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Journal of the Air & Waste Management Association

ISSN: 1096-2247 (Print) 2162-2906 (Online) Journal homepage: http://www.tandfonline.com/loi/uawm20

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To cite this article: Edwin S. Olson , Charlene R. Crocker , Steven A. Benson , John H. Pavlish & Michael J. Holmes (2005) Surface Compositions of Carbon Sorbents Exposed to Simulated Low-Rank Coal Flue Gases, Journal of the Air & Waste Management Association, 55:6, 747-754, DOI: 10.1080/10473289.2005.10464672

To link to this article: http://dx.doi.org/10.1080/10473289.2005.10464672

Published online: 01 Mar 2012.

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TECHNICAL PAPER

ISSN 1047-3289 *J. Air & Waste Manage. Assoc.* **55**:747–754
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Surface Compositions of Carbon Sorbents Exposed to Simulated Low-Rank Coal Flue Gases

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ABSTRACT

Bench-scale testing of elemental mercury (Hg^0) sorption on selected activated carbon sorbents was conducted to develop a better understanding of the interaction among the sorbent, flue gas constituents, and Hg^0. The results of the fixed-bed testing under simulated lignite combustion flue gas composition for activated carbons showed some initial breakthrough followed by increased mercury (Hg) capture for up to ~4.8 hr. After breakthrough, the Hg in the effluent stream was primarily in an oxidized form (>90%). Aliquots of selected activated carbons were exposed to simulated flue gas containing Hg^0 vapor for varying time intervals to explore surface chemistry changes as the initial breakthrough, Hg capture, and oxidation occurred. The samples were analyzed by X-ray photoelectron spectroscopy to determine changes in the abundance and forms of sulfur, chlorine, oxygen, and nitrogen moieties as a result of interactions of flue gas components on the activated carbon surface during the sorption process. The data are best explained by a competition between the bound hydrogen chloride (HCl) and increasing sulfur [S(VI)] for a basic carbon binding site. Because loss of HCl is also coincident with Hg breakthrough or loss of the divalent Hg ion (Hg^{2+}), the competition of Hg^{2+} with S(VI) on the basic carbon site is also implied. Thus, the role of the acid gases in Hg capture and release can be explained.

IMPLICATIONS

On March 15, 2005, the U.S. Environmental Protection Agency issued federal rules to reduce Hg emissions from coal-fired power plants, resulting in the need to control Hg currently being emitted from coal-fired combustion systems 69% by 2018. Since the most commonly considered strategy for removing Hg from coal combustion flue gas streams is the chemisorption of Hg species by a solid sorbent injected into the gas upstream of particulate control, a better understanding of the surface functions of the sorbent will provide insight into developing more effective sorbents.

INTRODUCTION

Mercury (Hg) is an immediate concern for the U.S. electric power industry because of the U.S. Environmental Protection Agency's (EPA) December 2000 decision that regulation of Hg from coal-fired electric utility steam-generating units is appropriate and necessary under Section 112 of the Clean Air Act (CAA). After extensive study, EPA determined that Hg emissions from power plants pose significant hazards to public health and must be reduced. The EPA *Mercury Study Report to Congress*[1] and the *Utility Hazardous Air Pollutant Report to Congress*[2] both identified coal-fired boilers as the largest single category of atmospheric Hg emissions in the United States, accounting for approximately one-third of the total anthropogenic emissions. On December 15, 2003, EPA proposed a rule to permanently cap and reduce Hg emissions from power plants.[3] EPA is proposing two approaches for controlling emissions of Hg from utilities and will take comments on the alternatives before taking final action. The alternatives are (1) requiring utilities to install controls known as Maximum Achievable Control Technologies (MACT) under Section 112 of the CAA—if implemented, this proposal would reduce nationwide emissions of Hg by 14 tons (29%) by the end of 2007, and (2) a proposed rule establishing "standards of performance" limiting Hg emissions from new and existing utilities. This proposal, under Section 111 of the CAA, would create a market-based "cap-and trade" program that, if implemented, would reduce nationwide utility emissions of Hg in two distinct phases. In the first phase, due by 2010, emissions will be reduced by taking advantage of "cobenefit" controls—that is, Hg reductions achieved by reducing sulfur dioxide (SO_2) and nitrogen oxides (NO_x) emissions. When fully implemented, Hg emissions will be reduced by 33 tons (69%).

