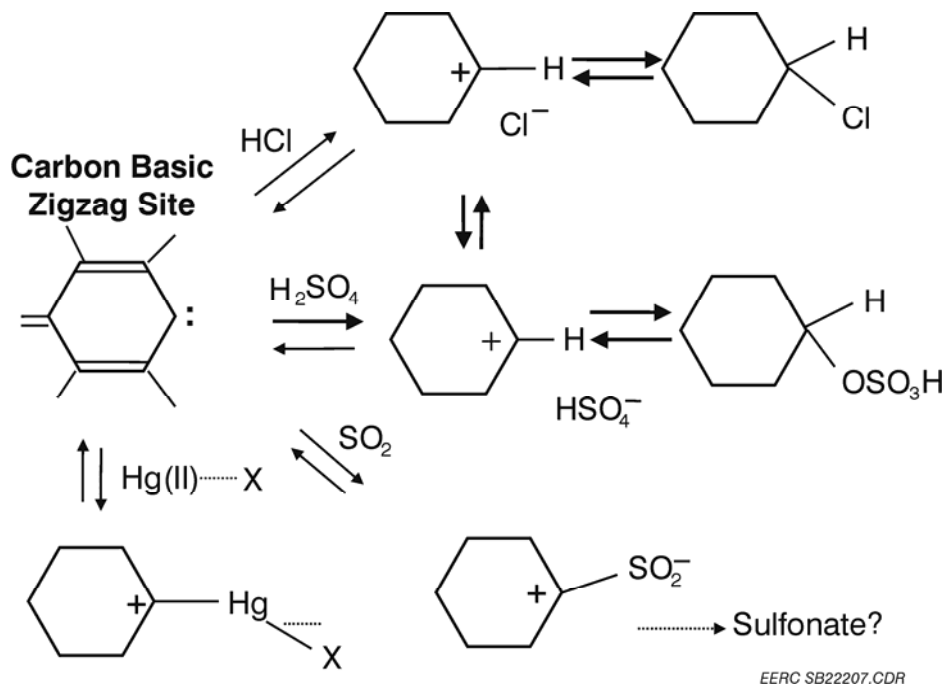


Figure 1. Binding site model for activated carbon.

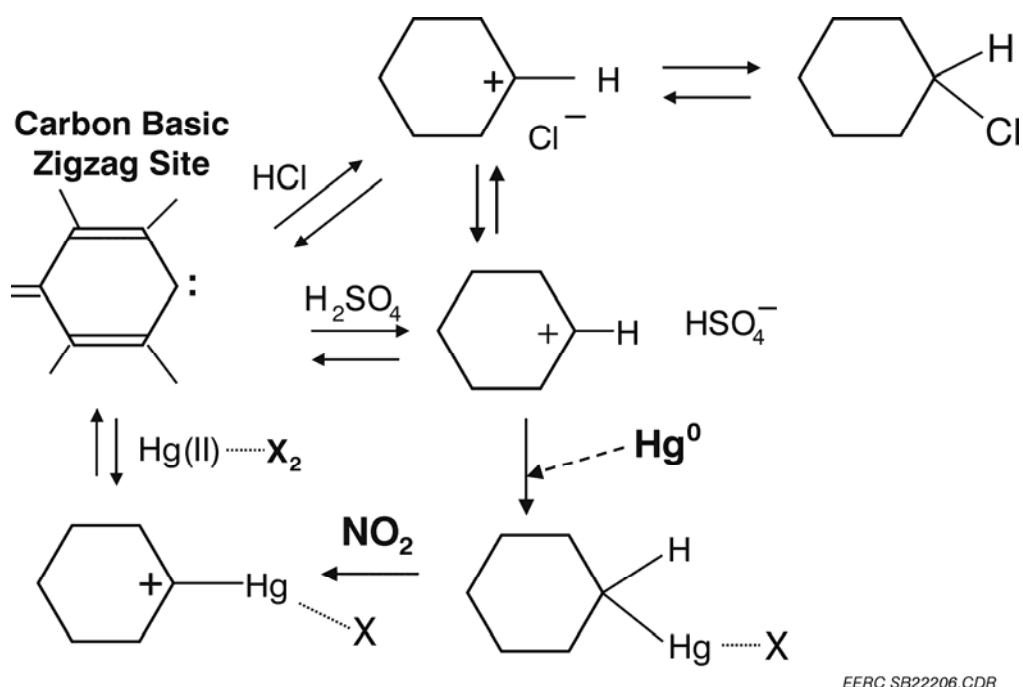


Figure 2. Oxidation site model for activated carbon—the role of hydrochlorination in generating carbenium oxidant (16).

