Impact of Sulfur Oxides on Mercury Capture by Activated Carbon

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Recent field tests of mercury removal with activated carbon injection (ACI) have revealed that mercury capture is limited in flue gases containing high concentrations of sulfur oxides (SO_x). In order to gain a more complete understanding of the impact of SO_x on ACI, mercury capture was tested under varying conditions of SO_2 and SO_3 concentrations using a packed bed reactor and simulated flue gas (SFG). The final mercury content of the activated carbons is independent of the SO_2 concentration in the SFG, but the presence of SO_3 inhibits mercury capture even at the lowest concentration tested (20 ppm). The mercury removal capacity decreases as the sulfur content of the used activated carbons increases from 1 to 10%. In one extreme case, an activated carbon with 10% sulfur, prepared by H_2SO_4 impregnation, shows almost no mercury capacity. The results suggest that mercury and sulfur oxides are in competition for the same binding sites on the carbon surface.

1. Introduction

Activated carbon injection (ACI) has been widely studied as an effective means for mercury capture from flue gas. Both unpromoted (e.g., Norit Darco Hg) (*1*, *2*) and halogen-promoted (e.g., Norit Darco Hg-LH) (*1*, *3*, *4*) activated carbons have been tested during full-scale field studies. Recent results indicate that brominated activated carbons are particularly effective and can capture 70−90% of the mercury from a sub-bituminous-derived flue gas at injection rates less than 2 lbs/MMacf (*5*). However, several studies also indicate that high concentrations of SO_x ($SO_x = SO_2+SO_3$) can interfere with the capture of mercury by activated carbon (*1*−*4*, *6*). For example, at Mississippi Power's Plant Daniel, increasing the SO_3 concentration in the flue gas from 0 to 6 ppm reduced native mercury capture by fly ash from 55% to 14% and reduced the effectiveness of ACI (Darco Hg at 10 lbs/MMacf) by 25−35% (*2*).

SO_x enters flue gas from one of three channels: (1) During combustion, coal-S is converted to SO_2; a small fraction of the sulfur is further oxidized to SO_3 (*7*). During combustion of high-sulfur coals, as much as 1−2% of the sulfur is converted to SO_3, leading to flue gas concentrations in the range of 10−40 ppm (*8*, *9*). High concentrations of SO_3 in flue gas have long been considered a nuisance because SO_3 can condense as sulfuric acid (H_2SO_4, the hydrated form of SO_3) and lead to increased corrosion and fouling as well as decreased efficiency (*9*). (2) SO_3 is sometimes added to flue gas upstream of an ESP as a conditioning agent and to improve ESP performance. SO_3 (and H_2SO_4) has a low vapor pressure and can condense on fly ash; this reduces the resistivity of the ash and allows it to be removed more efficiently by the ESP (*9*). (3) SO_2 can be oxidized to SO_3 by SCR (Selective Catalytic Reduction) catalysts installed for NO_x reduction (*7*). SCR catalysts typically contain vanadium oxides, which are known catalysts for the oxidation of SO_2 to SO_3 (*10*).

The inhibiting effect of SO_x on Hg capture by ACI is a particularly vexing problem for power plants burning high-sulfur bituminous coals; the flue gas generated from this fuel has high concentrations of both SO_2 (> 1000 ppm) and SO_3 (10−40 ppm). The poisoning effect upon activated carbons is also a concern for power plants injecting sulfur trioxide as a conditioning agent, with resulting flue gas SO_3 levels sometimes greater than 10 ppm.