Lignite coals generally contain comparable levels of mercury but significantly lower levels of chlorine (Cl) compared with bituminous coals. Lignite coals are also distinguished by their much higher alkali and alkaline-earth element contents. These compositional differences have important effects on the quantity and form of Hg

emitted from a boiler and on the capabilities of different control technologies to remove Hg from flue gas. The high Cl content (>200 ppm) characteristic of many bituminous coals increases the fraction of the more easily removable mercuric compounds (Hg^{2+}) in the total Hg emission. Conversely, experimental results and information collection request data indicate that low-Cl (<200 ppm) coal combustion flue gases contain predominantly elemental mercury (Hg^0), which is substantially more difficult to remove than Hg^{2+}.[4]

The most commonly considered strategy for removing Hg from coal combustion flue gas streams is the adsorption of Hg species by a solid sorbent injected upstream of a particulate control device such as a fabric filter (FF; baghouse) or electrostatic precipitator. The evaluations of potential Hg sorbents have demonstrated that the chemical speciation of Hg controls its capture mechanism and ultimate environmental fate.[5] Activated carbon injection is the most mature technology available for Hg control. Activated carbons can effectively sorb both Hg^0 and Hg^{2+}. Most activated carbon Hg control research has been performed in fixed-bed reactors that simulate relatively long residence time (min or hr) and imitate gas–solid contact mercury capture by a FF filter cake.[6–11]

Researchers are striving to attain a more thorough understanding of Hg species reactions on activated carbon surfaces to produce more efficient sorbents. The removal of Hg^0 from flue gas by activated carbon at typical filter bag temperatures in the range of 100–150 °C is believed to occur through surface-catalyzed oxidation (i.e., chemisorption). A major piece of evidence for a sorption mechanism involving oxidation of Hg^0 is the X-ray absorption near edge structure spectra of spent sorbents that show no peaks corresponding to Hg^0 but instead match Hg^{2+} sp(s), in which Hg^{2+} is likely bonded to some element other than oxygen.[12] Other evidence is that little sorption occurs on activated carbons in the absence of air or NO_2.[13]

The potential role of acidic and basic surface functional groups on mercury capture is unknown and needs to be investigated. By definition, for oxidation of Hg^0, electrons must be accepted by a Lewis acid on the activated carbon. The resulting Hg^{2+} is now a Lewis acid and could bind to a basic functionality on the carbon or to an anion residing on the carbon surface. Evidence for this basic functionality being on the carbon structure of the Norit flue gas desulfurization (FGD) sorbent, instead of on the 34% of mineral matter contained in that sorbent, was presented by Dunham et al.[9] The acidic gas components also bind to basic groups either on the carbon structure or the mineral matter or both.

The beneficial role of Cl and the impact of sulfur species in capturing mercury on activated carbons is well established.[9,14] However, Cl- and sulfur-bearing surface functional groups that form via addition of acid gases to the basic sorbent groups during exposure of carbons to flue gas are not well characterized.

To develop a better understanding of how mercury capture is related to acid gas effects on the sorbents, the surface chemistry of activated carbon in low–HCl-simulated flue gas was observed using X-ray photoelectron spectroscopy (XPS). XPS, also known as electron spectroscopy for chemical analysis, involves irradiating a sample with a monoenergetic X-ray beam that causes photoelectrons to be emitted from the samples. The photoelectrons are emitted from the first 30–50 Å of the sample surface. An energy analyzer is used to determine the binding energy of the emitted electrons. From the binding energy and intensity of the photoelectron peak, the elemental identity, chemical state, and surface concentration of an element are determined.

Previous XPS investigations at the Energy & Environmental Research Center (EERC) examined the surface chemistry of sorbents in simulated flue gases with varying compositions.[15] The experiments were intended to study the behavior in a relatively high HCl concentration (50 ppm) in the gas stream that would be representative of high-Cl coal combustion gases. That investigation clearly demonstrated that sulfur [S(VI)] builds up on the sorbents on exposure to flue gas, and, furthermore, both NO_2 and H_2O are necessary for oxidation of the bound SO_2 to S(VI). These studies also showed that Cl is present before breakthrough of mercury occurs but absent after completion of breakthrough. When SO_2 was omitted from the gas composition, a very large amount of Cl was present in the sorbent (and no breakthrough occurred).

The purpose in the investigation reported in this paper was to additionally verify and establish the relationship of HCl to SO_2 and its oxidation products under another set of conditions, specifically to determine if the behavior of HCl is the same when it is present in very low concentrations. Thus, a low HCl concentration was selected in this investigation, which is representative of the combustion of low-Cl coals. Furthermore, samples for observing changes in the surface concentrations were collected under a similar gas concentration, with time being the only variable. Thus the time of exposure to the gases was varied; the observation samples correspond to several stages of mercury exposure, including initial induction, max capture initiation, breakthrough initiation, and breakthrough completion. The previous work used a variety of gas compositions to scope and only one or two observation samples for each set of compositions.

