

XAFS Examination of Mercury Sorption on Three Activated Carbons

Frank E. Huggins* and Gerald P. Huffman

CME/CFFLS, University of Kentucky, Lexington, Kentucky 40506-0043

Grant E. Dunham

University of North Dakota—EERC, Grand Forks, North Dakota 58202

Constance L. Senior

Physical Sciences Incorporated, Andover, Massachusetts 01810

Received June 11, 1998. Revised Manuscript Received September 17, 1998

The sorption of mercury, as Hg^0 and HgCl_2 , in a synthetic flue gas (SFG) by three activated carbons has been examined by XAFS spectroscopy. The three carbons consisted of a sulfur-activated carbon, an iodine-activated carbon, and an activated carbon derived from lignite. In addition to mercury, the occurrence and behavior of sulfur, chlorine, calcium, and iodine were also examined by XAFS spectroscopy. These other elements were present either as activating species on the carbons or as reactive components (SO_2 , HCl) in the SFG. The XAFS results showed that each type of activated carbon behaves differently with respect to sorption of mercury and other species from the SFG. For the iodine- and sulfur-activated carbons, the XAFS data confirm that it is the activating element (I or S) that forms a sorption complex with mercury. However, the activated carbon from lignite exhibited a more variable behavior that reflected the conditions of the experiments, in particular whether HCl or HgCl_2 was present in the SFG. This study reveals some of the complexities that are involved in low-temperature sorption of mercury by activated carbons in that the sorption mechanism clearly involves acidic species of sulfur and chlorine in the gas phase, the affinity of the carbon for such species, and the nature of the active sites on the carbons, in addition to the mercury speciation.

1. Introduction

Even in quite small quantities, mercury (Hg) can be a potent toxin for humans due to its adverse effects on the gastrointestinal tract and the nervous system.¹ The most prevalent source of exposure to mercury for the general population is believed to be through ingestion of fish from natural waters that have been contaminated by mercury.² Mercury is thought to be introduced into such waters largely by atmospheric transport^{2,3} and is then transformed by bacterial agents to methylmercury ($(\text{CH}_3)_2\text{Hg}$), which accumulates in the body tissues of fish. Hence, mercury accumulates in the food chain and tends to become more concentrated the higher the

organism is up the food chain.^{2,3} The emission and dispersion of this element to the environment is, therefore, a topic of great concern for human health and the major reason mercury is included as a potential hazardous air pollutant (HAP) in Title III of the 1990 Amendments to the Clean Air Act.⁴ Further, as a result of the volatility of mercury and its compounds, the transport and residence lifetime of this element in the atmosphere are considerably greater than those of other HAP elements. Consequently, the dispersion of mercury has become a significant global environmental problem, particularly in the northern hemisphere.³

One of the more readily identifiable sources of anthropogenic mercury emissions is coal combustion for power generation. Despite the fact that mercury is the HAP element of lowest average abundance in coal (typically between 0.05 and 0.2 ppm by weight in U.S. coals),^{3,5,6} coal combustion in the United States is a significant contributor to atmospheric mercury because

* Corresponding author address: 533 South Limestone Street, Suite 111, University of Kentucky, Lexington, KY 40506. E-mail: fhuggins@engr.uky.edu.

(1) *Clinical Guide to Laboratory Tests*, 2nd ed.; Tietz, N. W., Ed.; Saunders: Philadelphia, PA 1990.

(2) Porcella, D. *EPRJ J.* **1990**, April/May, 46–49. Porcella, D. In *Proceedings, Second International Conference on Managing Hazardous Air Pollutants*, Report TR-104295; Electric Power Research Institute: Palo Alto, CA, 1994; pp IV.33–IV.41. Also see: Proceedings, 1995 Canadian Mercury Network Workshop Web Site: <http://www.cciw.ca/eman-temp/reports/publications/mercury95/main.html>. U.S. Geological Survey Web Site: http://water.usgs.gov/public/wid/FS_216-95/FS_216-95.html.

(3) Sloss, L. L. *Mercury Emissions and Effects—The Role of Coal*, IEAPER/19; International Energy Agency: London, 1995; 39.

(4) Amendments to the Clean Air Act. *U.S. Public Law 101–549*; U.S. Government Printing Office: Washington, DC, Nov. 15, 1990; 314.

(5) Bragg, L. J.; Oman, J. K.; Tewart, S.; Oman, C. L.; Rega, N. H.; Washington, P. M.; Finkelman, R. B. *Coal quality (COALQUAL) database*: version 1.3; U. S. Geological Survey, Open-File Report 94–205, 1994; 35Mb CD-ROM.

(6) Swaine, D. J. *Trace Elements in Coal*; Butterworth: Oxford, U.K., 1990.

the electrical power generation industry consumes over 0.5 billion tons of coal per year.⁷ Furthermore, on the basis of the assumption that about one-half of the mercury in coal is released via stack gases to the atmosphere during combustion,³ it is estimated that the annual release of mercury to the environment as a result of electrical power generation in the United States is between 25 and 50 tons. A more detailed estimate from the Electric Power Research Institute of 39 tons/year is said to represent approximately 16% of the total Hg emissions from human activities in the United States.⁸ Other sources such as municipal solid waste (MSW) incineration and smelting of heavy-metal (Zn, Pb, Cu, etc.) ores may be more significant.^{3,8}

Although some uncertainty remains as to the significance of the contribution of coal combustion to the overall global mercury cycle, it is one source of anthropogenic mercury emissions for which controls might be effectively implemented. In recent years, there has been much research devoted to developing sorbents that remove mercury from coal and MSW combustion flue gases at relatively low temperatures (<250 °C). Among the most promising sorbents for this purpose are activated carbons, which are reported to capture mercury by a physical adsorption process, unless activated by elements such as iodine, sulfur, or chlorine, which promote chemisorption of mercury.³ A wide variety of other sorbent materials have been⁹ and are being investigated.