In addition to removing mercury, activated carbon can also be used as a catalyst for the oxidation of SO_2 to sulfuric acid (*11*, *12*) and as an SO_2 sorbent (*13*−*15*). The oxygen source for SO_2 conversion to sulfuric acid can be either the flue gas or oxygen bound to the activated carbon surface (*12*). Both mercury and SO_x bind to Lewis base (electron-donating) sites on the activated carbon surface (*16*). Mercury is known to chemically adsorb to activated carbon (*16*); Huggins et al. showed that mercury exists on carbon surfaces as Hg^{2+} bound to a soft atom such as chlorine or carbon (*17*). SO_2 can form two different bonds with the carbon surface: a physical bond due to van der Waals forces with a heat of adsorption <50 kJ mol^{-1} or a chemical bond with a heat of adsorption >80 kJ mol^{-1} that is stable to temperatures above 200 °C (*13*, *18*). SO_2 and SO_3 compete with mercury for adsorption sites on activated carbon; this competition might inhibit mercury capture and limit the effectiveness of ACI. In fact, some activated carbon catalysts for converting SO_2 to H_2SO_4 are self-poisoned by SO_3 (*19*) or sulfate (*10*) buildup on the surface; a similar phenomenon might explain the inhibiting effect of SO_x on mercury capture. It has also been postulated that sulfuric acid that forms on the surface of activated carbon does not desorb and therefore inhibits mercury adsorption (*16*). Furthermore, activated carbon is a catalyst for the formation of sulfuryl chloride; hence sulfur dioxide may deplete the surface chlorine with a concomitant reduction in mercury capture (*20*).

In this study we investigate the effect of SO_x concentration on the performance of several activated carbons. We also present surface analyses of the tested activated carbons and identify the form of the sulfur on the surface of the carbon. Experiments were conducted with both unpromoted and halogenated activated carbons as well as an unpromoted activated carbon treated with sulfuric acid. The sulfuric acid treated carbon was used to test the hypothesis that sulfuric acid blocks adsorption of mercury on the carbon surface. Potential mechanisms explaining the inhibiting effects of SO_x are presented.

2. Experimental Procedures

Sorbent samples are exposed to mercury in a bench-scale packed bed reactor that is a larger version of an apparatus described previously (*21*, *22*). The assembly consists of a quartz tube reactor, 22 mm i.d. and 61 cm long, contained in a tube furnace. A 200 mg sorbent bed is placed in the reactor and is supported by approximately 1 g of glass wool. An additional 1 g plug of glass wool is placed above the sorbent bed. The sorbent is exposed to a simulated flue gas (SFG) containing N_2, O_2, CO_2, H_2O, HCl, NO, SO_2, SO_3, and Hg for 6 h (360 min). In this study, we will use 'mercury content'

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TABLE 1. Typical Simulated Flue Gas Concentrations for the Experiments Conducted in This Study

species	concentration
O_2 (%)	5.25
SO_2 (ppm)	0, 500, 1000, 1500, or 1870
NO (ppm)	500
CO_2 (%)	12.5
HCl (ppm)	50
H_2O (%)	0 or 1.0−1.5
SO_3 (ppm)	0, 20, 50, or 100
Hg (μg Nm^{-3})	9.3

to describe the amount of mercury (μg Hg/g sorbent) captured during the 6 h exposure.

Table 1 details the typical concentrations of the simulated flue gas components used in this study. Under typical experimental conditions, the flow rate of the simulated flue gas is 8 slpm, and the sorbent bed is held at 149 °C. Mercury is provided by a certified Dynacal permeation tube that is held at 90 °C in a water bath. The mercury concentration in the SFG is within the range typically observed in power plant flue gas. A total of 26.8 μg of mercury contacts the activated carbon bed during the 6 h experiment; the maximum mercury content for a 200 mg sample is therefore 134 $\mu g\ g^{-1}$. N_2 and O_2 are provided by the plant air and nitrogen supplies; each stream passes through a desiccant trap and a carbon trap prior to entering the process. CO_2, SO_2, HCl (2% in N_2), and NO (5% in N_2) are supplied from certified gas cylinders. Water vapor is added to the SFG by bubbling N_2 through a water saturator held at 52 °C.

SO_3 is supplied to the system by passing N_2 through a cylindrical saturator containing SO_3. The saturator is constructed of stainless steel and is cooled by a water/propylene glycol mixture maintained at subambient temperature (−15 to 6.4 °C) by a chiller/circulator. The SO_3 concentration in the SFG is calculated based on the vapor pressure of SO_3, the exterior temperature of the saturator, and the flow rate of the N_2 carrier gas. When calculating the vapor pressure, we assume that the SO_3 in the saturator exists as the γ phase. Given the uncertainties associated with the SO_3 saturator, specifically the exact value and the stability of the temperature inside of the saturator, we assume that our estimate of the SO_3 concentration in the SFG is accurate within ±20%.