Approach

The 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

Work Plan

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 for 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 the activity of the 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 SO₂ on the surface oxidation sites, it is important to identify activation conditions that improve selectivity of carbons for mercury and less selectivity for SO₂. 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 the 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

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

Activities focused on reducing the data from the XPS analysis. Samples prepared from the test matrix (Table 1) developed last quarter underwent XPS analysis to begin to examine the nature of the sorbent–chlorine bonds and potential effects on mercury capture. As described in the last quarterly report, DARCO FGD activated carbon was pretreated with 1%–2% chlorine using three application methods: aqueous HCl, gaseous HCl, and chlorine gas. Aliquots of 500 mg of the pretreated carbons were exposed to low-acid simulated flue gas (6% O₂, 12% CO₂, 15% H₂O, 580 ppm SO₂, 120 ppm NO, 6 ppm

Table 1. Test Matrix for Sample 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 capture (20 min)	Aqueous HCl
T1-3	10%–15% Hg breakthrough	Aqueous HCl
T1-4 (baseline)	None	HCl(g)
T1-5	Initial capture (20 min)	HCl(g)
T1-6	10%–15% Hg breakthrough	HCl(g)
T1-7 (baseline)	None	Gaseous Cl ₂
T1-8	Initial capture (20 min)	Gaseous Cl ₂
T1-9	10%–15% Hg breakthrough	Gaseous Cl ₂

NO₂, and 1 ppm HCl) on the bench-scale apparatus to provide enough material for further analysis. Exposure times represent optimum capture of the sorbent and 10%–15% mercury breakthrough as noted in Table 1. Actual exposure times for the 10%–15% breakthrough varied from 3 to 6 h.

All samples were analyzed by XPS at the Evans PHI Laboratory, Chanhassen, Minnesota, as the second step in the kinetic study. A survey scan was completed on each carbon, followed by a high-resolution scan for carbon-, oxygen-, sulfur-, and chlorine-binding energy regions. Table 2 presents the results of the survey scans. The actual carbon content of the samples was assumed to be constant since the loading temperature of the experiment is insufficient to evolve carbon compounds. Therefore, ratios of detected analytes were calculated normalized to carbon. In this format, it is easily seen that the surface became enriched in several mineral elements and oxygen during the aqueous application. Over the course of the test, the sulfur concentrations at the surface increased by a factor of 5 for the aqueous pretreatment and a factor of <15 for the gaseous-phase treatments. A similar trend of increasing oxygen concentrations was observed where the oxygen concentration of gaseous-phase treated carbons increased by a factor of about 2.5. Preliminary analysis of the survey scan data shows a greater effect of aqueous application of chlorine in the starting material than the gaseous application with regard to several elements, i.e., oxygen, magnesium, and aluminum. There also appears to be some enrichment of sulfur, silicon, and calcium. All three carbons show an increased chlorine concentration ranging from 1.2 to 1.8 at% as compared to <0.1 at% in the untreated carbon.

Table 2. Surface Characterization of Pretreated Sorbents Using XPS Analysis (survey scans normalized to carbon), at%

Test No.	C	O	N	Al	Ca	Cl	Fe	Mg	Na	P	S	Si
Untreated Carbon	86.4	9.3	0.3	0.5	0.9	0.1	0.1	0.1	1.4	0.1	0.1	0.3
T1-1 (baseline)	67	20.9	<0.1	1.7	1.8	1.4	0.3	4.7	<0.1	<0.1	0.8	1.4
T1-2	67.6	22	0.2	1.5	1.2	1	0.2	2.7	<0.1	<0.1	2.2	1.4
T1-3	67	29.8	0.22	0.97	1.62	0.65	0.11	0.86	<0.1	<0.1	5.19	1.62
T1-4 (baseline)	84.5	9.6	0.4	0.5	1.9	1.2	0.1	0.5	<0.1	0.2	0.2	0.9
T1-5	84.5	13.2	0.42	0.52	1.04	1.04	0.1	0.62	<0.1	0.21	1.35	0.94
T1-6	84.5	26.2	<0.1	0.72	1.8	<0.1	<0.1	0.96	0.24	0.12	5.04	0.72
T1-7 (baseline)	85.4	9.3	0.2	0.5	1.4	1.3	0.1	0.6	<0.1	0.1	0.3	0.8
T1-8	85.4	11.9	0.21	0.51	1.34	1.23	0.1	0.51	<0.1	<0.1	0.93	0.82
T1-9	85.4	24.5	0.36	0.48	1.91	0.95	0.12	0.6	<0.1	<0.1	4.65	0.6

