MERCURY SPECIATION IN COAL-FIRED POWER PLANT FLUE GAS - EXPERIMENTAL STUDIES AND MODEL DEVELOPMENT

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Principal Authors:
Dr. Radisav D. Vidic
Dr. Joseph R.V. Flora
Dr. Eric U. Borguet

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**U.S. Department of Energy
National Energy Technology Laboratory
3610 Collins Ferry Road
Morgantown, WV 26507-0880**

Submitted by:

**University of Pittsburgh
Department of
Civil and Environmental Engineering
Pittsburgh, PA 15261-2294**

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ABSTRACT

The overall goal of the project was to obtain a fundamental understanding of the catalytic reactions that are promoted by solid surfaces present in coal combustion systems and develop a mathematical model that described key phenomena responsible for the fate of mercury in coal-combustion systems. This objective was achieved by carefully combining laboratory studies under realistic process conditions using simulated flue gas with mathematical modeling efforts. Laboratory-scale studies were performed to understand the fundamental aspects of chemical reactions between flue gas constituents and solid surfaces present in the fly ash and their impact on mercury speciation. Process models were developed to account for heterogeneous reactions because of the presence of fly ash as well as the deliberate addition of particles to promote Hg oxidation and adsorption. Quantum modeling was used to obtain estimates of the kinetics of heterogeneous reactions. Based on the initial findings of this study, additional work was performed to ascertain the potential of using inexpensive inorganic sorbents to control mercury emissions from coal-fired power plants without adverse impact on the salability fly ash, which is one of the major drawbacks of current control technologies based on activated carbon.

EXECUTIVE SUMMARY

The overall goal of the project was to obtain a fundamental understanding of the catalytic reactions that are promoted by solid surfaces present in coal combustion systems and develop a mathematical model that described key phenomena responsible for the fate of mercury in coal-combustion systems. This objective was achieved by carefully combining laboratory studies under realistic process conditions using simulated flue gas with mathematical modeling efforts. Laboratory-scale studies were performed to understand the fundamental aspects of chemical reactions between flue gas constituents and solid surfaces present in the fly ash and their impact on mercury speciation. Process models were developed to account for heterogeneous reactions because of the presence of fly ash as well as the deliberate addition of particles to promote Hg oxidation and adsorption. Quantum modeling was used to obtain estimates of the kinetics of heterogeneous reactions. Based on the initial findings of this study, additional work was performed to ascertain the potential of using inexpensive inorganic sorbents to control mercury emissions from coal-fired power plants without adverse impact on the salability fly ash, which is one of the major drawbacks of current control technologies based on activated carbon.

The impact of fly ash on mercury speciation was evaluated for six different fly ash samples in simulated flue gas using a fixed bed reactor. Similar experiments were conducted with specific inorganic constituents to elucidate the key fly ash surface characteristics that affect mercury speciation in flue gas. No homogeneous mercury oxidation was observed at 140 °C. Mercury uptake tests with different fly ash samples revealed that loss on ignition (LOI), surface area, and particle size all had positive effects on mercury oxidation and adsorption (i.e., as the above parameters increased, mercury adsorption and oxidation also increased). Experiments with pure inorganic components showed that alumina (Al_2O_3), silica (SiO_2), calcium oxide (CaO), magnesium oxide (MgO), and titania (TiO_2) do not promote mercury oxidation or adsorption. Ferric oxide (Fe_2O_3) and unburned carbon, on the other hand, showed significant mercury oxidation and capture. Increases in LOI (unburned carbon content) and surface area of fly ash resulted in improvements in mercury capture and oxidation. Particle size also exhibited similar positive effects on mercury uptake and oxidation. Such behavior could be explained by the fact that the unburned carbon in fly ash has a relatively high surface area compared to other fractions and that it tends to be enriched in coarser fractions of fly ash samples. The interaction between flue gas components and surfaces is found to have significant impact on mercury transformation. NO , O_2 , H_2O , and SO_2 did not promote mercury oxidation or capture on carbon black. NO_2 can help oxidize and capture mercury on carbon black with or without O_2 . HCl showed the most profound effects on mercury oxidation and capture. O_2 plays an important role when combined with HCl , where the Deacon process could be involved. SO_2 inhibited mercury oxidation and capture probably by competing for electron acceptors with mercury and occupying the adsorption sites on the surface.

The second part of experimental studies focused on the finding that iron oxide (Fe_2O_3) can adsorb and oxidize mercury as a potential for the development of inexpensive mercury control technology. Abandoned mine drainage (AMD) sludge, which results from active or passive treatment of AMD, contains very high concentrations of iron and may be used as an effective and economical sorbent to capture or oxidize Hg^0 . The impact of flue gas composition and temperature on Hg uptake and oxidation was investigated in a fixed-bed reactor system, while the entrained flow system was utilized to test the performance of AMD sludge samples on mercury removal under typical conditions associated with powdered sorbent injection. AMD-

based sorbents promoted mercury oxidation, with mercury removal proportional to the percentage of Fe and to the overall Fe injection rate. The foam index of AMD sorbent was lower than that of fly ash and comparable to Portland cement, indicating that the use of this sorbent would not negatively impact beneficial reuse of fly ash for concrete production.

Modeling studies were performed to understand the kinetics of heterogeneous transformation of Hg in flue gases. The initial thrust in this research was to develop a process model describing detailed chemical reactions of mercury in the gas phase and on surfaces, and to fit the data to the model to obtain kinetic parameters. The complex nature of the reactions, and the absence of kinetic data involving Hg reactions on surfaces, required the use of quantum chemical models to extract surface reaction kinetic constants. These kinetic constants were then used in a process model that combined homogeneous and heterogeneous reactions.

The experimental data showed that HCl, NO₂, SO₂, and O₂ were critical in heterogeneous Hg reactions. Assuming a graphite layer with several diffused benzene rings to represent a model for carbon black, the binding energies of adsorption of various gaseous constituents on zigzag and armchair carbon models were calculated. Density functional theory calculations were performed using B3LYP parameterization with 6-31G(d) basis sets for all atoms except for Hg, which used the SBKJC effective core potential. Geometry optimization was run at different multiplicities to determine the minimum energy of the model systems, followed by frequency calculations to verify that the energy was at a minimum. HCl, SO₂, or NO₂ adsorption is favorable on carbon black surface. H or Cl atom attachment on the carbon edge does not significantly enhance elemental Hg adsorption on the carbon surface. The improved Hg removal in the presence of HCl might be caused by Hg oxidation reactions in the bulk phase or on the carbon black surface, possibly as a result of the detachment of released Cl from HCl. SO₂ attachment on the carbon surface does not enhance elemental Hg adsorption. NO₂ attachment improves elemental Hg adsorption on the zigzag carbon edge, but doesn't have a significant effect on the armchair edge. Mercury oxidation and removal in the presence of HCl and carbon black in the experiments are likely to be kinetically controlled. Gas phase reactions have been well studied and understood, and kinetic constants for these reactions are available. Mechanisms of Hg, HCl, and carbon black reactions were proposed and the kinetic constants for surface reactions were calculated.

Transition state calculations were performed and an intrinsic reaction coordinate (IRC) calculation was done subsequently to verify the reaction path. In cases where the transition state search was not successful, a potential energy surface (PES) scan was performed for the reaction to locate the transition state. Canonical transition state theory (CTST) was used to calculate the theoretical kinetic constants. Barrierless reactions were identified (e.g., H₂ and Cl₂ reactions with the carbon surface) and surface reactions related to HCl have barriers. The kinetic constants were applied to a batch process model and column process model to simulate the experimental reaction system. The process model results obtained could not predict the experimental results. The model results show slight elemental mercury removal within several seconds of the simulation, and no obvious elemental mercury removal was observed afterward. The failure of process model simulation is caused by competitive reactions occurring on the carbon surface. Computational results indicate that reaction rates of HCl on carbon surface are fast, and most of the active carbon sites are occupied immediately by H and Cl. After the active carbon sites are occupied, the reaction rates of surface reactions including Hg oxidation reaction on carbon surface are limited. It is postulated that other mercury species, such as Hg₂Cl₂, may exist in the system and must be considered in future studies.

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1 Project Goals.

The overall goal of the project was to obtain a fundamental understanding of the catalytic reactions that are promoted by solid surfaces present in coal combustion systems and develop a mathematical model that described key phenomena responsible for the fate of mercury in coal-combustion systems. This objective was approached by carefully combining laboratory studies under ultra high vacuum conditions and under realistic process conditions using simulated flue gas with mathematical modeling efforts. Laboratory-scale studies under ultra high vacuum conditions were performed at Temple University to understand the fundamental aspects of chemical reactions that are catalyzed by solid surfaces in coal-combustion gases and that cannot be elucidated in more complex and less sensitive systems at atmospheric pressures. The reactions studied included those between flue gas constituents and solid surfaces present in the fly ash and their impact on mercury speciation. The impact of these reactions on mercury speciation was then tested under more realistic process conditions in the entrained-flow reactor at the University of Pittsburgh. Process models were developed at the University of South Carolina that account for heterogeneous reactions because of the presence of fly ash as well as the deliberate addition of particles to promote Hg oxidation and adsorption. To build a complete process model of mercury removal and oxidation in a flue gas, kinetic constants for these heterogeneous reactions are required. Quantum modeling was used to obtain estimates of the kinetics of heterogeneous reactions.

2 Experimental Studies.

The experimental studies at atmospheric pressure consist of two sections. In the first section the impact of six fly ash samples on mercury speciation in simulated flue gas was studied. A fixed bed reactor system was used to study the catalytic effect of fly ash samples for mercury oxidation at a temperature of 140 °C. The simulated flue gas consisted of N₂, CO₂, O₂, NO, NO₂, SO₂, HCl, and H₂O. Mercury was introduced to the reactor using a temperature controlled permeation tube. Elemental and total mercury in the effluent were measured using a semi-continuous atomic fluorescence mercury monitor. Fly ash samples were characterized using SEM-EDAX, XRD, TGA, BET analyzer and particle size analyzer.

In the first section Fe₂O₃ (iron oxide) was found to be capable of moderately adsorbing and oxidizing mercury in simulated flue gas. Other studies (1,2,3) also indicated that Fe₂O₃ was a potential catalyst for elemental mercury oxidation in the flue gas from coal-fired power plants. Abandoned mine drainage (AMD) is produced by many flooded underground mines and it contains very high concentrations of iron. After active or passive treatment of AMD, very large quantities of iron oxide sludge are formed and are typically disposed by reinjection back into the mine. However, dewatered iron oxide can also be used as environmentally preferable pigments (4). Based on the previous findings of this study, it is possible that the AMD sludge can be used as an effective and economical sorbent to capture or oxidize Hg⁰. Therefore, the second section of experimental studies at atmospheric pressure was devoted to exploring the idea by collecting AMD sludge and testing it for Hg uptake and oxidation at simulated flue gas condition. The impact of flue gas compositions and temperature on Hg uptake and oxidation was investigated in a fixed-bed reactor system. Since fixed bed test results can not reflect the real reaction process under practical conditions, an entrained flow system was built up to test the performance of AMD sludge samples on mercury removal at typical experimental conditions similar to real flue gas condition.

2.1 Materials and Methods.

2.1.1 Fly Ash Samples.

Six ESP hopper fly ash samples were selected for this study. Four of them were collected at four different coal-fired electric utility boilers involved in Department of Energy's field testing programs. They are Southern Company's Gaston Plant, Wisconsin Electric Power Company's Pleasant Prairie Power Plant (PP), and PG&E Corp. National Generating Group's Brayton Point and Salem Harbor (SH) Plant. The coal types and particulate control devices at these power plants are summarized in Table 1. The other two ESP samples named as CE1 and CE2 were from Consol Energy's field tests with a power plant.

Table 1. General characteristics of power plants.

Site	Coal	Particulate Control Device
Salem Harbor (SH)	Low sulfur bituminous	Cold-side ESP
Brayton Point	Low sulfur bituminous	Cold-side ESP
Pleasant Prairie (PP)	PRB sub-bituminous	Cold-side ESP
Gaston	Low sulfur bituminous	Hot-side ESP, COHPAC FF

A carbon black sample, Black Pearls 460 (Cabot Carbon Co., Boston, MA) was used to represent the unburned carbon in the fly ash samples. Reagent grade Al_2O_3 , CaO , MgO , Fe_2O_3 , and TiO_2 were used to represent different inorganic compounds in fly ash. Sand (50-70mesh) was used as SiO_2 . Unwashed glass beads of 150-212 μm from Sigma – Aldrich were used as a bed support after a pretreatment with aqua regia and half an hour of heat at 500 °C.

2.1.2 Abandoned Mine Drainage Sludge Samples.

Four samples named Site A, Site1, Site 2 and Site 3 from four different abandoned mine drainage treatment sites were used in this research. The following paragraphs describe these four sites.

Site A sample is recovered from a site of a large system of ponds and wetlands that passively treats a large AMD discharge. The system precipitates most of the iron contamination in ponds designed for sludge removal, while residual iron is removed in a constructed wetland and then recovered to produce pigment-quality iron oxide.

Site 1 sample is produced from an AMD treating water from a mined-out, flooded, Pittsburgh seam mine. The raw water was rich in bicarbonate content and relatively low ferrous iron content. Unit operations at the treatment plant include: 1) preaeration using high speed mechanical aerators, 2) Addition of hydrated lime with more mechanical aeration and 3) gravity sedimentation in an open pond. After drying, Site 1 AMD solids were composed primarily of calcium carbonate (a reaction product of the lime and the native bicarbonate present in the raw water) and iron oxyhydroxides. Site 1 sample and Site B sample were from the same site, but Site B sample was collected before lime addition.

Site 2 utilizes the High Density Sludge process in which the sludge is settled in a clarifier (settling is aided by the addition of a floc) rather than an open pond. The majority of the settled sludge from the underflow of the clarifier is recycled through a high pH zone and returned to the process at the aeration basin. Recirculation of high pH sludge is supposed to impart a negative surface charge to the particles that will attract the dissolved ferrous iron to the particle surface. The objective is for iron oxidation to occur at the surface of an existing particle so that particle growth is achieved and new particle formation is avoided.

Site 3 treats water that is a combination of water from a mined-out, flooded Freeport seam mine water from overlying Pittsburgh seam deep mines and runoff/leachate from a refuse disposal area (largely Freeport refuse). The raw water is highly mineralized (ferrous iron, acidity due to dissolved metals, and sulfate are all high) and has a higher manganese content than the other waters. The unit operations for the treatment plant are the same as for Site B, but the water was treated to a higher pH (~9.0) to remove the manganese effectively. The sludge is highly expected to contain ferric oxyhydroxide, calcium sulfate and calcium carbonate as major components with a somewhat higher manganese and aluminum content than the other sites.

Site A, Site 1 and 2 are ground and sieved to a particle size below $37\mu\text{m}$ for fixed bed and entrained flow experiments. Site 3 sample is used without sieving since particle size analysis of Site 3 sample after grinding shows that it is not necessary to sieve it.

2.1.3 Fixed Bed Experiments.

The impact of fly ash or single synthetic fly ash component was studied in an experiment setup consisting of the following parts: 1) flue gas simulation, 2) mercury generator, 3) reactor and 4) mercury analyzer. A schematic of the setup is shown in Figure 1.

Figure 1. Schematic of the Hg uptake test setup.

A simulated flue gas consisting of N_2 , CO_2 , O_2 , NO , NO_2 , SO_2 and HCl was generated. A typical bituminous flue gas composition as listed in Table 2 was chosen for this study. The total flow rate is 1 L/min. Flow rates of different gases were controlled by digital mass flow controllers.

Table 2. Composition of simulated flue gas.

Gas	Concentration in eastern coal flue gases	Concentration in PRB flue gases
CO ₂	13.5%	13.5%
O ₂	6%	6%
HCl	50 ppm	10ppm
NO	300 ppm	300 ppm
NO ₂	20 ppm	20 ppm
SO ₂	0.15%	300 ppm
N ₂	Balance	Balance

A mercury permeation tube (VICI Metronics, Santa Clara, CA) was used as the source of elemental mercury. The 1 L/min simulated flue gas was then fed into a fixed bed quartz reactor (25cm long with 20mm ID), which was placed vertically in a tubular furnace (Lindberg Heavy-Duty, Watertown, WI) with a temperature controller. The effluent stream was then sent to an atomic fluorescence mercury detector to analyze total and elemental mercury concentration.