As discussed below, the literature on speciation and reaction mechanisms in mercury capture by sorbents at low temperatures appears contradictory and confusing. However, much of the confusion can be attributed to differences in experimental frameworks, which, because of the ultralow concentrations of mercury and the lack of establishment of chemical equilibria, make it impossible to compare and contrast different studies with much certainty or validity. However, even the basic question of what *is* the gas-phase mercury speciation in flue gas, let alone what are the basic factors controlling mercury speciation, cannot be readily answered. Further, recent studies are contradictory regarding whether the mercury speciation on the sorbent reflects the gas-phase mercury speciation. Work summarized by Senior et al.¹⁰ suggested that the speciation of mercury in the vapor phase is important in determining its capture mechanism on activated carbon. Their evidence suggests that elemental mercury is captured by chemisorption, whereas oxidized mercury (HgCl₂) is captured by physisorption. However, in apparent contradiction, earlier work by Chang¹¹ showed that mer-

cury sorption by activated carbon in a pilot-scale baghouse showed no dependence on gas-phase mercury speciation. In a study by Young et al.,¹² it was shown that there were differences in mercury removal efficiencies among different coals that were attributed to possible differences in mercury speciation in the coal. It was also noted by the same authors¹² and by others^{13,14} that the capture efficiency of oxidized mercury by activated carbon was highly temperature dependent. Work by Gullett et al.^{13,14} indicates that physisorption is more prevalent than chemisorption at low temperatures. Further, work by Felsvang et al.¹⁵ implies that the chlorine abundance in the coal controls the mercury speciation in the combustion gas.

From the above brief review, it is apparent that the reaction mechanisms involved in mercury capture are complex. It would appear that the gas-phase speciation of mercury and other elements such as chlorine and sulfur, the presence of activating species and active sites on the carbon, and the temperature and other conditions of sorption may all play a significant role in determining the rate and mechanism of mercury sorption. One technique that is capable of providing detailed speciation information about the elements of interest is X-ray absorption fine structure (XAFS) spectroscopy. The XAFS technique is well-suited to obtaining information on the local structure and bonding of elements in noncrystalline materials, such as activated carbons. In this paper, we present some observations and conclusions made with this technique on mercury and other elements in various activated carbons that have been used for mercury sorption in a simulated combustion flue-gas environment.

Experimental Section

(i) Mercury Sorption Experiments. Three different activated carbons were used in the mercury sorption experiments performed at the University of North Dakota Energy and Environmental Research Center (EERC): a lignite-derived activated carbon (LAC), an iodine-activated carbon (IAC), and a sulfur-activated carbon (SAC). Aliquots of these carbons were used to sorb mercury from a simulated combustion flue gas in a bench-scale reactor. In a typical experiment, about 400 mg of sorbent was held in the simulated flue gas at a temperature between 380 (225 °F) and 435 K (325 °F) for a period of up to 16 h. The base line flue gas consisted of a synthetic mixture of 6% O₂, 12% CO₂, 1600 ppm SO₂, 50 ppm HCl, 8% H₂O, and the balance N₂. Elemental mercury was added to the base line flue gas at a concentration of 60 μg/m³, although some experiments were run with addition of HgCl₂ at 12 μg/m³. Three different sets of experiments were performed: the first set consisted of a comparison of the three sorbents before and after exposure to the simulated flue gas containing elemental mercury; the second set consisted of the three sorbents exposed to a simulated flue gas containing mercuric chloride (HgCl₂); and the third set consisted of the

(7) 1980 *Keystone Coal Industry Manual*; Richardson, C. V., Nielsen, G. F., Eds.; McGraw-Hill: New York, 1980.

(8) EPRI, *Electric Utility Trace Substances Synthesis Report*; Report TR-104614-V3; Electric Power Research Institute: Palo Alto, CA, 1995; Vol. 3.

(9) Hyatt, D. E.; Schlagger, R. J.; Stewart, R. M.; Sagan, F. J. In *Proceedings, Second International Conference on Managing Hazardous Air Pollutants*; Report TR-104295; Electric Power Research Institute: Palo Alto, CA, 1994; pp VI.21–VI.37.

(10) Senior, C. L.; Morency, J. R.; Huffman, G. P.; Huggins, F. E.; Shah, N.; Peterson, T.; Shadman, F.; Wu B. In *Proceedings, Fourth International Conference on Managing Hazardous Air Pollutants*; Electric Power Research Institute: Palo Alto, CA, in press.

(11) Chang, R.; Bustard, C. J.; Schott, G.; Hunt, T.; Noble, H.; Cooper, J. In *Proceedings, Second International Conference on Managing Hazardous Air Pollutants*; Report TR-104295; Electric Power Research Institute: Palo Alto, CA, 1994; pp VI.41–VI.57.

(12) Young, B. C.; Miller, S. J.; Laudal, D. as quoted in ref 3; In *Proceedings, Eleventh International Pittsburgh Coal Conference*, 1994; Vol. 1, pp 575–580.

(13) Josewicz, W.; Krishnan, S. V.; Gullett, B. K. In *Proceedings, Second International Conference on Managing Hazardous Air Pollutants*; Report TR-104295; Electric Power Research Institute: Palo Alto, CA, 1994; pp VII.85–VII.99.