For all experiments, the concentrations of Hg, CO_2, HCl, and NO are held constant at the values shown in Table 1. The H_2O concentration is varied between 0% ('dry') and 1.0−1.5% ('wet'). Real flue gas contains higher concentrations of H_2O than what is present in the SFG; we are limited by our ability to maintain H_2O as a vapor, particularly in the room-temperature exhaust ductwork, and therefore could not explore typical H_2O concentrations. Dry SFG is used because the addition of SO_3 significantly lowers the acid dew point and increases the likelihood of corrosion in the system; all experiments containing SO_3 use dry SFG. SO_3-free experiments are also conducted with dry SFG because previous results indicate that the mercury capacity of activated carbons is dependent upon the moisture content of the SFG (*23*). The concentrations of the two sulfur species, SO_2 and SO_3, are varied independently to investigate their impact on mercury capture.

Three different activated carbons were tested in this study: Norit Darco FGD, Norit Darco Hg-LH, and H_2SO_4-FGD. Both Darco FGD and Darco Hg-LH, a brominated activated carbon, were used as-received. H_2SO_4-FGD was prepared by adding 95% H_2SO_4 to Darco FGD to incipient wetness. The impregnated carbon was then heated to dryness in an oven at 110 °C.

The mercury ($\mu g\ g^{-1}$) and sulfur (%) contents of the activated carbon samples were determined by ICP-AES (Inductively Coupled Plasma−Atomic Emission Spectroscopy). The activated carbons were first digested by adding a 0.1 g sample to 10 mL of nitric acid and 2 mL of 30% H_2O_2. When the effervescence subsided, 5 mL of DI water was added, and the mixture was digested in a microwave at 230 °C for 30 min. These samples were then brought to volume with water and analyzed. All solutions were dark-particulate free; a few did have minute amounts of light precipitate present, but since no HF was used, aluminosilicate materials were not digested. In some cases, the undigested activated carbon was also analyzed using a DMA-80 Direct Mercury Analyzer. The ICP-AES and DMA-80 results agreed to within ±10%. Surface compositions of several samples of both fresh and Hg-exposed activated carbon were also analyzed using XPS (X-ray Photoelectron Spectroscopy). During the experiments, the concentrations of gas-phase species were monitored by an online mass spectrometer.

Table 2 details the experiments conducted in this study. The experiment name is derived from the activated carbon used ('F' for FGD, 'LH' for Hg-LH, and 'SA' for H_2SO_4-FGD), the SO_2 concentration (0, 500, 1000, 1500, or 1870 ppm), the SO_3 concentration (0, 20, 50, or 100 ppm), and the moisture content ('d' for dry and 'w' for wet). For example, in experiment LH-500-0-w, 200 mg of Hg-LH was exposed to a wet SFG containing 500 ppm SO_2 and no SO_3. Experiments were also conducted where the activated carbon sample was pre-exposed to SO_3 prior to mercury exposure. In experiment LH50-0-0-d, for example, the activated carbon sample was exposed to a mixture of 50 ppm SO_3 in N_2, O_2, and CO_2 (with HCl, SO_2, and NO turned off) for 1 h prior to adding mercury and the other trace species to the SFG. Table 2 also lists the mercury ($\mu g\ g^{-1}$) and sulfur (%) content of the exposed carbons as well as the mass fraction of the incident sulfur captured by the carbons. The mercury and sulfur contents of the unused activated carbons are included for reference.

All of the error bars plotted in this manuscript show the 1-σ level of precision, which is approximately ±25% for mercury content measurements and ±10% for sulfur content measurements. The large uncertainty in the mercury data arises from several sources. The uncertainty associated with the ICP-AES measurement is approximately ±10%. The mercury output from the permeation tube has an uncertainty of at least ±6%. The activated carbon samples are 200 mg of grab samples taken from a 5-lb bucket, which itself is taken from a much larger production batch of activated carbon. Thus, the possibility exists for using activated carbon samples that are not representative of the bulk material. When the activated carbon is placed into the packed bed, care is taken to produce a bed with uniform thickness. However, it is nearly impossible to produce a perfectly uniform bed. Several experiments were conducted with intentionally uneven packed beds; this resulted in significantly decreased mercury capture. Thus, we assume that the small, inherent variations in bed thickness can affect changes in the mercury content.