The mercury analysis system includes a wet conditioning system. The gas first passes through a heating box, which prevents the accumulation of oxidized mercury onto the tubing. The gas is split to two streams; one is directed to the elemental mercury side, and the other is directed to the total mercury side. On the elemental side, 10%KCl + 20%NaOH solution was pumped to the impinger in order to remove acidic gases and oxidized mercury. On the total side, 2%SnCl₂ + 20%NaOH solution was used to reduce oxidized mercury to metallic form and remove acidic gases. After reacting with chemical reagents, the gas carrying spent chemical solution passed through a chiller, where water vapor is removed from the gas phase.

After the wet conditioning system, mercury in the gas phase is analyzed by PSA 10.525 Sir Galahad II (P S Analytical Ltd, Orpington, Kent, England), a mercury semi continuous emission monitoring (SCEM) system. For all the tests in this study, a 200 mL/min flow rate of gas sample was sent to Sir Galahad II during a one-minute sample period. The rest of gas sample was sent to vent after going through an activated carbon trap to remove the toxic gases and Hg. In the fixed bed tests with fly ash, carbon black and other oxide chemicals, 50 mg sample is mixed with 4 g of prepared glass beads and placed on the glass frit in the quartz reactor at a certain temperature. When abandoned mine drainage sludge was studied in the fixed bed system, 1 g of prepared sand was used as the support layer on the glass frit and then another 1 g of prepared sand mixed with 50 mg sample was introduced into the reactor after a stable baseline was established.

2.1.4 Entrained Flow Experiments.

The entrained flow system in this research was comprised of following parts: 1) sorbent feeding system, 2) simulated flue gas system, 3) entrained flow reactor, 4) mercury analyzer system. Figure 2 shows the schematic of the setup.

Figure 2. Schematic of entrained flow set up.

A modified powder feeder (CH-1031, Sylvester and Co. Engineers, Cleveland, Ohio) was used in this study to provide the desired sorbent feeding rate. A new stainless steel screw, which has less carrying capacity of powder than the original one, was used to transport the AMD sludge material out of the sealed chamber with a N_2 carrier gas that carried the sorbent into the reactor. The rotating speed of the screw and the vibration setting of this feeder can be adjusted so that the sorbent feeding rate can be varied to accomplish a desired value. The simulated flue gas generating system and the mercury analyzer system used in entrained flow tests were the same as the ones used in the fixed bed tests.

As shown in Figure 2, the 2 cm ID entrained flow reactor with a total length of 65 cm was made of quartz. It was equipped with one sampling port. The reactor is designed to have a total simulated flue gas residence time of 1 second at a desired temperature. The simulated flue gas is introduced through the right port on top of the reactor and is mixed with the sorbent carried by N₂ from the top port. A flow rate of 200 mL/min of the effluent was non-isokinetically sampled from the sampling port in the reactor. The reactor was wrapped with a heating tape (Samox[®] insulated heating tape, Cole-Parmer Instrument Company) to be heated up to a desired temperature. The effluent sample was directed to the PSA Sir Galahad II system to measure total and elemental mercury concentration. In addition, a quartz wool filter wrapped with a heating tape (Fisher Scientific, Pittsburgh, PA) was added to the sample line to capture the solids that could be possibly coming out of the reactor with the sampling gas from the reactor. The rest of the simulated flue gas was vented to the hood.

An entrained flow test starts with establishing a stable baseline with a desired simulated flue gas flowing through the entrained flow reactor at a desired temperature. When a baseline is attained, the feeder is turned on to start sorbent injection. After certain period of feeding, the feeder is turned off while mercury monitoring continued for a given period of time after that.

2.1.5 Material Sample Characterization.

2.1.5.1 Surface Area Analysis on All Samples.

The surface area of the tested material was measured in a Micromeritics ASAP 2000 apparatus (Micromeritics Instrument Corporation, Norcross, GA). Brunauer-Emmett-Teller (BET) calculations were used to analyze adsorption results and calculate the surface area.

2.1.5.2 Particle Size Distribution Analysis on All Samples.

A Microtrac S3500 Tri-Laser particle analyzer (Microtrac Inc., Montgomeryville, PA) was used to analyze the particle size distribution of AMD solids. A method built in the software was used for AMD samples analysis.

2.1.5.3 SEM-EDAX Analysis on Fly Ash Samples.

SEM (Scanning Electron Microscope) – EDAX (Energy Dispersive Analysis, X-ray) analysis was conducted using a Philips XL30 SEM equipped with an EDAX detector. The SEM analysis yielded information on surface morphology of the fly ash samples, while the EDAX analysis provided information about surface elemental composition of the fly ash samples.

2.1.5.4 X-ray Diffraction Analysis on Fly Ash Samples.

The powder X-ray diffraction was performed with a Philips X'pert diffractometer to identify crystalline mineral components in fly ash samples. Scans were conducted from 10 to 80° 2 θ with 0.04° per step each 0.5s.

2.1.5.5 X-ray Photoelectron Spectroscopy (XPS) Analysis on Fly Ash Samples.

Due to the inaccuracy of EDAX results caused by the lack of proper standards, XPS analyses were used to characterize surface chemical properties of fly ash samples. The XPS analyses were carried out using a PHI 5600ci instrument. Monochromatic Al K(alpha) (1486.6 eV) X-rays were used at a power of 400 W, and the analysis chamber was typically maintained at about 10^{-8} Torr. The pass energy of the analyzer was 58.7 eV. Samples were analyzed after smearing them on a stainless steel sample holder at a sufficient thickness so that the sample holder could not be detected. Atomic concentrations were calculated using PHI sensitivity factors.

2.1.5.6 Loss On Ignition (LOI) and Moisture Analysis on Fly Ash Samples.

Loss on ignition (LOI) is a standard method to measure unburned carbon in fly ash. The analysis was carried out according to ASTM D3174-82 standard method. First, 2.0 ± 0.5 g fly ash sample was weighed and dried at 110 °C for 2 hours, and then cooled in a desiccator for 1 hour. The residual was weighed to calculate the moisture content. Then the sample was heated at 750 °C for 2 hours in a Type F62730 muffle furnace (Barnstead/Thermolyne, Dubuque, IA) and cooled in a desiccator for another hour before being weighed. LOI was calculated as difference in weight on a dry basis.

2.1.5.7 TPD Analysis on Carbon Black Samples.

Temperature programmed desorption (TPD) of the Carbon black samples tested for mercury uptake under atmospheric pressures was performed under high vacuum. Samples were supported on a Tungsten-grid (W-grid) by pressing them into the W-grid with a hydraulic press. The sample loaded W-grid was mounted with copper clamps on a TPD sample holder connected to a Dewar and placed into high vacuum chamber. After evacuation for at least 12 h, the chamber pressure decreased to $<10^{-8}$ Torr. The sample was then cooled to cryogenic temperatures (~ 110 K) and TPD of water dosed from background was performed in the range of temperatures 110-373 K (2 K sec^{-1}). The water desorption experiment serves as a criterion that the sample and thermocouple are in proper thermal and electrical contact with the W-grid. When the temperature reached 373 K the sample was kept at that temperature for 10 minutes to degas physisorbed species. The sample was then allowed to cool down to cryogenic temperature. Liquid nitrogen was removed from the Dewar and sample was allowed to heat up spontaneously (to allow condensed gases to evaporate from Dewar walls). When the sample reached about 220 to 230 K, the sample was heated (2 K sec^{-1}) to 1400 K while monitoring desorbing species in the 1-100 a.m.u. range with a mass spectrometer (RGA 300, Kurt Lesker). For some samples, masses were recorded in 1-300 a.m.u. range.

2.1.5.8 Elemental Analysis of Abandoned Mine Drainage Samples.

Inductively Coupled Plasma Mass Spectrometry (ICP-MS) was used to analyze the elemental composition in the Site A sample. Fusion Inductively-Coupled Plasma (FUS-ICP) was used for the elemental analysis of Site B, Site C, Sites 1, 2 and 3 samples. All the samples were sent to a commercial laboratory (Activation Laboratories Ltd, 1336 Sand Hill Drive, Ontario, USA) for analysis.

2.1.5.9 Foam Index Test of Abandoned Mine Drainage Samples.

Foam index test is a rapid method to determine the interference of a given material with the air entraining admixture requirement for concrete preparation. In this study Portland cement was applied as the standard cement in this test. The procedure for the foam index test is as follows:

1. Place 20 g of cement in a 125 mL glass jar.
2. Add 50 mL of water to the jar, then cap and shake the jar and its contents for 1 minute.
3. Add diluted AEA solution (Darex II, Grace diluted to 1:20 with DI water) in small increments of 2 to 5 drops at a time. After each addition, cap and shake the jar vigorously for 15 seconds. Observe the stability of the foam.
4. The minimum amount of diluted AEA needed to produce a stable foam (i.e., bubbles exist over the entire surface) for 45 seconds is the foam index of the cement mixture.
5. Repeat steps 1 through 4 using 16 g of cement and 4 g of material tested to develop the foam index of the cement and fly ash mixture.

2.2 Results and Discussion.

2.2.1 Fly Ash Samples Characterization.

2.2.1.1 Surface Area, LOI, and Moisture Analysis of Fly Ash Samples.

Six fly ashes samples and one carbon black sample (Cabot, Black Pearl 460) were analyzed for surface area, and the results are shown as in Table 3. Salem Harbor fly ash has the highest surface area among the fly ash samples. It also has the highest LOI value (i.e., the highest amount of unburned carbon). According to the literature, surface area is strongly influenced by carbon content and a positive correlation were found between surface area and carbon content. The results agreed with the literature findings, though the R^2 is not as high.

Table 3. Surface area, LOI, and moisture content of fly ash samples.

Sample	Surface Area (m ² /g)	LOI (%)	Moisture (%)
SH	17.9	37.20	0.14
Brayton	5.8	18.06	0.12
Gaston	2.1	11.94	0.20
PP	3.0	0.96	0.17
CE1	2.5	5.97	0.07
CE2	1.1	3.07	0.11
Carbon Black	71.4	—	—

2.2.1.2 SEM Graphs.

Figure 3. 200X SEM graphs of fly ash sample a) SH, b) Brayton, c) Gaston, d) PP, e) CE1 and f) CE2.

The SEM graphs shown in Figure 3 are backscattered images. In a backscattered image, heavier atoms appear lighter in color. As shown in the images, diverse morphology was found in

different samples. Irregular shaped soot (sponge like particles in a)), aluminosilicate glassy spheres, angular quartz, and occasionally mullite spheres were identified by the SEM-EDAX analysis.

2.2.1.3 Particle Size Distribution.

Results from a typical size distribution analysis are shown in Figure 4. The particle size falls in a broad range. Table 4 shows the mean particle sizes of the samples.

Figure 4. Particle size distribution of Brayton Point fly ash sample.

Table 4. Mean particle sizes of fly ash and carbon black.

Sample	D (µm)
SH	92.7
Brayton	77.6
Gaston	30.3
PP	48.0
CE1	32.7
CE2	23.4
Carbon Black	268

2.2.1.4 Surface Chemical Properties.

Table 5 shows the results from EDAX analysis on a surface elemental weight percentage.

Table 5. Surface elemental composition from EDAX analysis on fly ash samples.

Fly Ash	C	O	Na	Mg	Al	Si	P	S	K	Ca	Ti	Fe
SH	74.31	16.84	n.d.	0.09	1.98	4.40	n.d.	0.27	0.41	0.56	n.d.	1.08
Brayton	64.80	26.23	n.d.	0.19	2.78	3.94	n.d.	0.24	0.44	0.39	0.25	0.74
Gaston	49.20	24.94	0.31	0.28	5.72	7.62	0.27	0.93	1.24	1.30	0.81	7.38
PP	17.17	43.26	1.37	2.61	8.42	9.37	0.76	1.59	0.39	11.68	0.76	2.63
CE1	45.33	34.49	0.33	0.37	4.78	8.28	n.d.	0.45	0.72	0.86	n.d.	4.40
CE2	46.82	34.8	0.18	0.22	5.6	8.17	n.d.	0.27	0.82	0.42	0.41	2.31

n.d. = not detected

Due to the presence of carbon tape, the carbon content in all samples was much higher than suggested by LOI analyses. Further, these results could not be trusted due to insufficient calibration. XPS analysis was then used to give the information on surface chemical composition of these fly ash samples. Table 6 shows the results from the XPS analysis.

Table 6. Surface elemental composition (atom ratio) from XPS analysis.

Fly Ash	C	O	N	Na	Mg	Al	Si	P	S	Ca	Ti	Fe	Mn
SH	54.2	31.3	1.6	n.d.	0.2	2.6	6.1	n.d.	2.4	0.6	0.1	0.8	n.d.
Brayton	22.7	53.8	n.d.	n.d.	0.3	6.1	12.9	n.d.	2.4	0.5	0.2	1.0	n.d.
Gaston	15.5	58.3	n.d.	1.7	0.5	4.5	7.7	1.0	8.8	0.8	0.2	1.1	n.d.
PP	10.4	56.0	n.d.	2.9	1.4	2.7	4.8	2.4	9.0	8.1	0.2	0.6	n.d.
CE1	24.7	52.3	n.d.	0.6	0.1	4.7	10.7	n.d.	4.0	1.0	0.2	1.8	n.d.
CE2	24.4	51.7	n.d.	0.5	0.2	5.7	12.3	n.d.	2.8	0.7	0.2	1.5	n.d.

n.d. = not detected

The weight percentage for every element was also calculated based on the atom ratio and is shown in Table 7. Compared with the results from EDAX and LOI, results from XPS analyses are more reasonable.

Table 7. Surface elemental composition (weight ratio) from XPS analysis.

Fly Ash	C	O	N	Na	Mg	Al	Si	P	S	Ca	Ti	Fe	Mn
SH	41.4	31.9	1.4	n.d.	0.3	4.5	10.9	n.d.	4.9	1.5	0.3	2.9	n.d.
Brayton	14.9	47.1	n.d.	n.d.	0.4	9.0	19.8	n.d.	4.2	1.1	0.5	3.1	n.d.
Gaston	9.7	48.4	n.d.	2.0	0.6	6.3	11.2	1.8	14.6	1.7	0.5	3.2	n.d.
PP	6.0	43.3	n.d.	3.2	1.6	3.5	6.5	4.1	13.9	15.7	0.5	1.6	n.d.
CE1	16.0	45.1	n.d.	0.7	0.1	6.8	16.2	n.d.	6.9	2.2	0.5	5.4	n.d.
CE2	15.9	44.8	n.d.	0.6	0.3	8.3	18.7	n.d.	4.9	1.5	0.5	4.6	n.d.

n.d. = not detected

Based on the elemental analyses, metal oxides (MgO, Al₂O₃, SiO₂, CaO, TiO₂, Fe₂O₃) and unburned carbon were selected as fly ash components for tests in flue gas. Carbon black was used in this study to represent unburned carbon in the samples due to the similarity between unburned carbon in fly ash and carbon black (5).

2.2.2 Abandoned Mine Drainage Sludge Sample Characterization.

2.2.2.1 Particle Size Distribution and Surface Area of Abandoned Mine Drainage Samples.

The mean particle sizes of the samples in this study are listed in Table 8. Four AMD sludge material samples were analyzed for surface area and the results are also listed in Table 8. Site 1 sample shows the lowest surface area among all the samples. This sample is from the same site after lime addition. The reason for the significant difference in surface area in this sample is not clear.

Table 8. Mean particle sizes and surface area of abandoned mine drainage sludge samples.

Sample	D (μm)	Surface area (m^2/g)
Site A	18.38	127.7
Site 1	21.47	21.9
Site 2	20.27	102.9
Site 3	18.80	144.3

2.2.2.2 Elemental Analysis.

Elemental analysis of AMD samples is shown in Table 9. For Site A sample, Fe is the main metal in the AMD sludges. In general, Site A sample was produced by passive treatment technology and no lime addition process was involved. Thus, these results are in agreement with the sources description of this sample. In Site 1, 2, 3 samples, both Ca and Fe are the dominant metals. The site description for Site 1 and 3 samples indicates the treatment method includes lime addition, so the sludge should have certain amount of Ca, which also agrees with the elemental analysis in Table 9. All the sludge samples tested in this study were dried at 110 °C to remove the water content in the wet sludge.

Table 9. Elemental analysis of acid mine drainage samples.