(14) Krishnan, S. V.; Gullett, B. K.; Josewicz, W. *Environ. Sci. Technol.* **1994**, *28*, 1506–1512.

(15) Felsvang, K.; Gleiser, R.; Juip, G.; Nielsen, K. K. In *Proceedings, Second International Conference on Managing Hazardous Air Pollutants*; Report TR-104295; Electric Power Research Institute: Palo Alto, CA, 1994; pp VI.1–VI.17.

Table 1. Experimental Details for Sorption Experiments

sample	filter temp (° F)	Hg species	sorbent mass (mg)	flue gas Hg conc ($\mu\text{g}/\text{m}^3$)	gas flow rate (m^3/h)	length test (h)	comments
Set 1: Before and After Flue Gas Exposure							
IAC-1	225	Hg	300	60	0.85	3.37	unreacted
IAC-2							
LAC-1	275	Hg	400	60	0.85	NA	
LAC-2	325	Hg	500	60	0.85	NA	unreacted
LAC-3							
SAC-1	225	Hg	300	60	0.85	12.42	
SAC-2							unreacted
Set 2: Exposure to HgCl_2 in Flue Gas							
IAC-400	225	HgCl_2	400	12	0.85	12.17	
LAC-400	225	HgCl_2	400	12	0.85	16.15	
SAC-400	225	HgCl_2	400	12	0.85	7.2	
Set 3: Exposure to Variations in Flue Gas							
LAC-5	225	Hg	400	60	0.85	4.0	10% O_2 , balance N_2
LAC-6	225	Hg	400	60	0.85	4.0	8% H_2O , 10% O_2 , N_2
LAC-7	225	Hg	400	60	0.85	4.0	base line – HCl
LAC-8	225	Hg	400	60	0.85	4.0	base line – SO_2

LAC sorbent exposed to different formulations of the flue gas containing elemental mercury under otherwise identical conditions. Details of specific experiments are summarized in Table 1.

(ii) XAFS Experiments. The forms of mercury and other elements present in the activated carbons before and after the sorption experiments were investigated using XAFS spectroscopy performed at either the Stanford Synchrotron Radiation Laboratory (SSRL), Palo Alto, CA, or the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory, NY. At both synchrotrons, a 13-element germanium detector,^{16,17} gated electronically to record the L-edge fluorescence from mercury, was used to record the mercury L_{III} XAFS spectra. A 6 μm gallium filter was also employed to maximize the signal/noise ratio. The XAFS spectra of other elements (S, Cl, Ca, I) were recorded at NSLS using a conventional Lytle fluorescence detector.¹⁸ Zero-points of energy for the XAFS spectra of the different elements are defined as follows: sulfur K-edge—white line peak in elemental sulfur at 2472 eV; chlorine K-edge—major derivative peak in NaCl at 2825 eV; calcium K-edge—major derivative peak in CaCO_3 at 4038 eV; iodine L_{III} edge—major derivative peak in elemental iodine (I_2) at 4557 eV; and mercury L_{III} edge—major derivative peak in elemental mercury at 12 284 eV. Data reduction followed well-established procedures:^{19,20} first, the XAFS spectrum was divided into X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) spectral regions, and each of these regions was then examined separately. Whereas the XANES spectrum (or its first derivative) was used without further modification to identify elemental occurrences, the EXAFS region was used to develop a “radial structure function” (RSF). The step-height, determined from the XAFS spectrum as the difference in background absorption above and below the edge, was used as a semiquantitative measure of the relative concentration of the elements in different sets of samples (Table 2).

Table 2. Relative Step-Heights Determined from XAFS Spectra^a

sample	S	Cl	Ca	I	Hg
IAC-1	20	0		0.1	1
IAC-2	1	1		1	0
LAC-1	15	60	6.5	0	2.1
LAC-2	18	42	6.0	0	1.5
LAC-3	7	1		0	0
SAC-1	60	3	0.9	0	2.8
SAC-2	65	0	1	0	0
IAC-400					1.5
LAC-400					1.7
SAC-400					1
LAC-5	1	1			1.6
LAC-6	1	0.3			1
LAC-7	2.6	0.3			2.0
LAC-8	0.7	100			6.7

^a Blank field indicates no determination made. 0 indicates no significant edge detected for that element.

Results and Discussion

(a) Sulfur. Sulfur XAFS experiments were carried out on the first and third suites of activated carbons (Table 2). Except for sample IAC-2, the sulfur XAFS spectra were quite strong and different forms of sulfur were readily apparent in the XANES spectra of different samples (Figure 1). Whereas the two SAC samples contained predominantly elemental sulfur (indicated by the major peak at 0 eV), the other samples (IAC-1, LAC) were predominantly sulfate sulfur (indicated by the major peak at 10 eV). The LAC samples also contained a minor amount (<20%) of elemental sulfur. The increases in step-height noted between IAC-1 and IAC-2 and between LAC-1, LAC-2, and LAC-3 suggest that the IAC and LAC carbons incorporate sulfate species from the SO_2 added to the flue gas. In the case of sample IAC-1, the broadness and shape of the sulfate absorption peak are indicative of a *bisulfate* species, whereas the narrowness and shape of the sulfate peak for the LAC samples are consistent with a sulfate species.

For the two SAC samples, however, there is little change in the sulfur concentration and, moreover, the dominant sulfur form in both samples is elemental. In the case of this carbon, relatively little SO_2 appears to have been adsorbed from the SFG compared to the amount of sulfur initially present. However, the most obvious difference between the SAC-1 and SAC-2 sulfur

(16) Cramer, S. P.; Tench, O.; Yocum, N.; George, G. N. *Nucl. Instrum. Methods* **1988**, *A266*, 586–591.