Results from full-scale field studies also indicate significant variability in mercury capture efficiency during ACI. Specifically, during long term injection tests, individual measurements of mercury capture efficiency (time scale of minutes − hours) can differ significantly from the long-term results (time scale of months) (*4*). When all of the potential sources of experimental uncertainty are considered, it is our opinion that the precision presented for the mercury capture data is appropriate for our experimental system and is consistent with previous work from this laboratory (*21*).

3. Results

3.1. SO_3-Free Experiments. During SO_3-free experiments, the SO_2 concentration was varied from 0 to 1870 ppm to investigate the effect of SO_2 on mercury capture. Figure 1

TABLE 2. Experiments Conducted in This Study

experiment	Hg content[a] ($\mu g\ g^{-1}$)	S content[a] (%)	fraction S captured[b] (%)	experiment	Hg content ($\mu g\ g^{-1}$)	S content (%)	fraction S captured (%)
F-1870-0-d	84.8	2.00	0.022	LH-0-20-d	12.2	3.00	5.2
F-1500-0-d	60.6	1.74	0.020	LH-0-50-d	6.13	7.04	6.0
F-1000-0-d	72.9	1.75	0.030	LH-0-100-d	4.59	8.56	3.7
F-500-0-d	81.0	1.54	0.038	LH50-0-0-d	9.26	2.36	8.8
F-0-0-d	71.3	1.28	N/A	LH50-0-50-d	4.70	5.69	4.0
F-1870-0-w	54.1	2.58	0.038	LH-1870-20-d	8.86	4.47	0.093
F-1500-0-w	45.3	2.45	0.042	LH-1870-50-d	7.55	5.19	0.11
F-500-0-w	39.3	2.82	0.16	LH-1870-100-d	4.17	8.50	0.19
F-0-0-w	54.8	1.19	N/A	LH50-1870-0-d	14.3	5.30	0.14
				LH50-1870-50-d	4.61	7.35	0.16
LH-1870-0-d	68.1	2.56	0.044				
LH-1500-0-d	42.7	2.25	0.044	F-0-20-d	16.5	1.83	1.7
LH-1000-0-d	50.0	2.04	0.058	F-0-50-d	20.0	2.11	0.95
LH-500-0-d	50.1	1.61	0.072	F-0-100-d	15.6	4.47	1.6
LH-0-0-d	58.4	0.69	N/A	F-1870-50-d	8.66	4.50	0.085
				F-1870-100-d	4.52	6.00	0.12
LH-1870-0-w	35.4	3.66	0.072				
LH-1500-0-w	33.2	3.34	0.080	SA-0-0-d	4.13	10.6	N/A
LH-1000-0-w	41.9	3.39	0.12				
LH-500-0-w	25.2	2.40	0.15	Raw FGD	3.04	0.92	N/A
LH-0-0-w	41.3	1.16	N/A	Raw Hg-LH	0.02	0.72	N/A

[a] The Hg and S contents were determined by ICP-AES. The maximum possible Hg content is 134 $\mu g\ g^{-1}$. [b] The mass fraction of sulfur captured by the carbons assumes that the initial sulfur contents for Darco FGD and Hg-LH are 1.13% and 0.86%, respectively. These values represent the arithmetic mean of the sulfur content for the virgin material and the final sulfur content for the experiments that used neither SO_2 nor SO_3. In the absence of SO_3 a small fraction of the incident sulfur, typically less than 0.1%, was captured by the activated carbons. The maximum fractional capture of sulfur occurred in experiments that used SO_3 but not SO_2. When SO_2 and SO_3 were both present, SO_3 was captured preferentially, and the fractional sulfur capture was lowered relative to the SO_3-only case by the large concentration of SO_2.

shows the mercury capture results for Darco FGD and Hg-LH. A statistically significant relationship between SO_2 concentration and mercury content is not apparent for either activated carbon under wet or dry conditions.