Sample	Fe%	Mg%	Al%	Ca%	K%	Na%	Mn%	P%
Site A	42.7	0.04	0.69	0.08	0.05	0.005	0.03	0.019
Site 1	2.59	0.42	0.22	34.6	0.008	0.007	0.08	0.009
Site 2	19.01	1.55	0.22	19.73	0.158	0.46	0.50	<0.04
Site 3	27.30	0.97	0.20	19.16	0.050	0.245	0.30	<0.04

2.2.3 Mercury Uptake

2.2.3.1 Mercury Uptake Tests with Fly Ash Samples in Fixed Bed System

Figure 5 shows the results of mercury uptake test with 50mg CE1 fly ash sample using a simulated eastern coal flue gas. Mercury concentration in the effluent was normalized to the influent concentration, and is shown on the left hand vertical axis. The percentage of oxidized Hg was calculated using equation (1).

$$Hg_{oxidized} = \left(1 - \frac{Hg_{elemental}}{Hg_{total}} \right) \times 100\% \quad (1)$$

The percentage of oxidized mercury is shown on the right hand vertical axis.

Figure 5. Hg uptake test with 50 mg CE1 fly ash at 140 °C in eastern coal flue gas.

After the introduction of CE1 fly ash sample into the reactor, mercury concentration in the effluent dropped to around 70% of the inlet level. As the fly ash sample slowly picked mercury up and lost some of its capacity, the effluent mercury concentration increased. However, there was a difference between elemental and total mercury concentration constantly, which means the CE1 fly ash also has an oxidation capacity for mercury besides adsorption of elemental mercury. The oxidation capacity decreased slightly during the test.

The test with CE2 fly ash showed similar trend (see Figure 6). 100% breakthrough was slowly approached, and the oxidized Hg percentage decreased gradually.

Figure 6. Hg uptake test with 50 mg CE2 fly ash at 140 °C in eastern coal flue gas.

Figure 7. Hg uptake test with 50 mg PP fly ash at 140 °C in eastern coal flue gas.

Figure 8. Hg uptake test with 50 mg Gaston fly ash at 140 °C in eastern coal flue gas.

Figure 9. Hg uptake test with 50 mg Brayton fly ash at 140 °C in eastern coal flue gas.

Figure 10. Hg uptake test with 50 mg SH fly ash at 140 °C in eastern coal flue gas.

Figure 5 to Figure 10 shows the results from tests with Please Prairie, Gaston, Brayton Point, Salem Harbor fly ash samples. In summary, fly ash not only captures mercury, but also promotes mercury oxidation. After the fly ash sample was introduced to the reactor, part of the Hg^0 got captured on the surface; part of the Hg left the reactor in either Hg^0 or Hg^{2+} form. The sample slowly reached its maximum capacity, but oxidation still took place. The results with different fly ash samples were different, though the trends were similar, indicating that the adsorption capacity and catalytic oxidation depended on fly ash characteristics. In order to compare the performance of different fly ash samples, the mercury load on the fly ash and the oxidized mercury ratio in the effluent after four hours of exposure were calculated and presented in Table 10.

Among these samples, the SH fly ash showed the highest capacity for mercury as well as the highest oxidized mercury percentage in the effluent. With the presence of SH fly ash, there was still around 20% of oxidized Hg in the effluent after an 8-hr exposure to flue gas (Figure 10). According to the surface characterization, SH fly ash sample also has the highest surface area. Surface area was found to have positive correlations with both mercury uptake and oxidation, as indicated in Figure 11. Such findings are in agreement with other studies (3,6,7,8).

Table 10. Hg uptake and oxidation after four-hour exposure with fly ash.

Sample	Mercury Load ($\mu\text{g/g}$)	Oxidized Hg%
SH	47.9	22.9%
Brayton	38.3	9.3%
Gaston	14.6	7.3%
PP	8.8	8.1%
CE1	13.1	1.6%
CE2	13.2	5.2%

Figure 11. Effects of surface area on Hg uptake and oxidation at 140 °C in eastern coal flue gas.

There is also a positive correlation between oxidized Hg percentage and Hg uptake, as shown in Figure 12. Higher mercury oxidation was associated with higher levels of mercury capture (3). Conversely, less mercury uptake may lead to less mercury oxidation (9). This may indicate that the sorption of the reagent molecules onto the surface is a critical step for oxidation. According to Kwon et al. (10), physisorption is most probably the limiting step based on the observations that increases in temperature will cause a decrease in mercury adsorption and oxidation.

Figure 12. Correlation between Hg uptake and oxidation at 140 °C in eastern coal flue gas.

Other than surface area, the effects of particle size were also studied. Mercury capture and oxidation also increased with particle size (Figure 13). Such findings could be explained by the fact that unburned carbon is enriched in the coarser fractions in the fly ash samples used in this study according to SEM-EDAX analyses and is in agreement with results from Suraez-Ruiz et al. (11) and Hwang et al. (12).

Figure 13. Effects of particle size on Hg uptake and oxidation at 140 °C in eastern coal flue gas.

Not surprisingly, Hg load and oxidation were found to be proportional to LOI values (see Figure 14), suggesting the unburned carbon is actively involved in both mercury oxidation and adsorption processes. The similarity between effects of LOI, surface area and particle size on Hg load and oxidation is likely due to the fact that carbon has a higher surface area than other fractions (12) and tends to be enriched in coarser fractions in fly ash.

Figure 14. Effects of LOI% on Hg uptake and oxidation at 140 °C in eastern coal flue gas

Experiments were done in order to verify whether unburned carbon itself has an important impact as suggested above and to find out what the effects of other components of fly ash are on mercury uptake and oxidation. The results are discussed in the following section.

2.2.3.2 Mercury Speciation Tests with Synthetic Single Components

Similar uptake tests to the ones with fly ash were performed with carbon black and oxides typically present in fly ash, such as SiO_2 , Al_2O_3 , MgO , CaO , TiO_2 , and Fe_2O_3 . Tests with Al_2O_3 , MgO , CaO , SiO_2 and TiO_2 in simulated eastern coal flue gas showed similar results with Figure 15. None of these oxides exhibited capacity for oxidizing or capturing Hg^0 since total mercury and elemental mercury readings were the same as the baseline level. Such findings agrees with results from Ghorishi et al. (1) and Thorwarth et al. (13).

Ferric oxide showed a significant oxidation capacity at the beginning of the test as shown in Figure 16. Oxidized mercury in the effluent was as high as 80%. As the test proceeded, the oxidation rate decreased to around 40% in four hours. Based on this study, it can be concluded that ferric oxide has the potential to be a mercury oxidation catalyst in flue gas, which has also been suggested by others (9).

Figure 15. Hg uptake test with 50 mg CaO at 140 °C in eastern coal flue gas.

Figure 16. Hg uptake test with 50 mg Fe₂O₃ at 140 °C in eastern coal flue gas.

Carbon black was used to simulate unburned carbon in fly ash samples. It showed a much higher capacity for adsorbing mercury than the oxides tested in this study (see Figure 17). The oxidized mercury was consistently around 20%-30% in the effluent during the 5-hr experiment except for a slight increase in the very beginning of the test. Carbon black showed a remarkable ability to

catalyze the oxidation of Hg^0 under the conditions of this study, which explains why mercury uptake and oxidation increased with increases in LOI values. Other studies have also shown that mercury oxidation is related to the extent of unburned carbon (3,6,9).

Figure 17. Hg uptake test with 50 mg carbon black at 140 °C in eastern coal flue gas.

The effects of Fe_2O_3 and carbon black on mercury oxidation and capture are summarized in Table 11. They showed comparable mercury capture capacity; but the Hg oxidation capacity of Fe_2O_3 is much higher than carbon black. However, the carbon content of the fly ash samples used in this study ranged from 10 to 54 atom %, while Fe_2O_3 was only present at 0.6 - 1.5 atom %. Therefore, Fe_2O_3 is relatively less important than unburned carbon for mercury oxidation and adsorption. It could be concluded that unburned carbon is the most important component in fly ash for mercury oxidation and adsorption.

Table 11. Hg uptake and oxidation after four-hour exposure with fly ash components.

Sample	Mercury Load ($\mu\text{g/g}$)	Oxidized Hg%
Fe_2O_3	42.5	41.00%
Carbon black	39.0	19.44%

From all experiments done with oxides, it was concluded that Al_2O_3 , MgO , CaO , SiO_2 and TiO_2 did not promote either mercury oxidation or mercury capture under flue gas conditions in this study. Both Fe_2O_3 and carbon black showed profound impacts on mercury adsorption and oxidation. Carbon is more important due to its higher amount. However, the SH fly ash sample having a lower carbon content and a lower surface area than carbon black showed comparable capacities for mercury oxidation and adsorption to carbon black, suggesting that the heteroatoms on the fly ash sample and the conditions the fly ash previously exposed to would be important for mercury transformation. It also indicates that the effects of fly ash are more complex than single fly components.

In order to examine the effects of different flue gas combination (without Hg) on the surface chemical properties, 50 mg of carbon black sample was exposed to each flue gas combination listed in Table 12 at 140 °C for either 3 hrs (XPS analysis) or about 12 hrs (TPD analysis). Figure 18 shows a sample of the TPD analysis performed, and Table 12 shows the summary of the results from the TPD and XPS analyses.

Full TPD spectrum of as received C-black sample (#0). Heating of as received C-black sample is accompanied by desorption of CO and CO_2 associated with the surface oxygen groups. Hydrogen desorbs as a product of cracking of surface C-H bonds.

Figure 18. TPD analysis of as-received carbon black.

Table 12. TPD and XPS analyses of carbon black samples treated with different flue gas combinations.

Carbon Black Samples (Flue gas combination)	TPD (Desorption temperature)		XPS (Atomic %)				
	CO/CO ₂	SO ₂	C	O	S	N	Cl
0: As-received	600-800 K (Signal intensity is on the same order of magnitude)	n.d.	98.6	0.7	0.6	0	0
1: SO ₂ +CO ₂ +O ₂ +NO ₂ +NO+HCl		400-900K	98.2	1.0	0.7	0	0.1
2: HCl+N ₂		n.d.	98.8	0.6	0.6	n.d.	0
3: CO ₂ +O ₂ +HCl+N ₂		n.d.	98.4	1.0	0.7	n.d.	0
4: SO ₂ +CO ₂ +O ₂ +HCl+N ₂		400-900K	98.8	0.5	0.6	0	0
5: SO ₂ +CO ₂ +O ₂ +N ₂	/	/	98.4	0.9	0.7	n.d.	n.d.
6: NO ₂ +N ₂	/	/	98.6	0.7	0.6	0	n.d.

/ = No analyses; n.d. = not detected.

As illustrated by the TPD analyses in Table 12, surface oxygen functionalities were present in all the analyzed samples including the as-received carbon black. SO₂ species was desorbed during the analyses on Samples 1 and 4, which had been exposed to SO₂. No nitrogen or chlorine related species were desorbed from the surface in the TPD tests. The differences in surface chemical composition between samples 0-6 prepared for XPS analyses were not significant.

In the following two experiments a stable baseline of Hg was reached in both N₂ and N₂ + CO₂ + O₂. After that, 50 mg carbon black was introduced into the reactor afterwards and mercury in the effluent was monitored until 100% breakthrough was reached. Then flue gas composition was altered while still keeping a flow rate of 1 L/min, and mercury speciation in the effluent was monitored.

As shown in Figure 19 and Figure 20, a 100% breakthrough was achieved immediately in either N₂ or N₂ + CO₂ + O₂. It can be concluded that carbon black itself does not adsorb much elemental mercury. However, TPD analysis of as-received carbon black revealed the presence of surface oxygen functionalities on these carbon black samples (see Figure 18). These results indicated that oxygen functionalities are not able to adsorb mercury or oxidize mercury by themselves, though they may play a role in capturing mercury under conditions that are different from those in experiments shown in Figure 19 and Figure 20.

Figure 19. Hg uptake by carbon black in N_2 at 140 °C.

Figure 20. Hg uptake by carbon black in $\text{N}_2 + \text{CO}_2 + \text{O}_2$ at 140 °C.

After the 100% breakthrough occurred, 1500 ppm of SO_2 was introduced to the influent stream. However, it did not promote mercury oxidation or mercury capture under both conditions (Figure 21 and Figure 22). These results do not necessarily mean that SO_2 will not inhibit mercury

capture or oxidation, since no mercury was captured or oxidized under these flue gas conditions. The effects of SO₂ will be discussed later regarding its interaction with HCl.

Figure 21. Effects of SO₂ on Hg uptake by carbon black in N₂ at 140 °C.

Figure 22. Effects of SO₂ on Hg uptake by carbon black in N₂ + CO₂ + O₂ at 140 °C.

Similar to SO₂, NO was found not to promote mercury oxidation or adsorption in either N₂ or N₂ + CO₂ + O₂, as illustrated in Figure 23.

Figure 23. Effects of NO on Hg uptake by carbon black at 140 °C.

Water vapor did not promote mercury adsorption or oxidation in the presence of $\text{N}_2 + \text{CO}_2 + \text{O}_2$ (Figure 24).

Figure 24 Effects of H_2O on Hg uptake by carbon black in $\text{N}_2 + \text{CO}_2 + \text{O}_2$ at 140 °C.

Previous experiments with fly ash or its components were all done without water vapor. One experiment with SH fly ash was done in a full flue gas with water vapor, as depicted in Figure 25.

Figure 25. Effects of H₂O on Hg uptake by SH fly ash in flue gas at 140 °C.

An initial breakthrough of ~30% occurred immediately after the introduction of fly ash into the moisture containing flue gas, which was much higher than that (~5%) of the experiment with SH in flue gas without water vapor (Figure 14). However, 80% breakthrough occurred 1 hr later with water vapor than that without water vapor. As a result, a higher mercury adsorption onto fly ash was achieved with the presence of moisture (Table 13). It may be caused by changes on fly ash surfaces under long time exposure to water vapor containing flue gas. Water vapor seems to suppress mercury oxidation as shown from the comparison of oxidized mercury percentage in the effluent after 4-hr exposure. However, under real power plant operating conditions, water vapor may inhibit mercury adsorption onto fly ash since the contact time between water vapor and fly ash particles would be 1 – 5 s, much shorter than that in the experiment in Figure 24.

Table 13. Hg uptake and oxidation after four-hour exposure with SH fly ash in flue gas with and without water vapor.

Flue gas	Mercury Load (μg/g)	Oxidized Hg%
With H ₂ O	54.0	14.26%
Without H ₂ O	47.9	22.89%

After NO_2 was introduced into N_2 , an immediate drop of both elemental and total mercury occurred (Figure 26). The elemental mercury in the effluent remained almost constant, while the total mercury slowly increased towards 100% breakthrough. Addition of $\text{CO}_2 + \text{O}_2$ did not have a significant impact on either oxidation or adsorption in the presence of NO_2 (Figure 27).

Figure 26. Effects of NO_2 on Hg uptake by carbon black in N_2 at 140 °C.

Figure 27. Effects of NO_2 on Hg uptake by carbon black in $\text{N}_2 + \text{CO}_2 + \text{O}_2$ at 140 °C.

In Figure 26 and Figure 27, a 90% breakthrough occurred initially. After 100% breakthrough was achieved, oxidation still took place. It is generally believed that NO₂ could oxidize mercury and promote mercury capture onto carbon surface (6,14,15). However, the exact mechanism is still unknown. Hg⁰ is suggested to be oxidized by NO₂ and form Hg(NO₃)₂ or HgO on the carbon surface, and part of NO₂ was reduced to NO by dismutation (15,16). NO is believed to transform into NO₂ in the presence of O₂ on the surface (17). However, experiments summarized in Figure 23 revealed that with NO and O₂ in the gas phase, no mercury uptake or oxidation occurred. A possible mechanism for Hg oxidation by NO₂ could be oxidation only occurs between adsorbed Hg and gas-phase NO₂, which is known as Eley-Rideal reaction (9),

For the case of mercury oxidation by NO₂, A is Hg⁰ and B is NO₂.

HCl is an important parameter for mercury chemistry in coal-fired power plants. After HCl was introduced to N₂ gas flow, effluent Hg immediately dropped to around 70% of the inlet concentration (Figure 28). The behavior was similar to that observed for NO₂. Elemental mercury in the effluent remained at 70% of the inlet level during the 12-hr test, while oxidized mercury slowly increased from 0 to 20% during that time. As HCl is not an oxidant, and the reaction between HCl and Hg is hindered by a very high energy barrier (18), the surface must be responsible for electron transfer.