(17) Huggins, F. E.; Huffman, G. P. *Int. J. Coal Geol.* **1996**, *32*, 31–53.

(18) Lytle, F. W.; Greeger, R. B.; Sandstrom, D. R.; Marques, E. C.; Wong, J.; Spiro, C. L.; Huffman, G. P.; Huggins, F. E. *Nucl. Instrum. Methods* **1984**, *226*, 542–548.

(19) Lee, P. A.; Citrin, P. H.; Eisenberger, P. A.; Kincaid, B. M. *Rev. Mod. Phys.* **1981**, *53*, 769–808.

(20) Brown, G. E., Jr.; Calas, G.; Waychunas, G. A.; Petiau, J. In *Spectroscopic Methods in Mineralogy and Geology*; Hawthorne, F. C., Ed.; Reviews in Mineralogy 18; Mineralogical Society of America, Washington, DC, 1988; Chapter 11, pp 431–512.

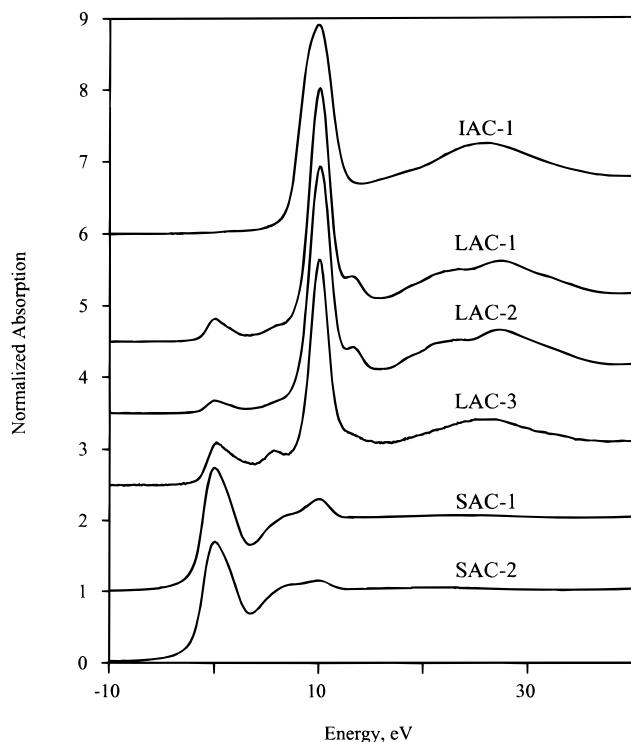


Figure 1. Sulfur K-edge XANES spectra of six activated carbon samples. Samples IAC-1, LAC-1, LAC-2, and SAC-1 were exposed to a synthetic flue gas (SFG) containing SO_2 , HCl, and Hg^0 .

XANES spectra (Figure 1) does occur in the vicinity of the sulfate peak, indicating that this carbon may also sorb some sulfur in the form of a sulfate.

For the suite of four LAC samples (LAC-5–LAC-8) exposed to different formulations of the synthesis gas, the sulfur XANES spectra are very similar to those shown for the LAC samples in Figure 1. Sulfate forms dominated the spectrum, with a minor (up to 25%) contribution from elemental sulfur. As indicated in Table 2, there was some variation in the XAFS step-height: as expected, LAC-7, the sample exposed to the synthetic flue gas containing SO_2 had the biggest step-height. Furthermore, the same sample had the highest sulfate/elemental sulfur ratio, indicating that the SO_2 in the SFG ends up attached to the activated carbon in the form of a sulfate.

These observations on sulfur suggest quite strongly that H_2SO_4 is a significant component in the synthetic flue gas at temperatures as low as 200–350 °F. The reaction



is indicated. The sulfuric acid species then interacts with the activated carbon, forming either a bisulfate species (IAC) or a sulfate species (LAC), most likely depending on the concentration of suitable cationic species that are present on the carbon. The alternative possibility that the sorbed sulfur species on the carbon is SO_2 , which then reacts with gas-phase O_2 and surface cationic species on the carbon to form the sulfate species, would appear to be less plausible, especially in view of the fact that the sulfur XANES spectra indicate no evidence for the S(IV) oxidation state.

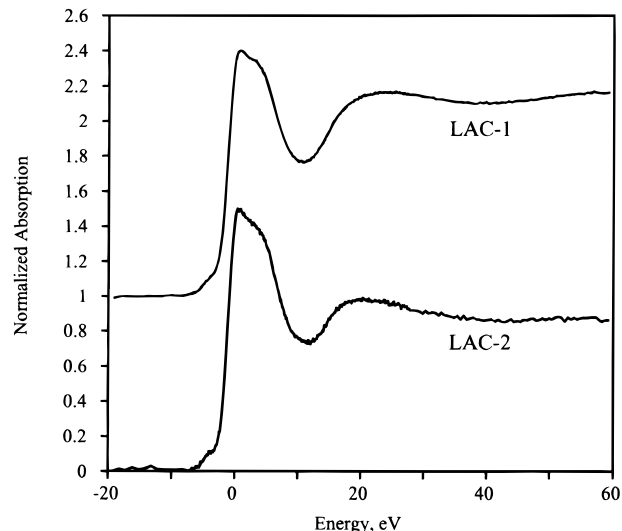


Figure 2. Chlorine K-edge XANES spectra of LAC activated carbon samples exposed to SFG.