Contact times between flue gas and sorbent particles on a FF may be on the order of minutes rather than hours. Thus, only the first sample (1332) may be representative of an actual field combustion condition. However, it necessary to understand how the sorption process runs its course to gather all of the clues that are accessible over both short and long periods of time to be able to put together a mechanism for the sorption process.

EXPERIMENTAL METHODS

The experimental design was to prepare activated carbon from a Fort Union lignite coal and load aliquots with elemental mercury in the fixed bed under low–acid-simulated flue gas conditions for increasingly long time intervals to observe changes in surface area chemistry over time using XPS. Activated carbons were prepared by carbonizing relatively high sodium lignites in a quartz tube reactor followed by steam activation in a vertical stainless steel tube reactor. One hundred grams of char produced by Luscar Ltd. from Ravenscrag lignite (Fort Union Formation from the Bienfait Mine) was steam-activated in a vertical steel tube reactor. The tube reactor was heated to 800 °C (1472 °F) in a gentle flow of nitrogen. Steam at 450 °C (842 °F) was then introduced into the bottom of the reactor at 65 cm^3/min for 30 min. After the activation process, the reactor was cooled to room temperature in flowing nitrogen. The activated carbon was removed from the reactor, weighed, and stored in a nitrogen atmosphere. The iodine number of the activated carbon, ground to pass through a 200-mesh sieve, was determined according to ASTM Procedure D4607–94 (1999) Standard Test Method for Determination of Iodine Number of Activated Carbon to approximate surface area. The yield of activated carbon from the char produced was 66%. The iodine number as determined by ASTM D4607 was 427 mg I_2/g. This is roughly equivalent to the surface area in m^2/g.

Four 500-mg aliquots of activated carbon were loaded with Hg^0 using a fixed-bed bench-scale apparatus at 135 °C (275 °F) using 12 $\mu g/m^3$ for inlet Hg^0 concentration and the simulated lignite flue gas (6% O_2, 12% CO_2, 15% H_2O, 580 ppm SO_2, 120 ppm NO, 6 ppm NO_2, and 1 ppm HCl in N_2) according to the conditions listed in Table 1. The 500-mg sample size provided adequate material for XPS analysis. The samples were separately exposed in four repetitions of the experiment for contact times of 0.33, 1.5, 4.8, and 11 hr (Table 1). Previous research conducted on this unit using smaller samples showed high reproducibility in subsequent runs under the same conditions.[10]

Figure 1 shows the approximate state of Hg loading level for each sample with respect to time by indicating the percentage of Hg^0 from the inlet measured as total mercury at the outlet. After breakthrough, the actual total mercury concentration at the outlet is 10–20% higher than the inlet concentration, indicating that Hg^{2+} species desorbed from the activated carbon. Once each sample was exposed for the appropriate time, the sample was recovered by tapping the inverted filter onto weigh paper and storing the powder under nitrogen in a vial.

Table 1. Conditions for loading activated carbons with mercury at 135°C (275°F).

Sample	Description	Load Point/ Exposure Time
Baseline material	Baseline activated carbon	Not exposed
BS-1332	Initial induction	Onset of testing (20 min)
BS-1331	Maximum capture rate achieved	Efficient Hg capture (90 min)
BS-1330	Breakthrough began	Hg evolution increased (4.8 hr)
BS-1329	Breakthrough condition	Hg began to evolve at the same rate as applied (11 hr)

Note: Simulated flue gas conditions: 6% O_2, 12% CO_2, 15% H_2O, 580 ppm SO_2, 120 ppm NO, 6 ppm NO_2, 1 ppm HCl, and 11 $\mu g/m^3$ Hg^0.

The five samples listed in Table 1 were analyzed by XPS at Physical Electronics in Eden Prairie, MN, with a Physical Electronics 5802 spectrometer using monochromatic Al Kα x-radiation. The X-ray source operated at 350 W, and data were collected from 800-μm analysis areas. Low-resolution survey scans (1.8-eV resolution) provided a full spectral analysis of elemental composition on the surface of the samples. High-resolution scans (0.3-eV resolution) of individual photoelectron peaks revealed the chemical state(s) of the associated elements. Carbon, nitrogen, oxygen, sodium, magnesium, calcium, iron, aluminum, silicon, phosphorus, sulfur, and chlorine were detected in the analyses.

RESULTS

Elemental Composition

Table 2 shows the results of the survey scan as atom percent (>0.1 atom %) for the most concentrated elements, as detected by XPS in the first thin layer of the activated carbon. Hg was not present in sufficient quantities to be detected by XPS.