For both FGD and Hg-LH, the mercury content was ~50% higher in dry SFG than wet SFG. The decrease in mercury content in wet SFG is consistent with previous results presented by Yan et al. (*23*). Darco FGD captured approximately 40% more mercury than Hg-LH in both wet and dry SFG. This result contradicts results from several full-scale tests of ACI, where brominated carbons consistently outperform unpromoted activated carbons such as FGD (*3*, *5*). These results suggest that, with excellent gas−solid contact provided by a packed-bed reactor, unpromoted carbons display good capacity for mercury and bromine promotion does not increase capacity. This is in contrast to the situation found during in-flight capture of mercury within the ductwork of a power plant; in this situation gas−solid contact is poor.

In addition to capturing mercury, the activated carbons also captured SO_2. Figure 2 shows the sulfur captured as a function of SO_2 concentration in the SFG. Hg-LH typically captured more sulfur than FGD under similar (i.e., wet or dry) conditions, and more sulfur was captured in wet SFG than dry SFG.

XPS data indicated that the sulfur on the activated carbon surface was primarily sulfate. The sulfur present in a raw sample of Hg-LH was 87% sulfate, with the remainder present as elemental sulfur. Exposure of Hg-LH samples to SFG containing 500, 1000, and 1870 ppm of SO_2 resulted in the surface sulfur being at least 97% sulfate. The large fraction of sulfate is consistent with the role of activated carbon as a catalyst for the oxidation of SO_2 to sulfuric acid (*11*, *12*). The larger amount of sulfur captured in the wet SFG may result from enhanced production of sulfuric acid in the presence of water.

3.2. Experiments Containing SO_3. We explored two routes of SO_3 exposure for the activated carbon samples: varying the SO_3 concentration in the SFG from 20 to 100 ppm and pre-exposing the activated carbon to 50 ppm SO_3 for 1 h prior to mercury exposure. Table 2 shows the mercury and sulfur contents for activated carbons exposed to SO_3 and mercury. SO_3 exposure led to higher final sulfur contents than were observed in SO_3-free SFG. Adding 20 ppm SO_3 to dry SFG produced a final sulfur content of 3% for Darco Hg-LH; in contrast, the maximum sulfur content observed for Hg-LH in dry SO_3-free SFG was 2.5%. The higher sulfur content after exposure to SO_3 is expected; SO_3 has a significantly lower vapor pressure than SO_2 and should be captured more efficiently by sorbents such as activated carbon.

Adding SO_3 to the SFG significantly reduced the final mercury content of the activated carbon samples. The addition of 20 ppm SO_3 to the SFG reduced mercury capture by nearly 80%, and higher SO_3 concentrations led to further reductions in mercury capture. This observation is consistent with the effect of SO_3 on ACI observed during full-scale field tests (*2*). Recent results also indicate that very low concentrations of SO_3 (<2 ppm) adversely impact the performance of ACI for mercury control (*24*). The effect of SO_3 on mercury capture presented here may be exaggerated relative to ACI because of the excellent gas−solid contact provided by the packed bed reactor.

As with the SO_3-free experiments, the SO_2 concentration in the SFG does not have a strong effect on the final mercury content. For example, the final mercury content is nearly identical for experiments LH-0-100-d (no SO_2 and 100 ppm SO_3) and LH-1870-100-d (1870 ppm SO_2 and 100 ppm SO_3). It is evident from the data that SO_3 has a stronger inhibiting effect on mercury capture than SO_2; possible explanations for the effect of SO_3 on mercury capture by activated carbon are discussed in the next section.

4. Discussion

We consider two hypotheses to explain the inhibition of mercury capture by sulfur oxides: (1) depletion of surface chlorine through the formation of sulfuryl chloride (*20*) and (2) competitive adsorption between sulfur oxides, particularly SO_3 and Hg (*25*, *26*).