High-resolution XPS scans were performed on the samples to examine specific species for selected elements. The high-resolution scans show the specific chemistry of each desired element. Elements of interest for this experiment were carbon, oxygen, chlorine, and sulfur species as previous work indicated that there is insufficient mercury in the samples to overcome the interference of the overlapping silicon peak. Analysis of the results indicated that the carbon 1s binding region contained one large peak of asymmetric shape typical for carbon black powders or graphitic materials. The main component is associated with single C–C bonding (this may also include some C–H bonding, which overlaps the C–C region). There is also a broad shake-up structure centered at approximately 291 eV, which is consistent with aromaticity. A low-level C–O band of various intensities is also detected in all the carbon 1s spectra.

XPS Analysis of the Starting Materials

The oxygen 1s binding region included one large peak at 532.6 eV for the samples treated with gaseous chlorine (Cl_2 and HCl) and 533.0 eV for the sample treated with aqueous HCl . The aqueous application of HCl increased the oxygen concentration at the surface as compared to untreated DARCO FGD, whereas the gaseous applications had no effect. The nearly 200% increase is likely a result of the inorganic constituents deposited at the surface. The additional inorganic chemical bonds on the surface would alter the peak maximum and peak shape, which was observed.

The sulfur 2p binding region contained complex sets of peaks of sulfur ranging from reduced sulfur species (S[II]) to fully oxidized sulfur species (S[VI]). The sulfur content of the three starting materials showed the effects of the chlorine application methods. Based on the binding energies, the gaseous applications had lower sulfide (S[II]) and thiophene compound content than the untreated DARCO FGD (11%–16% vs. 33% each). The remaining sulfur in the gas-treated carbons (70%–76%) was determined to be sulfite compounds (S[IV]). In contrast, the aqueous application of HCl resulted in the complete loss of sulfide as H_2S evolved and a decrease of thiophene and sulfite compounds (S[IV]) to 9% and 51%, respectively. The remaining 40% of the sulfur was present as oxidized S(VI) compounds, possibly from mineral deposition.

The chlorine additions resulted in a similar chlorine at% content in the three applications (1.2%–1.4%). Since chlorine was not detected in the untreated DARCO FGD, all of the chlorine present came from the chlorine addition. The chlorine 2p region included overlapping singlet and doublet peaks representing both organically associated chlorine and inorganic chloride species. Interestingly, the method of application affected the surface chemistry more than the form of chlorine applied. The partitioning of chlorine in the gaseous Cl_2 and $\text{HCl}(g)$ -treated starting materials was 70/30 organochlorine to chloride. In contrast, approximately half of the chlorine in the $\text{HCl}(aq)$ -treated carbon was present as chloride.

XPS Analysis of the Activated Carbons Post-Simulated Flue Gas Exposure

Figure 3 shows the mercury content of the flue gas after passing through the fixed-bed activated carbon during the preparation of carbon samples 1 month prior to XPS analysis. As the figure indicates, all of the treated carbons captured most of the mercury from the start of the test in contrast to the untreated DARCO FGD. The activated carbon treated with $\text{HCl}(aq)$ provided the best capture at the start of the test, capturing more than 95% of the mercury for nearly 2 h. The gaseous applications captured >90% of the mercury during the first 1.5 hr. Overall, the performance of the gaseous HCl treated carbon was comparable to the aqueous treated carbon. The Cl_2 -treated carbon lost capture capacity over time and reached 15% breakthrough 3.7 h into the test. Therefore, the test was terminated early compared to the other loading tests.