Figure 28. Effects of HCl on Hg uptake by carbon black in N₂ at 140 °C.

A possible mechanism is that gas phase HCl impregnates the surface and creates Cl sites, which then react with Hg^0 (19). However, neither TPD analyses nor XPS analyses of carbon black samples treated by $\text{N}_2 + \text{HCl}$ (without Hg) revealed the existence of Cl on carbon surface (Table 11). It is possible that the binding energy between Cl and carbon surface (20) is so low that Cl are removed under the ultra high vacuum conditions used in TPD and XPS analysis. However, previous studies (21,22,16) have detected Cl on carbonaceous surfaces upon exposure to flue gas containing Hg. The difference could be due to the presence of Hg in these previous studies: Hg reacted with Cl containing species, and formed HgCl_2 , which being on the surface, resulted in increased Cl concentration in the samples.

Another hypothesis could be that Cl is catalytically generated by the interaction between HCl and the carbon surface (23), while oxygen containing SFGs like oxygen functionalities may help to stabilize the H atom attached on the surface (24). In that case, Reaction 1: $\text{Hg} + \text{Cl} \rightarrow \text{HgCl}$ could proceed. The resulted oxidized Hg species could be partially or completely adsorbed to surface, since the adsorption rate of HgCl_2 is higher than that of Hg^0 (25).

The amount of elemental Hg remained at the same level during the experiment, which means the sum of adsorbed mercury and oxidized mercury remained constant too. Most likely, the surface has a constant capacity for mercury oxidation under the conditions of this experiment; some of the oxidized mercury is then adsorbed onto the carbon black, and as carbon black reaches its maximum capacity for oxidized mercury, 100% breakthrough occurs. If this is the case, the adsorption sites for elemental mercury would be different from oxidation sites and adsorption sites for oxidized mercury, and they were not present on the carbon black surface under the conditions in this experiment.

Addition of O_2 in the gas flow significantly improved mercury capture and oxidation (Figure 29). Elemental mercury in the effluent was decreasing in the first eight hours, which means that capacity of the surface for converting elemental mercury to oxidized mercury and adsorbed Hg increased during that time. It is probably due to the changes in surface chemical properties under exposure to flue gas. However, as shown before (Figure 20), carbon black did not adsorb or oxidize any mercury in $\text{N}_2 + \text{CO}_2 + \text{O}_2$. Therefore, it is the interaction between O_2 and HCl on the surface caused the promotion of mercury uptake and oxidation.

Figure 29. Effects of HCl on Hg uptake by carbon black in N₂+CO₂+O₂ at 140 °C.

A possible mechanism, the Deacon process, could be used to explain the effects of O₂. However, the Deacon process is generally catalyzed by metal compounds (26). XPS analysis of the as-received carbon black revealed no metal elements existing on the surface (Table 12). The presence of mercury may drive the reaction forward without metal catalyst. The overall reaction could be,

In order to verify the effects of oxygen, 50 mg carbon black was exposed to 135 mL/min O₂ at 140 °C for 4 hrs. 1 L/min N₂ with Hg was then sent to the treated sample for 20 min to get rid of O₂ in the gas phase before introducing HCl. There was no oxidation or capture of mercury during the 20 min exposure to N₂ (Figure 30).

Figure 30. Hg baseline in N₂ and its concentration in N₂ passed through O₂-treated carbon black bed at 140 °C.

Introduction of HCl caused mercury capture instantly with the carbon black pretreated with O₂ (Figure 31, diamond symbols). Chemisorbed O₂ from the pretreatment accounts for the improvement in mercury capture and oxidation compared to the as-received carbon black (Figure 31, circle symbols). However, even with a four-hour exposure to O₂, the carbon black sample still showed a higher initial mercury breakthrough than the one with O₂ in the gas stream (Figure 31, square symbols). This implied that O₂ in the gas phase more readily participates in the reaction than chemisorbed O₂ on carbon black. The net effect of oxygen functionalities can be similar to O₂ in gas phase, though the mechanisms involved are possibly much more complex.

* Experiment with O₂ pretreated carbon black was then conducted in N₂ + HCl

Figure 31. Effects of HCl on Hg uptake by carbon black in different gases at 140 °C.

Figure 32 depicts the effect of SO₂ in the influent flow of HCl + N₂ + CO₂ + O₂ on mercury capture and oxidation. SO₂ caused an appreciable decrease in mercury capture and oxidized mercury percentage in the effluent. It most likely inhibited mercury capture and oxidation by competing for adsorption sites and electron acceptors. Both TPD and XPS analyses (Table 12) indicated the adsorption of S on the surface, which at least supported the idea of competition for adsorption sites (27). Previous experimental findings showed that SO₂ is generally being adsorbed on the carbon surface in S(VI) form (21,28,22), which means it would compete with Hg for electron acceptors in order to be oxidized. SO₂ may inhibit the adsorption of O₂ onto the surface, and then result in a decrease in mercury oxidation.

Figure 32. Effects of SO₂ on Hg uptake by carbon black in HCl + N₂ + CO₂ + O₂ at 140 °C.

From experiments with carbon black in different gas combination, it could be concluded that carbon black does not adsorb or oxidize mercury in N₂ even in the presence of O₂. NO₂ could promote mercury oxidation and adsorption without HCl and O₂. NO, SO₂ or H₂O does not promote mercury oxidation or adsorption by itself. H₂O seems to inhibit mercury adsorption upon its introduction into gas stream. However, over time its effect on mercury adsorption diminished, though it suppressed mercury oxidation. HCl has profound effects on mercury adsorption and capture, especially when oxygen is present. SO₂ tends to diminish the effects of HCl by occupying the binding sites and competing for electron acceptors with mercury. It can also be concluded that the flue gas composition and the interaction between flue gas and the surfaces are more important than the fly ash composition, though the presence of fly ash samples play a predominant role in mercury oxidation (6).

2.2.3.3 Mercury Uptake Tests with Abandoned Mine Drainage Samples

Due to the abundance of Site A sample for various tests, this sample was selected for the following set of experiments. In Figure 33, "baseline with reactor" means that this baseline was established with empty reactor and simulated flue gas. Then 1 g of treated sand was placed into the reactor and the baseline with reactor and 1 g sand was established again. Figure 33 shows that the two baselines are almost identical, which indicates that the treated sand has no capacity for Hg and it does not cause any effect on Hg speciation in the reactor. Therefore, the sand used in this study can be considered as an inert material to Hg uptake and oxidation. In all of the following tests, the baseline in the figure will indicate the baseline attained with reactor and 1 g treated sand inside.

Figure 33 shows that it took around 400 minutes to reach full mercury breakthrough at 140°C in eastern coal flue gas, while in PRB flue gas the time for breakthrough is about 1000 minutes. At the breakthrough point for both tests, about 30% of mercury in the outlet gas existed as oxidized mercury. The mercury uptake capacity for this Site A material was calculated to be 92.2 $\mu\text{g Hg/g}$ in eastern coal flue gas and 174.6 $\mu\text{g Hg/g}$ in PRB flue gas.

Figure 33. Hg uptake on Site A sample in eastern coal and PRB flue gas at 140°C.

The impact of temperature on Hg uptake by Site A sample is shown in Figure 34, where the results obtained at 140°C are compared with those obtained at 370°C. This figure clearly shows that higher temperature results in lower Hg capture, which is in agreement with the common adsorption principles. The mercury uptake capacity for Site A sample in eastern coal flue gas is calculated to be 20.5 $\mu\text{g Hg/g}$ at 370°C. As shown in Figure 34, oxidation percentage increased from 25% to 40% when reaction temperature increased from 140°C to 370°C. Borderieux et al. (29) reported that at higher temperature Fe_2O_3 nanoparticles showed increased Hg oxidation efficiency, which agrees with the findings shown in Figure 34. The mechanism could be that high temperature causes high activity of Site A sample as a catalyst, which could lead to high catalytic efficiency.

Figure 34. Impact of temperature on Hg uptake with Site A sample in eastern coal flue gas at 140°C.

Since AMD sludge material has never been studied to remove Hg in coal-fired power plant flue gas, it is necessary to understand the transformation of mercury species and propose the possible mechanism of the reaction with this novel material. In this section the impact of flue gas compositions on Hg uptake and oxidation with Site A sample were investigated. Table 14 shows the experimental conditions investigated.

Table 14. Combinations of flue gas compositions in flue gas.

Number	Combinations of flue gas compositions
1	$\text{N}_2 + \text{CO}_2$
2	$\text{N}_2 + \text{CO}_2 + \text{O}_2$
3	$\text{N}_2 + \text{CO}_2 + \text{HCl}$
4	$\text{N}_2 + \text{CO}_2 + \text{O}_2 + \text{HCl}$
5	$\text{N}_2 + \text{CO}_2 + \text{SO}_2$
6	$\text{N}_2 + \text{CO}_2 + \text{O}_2 + \text{SO}_2$
7	$\text{N}_2 + \text{CO}_2 + \text{NO}_2$
8	$\text{N}_2 + \text{CO}_2 + \text{NO}_2 + \text{O}_2$
9	$\text{N}_2 + \text{CO}_2 + \text{NO}$
10	$\text{N}_2 + \text{CO}_2 + \text{O}_2 + \text{NO}$
11	$\text{N}_2 + \text{CO}_2 + \text{O}_2 + \text{HCl} + \text{SO}_2$
12	$\text{N}_2 + \text{CO}_2 + \text{O}_2 + \text{HCl} + \text{NO}$
13	$\text{N}_2 + \text{CO}_2 + \text{O}_2 + \text{HCl} + \text{NO}_2$
14	$\text{N}_2 + \text{CO}_2 + \text{O}_2 + \text{HCl} + \text{SO}_2 + \text{NO}$
15	$\text{N}_2 + \text{CO}_2 + \text{O}_2 + \text{HCl} + \text{SO}_2 + \text{NO}_2$
16	$\text{N}_2 + \text{CO}_2 + \text{O}_2 + \text{HCl} + \text{SO}_2 + \text{NO}_2 + \text{NO}$

Table 15 shows the Hg removal efficiency and percent oxidized mercury in the effluent from the reactor ($[\text{Hg}^{2+}] / \text{inlet} [\text{Hg}]$) after 2 hrs of contact with different flue gas compositions. This table indicates that NO_2 and NO did not affect Hg oxidation by AMD sludge material when they are combined with HCl individually or simultaneously in flue gas. Combination of SO_2 , HCl and NO showed similar behavior. However, combination of SO_2 , HCl and NO_2 shows significant negative impact on Hg oxidation. Dunham et al. (3) suggested a heterogeneous model for mercury capture explaining potential impact of SO_2 and NO_2 as shown in Figure 35. However, this model is proposed for carbon surface. The mechanisms responsible for the observations in

this research are not clear. As the Table 3.3.3.4 shows, when NO is added into flue gas with HCl or combination of HCl and SO₂, Hg removal efficiency is 41.6% or 46.3% (vs. 62.2% in HCl). Therefore, NO shows inhibitory effect on Hg adsorption not only by itself but also with combination of HCl and SO₂, Miller et al. (30) reported an increase in mercury uptake capacity of activated sorbent when adding NO to the flue gas. The test result with AMD sludge material was contradicted with these findings but the mechanisms are still unclear.

Table 15. Hg removal efficiency and outlet [Hg²⁺] / inlet [Hg] after 2 hrs of contact with different flue gas compositions in fixed bed tests with site A sample at 140 °C.

Flue gas compositions	Hg removal efficiency	Outlet [Hg ²⁺]/ inlet [Hg]
N ₂ +CO ₂ +O ₂	0	0
N ₂ +CO ₂ +O ₂ +SO ₂	4.7%	0
N ₂ +CO ₂ +O ₂ +NO ₂	11.1%	0
N ₂ +CO ₂ +O ₂ +NO	10.8%	0
N ₂ +CO ₂ +O ₂ +HCl	62.2%	79%
N ₂ +CO ₂ +O ₂ +HCl+SO ₂	65.5%	78.4%
N ₂ +CO ₂ +O ₂ +HCl+NO	41.6%	86.9%
N ₂ +CO ₂ +O ₂ +HCl+NO ₂	57.5%	75.5%
N ₂ +CO ₂ +O ₂ +HCl+ SO ₂ +NO	46.3%	76.2%
N ₂ +CO ₂ +O ₂ +HCl+ SO ₂ +NO ₂	51.9%	39.5%
N ₂ +CO ₂ +O ₂ +HCl+SO ₂ +NO ₂ +NO	57.2%	25.6%

Figure 35. Role of SO₂ and NO₂ on Hg capture (adapted from (3)).

2.2.3.4 Mercury Uptake Tests in Entrained Flow System

In this section, Site A, Site 1, Site 2 and Site 3 samples were injected into the entrained flow system at certain injection rate to test their ability for Hg removal and oxidation in eastern coal and PRB coal flue gas at 140°C. The effect of temperature and injection rate on Hg removal by the injection of Site A sample was also investigated in this section. In addition, removal efficiency of AMD Site A sample in the entrained flow system was compared with the performance of commercial powdered activated carbon (FGD Activated carbon, Norit America, Marshall, TX)

The Site A solids feeding rate provided by modified powder feeder was set at 0.29 g/hr, which resulted in sorbent loading in the simulated flue gas of 0.39 g/m³ and the sorbent to Hg ratio of about 22,100. As shown on Figure 36, the total and elemental Hg concentration in both eastern coal and PRB coal flue gas approached steady-state values after about 50 minutes of AMD injection. Hg removal was at about 80% and no obvious Hg oxidation was observed in this experiment. Such behavior could be explained by the fairly short residence time in the reactor. No obvious difference in Hg removal under these two flue gas conditions was observed in the entrained flow tests. As observed in fixed bed tests, there was no difference in Hg adsorption and oxidation with this AMD sample in simulated eastern coal and PRB flue gas during the first several minutes of fixed bed tests. The residence time in the entrained flow reactor was only 1 second and the effect of flue gas composition on Hg removal could not be displayed in such short residence time.

Figure 36. Hg removal in entrained flow test with Site A at 140°C in PRB and eastern coal flue gas.

Site A material was injected at the same conditions as in Figure 36 but at temperatures of 140 °C and 370°C. The results of two tests were compared as shown in Figure 37. After reaching steady state, Hg removal efficiency with Site A injection in entrained flow reactor was about 80% at 140°C and 58% at 370°C in eastern coal flue gas. This figure clearly shows that lower temperature results in higher Hg capture in the entrained flow test, which agrees with the common adsorption principles and the fixed bed test results.

Figure 37. Hg removal in entrained flow test with Site A at 140°C and 370°C in eastern coal flue gas

In order to investigate the effect of Site A sample injection rate on Hg removal in the entrained flow system, Site A sample was injected at two different rates, namely 0.29 g/hr and 0.56 g/hr. The sorbent loading in the simulated flue gas was 0.39 g/m³ and 0.76 g/m³ respectively, and the ratio of sorbent / Hg was about 22,100 and 43,000, respectively. The test result with these injection rates in eastern coal flue gas are compared to Figure 36. Figure 38 shows that the steady state at higher injection rate was achieved a bit earlier (35 minutes versus 45 minutes). Also Hg removal efficiency at higher injection rate was higher (95% vs. 80%). These encouraging results indicate that higher Site A injection rate can help achieve higher Hg removal performance in the entrained flow test.

Figure 38. Hg removal in entrained flow test with Site A at injection rate of 0.76 g/m^3 and 0.39 g/m^3 in eastern coal flue gas

Commercially available FGD activated carbon was injected at 140°C in eastern coal flue gas at the injection rate of 0.19 g/hr , resulting in activated carbon load in simulated flue gas of 0.26 g/m^3 and the ratio of activated carbon/Hg of 14480. The surface area of FGD activated carbon used in this test is $600 \text{ m}^2/\text{g}$. Performance of FGD carbon is compared with the performance of Site A sample in Figure 39. It can be seen that FGD activated carbon injection took about 15 minutes to reach steady state Hg removal. Compared with Site A injection test, less time was required for the system performance to reach the steady-state behavior with FGD activated carbon and the final Hg removal efficiency was almost 100%. In industrial PAC injection the injection rate of activated carbon varies between 1 and 10 lb/MMacf (31), which is equivalent to 0.016 g/m^3 and 0.16 g/m^3 . This result shows that about 30% lower injection rate of FGD activated carbon in this entrained flow test resulted in about 30% higher Hg removal efficiency and shorter time to achieve steady state. It indicates that the capability of Hg removal with Site A material is lower than the one with FGD activated carbon.