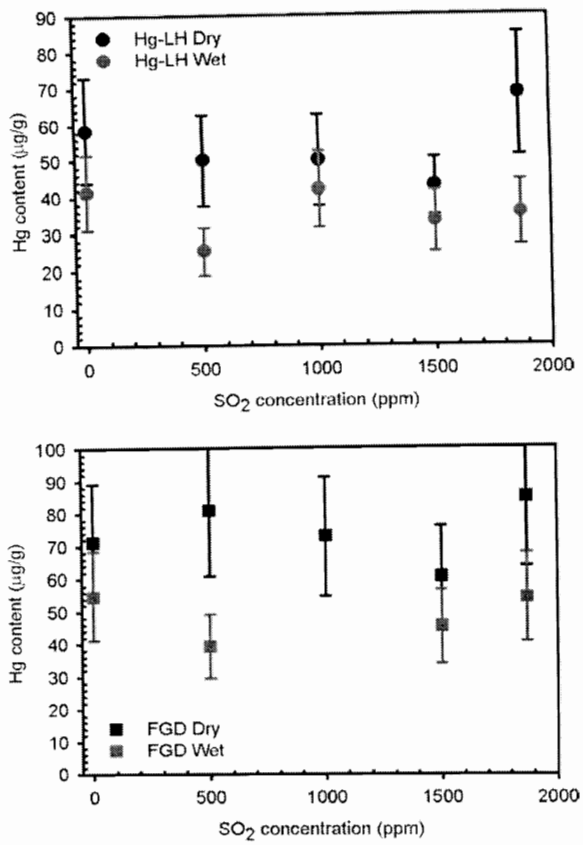

FIGURE 1. Mercury content ($\mu g\ g^{-1}$) as a function of SO_2 concentration for Darco FGD and Hg-LH under wet and dry SFG conditions. Error bars show the 1-σ level of confidence. Hg content is independent of the SO_2 concentration and reduced in the presence of water vapor.

The loss of surface chlorine via the formation of sulfuryl chloride could reduce mercury capture by altering the surface composition of the activated carbon. Halogenated (i.e., brominated or iodated) activated carbons are typically better mercury adsorbents than nonhalogenated activated carbons; (*16*) removing halogens from the surface could therefore negatively impact mercury capture. The presence of sulfuryl chloride or other flue gas halides, such as phosgene, in the SFG downstream of the packed bed would serve as a possible indication of mercury capture inhibition by this mechanism. Online mass spectrometer data show no presence of flue gas halides, but this does not rule out their formation. Flue gas halides are easily hydrolyzed and may be removed from the SFG via reaction with water prior to reaching the mass spectrometer (*27*).

Removal of surface halogens is unlikely to produce the profound drop in mercury capture efficiency observed during ACI testing. XPS analysis of both fresh and used Hg-LH shows no drop in surface chlorine or bromine concentrations due to exposure to SFG, and online mass spectrometer data do not indicate a change in SO_2 concentration across the packed bed. Furthermore, the inhibiting effect of sulfur oxides on mercury capture by ACI has been observed for both halogenated and nonhalogenated activated carbons (*1*). While sulfuryl chloride formation may be catalyzed in the packed bed, the reaction is slow at the temperature used here (149 °C) (*20*). Thus, the extent of reaction, and therefore the impact on mercury capture, is low.

Inhibition of mercury capture because of competitive adsorption could occur because activated carbon is a catalyst

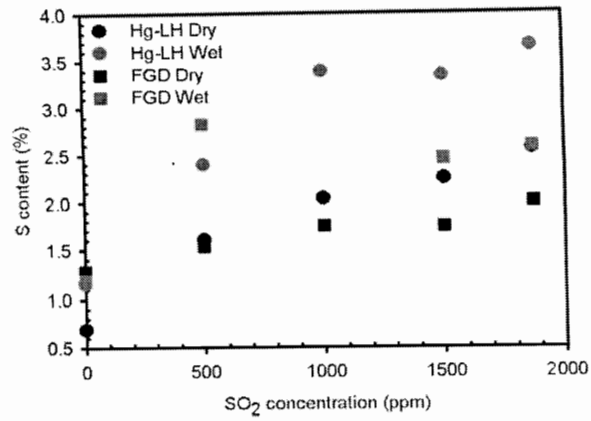

FIGURE 2. Sulfur content (%) as a function of SO_2 concentration for Darco FGD and Hg-LH under wet and dry SFG conditions. The mass fraction of the sulfur captured by the carbon is less than 0.2% in all cases.