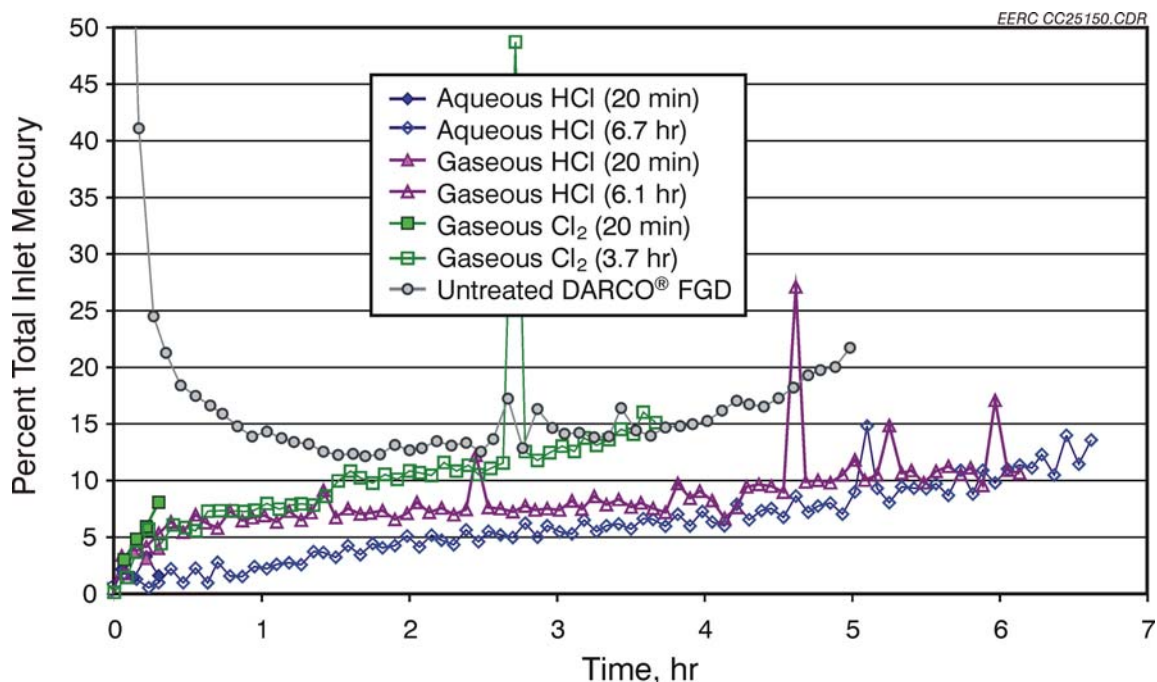


Figure 3. Outlet mercury profile during loading of pretreated activated carbons for XPS analysis.

As with the unexposed samples, the oxygen 1s binding region contained a single large shoulderless peak, which shifts over time. By the end of the test, the peak from the Cl_2 -treated carbon shifted down to 532.2 eV, and the peak from the $\text{HCl}(aq)$ -treated carbon shifted down to 532.6 eV. The source of these discrepancies has not yet been identified. The intensity of all peaks increased, indicating an increased concentration of oxygen at the sample surface.

As expected, the S(VI) peak in the sulfur 2p binding region increased while the thiophene (S(II)) peak diminished, and the sulfide (S(III)) peak disappeared for each sample. The total sulfur concentration of each sample exposed to simulated flue gas increased 6- to 25-fold over the course of the experiment from about 0.2 at% for the gaseous applications and 0.8 at% for the aqueous-treated carbon to around 5 at%, as indicated in Table 2. More than 95% of this sulfur is S(VI), and there is adequate oxygen at the surface to support the presence of sulfur as sulfate ions. The buildup of S(VI) on the surface coincides with mercury capture breakthrough and is hypothesized to interfere with the binding of oxidized mercury on the carbon surface.

$\text{Cl}_2(g)$ Treated Carbon

Aside from the peaks of the sulfur 2p region, the peaks in the chlorine 2p binding regions showed the greatest changes during the experiment. The surface of the Cl_2 -treated carbon maintained the greatest concentration of chlorine throughout the experiment. Changes in the spectra after 20 min occur mainly to the lower energy peaks, as would be expected for the loss of much of the HCl or chloride as HCl. This would be most easily displaced by the sulfuric acid (H_2SO_4) being formed. The intensity of the organochlorine peak stayed nearly constant, with no change in the binding energy. Very small changes occur at the higher-energy end of the spectra. By comparing the starting material with the 20-min sample, we see that a peak between the organochlorine doublet disappears. The 201.3 eV peak for the 20-min sample is lower, perhaps because of the loss of occluded Cl_2 .

The chloride/HCl peak is completely gone at 15% breakthrough (3.7 h). The 197.8 eV peak is likewise gone. Significant loss of organochlorine intensity occurred at 15% breakthrough. So the sample underwent a dehalogenation or dehydrohalogenation with the loss of chlorine as HCl from the organochlorine groups. Probably the remaining chlorines are relatively inert to the sulfuric acid-driven dehalogenation. The high-energy chlorine peak is also gone.