Figure 39. Hg removal in entrained flow test with Site A and FGD activated carbon injection at 140 °C in eastern coal flue gas

AMD sludge samples from Site 1, Site 2 and Site 3 sample were injected into the entrained flow reactor in PRB and eastern coal flue gas at 140°C. The feeding rate of AMD solids varied between 0.30 g/hr and 0.34 g/hr to yield the ratio of sorbent and Hg between 22,860:1 to 25,910:1. The test results for these AMD sorbents are compared in Figure 40 to Figure 42. Figure 40 shows that Site 1 sample displayed the lowest Hg removal efficiency in the entrained flow test among these 3 AMD sorbents. At steady-state, Hg removal efficiency with Site 1 injection was about 26% at 140°C in both eastern coal and PRB flue gas conditions.

Figure 40. Entrained flow test results with Site 1 in eastern coal and PRB flue gas at 140°C

Injection of Site 2 and Site 3 sample resulted in about 45% ~ 55% Hg removal in the entrained flow tests shown on Figure 41 and Figure 42, respectively. In eastern coal flue gas and PRB flue gas conditions, no significant difference in Hg removal efficiency was observed in PRB or eastern coal flue gas. In addition, no Hg oxidation was observed in these tests, which is in agreement with previous entrained flow tests with Site A sample.

Figure 41. Site 2 entrained flow test results in eastern coal and PRB flue gas at 140°C

Figure 42. Site 3 entrained flow test results in eastern coal and PRB flue gas at 140°C

The most likely reason for the different Hg removal performance with these AMD sorbents is the Fe_2O_3 content in the three samples. AMD Site 1 sample has only 3.7% of Fe_2O_3 while Site 2 sample and Site 3 sample have 27.1% and 39%, respectively.

A final test was performed to compare Fe_2O_3 powder (Fisher Scientific, Pittsburgh, PA) with the AMD samples. Fe_2O_3 was injected at 140°C in eastern coal flue gas at the injection rate of 0.23 g/hr resulting in sorbent loading in the simulated flue gas of 0.31 g/m^3 and the ratio of sorbent/Hg of 17200. Fe injection rate is calculated as 0.217 g/m^3 . The average particle size of Fe_2O_3 used in this test is $4.64 \mu\text{m}$. Performance of Fe_2O_3 is compared with the performance of Site A, 1, 2 and 3 samples in Figure 44. Compared with Site A injection test, the final Hg removal efficiency with Fe_2O_3 was about 17% lower (it was about 68%). On the other hand, compared with Site 1 and 2 samples, Fe_2O_3 shows higher Hg removal efficiency even at lower sorbent load in flue gas (0.31 g/m^3 vs. 0.33 g/m^3 , 0.34 g/m^3).

Figure 43. Fe_2O_3 chemical entrained flow test results compared with Site A, 1, 2 and 3 samples in eastern coal flue gas at 140°C .

Table 16 summarizes the injection test results with different sorbents with respect to Fe% in the sorbent, sorbent injection rate and Fe injection rate of each sample. Fe injection rate is calculated by multiplying Fe% with sorbent injection rate. This table shows that most iron content was injected in the test with Site A sample and the highest Hg removal efficiency was achieved with

Site A sample. In addition, Site 1 sample shows lowest Hg removal efficiency with lowest Fe injection rate.

Table 16. Fe%, sorbent injection rate, Fe injection rate and Hg removal efficiency results in the entrained flow tests with eastern coal flue gas.

Sample	Fe%	Injection rate, g/m ³	Fe injection rate, g/m ³	Hg removal efficiency, %
Site A at low injection rate	42.7	0.39	0.167	80
Site A at high injection rate	42.7	0.76	0.324	95
Site 1	2.59	0.34	0.009	26
Site 2	19.01	0.33	0.063	49
Site 3	27.30	0.30	0.082	53
Fe ₂ O ₃	70	0.31	0.217	68

Figure 44 shows Hg removal as a function of Fe injection rate for the tests with these five sorbents. It is clear that there is also a positive correlation between Hg removal and Fe injection rate as shown in this figure. Higher Fe injection rate resulted in higher level of mercury removal. Therefore, this finding suggests AMD sludge with high Fe content is preferred as sorbent for Hg removal.

Figure 44. Fe injection rate and Hg removal results with Site A, 1, 2, 3 and Fe₂O₃ injection.

2.2.4 Foam Index Test Results.

The test results summarized in Table 17 show that the foam index of Portland cement and AMD material used in this study is very close (between 24~ 31). On the other hand, the foam index of CE1 fly ash, which has 3.1% LOI, is more than 3 times higher (i.e.107).

Table 17. Foam index of Portland cement and AMD samples.

Sample	Foam Index
Portland Cement	31
Site A	30
Site 1	27
Site 2	26
Site 3	24
CE1	107

These results suggest that AMD sorbents will not have any adverse impact on the amount of AEA needed for concrete production. Therefore, when AMD sorbents are injected in the coal-fired power plants for Hg removal application, this material will not cause negative effect on the quality of fly ash for cement applications.

3 Modeling Studies.

Process modeling to evaluate the fate of mercury in coal fired power plants has been performed to understand different approaches to mercury control. For example, Flora et al. simulated elemental mercury removal via adsorption on powdered activated carbon injected for Hg control (32). Flora et al. also modeled mercury control in baghouse systems (33,34,35,36). Their models only account only for sorption and no Hg transformation in the system.

Process models of mercury fate in flue gas systems involving homogeneous mercury reactions were also developed. Not all of the kinetic constants for the homogeneous mercury reactions could be obtained from experiments. Quantum modeling was used to obtain kinetic parameters for homogeneous mercury oxidation that could not otherwise be directly evaluated (37,23,38,39,40).

Homogeneous mercury oxidation can not entirely account for mercury oxidation and removal in the flue gas systems. Process models must account for heterogeneous reactions because of the presence of fly ash as well as the deliberate addition of particles to promote Hg oxidation and adsorption. To build a complete process model of mercury removal and oxidation in a flue gas, kinetic constants for these heterogeneous reactions are required. Quantum modeling can be used to obtain estimates of the kinetics of heterogeneous reactions. However, because of complexities associated with the quantum modeling of surface reactions, reports of heterogeneous mercury reactions are quite limited, and these constants are currently not available in the literature. For example, Padak et al. calculated binding energies of elemental Hg on a 16 carbon model and concluded the attachment of Cl and O functional groups on carbon surfaces improves Hg adsorption (20). Heterogeneous mercury oxidation and adsorption on various surfaces is still not reported.

Our goal is to elucidate mercury adsorption and oxidation on fly ash surfaces (particularly unburned carbon and metal oxide surfaces) that are encountered in flue gas streams. Packed bed experiments show that HCl and NO₂ in a N₂ gas stream enhance elemental Hg removal on carbon surfaces, but SO₂ and O₂ do not have an effect. Al₂O₃, CaO, and MgO do not impact Hg removal, but Fe₂O₃ enhances Hg oxidation and removal. To understand the effects of various gaseous constituents, quantum modeling will be used to obtain equilibrium and kinetic parameters, and a process model will be developed to holistically evaluate chemistry and transport of Hg in a flue gas. In this project, we were only able to focus on reactions on carbon surfaces.

3.1 Background.

Process modeling is necessary to study the mechanism of mercury oxidation and removal in a flue gas. Flora et al. built process models to simulate elemental mercury uptake on injected powdered activated carbon (32) and mercury control in baghouse systems (33,35,34,36). Their models use partial differential equations to describe the diffusion of Hg into a carbon particle, accounting for both internal mass transfer and an external mass transfer boundary layer. In-flight Hg removal on carbon and subsequent transport and removal of Hg through a growing bed in a

baghouse filter was also modeled. The effects of a pressure drop on flow redistribution and subsequent Hg removal were also accounted for in their efforts. The primary chemistry accounted for in their models was equilibrium mercury sorption on activated carbon. All other homogeneous and heterogeneous chemical reactions were neglected.

Process models accounting for homogeneous reactions can also be found in the literature to simulate mercury reactions in the gas phase. Oxidized mercury is formed from the interaction of elemental mercury with other constituents in the flue gas stream. Oxidized mercury is more desirable because it can be removed more easily than elemental mercury in the flue gas. Most of the mercury emissions from coal-fired power plants is in elemental form, which brings researchers' attention to mercury oxidation reactions in coal-fired power plant process (37). Many researchers have used quantum modeling methods to study homogeneous mercury oxidation mechanisms (37,23,38,39,40). Sliger et al. (23) carried out experiments and also performed quantum modeling calculations at the B3LYP/LANL2DZ level to study the homogeneous mercury oxidation reactions with Cl species in the flue gas. They forwarded a mechanism for homogeneous mercury oxidation reactions and concluded that atomic Cl is the key oxidizing species. Oxidation reactions happen when temperature is between 400 and 700 °C. Xu et al. (40) built a process model to simulate homogeneous mercury speciation in combustion-generated flue gases with 107 reactions and 30 species. They proposed a mechanism for HgO formation in the flue gas. Wilcox et al. (38,39) evaluated theoretical reactions rate constants for mercury oxidation by HCl. Rate constants were calculated using transition state theory with QCISD and B3LYP and different effective core potentials for mercury were evaluated. Niksa et al. (37) modeled the homogeneous mercury oxidation process using the CHEMKIN software package and reported the effects of NO and H₂O in homogeneous mercury oxidation reactions. Their results show that NO can promote or inhibit homogeneous Hg oxidation at various concentrations.

Gas phase reactions can not entirely account for mercury oxidation in flue gas systems. To build a complete process model of mercury transformation and removal, kinetic constants of heterogeneous reactions that occur within the flue gas are required. Because of the importance of heterogeneous reactions on surfaces and the accessibility of computational resources, researchers show growing interest in theoretical calculations of heterogeneous reactions. Reports of heterogeneous mercury reactions are quite limited. Padak et al. (20) modeled elemental Hg adsorption on carbon with a 16 carbon model and concluded the attachment of Cl and O functional groups on carbon surfaces improve Hg adsorption. They calculated binding energies of different Hg species on the model carbon, but did not present any equilibrium or kinetic calculations.

As early as 1986, a theoretical study of hydrogen surface diffusion on copper was carried out with an embedded Cu cluster model by applying morse-spline potential function in the calculation (41). Computational resources and software before that time were not widely available, which limited studies of heterogeneous reactions. With the development of quantum chemistry computational software, such as Gaussian, Gamess, Q-Chem, VASP, and the development of powerful computing systems, heterogeneous reactions are studied more widely recently (42,43,44).

Ideal models for a heterogeneous system would be a large molecule that would describe the surface on which reactions occur. Ab initio modeling of a large molecule is computationally intensive. One approach is to use smaller models to describe the reaction center. Another approach is to use simplified Hamiltonians, such as in semi-empirical methods. Molecular dynamics methods have also been used. The application of semi-empirical methods and molecular dynamics strongly depend on the parameterizations of the atomic interaction and could not be generalized (45). One approach is to separate the system into two parts, applying a higher level of theory in the key parts of interest and lower levels of theory in the remaining parts of the molecular system. This method is called ONIOM and is implemented in the Gaussian 03 program. ONIOM has been applied in many large molecule system studies (46,47,48,49). By applying this method, the dangling bonds need to be connected by virtual atoms such as H, O. We tried to apply ONIOM method in our model system and compared the ONIOM results with high level calculations. However, using either the virtual C-H single bond or C=O bond in the calculation could not represent the actual C-C bond in graphite and caused a large difference between high level calculation on the full system and ONIOM calculations. Thus, the approach we used for our system was to focus on a cluster where the key reactions occur.

Carbon is one of the more widely studied heterogeneous reaction media. Carbon is encountered under numerous natural and engineered conditions. The graphite structure has been used extensively to represent a carbon surface. Chen and Yang (50,51) used such a structure to study carbon gasification reactions. HF/3-21G(d) calculations of 1 to 7 benzene ring models used to represent graphite carbon were compared to experimental frequencies and geometry of graphite. The 7-ring system could fit the experimental structure and properties better. Montoya et al. studied spin contamination of Hartree-Fock and density functional theory (DFT) in the modeling of graphite carbon (52) and found that DFT has less spin contamination than Hartree-Fock. More recent studies used DFT to evaluate reactions on graphite carbon (53,54,55,56,57,58,59).

N₂ adsorption on graphite carbon (54,55,56) and carbon gasification (50,51,53) were understood very well. Many other heterogeneous reaction systems, such as titanium oxide photocatalysts stabilized on an active carbon surface (60), SO₂ oxidation catalyzed by carbon (59), mercury binding on activated carbon (20), oxidation of graphite by gas phase nitric acid (58), and methane oxidation mechanism on Pt (61) were also studied. However, a theoretical study of the mercury oxidation reactions on carbon has not yet been reported.

3.2 Energetic and Thermodynamic Study.

3.2.1 Elemental Mercury Binding on Carbon Black in the Presence of Flue Gas Components.

3.2.1.1 Calculation Details

Because of the nature of coal, the exact molecular structure of unburned carbon on fly ash surfaces is highly uncertain. Carbon black was used to represent unburned carbon. Different structures of carbon also exist in carbon black, and the exact structure could not be determined. It is assumed that a graphite layer with several diffused benzene rings could be used as a model for carbon black based on the information provided by the manufacturer and the literature (50,51).

Two types of edges were cut from the graphite layer and the broken carbon-carbon bonds were substituted with carbon-hydrogen bonds. The zigzag and armchair carbon models are shown in Figure 45 and Figure 46, respectively. The zigzag and arm-chair structures were studied by other researchers, and the characteristics obtained from theoretical calculations were in good agreement with the experimental results (50,56).

PC-GAMESS 7.0 was used in the calculations (42). PC-GAMESS is based on the GAMESS software (44) and is freely available to registered users. PC-GAMESS was used for both optimization calculation and frequency calculation for a relaxed carbon system. Density functional theory calculations were performed using B3LYP/6-31G(d) basis sets for all atoms except for Hg which used the SBKJC effective core potential. Geometry optimization was run at different multiplicities to determine the minimum energy of the model systems, followed by frequency calculations to verify that the energy was a minimum. The adsorption of gas phase components on both zigzag edge model and armchair model were studied. Adsorptions on two positions of the armchair edge were also investigated. As shown in Figure 46, one position is called the “arm” position, and the other position is called “chair.”

Figure 45. Optimized structure of carbon zigzag edge model.

Figure 46. Optimized structure of carbon armchair edge model.

3.2.1.2 Results and Discussion

The structures of two carbon black graphite models, zigzag model and armchair model, were optimized with different multiplicities. The optimized structures were used as initial structures for the calculations in this section. The results of the zigzag and armchair carbon model optimizations are listed in Table 18 and Table 19, respectively. Minimum energies result when the multiplicities of zigzag and armchair models are 6 and 1, respectively, indicating that there are 5 and zero unpaired electrons distributed within the respective models.

Binding energies for elemental Hg adsorption on carbon edges were calculated as follows,

$$\text{Binding energy} = E_{\text{Hg on C}} - E_{\text{Hg}} - E_{\text{C}} \quad (5)$$

The same approach was used where the geometry was optimized using different multiplicities, and the binding energies are shown in Table 18 and Table 19. Hg binding energies on both armchair and zigzag models are more than -10 kcal/mol. Binding energy more than -28 kcal/mol are not favorable on carbon black at 140 °C. Therefore, elemental Hg adsorption on carbon black is not favorable, which is consistent with experiments in this study.

HCl, SO₂, NO₂, and O₂ are present in flue gases and can adsorb onto unburned carbon, impacting the sorption and removal of Hg from the gas phase. Geometry optimization was performed with H, Cl, HCl, SO₂, NO₂, and O adsorbing on different sites and at different approaches to the carbon surface. The minimum energy configuration in the presence of these species was used in subsequent geometry optimizations for Hg adsorbing onto the carbon surface. The results are shown in Table 18 and Table 19.

The binding energies of H, Cl, HCl, SO₂, NO₂, and O on the carbon surface range from -55.57 kcal/mol to -117.64 kcal/mol, indicating that attachment of these species onto the carbon is favorable. These species could adsorb first onto the carbon prior to Hg interacting with the carbon surface. The binding energies of Hg onto surfaces with these species range from -3.33 kcal/mol to -38 kcal/mol, indicating that only NO₂ will enhance Hg removal. Experiments show that Hg is removed and oxidized in the presence of HCl or NO₂, while SO₂ or O₂ alone do not impact Hg removal. The binding energy calculations are consistent with the experimental results except for HCl. Thus, HCl interaction with the carbon surface was further explored.