(b) Chlorine. Chlorine XAFS experiments have also been performed only on sample sets 1 and 3. For the LAC samples (LAC-1, LAC-2, LAC-8) exposed to HCl in the flue gas, a significant increase (approximately 50–100 times) in the chlorine concentration was indicated by the step-height data (Table 2) compared to the sample (LAC-3) that was not exposed to the flue gas or to the samples (LAC-5, -6, -7) for which HCl was absent from the flue gas. These data indicate that the LAC carbon readily sorbs a form of chlorine present in the synthetic flue gas. The chlorine XANES spectra are shown in Figure 2 and are consistent with the capture of chlorine on the LAC carbons as HCl and not as Cl_2 .²¹ The other two carbons, IAC and SAC, showed no such enrichment in chlorine concentration. The SAC sample showed a small increase in chlorine content, whereas the IAC sample actually indicated a loss of chlorine upon exposure to the simulated flue gas.

These results indicate that the acidic species, HCl, is efficiently sorbed from the gas phase onto the LAC activated carbon but that the SAC and IAC carbons are much less efficient at sorbing HCl. As with sulfur, a strong acid species is formed on the carbon by interaction of the LAC carbon with the synthetic flue gas. However, whereas the LAC carbon has an affinity to sorb both acidic species, the IAC carbon appears to have only a strong affinity for sorption of H_2SO_4 and little or none for HCl.

(c) Iodine. Iodine XAFS experiments were performed on all seven samples in set 1, but as expected, only the two IAC samples gave positive indications of iodine. The iodine L_{III} XANES spectra for the two IAC samples are shown in Figure 3; they can be compared with the spectra shown in Figure 4 for various iodine standards. The spectra for the activated carbons appear closest to elemental iodine, although the match is by no means exact. Whether the differences reflect a highly dispersed state for elemental iodine in the activated carbons compared to bulk I_2 or some other iodine form altogether remains to be demonstrated. The step-height data (Table 2) suggest that the iodine content of the carbon after exposure to the flue gas is

(21) Huggins, F. E.; Huffman, G. P. *Fuel* 1995, 74, 556–569.

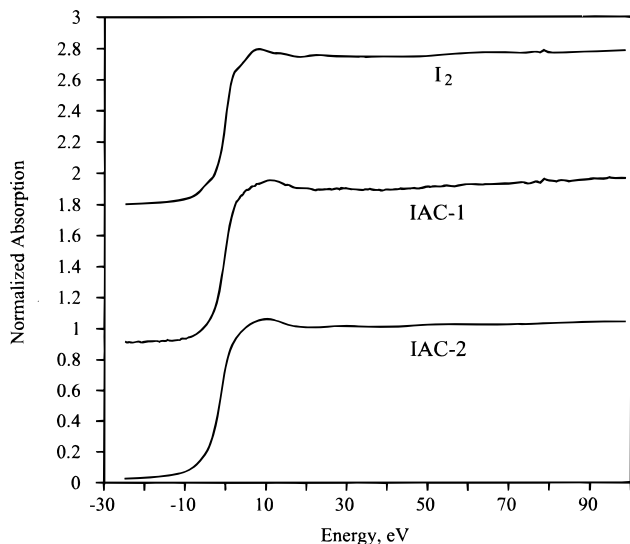


Figure 3. Iodine L_{III}-edge XANES spectra of IAC activated carbon samples and elemental iodine (I₂).

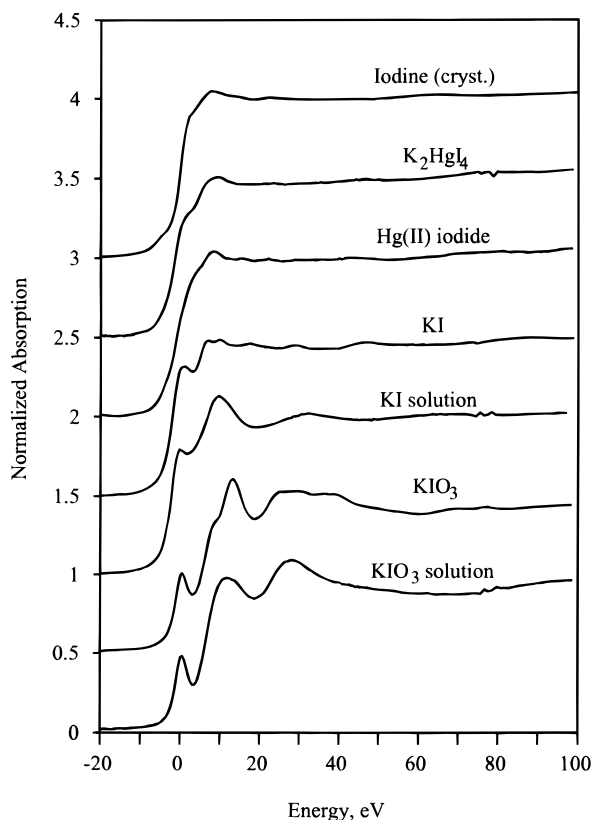


Figure 4. Iodine L_{III}-edge XANES spectra of various iodine standards.

much less than it was before, which would appear to indicate that significant volatilization of iodine from the carbon has occurred during exposure to the flue gas or possibly that reactive components in the flue gas have been exchanged for the iodine. In this regard, it should be recalled that there was an approximate 20-fold increase in sulfur concentration for the IAC sample (IAC-1) exposed to the flue gas relative to the unexposed sample (IAC-2). Hence, these observations raise the possibility that a bisulfate species [HSO₄⁻], derived from sulfur species in the gas phase, may have been exchanged for the iodine species during the exposure of the IAC carbon to the flue gas.