for the oxidation of SO_2 to sulfuric acid or through adsorption of SO_3 (which can hydrolyze to sulfuric acid). SO_2 and SO_3 compete with mercury for the same adsorption sites, specifically Lewis base sites, on the carbon surface. In flue gas, adsorption of SO_2 or SO_3 could be favored over mercury adsorption both kinetically and thermodynamically. Mercury concentrations in flue gas are typically ~1 ppb; this is orders of magnitude smaller than typical concentrations of SO_2 and SO_3, both of which are present at ppm levels. This concentration difference means that many more SO_x molecules collide with the surface of the activated carbon, thereby enhancing the adsorption of sulfur oxides versus mercury. Fast capture of SO_2 or SO_3 could exhaust the sites available for mercury capture and thereby inhibit mercury adsorption.

The XPS results presented earlier indicate that the sulfur on the activated carbon surface is present almost exclusively as sulfate. Sulfuric acid has a low vapor pressure, approximately 1 Torr at 150 °C (*28*), and is therefore unlikely to desorb from the activated carbon surface. Surface S(VI) can form from the direct adsorption of SO_3 or from the oxidation of chemically bound SO_2. SO_2 can form a strong bond with the carbon surface, with a heat of adsorption >80 kJ mol^{-1} (*13, 18*). Miller et al. (*29*) observed that exposing mercury-laden activated carbon to SO_2, with NO_2 present as an electron sink for SO_2 oxidation, caused the mercury to desorb from the surface with a concomitant increase in surface S(VI) concentration (*30*). From this observation we can infer that the bond formed between S(VI) and the carbon surface is stronger than the bond formed between mercury and the surface. Thus, under conditions of either high SO_3 concentration or oxidizing conditions for converting SO_2 to sulfuric acid, mercury capture could be inhibited by competition with SO_3 adsorption and/or SO_2 oxidation.

According to the data presented in Figure 1, the SO_2 concentration in the SFG does not appear to impact mercury capture by the activated carbons tested here. However, this fact alone does not disprove the hypothesis that sulfur oxides outcompete mercury for adsorption sites on the carbon surface. If mercury competes with S(VI) for binding sites on the activated carbon surface, then the S(VI) concentration of the activated carbon, and not the SO_2 concentration in the SFG, is the important variable. We tested an extreme case of sulfur uptake with H_2SO_4-FGD, an activated carbon sample prepared by soaking FGD in 95% H_2SO_4. As shown in Table 2, H_2SO_4-FGD had a sulfur content of 10.6% and had a mercury content after exposure to SFG (4.13 $\mu g\ g^{-1}$) similar to the raw FGD (3.04 $\mu g\ g^{-1}$). This test suggested that high concentrations of surface-bound sulfur inhibit mercury capture, perhaps because of competition for binding sites.

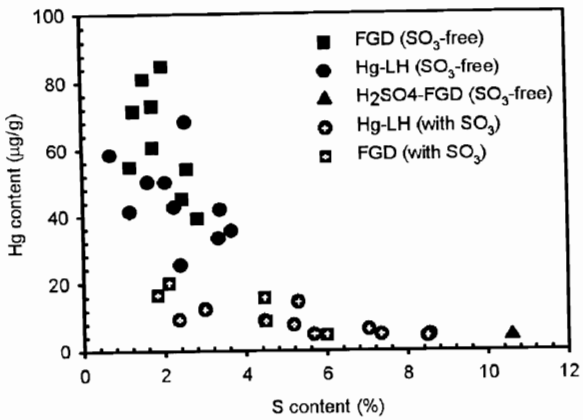

FIGURE 3. Mercury content ($\mu g\ g^{-1}$) as a function of sulfur content (%) for all of the experiments presented in this study. Mercury content decreases with increasing sulfur content, and almost no mercury is captured at the highest sulfur content (10.6%) tested here.