Apparent measurable change in surface elemental concentration over time occurred for carbon, sulfur, and oxygen. The atom percentage of carbon decreased from 86.4 to 70.2 atom % (20% change) owing to surface accumulation of sulfur and oxygen, which increased by factors of >40 and 2, respectively. The nitrogen concentration appeared constant over time. Whereas chlorine

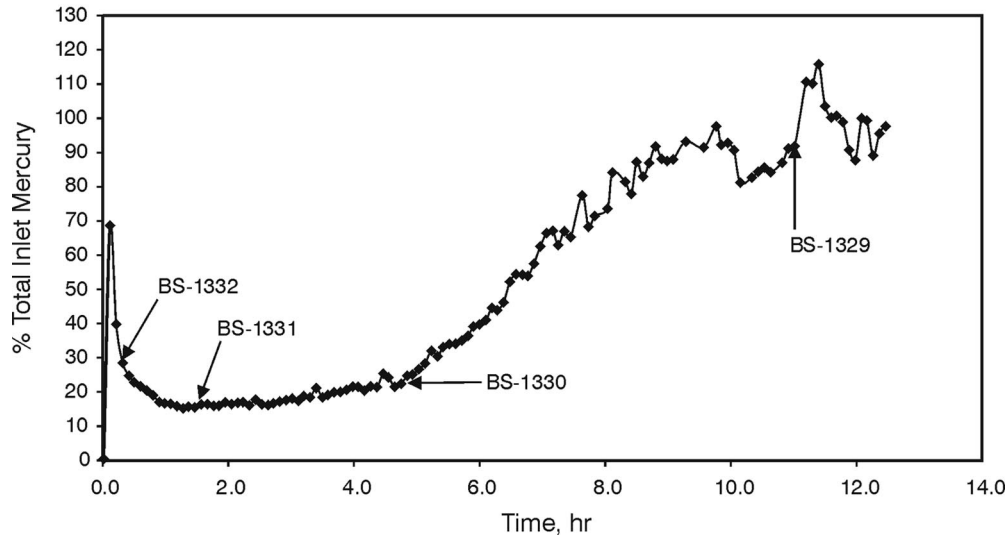

Figure 1. Hg loading rates of Luscar char-activated carbon.

was not present initially at a detectable concentration, its presence became detectable for the midtest samples. The chlorine concentration decreased when the Hg breakthrough level reached the inlet concentration. This was confirmed in the high-resolution scan.

The actual carbon content of the samples was assumed to be constant, because the loading temperature of the experiment is insufficient to evolve carbon compounds. Recalling that the XPS measures the presence of analytes at the surface relative to each other (versus absolute concentration), ratios of detected analytes were, therefore, calculated normalized to carbon and are presented in Table 3. In this format, it is easily seen that sulfur and oxygen concentrations at the surface increased by a factor of 60 and 3, respectively, relative to the carbon content. Concentrations of other analytes at the surface remained constant relative to the carbon content.

Speciation

High-resolution XPS scans were performed on the samples to examine specific species for selected elements. The high-resolution scans show the specific chemistry of each desired element. Elements of interest for this experiment were carbon, oxygen, nitrogen, sulfur, chlorine, and Hg species. The large energy of the incident X-ray is enough to exceed the binding energy of an inner electron and

Table 2. Concentration of elements from the XPS survey scan (atomic percentage).

Sample	Load Point/Time	C	S	O	N	Al	Ca	Cl	Fe	Mg	Na	P	Si
Baseline material	Not exposed	86.4	0.1	9.3	0.3	0.5	0.9	<0.1	0.1	0.1	1.4	<0.1	0.3
BS-1332	20 min	85.0	1.1	11.3	0.2	<0.1	0.8	<0.1	<0.1	<0.1	1.4	<0.1	0.4
BS-1331	90 min	80.3	2.5	14.5	0.2	<0.1	0.8	0.1	0.1	<0.1	1.4	<0.1	0.3
BS-1330	4.8 h	75.5	3.6	17.9	0.2	<0.1	0.9	<0.1	0.2	<0.1	1.3	0.1	0.2
BS-1329	11 h	70.2	4.1	22.5	0.4	<0.1	1.0	<0.1	0.1	<0.1	1.0	<0.1	0.4

Table 3. Atomic ratios of elements from the XPS survey scan, normalized to carbon at 86.4%.