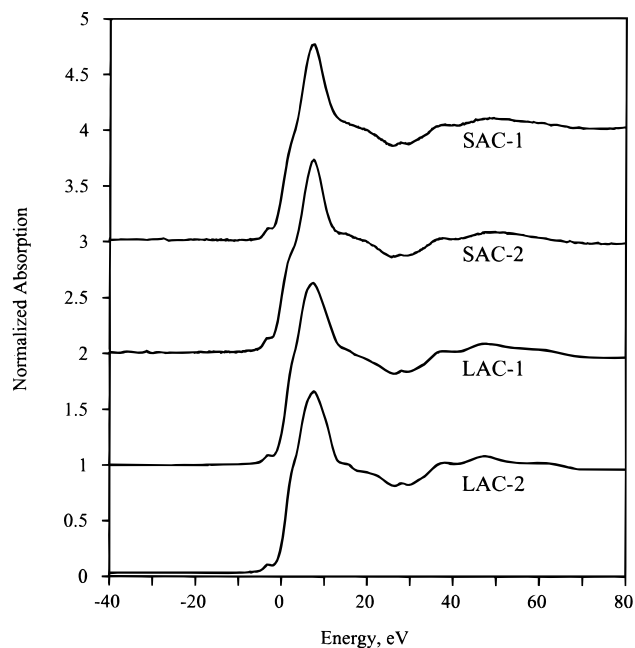


Figure 5. Calcium K-edge XANES spectra of four activated carbon samples. All samples except SAC-2 were exposed to a SFG.

(d) Calcium. The calcium XAFS spectra of some of the carbons were examined because calcium is a major constituent of lignites and also a reactive species for acidic gases such as HCl or SO₂. Calcium XAFS experiments were performed on the two SAC samples and on the two LAC samples exposed to the flue gas. The step-height data for calcium (Table 2) indicate little or no difference in concentration for calcium between the two SAC samples, suggesting that there is no net loss or gain of calcium during the exposure to the flue gas. The spectra (Figure 5) are distinct for each pair of samples. For the LAC samples, the calcium XANES spectra appear similar to that reported for calcium sulfate (CaSO₄);²² however, the calcium form that gives rise to the spectra for the SAC samples is not so readily identified.

(e) Mercury. The mercury XANES spectra of the four carbon samples in the first sample set that were exposed to the simulated flue gas are shown in Figure 6. As with all mercury XANES spectra, the fine structure is rather subtle and the first derivative spectrum has been used to accentuate differences among the spectra. As can be seen from the figure, the fine structure, consisting principally of two inflection points, becomes more pronounced in the order IAC-1 < LAC-1, LAC-2 < SAC-1 and is accompanied by an increased separation of the two peaks in the derivative spectra. On the basis of analysis of a suite of mercury standards²³ summarized in Table 3, it would appear that the separation of the peaks in the first derivative XANES spectra is highest for ionic mercury compounds and least

(22) Huffman, G. P.; Huggins, F. E.; Levasseur, A. A.; Durant, J. F.; Lytle, F. W.; Greeger, R. B.; Mehta, A. *Fuel* **1989**, *68*, 238–242.

(23) Huggins, F. E.; Huffman, G. P.; Yap, N. Unpublished data compilation. Also see: Senior, C. L.; Panagiotou, T.; Huggins, F.; Huffman, G. P.; Yap, N.; Wendt, J. O. L.; Seames, W.; Ames, M. R.; Olmez, I.; Zeng, T.; Sarofim, A. F.; Kolker, A.; Finkelman, R.; Helble, J. J. *Toxic Substances from Coal Combustion—A Comprehensive Assessment*, Quarterly Report No. 7; U.S. Department of Energy Contract No. DE-AC-95PC95101, July 1998.

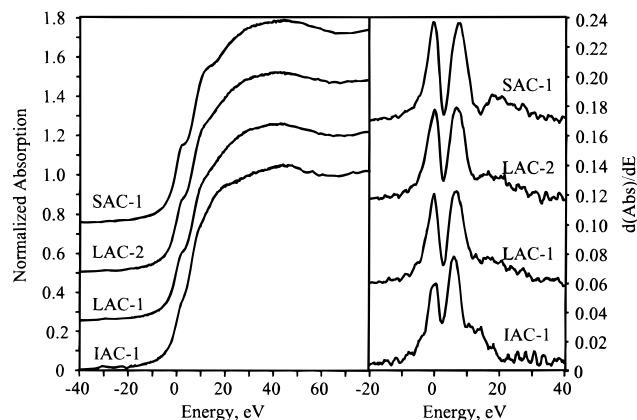


Figure 6. Mercury L_{III} -edge XANES spectra of four activated carbon samples exposed to SFG.

Table 3. Summary of Hg XAFS Data (Derivative XANES Peak Separations and Phase-Shift Uncorrected RSF Peak Positions) for Various Mercury Standards^a

mercury standard	deriv. XANES peak separation (eV)	RSF peak position (phase uncorr.) (Å)
HgO (yellow)	13.3	
HgO (red)	13.3	1.72
Hg acetate	10.6	1.68
HgSO ₄	9.6	
Hg ₂ SO ₄	9.5	
HgCl ₂	8.4	2.02
Hg ₂ Cl ₂	8.4	
HgS (metacinnabar)	7.7	2.12
HgS (cinnabar)	7.5	2.05
CH ₃ HgI	6.9	2.49
diphenylmercury	6.8	
HgI ₂	6.5	2.60
K ₂ HgI ₄	4.6	2.52
Hg (liquid)	0.0	

^a Errors: ± 0.2 eV for XANES peak separation; ± 0.03 Å for RSF peak position.