3.2.1.3 Conclusions

HCl, SO₂, or NO₂ adsorption is favorable on carbon black surface. H or Cl atom attachment on the carbon edge does not significantly enhance elemental Hg adsorption on the carbon surface. The improved Hg removal in the presence of HCl might be caused by Hg oxidation reactions in the bulk phase or on carbon black surface, possibly as a result of the detachment of released Cl from HCl. SO₂ attachment on the carbon surface does not enhance elemental Hg adsorption. NO₂ attachment improves elemental Hg adsorption on the zigzag carbon edge, but doesn't have a significant effect on the armchair edge. Further studies of the mercury reaction mechanism in flue gas system are required to completely explain heterogeneous Hg removal.

Table 18. Summary of zigzag model energetic results.

	Formula	Description	Energy Hartree	Multiplicity	Binding Energy of adsorbate kcal/mole
1	C ₂₅ H ₉	Bare Zigzag Carbon Edge	-957.82	6	N/A
2	H + C ₂₅ H ₉	H Adsorption on Bare Zigzag Carbon Edge	-958.51	5	-117.64
3	Cl + C ₂₅ H ₉	Cl Adsorption on Bare Zigzag Carbon Edge	-1418.11	5	-91.03
4	HCl + C ₂₅ H ₉	HCl Adsorption on Bare Zigzag Carbon Edge	-1418.79	4	-108.06
5	SO ₂ + C ₂₅ H ₉	SO ₂ Adsorption on Bare Zigzag Carbon Edge	-1506.59	4	-114.29
6	NO ₂ + C ₂₅ H ₉	NO ₂ Adsorption on Bare Zigzag carbon Edge	-1163.05	1	-98.94
7	O + C ₂₅ H ₉	O Atom Adsorption on Bare Zigzag carbon Edge	-1033.14	4	-159.85
8	Hg + C ₂₅ H ₉	Hg Adsorption on Zigzag Carbon Edge	-1111.66	4	-9.08
9	Hg + C ₂₅ H ₁₀	Hg Adsorption on H attached Zigzag Carbon Edge	-1112.34	3	-5.81
10	Hg + C ₂₅ H ₉ Cl	Hg Adsorption on Cl attached Zigzag Carbon Edge	-1571.93	3	-3.33
11	Hg + C ₂₅ H ₉ NO ₂	Hg Adsorption on NO ₂ attached Zigzag Carbon Edge, Hg close to NO	-1316.94	1	-38.11
12	Hg + C ₂₅ H ₉ NO ₂	Hg Adsorption on NO ₂ attached Zigzag Carbon Edge, Hg close to O	-1316.92	1	-37.58
13	Hg + C ₂₅ H ₉ SO ₂	Hg Adsorption on SO ₂ attached Zigzag Carbon Edge, Hg close to SO	-1660.44	2	-11.66
14	Hg + C ₂₅ H ₉ SO ₂	Hg Adsorption on SO ₂ attached Zigzag Carbon Edge, Hg close to O	-1660.44	4	-11.66
15	Hg + C ₂₅ H ₉ O	Hg Adsorption on O attached Zigzag Carbon Edge	-1186.98	2	-12.71

Table 19. Summary of armchair model energetic results.

	Formula	Description	Energy Hartree	Multiplicity	Binding Energy of adsorbate kcal/mol
1	C ₂₄ H ₈	Bare Armchair Carbon Edge	-919.05	1	N/A
2	H + C ₂₄ H ₈	H Adsorption on Bare Armchair Carbon Edge	-919.70	2	-93.40
3	Cl + C ₂₄ H ₈	Cl Adsorption on Bare Armchair Carbon Edge	-1379.29	2	-64.11
4	HCl + C ₂₄ H ₈	HCl Adsorption on Bare Armchair Carbon Edge	-1379.99	1	-86.95
5	SO ₂ + C ₂₄ H ₈	SO ₂ Adsorption on Bare Armchair Carbon Edge	-1467.73	1	-55.45
6	NO ₂ + C ₂₄ H ₈	NO ₂ Adsorption on Bare Armchair carbon Edge	-1124.21	4	-56.57
7	O + C ₂₄ H ₈	O Atom Adsorption on Bare Armchair carbon Edge	-994.29	3	-176.26
8	Hg + C ₂₄ H ₈	Hg Adsorption on Bare Armchair Carbon Edge	-1072.88	1	-3.98
9	Hg + C ₂₄ H ₉	Hg Adsorption on H attached Armchair Carbon Edge	-1073.54	2	-9.00
10	Hg + C ₂₄ H ₈ Cl	Hg Adsorption on Cl attached Armchair Carbon Edge	-1533.13	2	-10.56
11	Hg + C ₂₄ H ₈ NO ₂	Hg Adsorption on NO ₂ Arm position attached Carbon Edge, Hg close to O	-1278.06	4	-13.20
12	Hg + C ₂₄ H ₈ NO ₂	Hg Adsorption on NO ₂ Chair Position attached Carbon Edge, Hg close to N	-1278.06	4	-13.08
13	Hg + C ₂₄ H ₈ SO ₂	Hg Adsorption on SO ₂ attached Armchair Carbon Edge, Hg close to S	-1621.57	1	-10.78
14	Hg + C ₂₄ H ₈ SO ₂	Hg Adsorption on SO ₂ attached Armchair Carbon Edge, Hg close to O	-1621.61	1	-12.38
15	Hg + C ₂₄ H ₈ O	Hg Adsorption on O attached Armchair Carbon Edge	-1148.13	3	-11.94

3.2.2 Energetics and Thermodynamics of Mercury Oxidation in the Presence of HCl and Adsorption on Carbon.

In the previous section, the binding energy of elemental Hg in the presence of different flue gas components on carbon black was calculated. However, pure elemental Hg adsorption alone could not explain the removal of Hg from the gas phase. Figure 28 shows that Hg oxidation occurs in the presence of HCl and carbon black. Thus, in this section, the binding energies of elemental and oxidized Hg species were calculated, and a thermodynamic study involving possible oxidation and adsorption reactions of various species was performed.

3.2.2.1 Calculation Details

Quantum calculations. As discussed in Section 3.2.1, H and Cl functional group attachment on neighboring carbon sites does not affect Hg binding energy significantly, so it is reasonable to neglect the attachment of neighboring functional groups in the reaction mechanism study. In order to limit the available carbon sites for attachment and reduce computational cost, a 3-ring zigzag and armchair carbon edge model with edge carbon and dangling bonds terminated with hydrogen were fixed at crystallographic graphite coordinates. The 3-ring carbon models are shown in Figure 47. The energetic results of the 3-ring system were compared to the larger carbon system in Table 20. The order of magnitude of the binding energies of H, Cl, and Hg on the carbon surface is similar.

Figure 47. Structures of 3-ring carbon edge models.

Table 20. Comparison of energetic results of 3-ring model and larger ring carbon models.

	3-ring armchair	6-ring armchair	3-ring zigzag	7-ring zigzag
H binding energy (kcal/mol)	-101.25	-93.40	-117.18	-117.64
Cl binding energy (kcal/mol)	-67.50	-64.11	-91.41	-91.03
Hg binding energy (kcal/mol)	-4.38	-3.98	-6.50	-9.08

Similar to Section 3.2.1.1, PC-GAMESS 7.0 was used for geometry optimization. Frequency calculations were carried out using Gaussian 03W, with conversion of spherical basis functions to cartesian functions. DFT calculations were performed using B3LYP/6-31G(d) for all atoms except for Hg which used the SBKJC effective core potential. Geometry optimization was run at different multiplicities to determine the minimum energy of the model systems, followed by frequency calculations to verify that the energy was a minimum.

Equilibrium constant calculation. Surface reactions can be written as,

Where, a, b, c, d are the stoichiometric constants. The equilibrium constants K_s for surface reaction can be calculated based on the following thermodynamic relationship,

$$K_s = \text{EXP}\left(-\frac{\Delta G}{RT}\right) \quad (7)$$

$$\Delta G = \sum G_{\text{product}} - \sum G_{\text{reactant}} \quad (8)$$

Where ΔG is the Gibbs free energy change of the reaction; R is the gas constant; and T is the temperature. The Gibbs free energy can be obtained from the entropy and enthalpy from,

$$\Delta G = \Delta H - T\Delta S \quad (9)$$

The Gibbs free energy for each compound was calculated with thermal correction and zero point energy correction. The correction for Gibbs free energy can be obtained using the calculated frequencies for the optimized geometry (62). The absolute entropy can be written as a sum of various terms,

$$S = S_{\text{tr}} + S_{\text{rot}} + S_{\text{vib}} + S_{\text{el}} - nR[\ln(nN_0) - 1] \quad (10)$$

where

$$S_{\text{tr}} = nR\left\{\frac{3}{2} + \ln\left[\left(\frac{2\pi MkT}{2}\right)^{3/2} \left(\frac{nRT}{P}\right)\right]\right\} \quad (11)$$

$$S_{\text{rot}} = nR\left\{\frac{3}{2} + \ln\left[\frac{(\pi V_A V_B V_C)^{1/2}}{S}\right]\right\} \quad (12)$$

$$S_{\text{vib}} = nR \sum \{(u_i e^{u_i} - 1)^{-1} - \ln(1 - e^{-u_i})\} \quad (13)$$

$$S_{\text{el}} = nR \ln \omega_{\text{el}} \quad (14)$$

Where $V_A = \frac{h^2}{8\pi^2 I_A kT}$, $V_B = \frac{h^2}{8\pi^2 I_B kT}$, $V_C = \frac{h^2}{8\pi^2 I_C kT}$, $\mu_i = \frac{h\nu_i}{kT}$; n is the number of moles; M is the molecular mass; I_a , I_b , and I_c are the principal moments of inertia; s is the symmetry number; ν_i are the vibration frequencies and ω_{el} is the degeneracy of the electronic ground state; R is the gas constant; k is the Boltzmann's constant; h is the Planck's constant; and N_0 is the Avogadro's number.

Temperature corrections for enthalpy can be written as,

$$\Delta H(T) = H_{\text{tr}}(T) + T_{\text{rot}}(T) + \Delta H_{\text{vib}}(T) + RT \quad (15)$$

$$H_{tr}(T) = \frac{3}{2}RT \quad (16)$$

$$H_{rot}(T) = \frac{3}{2}RT \quad (17)$$

$$\Delta H_{vib}(T) = Nh \sum \frac{V_i}{e^{h\nu_i/KT} - 1} \quad (18)$$

The zero point energy correction can be written as,

$$\varepsilon_0 = \frac{1}{2}h \sum_i \nu_i \quad (19)$$

The above thermal correction and zero point energy correction were calculated within Gaussian 03W.

CSTR model. A CSTR model was built to simulate Hg oxidation and adsorption under equilibrium conditions in the presence of HCl and carbon. The equilibrium constant for each independent reaction is written as,

$$K_s = \frac{C_{product1} \times C_{product2}}{C_{reactant1} \times C_{reactant2}} \quad (20)$$

where K_s is the equilibrium constants calculated by statistical thermodynamics discussed above and C stands for both surface and bulk concentration.

The material balance for gas phase elements can be written as,

$$Q(C_{gas_in} - C_{gas_out}) = \sum \frac{dC_{surfacei}}{dt} S + \sum \frac{dC_{gas,i}}{dt} V \quad (21)$$

Where, i stands for the i th compound. The material balance of surface species for each carbon site can be written as,

$$C_{Carbon_site_{total}} = \sum C_{surface} \quad (22)$$

The equilibrium constants for Hg, HCl and carbon black reactions are listed in Section 3.2.2.2. The range of equilibrium constants for the independent reactions is huge, which presented difficulties in using differential algebraic packages for solving the system of equations. Thus, the ordinary differential equations were discretized using finite differences and the resulting system of algebraic equations at each time step was solved using DNEQNF.

3.2.2.2 Results and Discussion

Energetic study of HgCl and HgCl₂ on carbon black. Geometry optimization was performed for HgCl and HgCl₂ in the gas phase as well as for bulk Cl reacting with Hg attached onto a three-ring carbon. The binding energies are shown in Table 21. Assuming that Cl is released into the gas phase from the adsorption of HCl onto carbon black, numerous possible reactions occur, including the formation of HgCl and HgCl₂ in the gas phase, or reactions with Hg bound on the carbon surface. The binding energies show that if Hg is attached onto the carbon, Cl affinity to the Hg on the surface is significantly greater than for gas phase species. Thus, even if Hg binding

energies may not be significant on a bare carbon surface, Hg oxidation by Cl on the carbon surface could be a key mechanism for Hg removal. Table 21 also shows that HgCl₂ formation in the gas phase is more favorable than on the carbon surface, indicating the HgCl formed on the surface would have to be desorbed prior to reaction with Cl.

Table 21. Binding energy comparison of Hg-Cl bond in gas phase and with Hg attached on the carbon surface.

	Gas phase	Zigzag model	Armchair model
Hg-Cl (kcal/mol)	-21.85	-81.80	-81.84
Cl-Hg-Cl (kcal/mol)	-71.73	-11.63	-34.09

Table 22 shows binding energies of HgCl and HgCl₂ on the carbon surface. Adsorption of both species are favorable, particularly HgCl. The binding energies are still higher than the binding energies of H or Cl. Thus, when HCl is present, binding of H or Cl is more favorable than oxidized Hg species.

Table 22. Energetic results of 3-ring zigzag and armchair carbon model.

Formula	Description	Energy Hartree	Multiplicity	Binding Energy of attaching species, kcal/mol
C ₁₃ H ₇	Zigzag carbon model	-499.43	4	N/A
HgCl + C ₁₃ H ₇	HgCl adsorption on zigzag carbon edge	-1113.53	3	-66.44
HgCl ₂ + C ₁₃ H ₇	HgCl ₂ adsorption on zigzag carbon edge	-1573.69	4	-6.35
C ₁₄ H ₈	Armchair carbon model	-538.11	1	N/A
HgCl + C ₁₄ H ₈	HgCl adsorption on armchair carbon edge	-1152.27	2	-98.82
HgCl ₂ + C ₁₄ H ₈	HgCl ₂ adsorption on armchair carbon edge	-1612.46	1	-61.19

Thermodynamic calculations of Hg Adsorption on Bare Carbon Surface. Figure 19 show that carbon black does not remove elemental mercury at 140 °C. Equilibrium constants of Hg adsorption on bare carbon black are calculated with thermal and zero point energy corrections at 140 °C. The optimized structures and equilibrium constants are shown in Figure 48. The equilibrium constants are small, which indicate elemental mercury adsorption is not significant on bare carbon black. The model results agree with experimental results at 140°C.

Figure 48. Optimized structure and equilibrium constants of Hg adsorption on 3-ring carbon model.

Equilibrium constants for Hg oxidation and adsorption reactions in the presence of HCl and carbon black. Because of the multitude of possible reactions that may occur, an initial approach to elucidate possible mechanisms was to perform an equilibrium analysis of the system. In the presence of HCl, the following can also exist in the gas phase: H atom, Cl atom, H₂, and Cl₂. HCl, Cl and Cl₂ could oxidize Hg to form HgCl and HgCl₂. Therefore, there are 8 gas phase species that should be accounted for in the model. Gas phase species can also attach on the carbon surface and form surface species. Gas phase species can also react with surface species to form other surface species. 6 surface species are accounted for each type of carbon surface. A total of 20 species are accounted for in the investigation of Hg reactions on carbon black in the presence of HCl. A schematic of this reaction system is shown in Figure 49.

Figure 49. Schematic of Hg, HCl, and carbon reaction system

There are 15 independent equilibrium reactions in the system and a total of 35 reactions. The reactions and equilibrium constants calculated with statistical thermodynamics are listed in four groups. The first group contains reactions that do not involve mercury and chlorine transformation (see Table 23). The second group contains reactions pertaining primarily to Cl transformation but not including mercury oxidation (see Table 24). The third group involves the initial step of Hg oxidation to HgCl (see Table 25), while the fourth group involves the second step of Hg oxidation, where HgCl₂ is formed from HgCl (see Table 26). In these tables, K_s is the equilibrium constant calculated at 140 °C, [i] is the gas phase concentration of compound i, and (j) is the surface concentration of compound j.

Table 23. Reactions without Hg and Cl transformation.