Sample	Load Point/Time	C	S	O	N	Al	Ca	Cl	Fe	Mg	Na	P	Si
Baseline material	Not exposed	86.4	0.07	9.3	0.3	0.5	0.93	—	0.06	0.1	1.4	—	0.3
BS-1332	20 min	86.4	1.1	11.5	0.2	—	0.84	—	—	—	1.4	—	0.4
BS-1331	90 min	86.4	2.7	15.6	0.2	—	0.87	0.06	0.09	—	1.5	—	0.3
BS-1330	4.8 hr	86.4	4.1	20.5	0.2	—	1.05	—	0.17	—	1.5	0.09	0.2
BS-1329	11 hr	86.4	5.0	27.7	0.5	—	1.22	—	0.11	—	1.2	—	0.5

Note: Atom_C % and atom_E % from Table 2 are used to calculate the atom % of the element (E) according to the equation: $E_{\text{norm at\%}} = \left(\frac{86.4}{\text{atom}_C\%}\right) \times \text{atom}_E\%$.

cause its ejection from the atom. The photoelectron spectra represent the binding energies of photoelectrons ejected from an inner orbital, such as the 1s orbital for carbon and oxygen and the 2p orbital for sulfur and chlorine. These energy spectra can give information about the chemical state of the atoms of which the electrons are ejected. The carbon 1s binding region contained one large peak at the graphene binding energy with irresolvable trace peaks present in the graphene tail at increasing binding energy. The oxygen 1s binding region includes one large peak at 532.11 eV for all of the samples. Potential peaks in the nitrogen 1s region include nitrate at 407–408 eV, nitrite at 404 eV, and ammonium at 401–402 eV. The XPS nitrogen 1s species analysis indicated that a small amount of ammonium ion might have been present in the starting material. Consistent with the small increase in atom % N for the most exposed sample (1329) from the survey scans, the binding energy region (Figure 2) showed only a very small increase in the ammonium species with exposure time. No nitrate or nitrite species were identified at the sample surface.

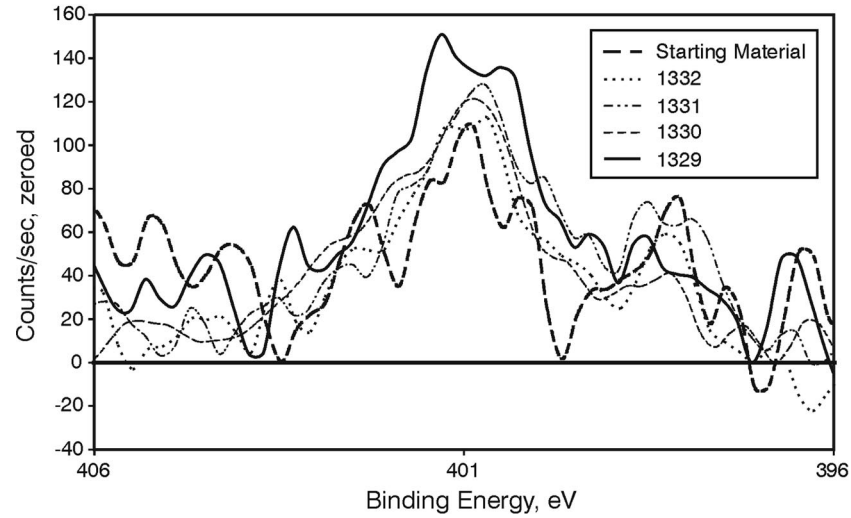

Figure 2. Nitrogen peak region. Potential peaks in the nitrogen 1s region include nitrate at 407–408 eV, nitrite at 404 eV, and ammonium at 401–401eV.

Figure 3 shows the peaks in the sulfur 2p region. Sulfur in the starting material occurred as S(VI; sulfates/sulfones), thiophenes, and S(II; sulfides) at 169, 165, and 161 eV, respectively. Mathematical integration of the peaks suggests a nearly even split between the three species—34, 34, and 32%, respectively. That is ~0.02 atom % of the sample. Within the first 20 min, the total sulfur concentration increased 10-fold. Most (>89%) occurred as S(VI), mostly sulfate, with a nominal concentration of the two other species, as indicated in Table 4. As the S(VI) concentration increased to 4 atom %, the thiophene concentrations leveled off at ~0.12 atom %, and the sulfide disappeared, possibly through displacement as H_2S or through oxidation. When normalized to carbon, the S(VI) ratio is 0.057, and the thiophene ratio is 0.002. The buildup of sulfur species on the surface of the sample suggests sorption and oxidation of SO_2 from the flue gas stream.