Table 4. Summary of Hg XAFS Data (Derivative XANES Peak Separations and Phase-Shift Uncorrected RSF Peak Positions) for Activated Carbon Samples^a

activated carbon	deriv. XANES peak separation (eV)	RSF peak position (phase uncorr.) (Å)
SAC-1	7.8	1.94
LAC-1	7.3	1.91
LAC-2	7.0	
IAC-1	6.1	2.57 (1.97)
SAC-400	8.0	1.99
LAC-400	8.0	1.96
IAC-400	5.1	2.57 (1.87)
LAC-5	7.6	1.96
LAC-6	7.2	
LAC-7	8.3	1.93
LAC-8	8.4	1.94

^a Errors: ± 0.4 eV for XANES peak separation; ± 0.05 Å for RSF peak position.

for covalent and metallic mercury compounds. Qualitatively similar trends have been reported for mercury compounds by other researchers, who have indicated that other factors may also influence such trends.²⁴ However, using the data in Table 3 as a scale, the observed values for the peak separation in the derivative XANES spectra of the activated carbons (Table 4) are consistent with Hg–S or possibly Hg–Cl bonding in the LAC-1, LAC-2, and SAC-1 carbons and Hg–I bonding in the IAC-1 carbon.

(24) Åkesson, R.; Persson, I.; Sandström, M.; Wahlgren, U. *Inorg. Chem.* **1994**, *33*, 3715–3723.

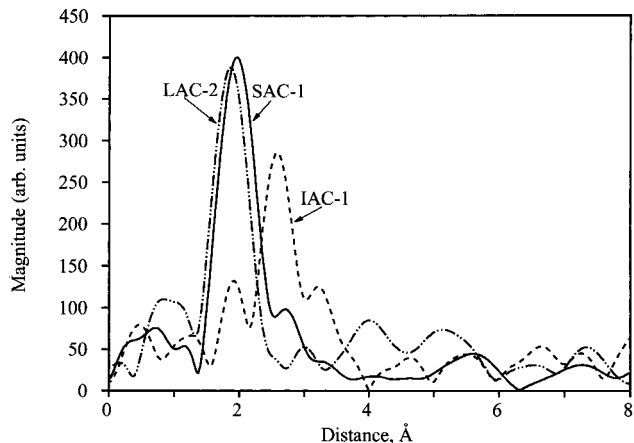


Figure 7. Radial structure functions derived from EXAFS spectra for mercury in LAC-2, SAC-1, and IAC-1 activated carbons.

Additional evidence about the structures of the Hg sorption sites on the activated carbons comes from analysis of the EXAFS regions of the XAFS spectra. The radial structure functions (RSFs) shown in Figure 7 and the data on RSF peak positions listed in Table 4 indicate a significantly different local structure for Hg in the iodine-impregnated carbon. In particular, the RSF for IAC-1 indicates that the Hg–X bond in this carbon is much longer than those for Hg in SAC-1 and LAC-1,2 carbons; such a bond distance is consistent with a Hg²⁺–I bond, as found in HgI₂ and other Hg–I compounds (Table 3). Although perhaps a little shorter, the Hg–X bond distances indicated in the RSFs for the LAC-1, and -2 and SAC-1 carbons appear consistent with Hg²⁺–Cl, as in HgCl₂, and/or Hg²⁺–S, as in HgS (cinnabar). However, the RSF distances are similar enough for both the standards and the activated carbons so that such values, by themselves, cannot be used justifiably to discriminate between Hg–S and Hg–Cl speciation. The Hg–S bond distance in HgS (cinnabar) is about 2.36 Å, the Hg–Cl bond distance in HgCl₂ is about 2.25 Å, and the bond distance for Hg–I in HgI₂ is about 2.78 Å. Wright et al.²⁵ and Jiang et al.²⁶ have reported similar XAFS structure and comparable Hg–S distances derived from RSFs for predominantly Hg–S species in mercury-bearing proteins²⁵ and metallothioneins²⁶ to those seen for the activated carbons.

Similar mercury XANES and RSF spectra to those shown in Figures 6 and 7 were obtained from the second set of three samples (IAC-400, SAC-400, LAC-400) that were exposed to the flue gas containing HgCl₂. However, as indicated in Table 4, the separation of the two peaks in the derivative spectrum was significantly greater for the LAC sample exposed to HgCl₂ than for the LAC samples exposed to Hg⁰ and closer to values observed for mercury chlorides (Table 3). The close similarity of the spectra of the SAC-400 and IAC-400 samples to those obtained from the corresponding samples exposed to the flue gas containing Hg⁰ vapor implies either that the mercury species in the flue gas is little different regardless of whether elemental mercury or mercuric chloride is initially added to the flue

(25) Wright, J. G.; Tsang, H.-T.; Penner-Hahn, J. E.; O'Halloran, T. V. *J. Am. Chem. Soc.* **1990**, *112*, 2434–2435.

(26) Jiang, D. T.; Heald, S. M.; Sham, T. K.; Stillman, M. J. *J. Am. Chem. Soc.* **1994**, *116*, 11004–11013.

gas or that the products of the chemisorption reactions on the carbons are not determined to any great extent by the speciation of mercury in the gas phase but, rather, are determined by the active species on the carbons. The fact that these two activated carbons appear to give rise to their own unique Hg XANES spectrum, which is little affected by the form of mercury added to the SFG, is a strong indication that it is the site-activating agent on the carbon that controls the speciation of the sorbed mercury. Further, the peak separation for the IAC-400 carbon and the position of the major peak in its RSF (Table 4) clearly demonstrate that I^- anions surround the mercury atom in this particular carbon. Hence, the $HgCl_2$ added to the SFG must have decomposed to a Hg^0 species in the gas phase or reacted at the active site, releasing Cl, to form the Hg-I complex on the carbon. Thermodynamic considerations²⁷ would appear to imply that it is highly unlikely that the mercury speciation in the gas phase at such low temperatures would be completely equilibrated; hence, it appears more likely that the decomposition of the $HgCl_2$ occurs at the active site itself.