HCl(g)-Treated Carbon

The peak profile of the HCl(g)-treated carbon was similar to the Cl₂-treated carbon, but with slightly lower intensities. Changes in the spectra after 20 min occur mainly to the lower-energy chloride peaks, as with the Cl₂-treated sample. HCl would be most easily displaced by the sulfuric acid being formed. Some decrease in intensity of the organochlorine peak occurred, with no change in the binding energy. Very small changes occur at the higher-energy end of the spectra. By comparing the starting material with the 20-min sample, we see that a peak between the organochlorine doublet disappears. The 201.3eV peak for the 20-min exposure is lower, again, perhaps because of the loss of occluded Cl₂.

All chlorine is completely gone at 10% breakthrough (6.1 h). So the sample underwent a dehalogenation or dehydrohalogenation with loss of HCl from the organochlorine groups. So all chlorine is labile to the sulfuric acid-driven dehalogenation in this sample, but it was exposed almost twice as long as the Cl₂-treated sample.

HCl(aq)-Treated Carbon

While initially different from the gaseous-treated carbons because of its high chloride ratio (54/40 versus 30/70), the peak profile of the HCl(aq)-treated carbon came to resemble the Cl₂-treated peak profile by the end of the experiment. Changes in the spectra after 20 min occur mainly to the lower-energy peaks, as with the Cl₂-treated sample. HCl would be most easily displaced by the sulfuric acid being formed. Some decrease in intensity of the organochlorine peak occurred, with no change in the binding energy. Very small changes occur at the higher-energy end of the spectra.

The HCl/chloride peak is no longer present at 10% breakthrough (6.7 h), but the organochlorine is still present. As with the Cl₂-treated sample and unlike the HCl(g)-treated sample, not all the chlorine is labile to the sulfuric acid-driven dehalogenation in this sample, even though it was exposed to simulated flue gas longer than the HCl(g)-treated sample.

With respect to all three samples, the HCl/chloride peak in the gaseous-treated carbons is initially small compared to the organochlorine and is lost rapidly in the flue gas. In the HCl(aq)-treated carbon, the HCl/chloride peak is initially comparatively large, but it, too, is lost rapidly in the flue gas as with the other samples. Since the organochlorine peak decreased but did not disappear at >10% mercury breakthrough for the Cl₂- and HCl(aq)-treated carbons, part of the chlorine in the sample is tightly fixed organochlorine and part is more easily displaced. In contrast, the organochlorine peak of the HCl(g)-treated carbon disappeared at 10% mercury breakthrough; being easily displaced, none of the chlorine in the sample is tightly fixed organochlorine.

The goal of this investigation is to elucidate the behavior of mercury on the carbon surface; however, because of its very low concentration in the sample and instrumental interference of silicon, mercury was not detected on the surface. Therefore, direct analysis of mercury bonding cannot be determined by this technique at these low concentrations even at the maximum mercury capture capacity of the sorbent. Even if the mercury peak were observed, there is little difference in energy between mercury compounds. Since chlorine has a large effect on mercury oxidation and capture, understanding

the chemical forms of chlorine on the sorbent and the change in its forms with exposure will be beneficial in understanding the mercury–sorbent interactions.

Reactivity Test of the Treated Activated Carbons

At the time of the XPS analysis, mercury reactivity tests were performed on the three pretreated carbon samples. These tests were performed on the bench-scale screening apparatus under conditions similar to the bench-scale flue gas exposure/mercury loading described at the beginning of the Progress section on Page 134. Important differences to note are that the reactivity tests took place approximately 5 weeks after the activated carbons were treated and that the test is carried out to 100% mercury breakthrough to evaluate the capacity of the sorbent. In addition, smaller aliquots of material (37.5 mg) diluted with sand (113.5 mg) provide a thin bed and shorter testing times to minimize cost. The system was operated at 29.9 scfh.

The results of the test are presented in Figure 4. The Cl_2 -treated carbon sample exhibited high initial activity (10% of inlet) but climbed rapidly to 17% of inlet. Thus no induction period was required to obtain good mercury capture. After the capture rate leveled out, the main mercury breakthrough was initiated at 33 min. The $\text{HCl}(g)$ -treated sample exhibited an initial mercury capture of 10% of inlet, then dropped down to <5% of inlet and leveled out—a very small induction period produced excellent mercury capture. Main breakthrough was initiated at 30 min. The $\text{HCl}(aq)$ -treated sample showed mediocre initial sorption at 28% of inlet, which increased slowly to 23% of inlet. Thus a long induction period was