Oxygen concentrations in the starting material were more than adequate to support the presence of S(VI) and S(IV) species. The increase in oxygen content at the surface over time of exposure to flue gas is expected as SO_2 is collected and oxidized on the surface.[16] There may also have been some oxidation of the carbon surface, because the gas had both O_2 and NO_2, but this is minimal at <150 °C.[17] The ratio of increased oxygen to increased sulfur in the 20-min sample was 2.2. The sample contained mostly S(VI), so this value is not consistent with a 4:1 ratio predicted for sulfate. Thus, much of the S(VI) may be a bound form of SO_3, or in other words, one or more of the S(VI) oxygens may be a pre-existing carbon oxygen, such as formation of a phenolic sulfate ester. Another possible outcome is that carbonate and inorganic oxides on the carbon were converted to sulfates with loss of CO_2 or incorporation of inorganic oxygen. In subsequent samples, the S increase-to-O increase ratio increased with time, reaching 3.7 at 11 hr (Table 3). Thus, not only do the S and O increase with time, but the ratio approaches that expected for sulfate (i.e., 4). This increase

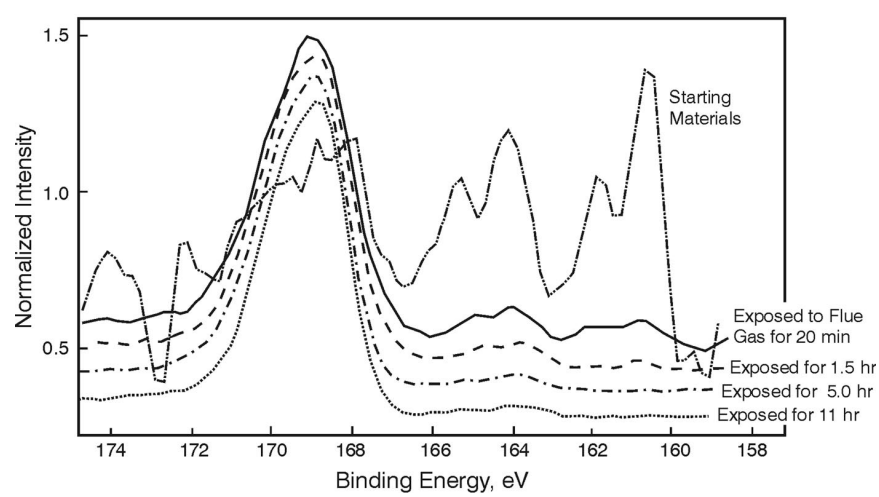

Figure 3. Sulfur peak region. Peaks in the sulfur 2p region include S(VI; sulfates/sulfones), thiophenes, and S(II; sulfides) at 169, 165, and 161 eV, respectively. The scans have been normalized and expanded and the baselines offset to illustrate qualitative differences in the peaks of the samples. Actual peak intensity ranged from 44 to 1261 counts/sec.

Table 4. XPS analysis of sulfur species apportionment.

	Atom %, Normalized to Carbon at 86.4%				% Sulfur Speciation		
Sample	**Total S**	**S(VI)**	**Thiophene**	**Sulfide**	**S(VI)**	**Thiophene**	**Sulfide**
Baseline material	0.07	0.02	0.02	0.02	34%	34%	32%
BS-1332	1.08	0.96	0.06	0.05	89%	6%	5%
BS-1331	2.73	2.57	0.14	0.03	94%	5%	1%
BS-1330	4.09	3.97	0.12	0.00	97%	3%	0%
BS-1329	5.04	4.88	0.15	0.00	97%	3%	0%

in the ratio could be attributed to S(VI) exhaustion of the sorbent oxides and carbonates and the formation of more hydrated forms, such as sulfuric acid, with time.

The peaks in the Cl(2p) species region are illustrated in Figure 4. The Cl(2p) region includes covalently bound chlorine (doublet at 200 and 201.6 eV) and ionic chloride (at 198 eV). The XPS chlorine speciation analysis indicated the absence of chlorine species in the starting material, consistent with the atom % survey scan. The sample obtained after 20 min of exposure to low-acid simulated flue gas (1331) showed peaks corresponding to the covalent and ionic chloride, clearly indicating that the sample surface accumulated covalently bonded chlorine. The 90-min sample exhibited a similar XPS spectrum. The signal-to-noise ratio of these peaks is ~9:1. In these samples, carbon is the likely covalent partner. Thus, these data are interpreted as an addition reaction of HCl to the unsaturated graphene edge of the carbon (hydrohalogenation) to form the organochlorine derivative. After longer exposure to the flue gas, chlorine was once again absent from the sample surface (Samples BS-1329 and 1330).