The situation for the LAC carbon is different. For this carbon, it would appear that the gas-phase speciation of mercury does make a difference. The sorbed mercury species under vapor-phase $HgCl_2$ appears to be most like a mercury chloride. However, under Hg^0 vapor, the XANES data suggest a different species is present. The derivative XANES peak separation values (Table 4) for the LAC carbons exposed to Hg^0 are significantly smaller and more like that observed for mercury sulfides and would indicate a different sorption mechanism altogether under Hg^0 . It is also worth noting that the $HgCl_2$ sorption experiments on the LAC carbons were carried out at a lower temperature than the Hg^0 sorption experiments. As noted before,¹²⁻¹⁴ temperature can have a great effect on the sorption behavior of mercury.

Except for differences in the mercury step-height (Table 2) or, equivalently, in the concentration of the mercury captured on the carbons, the XAFS spectral data (Table 4) for the LAC samples (LAC-5-LAC-8) exposed to different formulations of the flue gas were similar to those of other LAC samples investigated previously. However, there are also small but significant differences in the separations of the peaks in the Hg XANES derivative spectra, and the four samples exhibit a range in this parameter that was greater than that found for the previous LAC samples (LAC-1, LAC-2, LAC-400) discussed above. The samples subjected to Hg sorption under SO_2 and HCl have higher values, comparable with those for mercury chlorides but not mercury sulfates (Table 3). In these experiments, the duration, temperature, and other conditions were identical, except for the composition of the flue gas; hence, the differences in the mercury step-height must reflect the relative efficiency with which mercury is captured from the gas stream. On this basis, it would appear that moisture retards the sorption of mercury but that SO_2 (as H_2SO_4) and especially HCl enhance the sorption of elemental mercury. Exactly how this happens is not

clear, particularly with SO_2 , because there is no evidence of formation of a mercury sulfate. Whether such observations indicate that mercury does react with acidic species (HCl, H_2SO_4) in the gas phase or that the acidic species interact with the Hg sorption sites on the carbon remains to be demonstrated. Either alternative or both would facilitate the sorption of mercury on the carbon.

Conclusions

This work demonstrates that XAFS spectroscopy is a powerful technique for identifying elemental species on activated carbons and for examining reactions involved in the sorption of mercury from flue gases on such carbons. Although further work is needed to augment this investigation, a number of interesting conclusions appear to have been reached: (1) the sulfur and chlorine XAFS data suggest strongly that acidic components, H_2SO_4 and HCl, are the prevalent species that are sorbed on the surface of the activated carbons from the synthetic flue gas; (2) the mechanism involved in sorption of mercury appears to depend on the dopant element and/or method used to activate the carbon; (3) the LAC carbons are very efficient in extracting HCl from the flue gas, and both the IAC and LAC carbons and possibly the SAC carbons as well, appear to react with H_2SO_4 to form sulfate species; and (4) the mercury speciation in the gas phase appears to have little effect on the sorption mechanism for the SAC and IAC carbons but may be more important for the LAC carbons. It remains to be demonstrated whether the acidic species react with mercury in the gas phase or whether they interact solely with the carbon to facilitate the interaction between gas-phase mercury species and the carbon surface. Either type of interaction has the potential to affect the rate of sorption of mercury significantly, in agreement with observation.

These observations emphasize the complexity of mercury sorption. The following factors appear to be important in affecting either the mechanism or the rate of mercury sorption: the nature of the active sites on the carbons, the speciation of sulfur and chlorine in the gas phase, the gas-phase interaction of mercury with sulfur (H_2SO_4) or chlorine (HCl), temperature, etc. In this study, it would appear likely that a different mechanism is responsible for the mercury sorption by each different type of activated carbon. The chemisorption of Hg in the form of a Hg-I compound on the IAC carbon is clearly indicated by the Hg XAFS data. Although less clearly resolved, the XAFS results, supplemented by compositional data, appear to indicate the formation of Hg-Cl and Hg-S compounds (chemisorption) for sorption of Hg on the LAC and SAC carbons, respectively. However, the data do not eliminate the possibility of both mechanisms being operative, to different degrees, for these carbons, especially the LAC carbon. Also, it appears that the dominant sorption mechanism for the LAC samples may reflect the different gas-phase speciation (for S, Cl, as well as Hg), whereas those for the SAC and IAC samples are less dependent. A detailed systematic investigation of the peak difference in the derivative Hg XANES spectra could be quite revealing, and such work is now underway to define this parameter better with respect to the sorption behavior of mercury.

(27) Senior, C. L.; Morency, J. R.; Huffman, G. P.; Huggins, F. E.; Shah, N.; Peterson, T.; Shadman, F.; Wu, B. Paper 98-RA79B.04, AWMA 91st Meeting, San Diego, CA, June, 1998.

Acknowledgment. This work was supported by the U.S. Department of Energy through separate contracts to UND-EERC for preparation of the activated carbons and to PSI and UK for research on the "air-toxics" elements. Both contracts were also supplemented by the Electric Power Research Institute. We also acknowledge Tom Brown, U.S. DOE-FETC, in bringing these efforts

together. The U.S. DOE is also acknowledged for its support of the Synchrotron Radiation Laboratories, SSRL and NSLS, without which the XAFS experimentation could not have been carried out.

EF9801322