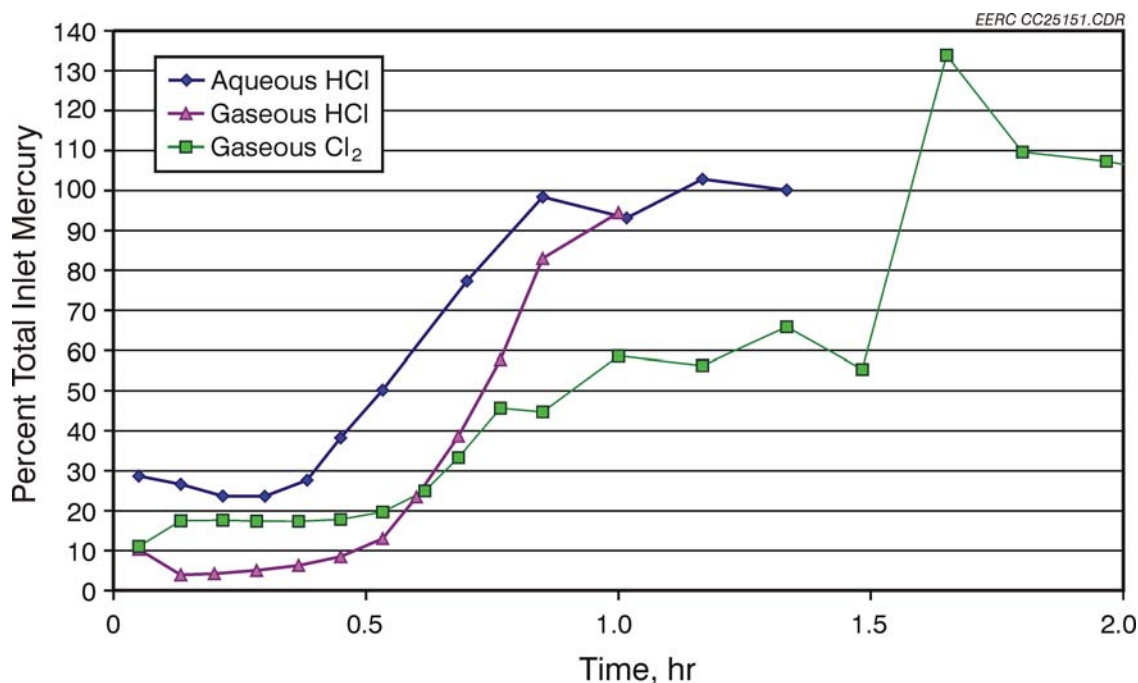


Figure 4. Mercury reactivity of the pretreated activated carbon sorbents.

required to obtain poorer mercury capture than either of the gaseous-treated carbons. The main mercury breakthrough began 20 min into the test.

None of the carbons exhibited superior performance. The Cl_2 -treated carbon started with excellent sorption but rapidly lost activity. The $\text{HCl}(g)$ -treated sample required a short induction period to achieve good activity. This was surprising based on all previous screening tests which have shown good activity from the start of the test. The $\text{HCl}(aq)$ -treated sample performed the poorest of all three and only slightly better than the untreated FGD. This result is in direct contrast to the mercury capture curves collected during the loading/exposure tests performed 5 weeks earlier (Figure 3). Although the results are not directly comparable—reactivity tests used 37.5 μg carbon mixed with 112.5 μg sand versus loading tests used 500 μg —one would expect similar trends to result from both types of tests. One reason that the results are in contrast may be the stability of the pretreatment techniques on the sorbents. Another possibility may be that the tests are not comparable. We plan to investigate this change in reactivity as the research continues.

Task 3 – Evaluation of Activated Carbons

As a preliminary experiment in producing activated carbon from Fort Union lignite, samples of coal obtained from three sponsors were charred and activated in a fixed-bed reactor. Aliquots of the product activated carbons were screened for mercury activity using the bench-scale mercury-screening apparatus.

All coals were sieved, and the $-1/8 + 20$ -mesh size was selected. Two coals, an Underwood coal from the Falkirk Mine and a Beulah Zap coal from the Dakota Westmoreland Mine, were carbonized and steam-activated in a single process. A nominal 1000 g of coal was placed in a 3-in. fixed-bed reactor and heated slowly to 400°C in a gentle flow of N_2 (250 cm^3/min). The 1-m-long reactor is vertically oriented with a gas and steam inlet at the base and an outlet at the top. The gases are introduced through a probe near the bottom of the carbon column, and a thermocouple measures the internal temperature of the reactor near the top of the heated zone. During the carbonization process, volatile organic compounds and tarry material exit the top of the reactor in the N_2 stream and travel to condensation pots where all but the most volatile compounds are collected. Once the flow of volatile material from the outlet ceased, the furnace temperature was increased in preparation for the activation step. Activation was carried out as reported in Table 3, varying temperature and exposure time. In all cases, the activation gas was superheated steam in a 250- cm^3/min N_2 flow. Once the activation time ended, the steam and furnace were turned off. N_2 continued to flow through the reactor until the material cooled and was removed to a plastic bag in a tin can and purged with N_2 before being sealed. The volume of the product carbon was considerably smaller than that of the initial coal aliquot.