$\text{H}_2 + \text{M} \leftrightarrow 2\text{H} + \text{M} \quad K_s = \frac{[\text{H}]^2}{[\text{H}_2]} = 1.47 \times 10^{-51}$
$\text{H} - \text{C}_{\text{zig}} + \text{M} \leftrightarrow \text{H} + \text{C}_{\text{zig}} + \text{M} \quad K_{s,6} = \frac{[\text{H}](\text{C}_{\text{zig}})}{(\text{H} - \text{C}_{\text{zig}})} = 6.82 \times 10^{-52}$
$\text{H} - \text{C}_{\text{am}} + \text{M} \leftrightarrow \text{H} + \text{C}_{\text{am}} + \text{M} \quad K_s = \frac{[\text{H}](\text{C}_{\text{am}})}{(\text{H} - \text{C}_{\text{am}})} = 5.39 \times 10^{-64}$
$\text{H}_2 + \text{C}_{\text{zig}} \leftrightarrow \text{H} - \text{C}_{\text{zig}} + \text{H} \quad K_s = \frac{[\text{H}](\text{H} - \text{C}_{\text{zig}})}{[\text{H}_2](\text{C}_{\text{zig}})} = 1.00$
$\text{H}_2 + \text{C}_{\text{am}} \leftrightarrow \text{H} - \text{C}_{\text{am}} + \text{H} \quad K_s = \frac{[\text{H}](\text{H} - \text{C}_{\text{am}})}{[\text{H}_2](\text{C}_{\text{am}})} = 1.05$
$\text{Hg} - \text{C}_{\text{zig}} + \text{M} \leftrightarrow \text{C}_{\text{zig}} + \text{Hg} + \text{M} \quad K_s = \frac{[\text{Hg}](\text{C}_{\text{zig}})}{(\text{Hg} - \text{C}_{\text{zig}})} = 58.1$
$\text{Hg} - \text{C}_{\text{am}} + \text{M} \leftrightarrow \text{C}_{\text{am}} + \text{Hg} + \text{M} \quad K_s = \frac{[\text{Hg}](\text{C}_{\text{am}})}{(\text{Hg} - \text{C}_{\text{am}})} = 2.73 \times 10^2$
$\text{HgCl} - \text{C}_{\text{zig}} + \text{M} \leftrightarrow \text{HgCl} + \text{C}_{\text{zig}} + \text{M} \quad K_s = \frac{[\text{HgCl}](\text{C}_{\text{zig}})}{(\text{HgCl} - \text{C}_{\text{zig}})} = 1.82 \times 10^{-29}$
$\text{HgCl} - \text{C}_{\text{am}} + \text{M} \leftrightarrow \text{HgCl}_2 + \text{C}_{\text{am}} + \text{M} \quad K_s = \frac{[\text{HgCl}](\text{C}_{\text{am}})}{(\text{HgCl} - \text{C}_{\text{am}})} = 5.61 \times 10^{-47}$
$\text{HgCl}_2 - \text{C}_{\text{zig}} + \text{M} \leftrightarrow \text{HgCl}_2 + \text{C}_{\text{zig}} + \text{M} \quad K_s = \frac{[\text{HgCl}_2](\text{C}_{\text{zig}})}{(\text{HgCl}_2 - \text{C}_{\text{zig}})} = 1.79 \times 10^{-4}$
$\text{HgCl}_2 - \text{C}_{\text{am}} + \text{M} \leftrightarrow \text{HgCl}_2 + \text{C}_{\text{am}} + \text{M} \quad K_s = \frac{[\text{HgCl}_2](\text{C}_{\text{am}})}{(\text{HgCl}_2 - \text{C}_{\text{am}})} = 5.77 \times 10^{-23}$

Table 24. Chlorine transformation reactions.

Table 25. Reactions involving Hg oxidation to HgCl.

Table 26. Reactions involving HgCl oxidation to HgCl₂.

$\text{HgCl} + \text{Cl} + \text{M} \leftrightarrow \text{HgCl}_2 + \text{M}$	$K_s = \frac{[\text{HgCl}_2]}{[\text{HgCl}][\text{Cl}]} = 1.09 \times 10^{36}$
$\text{HCl} + \text{HgCl} \leftrightarrow \text{HgCl}_2 + \text{H}$	$K_s = \frac{[\text{HgCl}_2][\text{H}]}{[\text{HgCl}][\text{HCl}]} = 4.79 \times 10^{-13}$
$\text{Cl}_2 + \text{HgCl} \leftrightarrow \text{HgCl}_2 + \text{Cl}$	$K_s = \frac{[\text{HgCl}_2][\text{Cl}]}{[\text{HgCl}][\text{Cl}_2]} = 1.94 \times 10^{11}$
$\text{HgCl} - \text{C}_{\text{zig}} + \text{Cl} + \text{M} \leftrightarrow \text{HgCl}_2 - \text{C}_{\text{zig}} + \text{M}$	$K_s = \frac{(\text{HgCl}_2 - \text{C}_{\text{zig}})}{[\text{Cl}](\text{HgCl} - \text{C}_{\text{zig}})} = 1.11 \times 10^{11}$
$\text{HgCl} - \text{C}_{\text{arm}} + \text{Cl} + \text{M} \leftrightarrow \text{HgCl}_2 - \text{C}_{\text{arm}} + \text{M}$	$K_s = \frac{(\text{HgCl}_2 - \text{C}_{\text{arm}})}{[\text{Cl}](\text{HgCl} - \text{C}_{\text{arm}})} = 1.06 \times 10^{12}$
$\text{HgCl} - \text{C}_{\text{zig}} + \text{HCl} \leftrightarrow \text{HgCl}_2 - \text{C}_{\text{zig}} + \text{H}$	$K_s = \frac{[\text{H}](\text{HgCl}_2 - \text{C}_{\text{zig}})}{[\text{HCl}](\text{HgCl} - \text{C}_{\text{zig}})} = 4.86 \times 10^{-38}$
$\text{HgCl} - \text{C}_{\text{arm}} + \text{HCl} \leftrightarrow \text{HgCl}_2 - \text{C}_{\text{arm}} + \text{H}$	$K_s = \frac{[\text{H}](\text{HgCl}_2 - \text{C}_{\text{arm}})}{[\text{HCl}](\text{HgCl} - \text{C}_{\text{arm}})} = 4.65 \times 10^{-37}$
$\text{HgCl} - \text{C}_{\text{zig}} + \text{Cl}_2 \leftrightarrow \text{HgCl}_2 - \text{C}_{\text{zig}} + \text{Cl}$	$K_s = \frac{[\text{Cl}](\text{HgCl}_2 - \text{C}_{\text{zig}})}{[\text{Cl}_2](\text{HgCl} - \text{C}_{\text{zig}})} = 1.88 \times 10^{-13}$
$\text{HgCl} - \text{C}_{\text{arm}} + \text{Cl}_2 \leftrightarrow \text{HgCl}_2 - \text{C}_{\text{arm}} + \text{Cl}$	$K_s = \frac{[\text{Cl}](\text{HgCl}_2 - \text{C}_{\text{arm}})}{[\text{Cl}_2](\text{HgCl} - \text{C}_{\text{arm}})} = 1.97 \times 10^{-14}$

All the mercury oxidation reactions involving HCl have equilibrium constants lower than 1, which indicate that these reactions are not thermodynamically favorable. For the initial step of Hg oxidation, reactions of Hg with Cl have equilibrium constants higher than 1, which indicate mercury could be oxidized to form HgCl in the gas phase and carbon surface. Hg could also be oxidized by Cl₂ on carbon surface. For the second step of HgCl oxidation to HgCl₂, only reactions with Cl are favorable. HgCl adsorption on both carbon black models have large equilibrium constants, which indicate HgCl adsorption could result in mercury removal from the gas phase. The equilibrium constants of the second step of gas phase mercury oxidation indicate Cl or Cl₂ can both oxidize HgCl to form HgCl₂. HCl does not release Cl in the gas phase, so HCl reaction on carbon black is the key reaction for mercury oxidation and removal in this reaction system. Comparing the equilibrium constants of HCl reaction on zigzag carbon, the reaction releasing H is more favorable than the reaction releasing Cl. For armchair carbon, the reaction

releasing Cl is more favorable than the reaction releasing H. Because of the higher binding energy of H-carbon bond on both zigzag and armchair edges, the attached Cl should be gradually replaced by H after the carbon surface is fully covered, and the released Cl could oxidize Hg.

Equilibrium CSTR model of Hg oxidation and adsorption reactions in the presence of HCl and carbon black. A CSTR model was built to study Hg oxidation by HCl under equilibrium conditions. The equilibrium constants are calculated for 15 independent reactions at 140°C. The model assumes 40% of the surface area is zigzag carbon. Figure 50 shows the model results and the experimental results from Figure 28.

Figure 50. Equilibrium model results vs experimental results of Hg uptake in HCl and carbon black system

The model was able to calculate the elemental mercury and oxidized mercury levels when the reaction system approaches equilibrium. The difference between experimental results and model results are at the beginning of reaction. Experiments show an immediate drop in elemental Hg with a gradual rise in oxidized Hg in the effluent. The model predicts a drop in elemental Hg about 35 minutes in the experiment, coupled with a sudden rise in oxidized Hg. These sudden changes in Hg levels occur when the carbon surface becomes saturated with H and Cl. The experiment shows a gradual rise in the level of oxidized Hg and the system approaches equilibrium gradually. Thus, it is likely that some of the reactions in the system are kinetically controlled. Furthermore, the model generated is for a CSTR, and not a column model for a plug flow system. Further work is needed to incorporate the equilibrium model into a PFR system, and to account for reaction kinetics.

3.2.2.3 Conclusions

The equilibrium constants for elemental Hg adsorption on carbon black predict that significant Hg adsorption should not occur, which is in agreement with the experimental results. The equilibrium constants provided some insight into the potential reaction mechanisms for mercury oxidation and removal. HCl initially reacts with the carbon surface to release Cl atom, which acts as the primary oxidizing agent in the system. Cl reacts with Hg species, and with another Cl to form Cl₂. Cl₂ can further react with elemental Hg in the gas phase or on the surface. The reactions could be visualized as shown in Figure 51.

Figure 51. Proposed mechanisms for Hg adsorption on carbon in the presence of HCl.

The kinetics of the various reactions are required to verify the mechanisms proposed and to describe Hg removal in the presence of HCl and carbon.

3.3 Kinetic Constants of Hg, HCl and Carbon Reactions.

As discussed in Section 3.2.2, mercury oxidation and removal in the presence of HCl and carbon black in experimental condition are likely to be kinetically controlled. The Hg, HCl and carbon black reaction system are proposed and listed in Table 23 to Table 26. Gas phase reactions have been well studied and understood, and kinetic constants for these reactions are available. Thus, kinetic constants for surface reactions must be calculated. Only gas-surface reactions are considered in the calculations as surface-surface reactions may be considered as a combination of two gas-surface reactions.

3.3.1 Calculation Details.

3.3.1.1 Locating Transition States.

The transition state is the highest energy state of the chemical reaction along the reaction path. The transition state of the reaction must be located, and the energy and frequencies are calculated to estimate the kinetic constant of the chemical reaction. To locate the transition state, a geometry optimization was performed starting with the product species. The bond to be broken was modified towards the reactant species based on the optimized geometry. Transition state calculations were performed at the B3LYP/6-31G(d) level for all atoms except for Hg, where the SBKJC effective core potential was used. The modified structure was used as the initial guess for the transition state structure. An intrinsic reaction coordinate (IRC) calculation was done

subsequently to verify the reaction path. In cases where the transition state search was not successful, a potential energy surface (PES) scan was performed for the reaction to locate the transition state. Because the computational cost of the PES scan is extremely high, the scan was limited to the carbon plane. Previous relaxed scans of single atom adsorption showed that the energy minima are always located along the carbon plane. For multiple atoms, a PES scan was performed with the attaching atom in the carbon plane and the other atoms relaxed, or with the other atoms fixed at locations relative to the attaching atom based on the optimized geometry during attachment.

3.3.1.2 Calculation of Kinetic Constants.

Canonical transition state theory (CTST) has been widely used to predict theoretical kinetic constants. CTST assumes that transition states are effectively in equilibrium with reactant molecules. If this transition state is considered as a unique compound in itself whose energy is at a maximum between products and reactants, the rate of reaction is given by the product of the concentration of the transition state and the frequency associated with this motion. This frequency is given by kT/h and the concentration of the transition state is calculated from the statistical mechanical expression for the equilibrium constant $k^\pm$ in terms of the appropriate partition functions (63).

For a reaction $A + B \rightarrow \text{products}$, the scheme can be written as:

and the overall rate constant k_+ is then given by the equation

$$k^\pm = \frac{kT}{h} \frac{Q^\ddagger}{Q_A Q_B} \exp(-E_0/kT) \quad (24)$$

Where E_0 is the activation energy, Q_A and Q_B are the complete partition functions per unit volume for the reactants, and $Q^\ddagger$ is the partition function for all the degrees of freedom of the transition state except the reaction coordinate. The motion in the reaction coordinate has been considered separately and its partition function included in the factor kT/h . CTST is also applied to unimolecular reaction kinetic constants calculations in this study.

Kinetic constants calculations are carried out for the 30 gas phase and surface interface reactions listed in Section 3.2.2.2. Transition state theory is used to calculate forward bimolecular reaction kinetic constants for both of the bimolecular and unimolecular reactions. Barrierless reactions are a special case. Because the transition state for barrierless reaction is close to the higher energy structure, the geometry and frequency of higher energy structure could be used as transition state geometry and frequency in the calculation (64). The backward reaction for the barrierless reaction will be calculated based on the following equation.

$$k_s = \frac{k_f}{k_b} \quad (25)$$

Where, k_s is the equilibrium constant of the reaction; k_f is the kinetic constant for the forward reaction; k_b is the kinetic constant for the backward reaction.

Unit corrections were applied to the translational partition function. Units of the kinetic constant for each reaction are either 1/s or cm³/s.mol, depending on each reaction.

3.3.2 Results and Discussion.

3.3.2.1 Kinetic Constants for Adsorption Reactions on Carbon Surface.

As discussed in the previous section, the B3LYP/6-31G(d) theory with SBKJC relativistic effective core potentials for Hg was used in the study of reactions. Transition state calculations were performed to locate the transition state structures and estimate the activation energy of the adsorption reactions. However, the direct calculations failed to locate the transition state. Potential energy scans are necessary for kinetics estimation. Single atom adsorptions show that the energy minima are always located along the carbon plane. PES scans on the carbon sheet surface were performed to study the reaction potential energy surface. PES scan was performed with the attaching atom in the carbon plane relaxed, and the other atoms fixed at locations relative to the attaching atom based on the optimized bare carbon model geometry.

The adsorption reactions which are going to be discussed in this section are listed below.

Based on the PES scan results, the adsorption reactions on carbon surface are all barrier-less reactions. Hydrogen atom adsorption on carbon surface is analyzed as one example of the barrier-less reactions. PES results of hydrogen adsorption on zigzag carbon surface are shown in Figure 52 and Figure 53. The Y axis is the direction along carbon active site edge, and the X axis is the direction which is vertical to carbon edge. The PES was scanned within one active site. As shown in figures, energy results change continuously without a peak or a valley occurring on the surface, which tells that the reaction is a barrier-less reaction. The potential energy surfaces of all the other reactions listed in this section are similar to Figure 52 and Figure 53 and are not presented.

Figure 52. Contour plot for PES of $\text{H} + \text{Czig} = \text{H-Czig}$.

Figure 53. Three-dimensional plot for PES of $\text{H} + \text{Czig} = \text{H-Czig}$.

CTST was applied to calculate kinetic constants. The reactants are considered as the transition states for barrier-less reactions. The statistical and energetic results of barrier-less reactions are estimated with the results of reactants. Transition state energies are estimated with the total energy of reactants. Products of the reactant partition functions were used as partition functions of transition states in CTST calculations. The results of the reactions are summarized in Table 27.

Table 27. Kinetic constants of barrier-less adsorption reactions on carbon surface in HCl and Hg and carbon black reaction system.