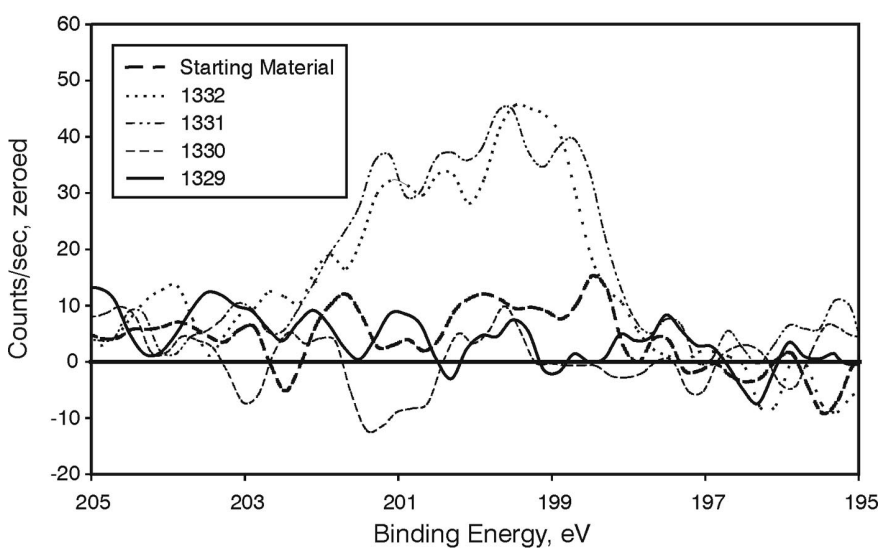

Figure 4. Organic chlorine peak region. Potential peaks in the Cl(2p) region include covalently bound chlorine (doublet at 200 and 201.6 eV) and ionic chloride (at 198 eV).

Addition of HCl to a carbon surface has been investigated,[18] but XPS has not been previously utilized to elucidate the binding interactions. Cl(2p) spectra very similar to the that of the flue gas-exposed sample were reported for a sample prepared from a metalized chlorinated organic precursor[19] and for carbons treated with molecular chlorine.[20,21] The published spectrum clearly showed the Cl (2p) peaks (200 and 201.6 eV) attributed to organochlorine, as well as the ionic chloride peak. Similar spectra were also obtained for Norit FGD and North Dakota lignite-derived carbons exposed to flue gas containing much larger amounts of HCl (50 ppm), but did not appear in spectra from a similar carbon exposed to flue gas that did not contain HCl.[15]

Because of its very low concentration in the sample and instrumental interference of silicon, Hg was not detected on the surface; therefore, direct analysis of mercury bonding cannot be determined by this technique at these low concentrations, even at the maximum Hg capture capacity of the sorbent.

DISCUSSION

The results showing the progressive accumulation of S(VI) in the set of sorbents exposed to flue gas verified the results obtained in the earlier investigation for before and after Hg breakthrough samples. In the present investigation, we were able to show that the S(VI) forms and collects rapidly on the surface.

The accumulation of chlorine was also observed from the 1-ppm HCl flue gas in the 20-min and 90-min samples and was not observed in experiments conducted for longer times. This also verifies the earlier results conducted with 50 ppm HCl, where a long exposure to full flue gas gave no chlorine after Hg breakthrough (8 hr) but 0.19 atom % before Hg breakthrough (2 hr). Previous work showed that HCl-treated carbons are very thermally stable and, therefore, no HCl adsorbed to the surface, further weight to the supposition that the chlorine is organically bound and not just HCl at the surface.[18] Had HCl simply collected in a water film on the surface, it would have ionized, and chloride would have been evident in

the XPS spectrum. The high-resolution results were consistent with formation of organochlorine (hydrochlorination).

The samples exposed for longer periods (1330 and 1329) showed no chlorine in the survey scan, and the Cl (2p) peaks that were attributed to organochlorine disappeared in the high-resolution scan (dehydrochlorination). In the previous research, we showed that when no SO_2 is present in the flue gas, the atom % chlorine continues to build up, reaching 2 atom % after 4 hr.[15] These data demonstrate that in the present experiment, HCl had formed covalent bonds reversibly to the surface. During the initial exposure times, HCl hydrochlorinates the surface carbon structures, and during the later times when sulfuric acid concentrations reach a high level, the chlorine is displaced. Secondly, because no chlorine is displaced when SO_2 is omitted, the data suggest that sulfuric acid is the main poison for the basic sites. Binding of SO_2 is not important in this equilibrium, because most of it converted to S(VI), and it does not build up.