Hagel A from the Center Mine was carbonized in the 6-in.-i.d. rotary kiln at 425°C and fed through the kiln at the rate of about 4 kg/hr (9 lb/hr). A 1000-g aliquot of the devolatilized char was steam-activated in the 3-in. fixed-bed reactor under the conditions listed in Table 3. Therefore, the amount of char present at the start of the steam activation step was greater for this material than for the other coals. The thermocouple inserted at the top of the reactor was long enough to contact the char during the activation step. It, rather than the furnace temperature, was used to determine the activation temperature. In order to maintain the internal temperature at 800°C , the furnace temperature was set at 650°C as noted in the table. The cooling and storage process was the same as for the other tests.

Table 3 also shows the yields of the various materials. The two activated carbons prepared at a furnace temperature maintained at 800°C had lower-than-expected yields of 27%–28% (CC-2 and CC-1, respectively). Table 4, which provides a comparison of several carbonization and activation tests carried

Table 3. Preparation of Activated Carbons from North Dakota Lignites in the 3-in. Fixed-Bed Reactor

Sample ID	Feedstock	Carbonization Conditions		Activation Conditions		Yield, %	I ₂ No., g/m ²
		Time, min	Temperature, °C	Time, min	Temperature, °C		
CC-1	Falkirk Coal	130	400	57	800	28.3	564
CC-2	Beulah Zap Coal (WCC)	110	400	35	800	27.2	543
CC-3	Center Char (BNI) ¹			39	650	64.9	336
CC-4	Falkirk Coal	120	400	37	650	34.8	310

¹ Carbonization of the Center coal was carried out in the 6-in. rotary kiln reactor.

Table 4. Comparison of Several Carbonization and Activation Tests Carried Out in the Reactors for Either 30 or 60 Minutes

	Carbonization		Activation		Carbon/Coal Yield, %
	No. of Tests	Yield, %	No. of Tests	Yield, %	
1-in. Reactor at 750°C ¹	5	50.0	4	71.6	36.6
1-in. Reactor at 800°C ¹	NA ²	NA	3	65.4	35.1
3-in. Reactor at 750°C ³	14	56.3	9	71.4	40.0
3-in. Reactor at 800°C	2		2		27.8

¹ Data from Ref. 17.

² Not applicable.

³ Data from Ref. 18.

out in the reactors for either 30 or 60 minutes, shows that this is less than was previously determined in the 1-in. fixed-bed reactor at either 750° or 800°C. Since all previous attempts at making activated carbon from coal were carried out in two separate carbonization and activation runs, potential effects of the multistage run were unknown. It was thought that the temperature at the top of the vertical reactor might be too high since the volume of material had diminished at the start of the activation test. Therefore, two tests (CC-3 and CC-4) were carried out based on maintaining the internal furnace temperature at 800°C instead of the furnace temperature being set to 800°C. In order to achieve this, the furnace was set at 650°C to maintain a thermocouple temperature in the reactor near 800°C. The resulting yields of 64.9% from char and 34.8% from coal were closer to those achieved in previous tests. It is possible that the excess steam at the higher temperature was responsible for the higher burnout rate of the first two tests.

Results of the surface area analysis show that the samples activated at the 800°C range, CC-1 and CC-2, had much greater surface area than those activated at a furnace temperature of 650°C. CC-1, which was exposed to steam at >800°C for 57 min, had a slightly higher iodine number at 564 g I₂/m² than CC-2, which was exposed for 35 min, resulting in a surface area of 543 g I₂/m². The internal temperature near the top of the reactor was likely close to 900°C during these tests. Carbons activated at the internal reactor temperature of 800°C were insufficiently activated, resulting in products of inferior quality. The surface areas were only in the 310 to 340 g I₂/m² range, which is lesser than in carbons produced previously. However, the most telling data will likely be the results of the bench-scale screening tests.