Reaction	Reactant Energy (J/mol)	Product Energy (J/mol)	Activation Energy (backward) (J/mol)	Kinetic constant forward	Kinetic constant backward
H+Carm=H-Carm	-538.5657	-538.7784	558469.6240	2.5786E+13	3.0403E-30
H+Czig=H-Czig	-499.8915	-500.0667	459809.2913	2.6817E+12	1.7379E-18
Cl+Carm=Cl-Carm	-998.2017	-998.3750	455256.8280	2.1197E+13	8.9536E-17
Cl+Czig=Cl-Czig	-959.5275	-959.6642	358922.6097	1.4041E+10	3.1709E-04
Hg+Carm=Hg-Carm	-691.8884	-691.9471	154030.2579	4.9206E+08	1.6543E+20
Hg+Czig=Hg-Czig	-653.2142	-653.2227	21979.9437	2.9588E+08	3.1210E+35
Hg-Cl+Carm=HgCl-Carm	-1152.0581	-1152.2106	400107.4374	1.8292E+14	2.6468E-08
Hg-Cl+Czig=HgCl-Czig	-1113.3840	-1113.4841	262751.1669	1.2147E+12	2.5784E+09
Cl+Hg-Carm=HgCl-Carm	-1152.0819	-1152.2106	337756.5435	3.2999E+14	1.8561E-02
Cl+Hg-Czig=HgCl-Czig	-1113.3575	-1113.4841	332450.5872	3.0285E+11	7.9643E-02
HgCl ₂ +Carm=HgCl ₂ -Carm	-1612.3028	-1612.3957	243921.7168	2.7682E+07	7.7013E+11
HgCl ₂ +Czig=HgCl ₂ -Czig	-1573.6286	-1573.6436	38937.4756	1.9378E+12	2.0918E+32
HgCl-Carm+Cl=HgCl ₂ -Carm	-1612.3454	-1612.3957	131979.4281	9.2786E+09	5.8662E+22
HgCl-Czig+Cl=HgCl ₂ -Czig	-1573.6189	-1573.6435	64351.4574	9.7810E+16	1.6356E+26

3.3.2.2 Kinetic Constants for Oxidation Reactions

In general, direct transition state calculations were performed with QST2, QST3 and TS options using G03W software. When transition state calculations would not converge, a rigid PES scan

Figure 55. Three-dimensional plot for PES of $\text{HCl} + \text{Czig} = \text{H-Czig} + \text{Cl}$.

In order to study the reaction path of this reaction, PES data were also carefully analyzed in addition to the PES graph. Two local minima were located from the PES results, which indicate that there are intermediates on the reaction path from reactant to product. One is on the reactant side and the other one is on the product side. The two minima are difficult to visualize on the PES graph of this reaction because of the shallow energy change. Because of the existence of the two minima, the entire reaction was divided into 3 reactions, one is from reactant to the intermediate close to reactant, one is from intermediate close to reactant to intermediate close to product, and the third is from intermediate close to product to the product. The three reactions are listed below. The energetic and kinetic results for these reactions and the other critical reactions are summarized in Table 28.

Table 28. Energetic and kinetic results for HCl releasing Cl reaction on zigzag carbon surface.

Reaction	Reactant Energy (J/mol)	Product Energy (J/mol)	Activation Energy (backward) (J/mol)	Kinetic constant forward	Kinetic constant backward
HCl releasing Cl reaction on zigzag carbon surface.					
HCl + Czig = Cl--H-Czig	-2.5208E+09	-2.5211E+09	3.6076E+05	2.3586E-27	1.1360E-03
H-Czig + Cl = Cl--H-Czig	-2.5208E+09	-2.5211E+09	3.2511E+05	4.4482E-26	5.7071E-01
Czig—HCl = Czig-H--Cl	-9.6023E+02	-9.6028E+02	2.4498E+05	1.2784E-1	6.3517E-17
HCl releasing Cl reaction on armchair carbon surface.					
HCl + Carm = Cl--H-Carm	-2.6224E+09	-2.6226E+09	2.3043E+05	2.0794E+03	8.9656E+09
H-Carm + Cl = Cl--H-Carm	-2.6226E+09	-2.6226E+09	7.0668E+04	8.4228E+08	6.3395E+29
ClH—Carm = Cl--H-Carm	-2.6226E+09	-2.6226E+09	8.3724E+04	3.7961E+19	6.8833E+04
HCl releasing H reaction on zigzag carbon surface					
Cl-Czig + H = H--Cl-Czig	-2.5207E+09	-2.5209E+09	1.6312E+05	4.2358E+03	1.3933E+13
HCl + Czig = HCl—Czig	-2.5208E+09	-2.5209E+09	1.2068E+05	1.3946E-01	1.9876E+23
Czig—ClH = Czig-Cl--H	-2.5208E+09	-2.5209E+09	4.2526E+04	5.6841E+02	2.0109E+05
HCl releasing H reaction on armchair carbon surface					

HCl + Carm = HCl--Carm	-2.6224E+09	-2.6225E+09	1.2779E+05	1.2489E+07	6.9802E+20
Cl-Carm + H = H--Cl-Carm	-2.6225E+09	-2.6225E+09	4.2014E+04	5.8088E+10	7.3666E+03
HCl—Carm = Cl-Carm+H	-2.6225E+09	-2.6225E+09	-3.0108E+04	2.4209E+51	8.8895E+36
H ₂ and Cl ₂ reactions on carbon surface					
H ₂ + Carm = H-Carm + H	-5.3923E+02	-5.3928E+02	1.2750E+05	8.6282E+10	4.7794E-02
H ₂ + Czig = H-Czig + H	-5.0055E+02	-5.0057E+02	2.8838E+04	7.5262E+09	2.7319E+10
Cl ₂ + Carm = Cl-Carm + Cl	-1.4584E+03	-1.4585E+03	2.5822E+05	4.7825E+10	3.4722E-16
Cl ₂ + Czig = Cl-Czig + Cl	-1.4197E+03	-1.4198E+03	1.6188E+05	2.5981E+07	1.0085E-03
HCl + Hg-Czig = ClHg-Czig + H					
HCl + Hg-Czig = HCl--Hg-Czig	-2.9246E+09	-2.9247E+09	1.2788E+05	3.3705E+04	1.4770E+18
HCl-Hg-Czig = H-ClHg-Czig	-2.9246E+09	-2.9248E+09	1.2407E+05	6.8478E-03	3.5559E+23
H-ClHg-Czig = H + ClHg-Czig	-2.9248E+09	-2.9247E+09	1.6960E+04	1.4902E-01	1.0916E+06
HCl + Hg-Carm = ClHg-Carm + H					
HCl + Hg-Carm = HCl--Hg-Carm	-3.0263E+09	-3.0263E+09	9.1259E+03	1.2771E+14	4.3347E+32
HCl-Hg-Carm = H-ClHg-Carm	-3.0264E+09	-3.0264E+09	1.4495E+04	9.6815E+10	7.3405E+33

$\text{H-ClHg-Carm} = \text{H} + \text{ClHg-Carm}$	-3.0264E+09	-3.0263E+09	1.2728E+04	3.3951E+00	9.8677E+08
$\text{HCl} + \text{HgCl-Czig} = \text{Cl}_2\text{Hg-Czig} + \text{H}$					
$\text{Czig-HgCl}_2 + \text{H} = \text{H--HgCl}_2\text{-Czig}$	-4.1327E+09	-4.1330E+09	2.4753E+05	8.8650E-03	4.2669E+10
$\text{HCl} + \text{HgCl-Czig} = \text{H--HgCl}_2\text{-Czig}$	-4.1330E+09	-4.1330E+09	1.1461E+05	3.0297E-10	6.1255E+00
$\text{HCl} + \text{HgCl-Carm} = \text{Cl}_2\text{Hg-Carm} + \text{H}$					
$\text{Carm-HgCl}_2 + \text{H} = \text{H--HgCl}_2\text{-Carm}$	-4.2345E+09	-4.2346E+09	6.6378E+04	3.0958E+10	3.7769E+26
$\text{HCl} + \text{HgCl-Carm} = \text{HCl--HgCl-Carm}$	-4.2348E+09	-4.2348E+09	2.6257E+04	1.4888E+09	4.4194E+33
$\text{HCl--HgCl-Carm} = \text{H--HgCl}_2\text{-Carm}$	-4.2348E+09	-4.2346E+09	2.2597E+04	4.4450E-21	1.0190E+09
$\text{Cl}_2 + \text{Hg-C} = \text{C-HgCl} + \text{Cl}$ and $\text{Cl}_2 + \text{HgCl-C} = \text{C-HgCl}_2 + \text{Cl}$					
$\text{Cl}_2 + \text{Hg-Carm} = \text{Carm-HgCl} + \text{Cl}$	-1.6123E+03	-1.6123E+03	1.4072E+05	2.0813E+07	2.0122E-06
$\text{Cl}_2 + \text{Hg-Czig} = \text{HgCl-Czig} + \text{Cl}$	-1.5736E+03	-1.5736E+03	1.3541E+05	5.6039E+08	2.5331E-01
$\text{Cl}_2 + \text{HgCl-Carm} = \text{HgCl}_2\text{-Carm} + \text{Cl}$	-2.0725E+03	-2.0726E+03	6.5060E+04	4.8572E+18	4.4696E+02
$\text{Cl}_2 + \text{HgCl-Czig} = \text{HgCl}_2\text{-Czig} + \text{Cl}$	-2.0338E+03	-2.0338E+03	1.3269E+05	4.6077E+11	1.6031E-01

3.3.3 Conclusions

PES and kinetic constants for the surface reactions were calculated in this chapter. According to the PES results, the adsorption reactions from equation (26) to (33), and the H_2 and Cl_2 reactions on carbon surfaces are barrier-less. The kinetic constants of barrier-less reactions are calculated with canonical transition state theory based on the assumption that the transition state is very

close to the higher energy reactants. Kinetic constants are listed in the tables are ready to be used for process model calculation.

In the Hg, HCl and carbon black reaction system, the surface reactions related to HCl have barriers. The intermediates were located on the PES of HCl related reactions, which implies that the HCl surface reactions can be divided in to several steps. Quantum calculations and kinetic calculations of each step of the reactions were performed to complete the reaction kinetic constant estimation. The reaction constants calculated in this section will be applied in process model calculations.

3.4 Process Model Simulations.

3.4.1 Model Details.

The process models were equilibrium based or kinetic based. The equilibrium based model for a CSTR was discussed in Section 3.2. This was expanded for a packed bed column reactor and will be modeled as a plug flow system. The material balance for gas phase elements in a PFR can be written as,

$$\rho_a \varepsilon_{ab} \sum \frac{\partial C_{\text{surface},i}}{\partial t} + \varepsilon_b \sum \frac{\partial C_{\text{gas},i}}{\partial t} + \varepsilon_b v \frac{\partial C_{\text{gas},i}}{\partial x} = 0 \quad (37)$$

where ε_b is the porosity of the column (volume of pores divided by total column volume), ε_{ab} is the adsorbent porosity (volume of adsorbent divided by the total column volume), ρ_a is the adsorbent density, and v is the interstitial velocity. Dispersion was neglected. PFR systems have been modeled as n-CSTRs-in-series. Thus, the partial differential equations were solved first by discretizing the equation in space, resulting in sequential CSTRs. The resulting ordinary differential equations in time were discretized using finite differences and the resulting system of algebraic equations at each time step were solved using DNEQNF.

The partial differential equations for kinetic based models are similar to equilibrium based models except for reaction terms. For a PFR,

$$\rho_a \varepsilon_{ab} \sum \frac{\partial C_{\text{surface},i}}{\partial t} + \varepsilon_b \sum \frac{\partial C_{\text{gas},i}}{\partial t} + \varepsilon_b v \frac{\partial C_{\text{gas},i}}{\partial x} = \sum r_j \quad (38)$$

where r_j refers to the rate of reaction and will be of general the form,

$$r_j = k_{\text{forward}} C_{\text{reactant}_1}^a C_{\text{reactant}_2}^b - k_{\text{reverse}} C_{\text{product}_1}^c C_{\text{product}_2}^d \quad (39)$$

Where, surface species concentration is in mol/m². The equilibrium reactions were replaced by the relevant kinetic reactions. The model was solved by discretizing the space component. The resulting system of differential equations were solved using DDASSL within the Sci-lab software (65). Batch reactors are similar to equations (37) and (38), but without the space component.

3.4.2 Results and Discussion.

Reaction kinetic constants are required for process modeling. The kinetic constants of surface reactions were calculated in Section 3.3. The kinetic constants for gas phase reactions were collected from the literature (38,39,40) and are shown in Table 29.

Table 29. Kinetic constants for gas phase reactions.

Reaction	Forward Kinetic constant (/s)	Backward Kinetic Constants (/s)
$\text{HgCl} + \text{M} = \text{Hg} + \text{Cl} + \text{M}$	4.0102E+04	3.7857E+13
$\text{Hg} + \text{HCl} = \text{HgCl} + \text{H}$	7.5993E-42	3.8110E-01
$\text{Hg} + \text{Cl}_2 = \text{HgCl} + \text{Cl}$	1.0399E+01	1.2153E+17
$\text{HgCl}_2 + \text{M} = \text{HgCl} + \text{Cl} + \text{M}$	2.9403E-22	3.0737E+05
$\text{HgCl} + \text{HCl} = \text{HgCl}_2 + \text{H}$	9.4734E-06	2.3554E+14
$\text{HgCl} + \text{Cl}_2 = \text{HgCl}_2 + \text{Cl}$	9.7541E+09	1.2426E-02
$\text{Cl}_2 + \text{M} = \text{Cl} + \text{Cl} + \text{M}$	3.0467E+03	3.3612E+28
$\text{H}_2 = 2\text{H}$	1.7401E-39	1.4904E+11
$\text{HCl} = \text{H} + \text{Cl}$	1.8450E-32	7.2296E+17

The kinetic constants were applied to the batch process model and column process model to simulate the experimental reaction system. The process model results obtained from the current model could not predict the experimental results. The model results show slight elemental mercury removal within several seconds of the simulation, and no obvious elemental mercury removal was observed afterward. The failure of process model simulation are caused by competitive reactions occurring on the carbon surface. Computational results indicate that reaction rates of HCl reactions on carbon surface are fast, and most of the active carbon sites are occupied immediately by H and Cl. After the active carbon sites are occupied, the reaction rates of surface reactions including Hg oxidation reaction on carbon surface are limited. As a result, elemental mercury removal is limited in the simulations.

Two possibilities must be considered to improve the model. First, the major components of glass beads in the column might react with the gas phase components in the presence of catalytic reactions by carbon black. The reactions on SiO₂ surface must be considered included in future studies. Second, other mercury species such as Hg₂Cl₂, may exist in the reaction system and must be considered in future studies.

4 Conclusions and Recommendations

Increases in LOI value (unburned carbon) of fly ash samples resulted in improvements in mercury capture and oxidation. Mercury capture and oxidation were proportional to surface area for different samples. Particle size exhibited similar effects to surface area. The impacts of surface area and particle size were similar to those of LOI, which could be explained by the facts that unburned carbon in fly ash has a relatively high surface area than other fractions, and it tends to be enriched in coarser fractions compared with other fractions in the samples.

Tests with single fly ash components indicated that SiO_2 , Al_2O_3 , MgO , CaO , and TiO_2 had little effect on promoting mercury oxidation or adsorption. Fe_2O_3 and carbon black promoted both mercury oxidation and adsorption. However, carbon was considered as the most important component because of its higher content in different samples compared with iron.

The interaction between flue gas components and surfaces is found to have significant impact on mercury transformation. NO , O_2 , H_2O , and SO_2 did not promote mercury oxidation or capture on carbon black by themselves. NO_2 can help oxidize and capture mercury on carbon black with or without O_2 . HCl showed the most profound effects on mercury oxidation and capture. O_2 plays an important role when combined with HCl , where the Deacon process could be involved. SO_2 inhibited mercury oxidation and capture probably by competing for electron acceptors with mercury and occupying the adsorption sites on the surface.

Acid mine drainage based sorbents promoted mercury oxidation, with mercury removal proportional to the percentage of Fe and to the overall Fe injection rate. The foam index of AMD sorbent was lower than that of fly ash and comparable to Portland cement, indicating that this would not negatively impact concrete production. AMD sorbent injected in coal fired power plants for Hg control would not have a negative effect on the quality of fly ash for cement application.

Theoretical investigation into the interaction of flue gas constituents and carbon surfaces were studied with quantum modeling. Binding energies and equilibrium constants qualitatively agree with the experimental results. Kinetic constants calculated with the quantum models were coupled to reactor models. The process model could not predict the experimental results. Further studies are required to elucidate the heterogeneous reaction mechanisms.

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