The reversible binding of HCl to carbons has been previously demonstrated, the desorption mode being mostly thermal.[18] The conditions on the surface become highly acidic with the buildup of sulfuric acid. It is well known that HCl is liberated most easily from a warmed H_2SO_4 solution. Of the potential molecules formed by the departing chlorine with other flue gas constituents (e.g., SO_2Cl_2, $SOCl_2$, HOCl, and Cl_2), HCl has the most favorable heat of formation and, thus, is the likely form of the detaching chlorine. Irrespective of the bond energies of substituents on the carbon atoms, the high volatility of HCl compared with the low volatility of H_2SO_4 (and large increase in concentration) means the equilibria will favor displacement of HCl from the surface.

Finally, we consider how the acid gas interactions relate to the mercury breakthrough. We argue that the same principle applies to mercury binding as that involved in competitive chlorine binding discussed above. This argument is based on the extensive series of sorption runs conducted with a variety of concentrations of each of the major flue gas components.[10] The Hg breakthrough time was inversely related to the SO_2 concentration. The Hg^{2+} is a Lewis acid, and reversible binding to a carbon basic site must compete with sulfuric acid. So higher concentrations of SO_2 produce higher sulfuric acid concentrations at a faster rate. When all of the carbon basic sites are filled, no additional Hg^{2+} can bind, and in fact the Hg^{2+} already present is displaced, as evidenced by effluent Hg^{2+} that is 120+% of the inlet.[10] The competition model for Hg capture developed in those breakthrough experiments is consistent with the competition demonstrated in the present article. To be perfectly clear, we restate that mercury binding competes with HCl and sulfuric acid binding on the carbon structure, and this does not at all imply that chlorine and sulfur constitute a binding site. They may comprise part of an oxidation site, but that will be discussed in a future publication.

CONCLUSIONS

Results of this experiment led to several conclusions regarding the surface chemistry of activated carbon in a fixed bed exposed to mercury under low-acid flue gas conditions.

With regard to nitrogen species, XPS analysis showed little increase in ammonium concentrations over time as the sample was exposed to simulated flue gas. Oxidized nitrogen species were not detected in the analysis.

X-ray photoelectron spectroscopy analysis showed that most sulfur occurred initially as sulfate, thiophene, and sulfide. S(VI) concentration (as sulfate, bisulfate, or sulfuric acid) increased significantly as the sample was exposed to simulated flue gas.

Oxygen concentration on the sample increased over time, resulting from both addition of SO_2 and oxidation and hydration of constituents such as SO_2 chemisorbed to the sample surface and surface carbons.

The organic chlorine content increased during the period of optimal Hg capture and then decreased as S(VI) concentrations increased.

There is competition for active basic sites by acidic chlorine and S(VI) species, which the S(VI) species ultimately dominate.

Mercury sorption on the surface correlates inversely to S(VI) accumulation. This is interpreted as competition by Hg^{2+}, S(VI), and HCl for the basic carbon sites, which eventually are occupied entirely by S(VI) species.

This work provides greater insight into changes in the surface chemistry of lignite-based activated carbons over time when exposed to the low-acid flue gas conditions encountered in lignite (and western subbituminous)-fired combustion systems. These findings are also consistent with results using lignite-based activated carbon in high HCl, SO_2 conditions.[22] Understanding the surface interactions required to oxidize and bind Hg allows for the engineering of effective sorbents to capture and control mercury in anticipation of federally mandated emission reduction requirements.

The conclusions of this research are consistent with the hypothesized bonding site for Hg as a base site that may be a carbon-edge structure having Lewis base characteristics.[23] Other basic sites may be situated on the basal planes[24] or on surface oxides (pyrones). The zigzag sites were favored in molecular orbital calculations[25] on the sites for SO_2 oxidation to S(VI). The base can donate electrons to Hg^{2+}, HCl, H_2SO_4, and SO_2. The reactions are

reversible as demonstrated by loss of HCl at breakthrough. The final equilibrium state favors the sulfate form. Thus, the acid gases will poison the Hg-bonding sites after prolonged exposure, leading to desorption of oxidized mercury species.

ACKNOWLEDGMENTS

This work is supported by an international consortium of Saskatchewan Power Corp., Environment Canada, Luscar Ltd., Basin Electric Power Cooperative, Minnkota Power Cooperative, Inc., Otter Tail Power Company, EPRI (through tailored collaboration with Great River Energy, Minnesota Power, Inc., and Xcel Energy), the North Dakota Industrial Commission, the U.S. Department of Energy (DOE) National Energy Technology Laboratory under Cooperative Agreement DE-FC26–98FT40321 through the EERC's Jointly Sponsored Research Program, and the U.S. Environmental Protection Agency (EPA; Grant Number R827649.01) through the Energy and Environment Research Center's (EERC) Center for Air Toxic Metals Program. Any opinions, findings, conclusions, or recommendations expressed herein are those of the authors(s) and do not necessarily reflect the views of DOE or EPA.

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