The elemental mercury capture characteristics for the North Dakota lignite-derived activated carbons were determined by testing in a bench-scale apparatus using synthetic low-acid flue gas under high-flow conditions. The composition of the flue gas includes the following: 6% O₂, 12% CO₂, 15% H₂O, 580 ppm SO₂, 120 ppm NO, 6 ppm NO₂, and 1 ppm HCl; samples were diluted with powdered sand in a 1:3 ratio (-325 mesh). Each bed consisted of 37.5 mg of carbon with 112.5 mg sand (one-quarter of the amount used in the previous test protocol) in order to distinguish reactivity of similar carbons. The

flow rate was the same as in the previous test protocol, i.e., 30 scfm. The control sample was NORIT Americas Inc.'s commercial DARCO FGD carbon.

Aliquots of the activated carbons and of halogenated samples of the carbons were tested for reactivity and capacity on the bench scale with full low-acid flue gas composition at the fast-flow condition. Total mercury in the effluent was determined and converted to % of inlet. Elemental mercury in the effluent was determined after breakthrough as an indication of the number of active sites available for oxidation on the carbon.

The results of the screenings are presented in Table 5. A large induction period was obtained for the DARCO FGD carbon, which is normal for low-acid-gas tests. Starting concentrations are typically 40%–50% of inlet, and 20 min is required for maximum capture. The elemental mercury fraction following breakthrough was 20%, indicating an oxidation rate of 80%. Thus the initial rate, maximum rate, capacity, and oxidation rate were normal for the diluted sample in a fast-flow stream.

The CC-1 exhibited mediocre capture at the start and did not improve much, that is, the induction effect was relatively minor. Breakthrough initiated early as well. Only 50% of the mercury was oxidizing following breakthrough. Thus the performance was far inferior to the DARCO FGD with respect to maximum capture rate capacity and oxidation rate.

For the CC-2 carbon, the initial capture was much better (80%) compared to DARCO FGD, and a very small induction period was observed (7 min), giving a better maximum capture rate. The 50% breakthrough time was also longer than for the DARCO FGD carbon. Oxidation following breakthrough was similar to the DARCO FGD.

The CC-2 sample that was chlorinated under dry conditions showed high initial activity with elimination of the induction period, as expected, but also a faster breakthrough. Oxidation following breakthrough was 60%, which was somewhat disappointing.

The CC-2 sample that chlorinated under wet conditions showed similar good initial activity and no induction, but it also broke through relatively quickly. Oxidation following breakthrough was 50%.

Both the CC-3 sample and the chlorinated CC-3 sample were extremely poor sorbents, exhibiting instant breakthrough and only slight promotion with chlorine. No mercury was oxidizing in either

Table 5. Mercury Emissions as % of Inlet Mercury at Critical Times in the Test and Breakthrough Times for Test Samples

Sample	50% Breakthrough, min	Start of Test, % of inlet	Maximum Capture, % of inlet	Time for Maximum, min	Hg ⁰ Fraction after Breakthrough, % of inlet
FGD	40	50	18	21	20
CC-1	25	47	43	8	50
CC-2	46	20	16	7	22
CC-2 (dry Cl)	30	<10	<10	0	40
CC-2 (wet Cl)	17	<10	<10	0	50
CC-3	<1	92	87	10	100
CC-3 (wet Cl)	<1	72	72	0	100

sorbent. The chief difference between this and the two previous carbons was the lower activation temperature. Thus CC-4 was not evaluated on the screening apparatus.

Quality Assurance/Quality Control (QA/QC)

Quality Objectives

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 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 will be evaluated for accuracy, validity, and completeness.

Measurement/Data Acquisition

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

XPS analysis will be performed at Physical Electronics, Inc. (PHI), in Eden Prairie, Minnesota will perform XPS analyses. PHI has established QA/QC protocols for instrument calibration and sample analysis.

Assessment and Validation

The compiled data will be 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 prove results within known confidence limits. Periodic analysis of a baseline sorbent provides assurance for consistent results. Where possible, results will be based on independent collaborating measurements to ensure that valid conclusions are drawn.

Status

This project is about 50% completed. The experimental components of Task 1.1 have been completed, but may bear repeating if sufficient funds are available. We have also evaluated several Fort Union lignite-derived activated carbons under Task 3.

The remainder of the project will focus on an examination of other analytical techniques that elucidate the surface of the carbon (such as XAFS, Raman spectroscopy, and Boehm titrations), the effectiveness of modifications to the surface, and the evaluation of coal characteristics of Fort Union

coals. There are still many remaining questions in the mechanism of the carbon–mercury oxidation and binding. It is unlikely that all questions can be answered by the results of this project, but we have already learned much about the state of the carbon surface.

Potential Applications and Benefits

Potential Users and Real-Life Applications (applies to all projects)

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.

Technology Transfer

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.

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 (applies to all projects)

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

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