Figure 3 shows that, for all of the experiments presented here, the mercury content decreases as sulfur content increases. It should be noted that Figure 3 convolves the effects of sulfur content and water vapor concentration; as shown in Figure 1, the mercury content is reduced in wet flue gas even when no sulfur is present in the SFG. Regardless, the data shown in Figure 3 are strong evidence for the direct competition between mercury and sulfur for binding sites on the carbon surface.

The data in Figure 3 suggest that SO_3 has a stronger impact on mercury capture than SO_2. For example, at 3% S, approximately 40 $\mu g\ g^{-1}$ of Hg was captured in SO_3-free SFG, compared to ~10 $\mu g\ g^{-1}$ in SO_3-laden SFG. A possible explanation for the enhanced effect of SO_3 may be the form of sulfur present on the activated carbon surface. As noted previously, SO_2 can form two different bonds with the carbon surface: a physical bond due to van der Waals forces with a heat of adsorption <50 kJ mol^{-1} or a chemical bond with a heat of adsorption >80 kJ mol^{-1} (*13, 18*). XPS results indicate that >97% of the sulfur captured in SO_3-free SFG is sulfate, suggesting the stronger, chemical bond. However, the surface concentration of sulfur measured by XPS is significantly lower than the bulk sulfur content determined by digesting the activated carbon in solution; the latter quantity is shown in Table 2 and Figure 3. One possible explanation for the discrepancy in sulfur concentration may be that a significant portion of the sulfur captured in the SO_3-free SFG is physically bound; the physically bound sulfur would be measured by the solution method but could desorb from the activated carbon surface under the vacuum conditions used for XPS. We assume that the SO_3, which is already oxidized to S(VI), exists on the activated carbon surface exclusively in the chemically bound form.

Previous research has suggested that sulfate competes with mercury for binding sites on the activated carbon surface (*25, 26*). Currently, it is not clear whether physically bound sulfur intereferes with mercury capture by activated carbon, though it likely has a weaker effect than chemically bound sulfur, if there is any effect at all. Thus, the presence of physically bound sulfur from the SO_3-free SFG could explain the discrepancy between SO_3-free and SO_3-containing experiments in Figure 3. The current hypothesis is that all of the sulfur captured from the SO_3-laden SFG is chemically bound and therefore inhibits mercury capture, whereas a portion of the sulfur captured from SO_3-free SFG is physically bound and does not inhibit mercury capture.

It is important to note that both routes of exposing the activated carbon to SO_3, whether as a constituent of the SFG or pre-exposing the sorbent, lead to significant reductions in mercury capture. This result further indicates that mercury and SO_3 compete for the same adsorption sites on the activated carbon surface and suggests that SO_3 adsorption is favored both kinetically and thermodynamically to mercury adsorption. Adding SO_3 to the SFG, and placing it in direct competition with mercury for adsorption sites on the activated carbon surface, leads to reduced mercury capture. Similarly, the pre-exposure experiments as well as the experiment with the H_2SO_4 treated activated carbon show that mercury cannot dislodge sulfur species from the activated carbon surface.

The competition between SO_x, particularly SO_3, and mercury for binding sites on the surface of activated carbon will likely limit the effectiveness of ACI for mercury removal in any high-SO_x flue gas. Recent research has led to the development of chemical alterations, notably bromination, that enhances the mercury capture efficiency by increasing the reactivity of the activated carbon. However, as shown here and in previous studies (*1*), SO_3 impedes mercury capture by brominated carbons as well as unpromoted activated carbons. This occurs because bromination increases the reactivity of the mercury-accepting sites; thus bromination also makes the activated carbons more reactive toward sulfur oxides, as shown in Figure 2.

Potential options for overcoming the impact of SO_x on ACI include removing sulfur species prior to carbon injection, removing SO_x and mercury concurrently by injecting basic sorbents (i.e., hydrated lime) along with activated carbon (*24*), or in cases where SO_3 is used for flue gas conditioning, injecting the carbon upstream of the SO_3. Each of these approaches has advantages and disadvantages. Removing SO_x, specifically SO_3, prior to carbon injection should improve the efficiency of ACI. However, including flue gas desulfurization upstream of ACI poses potential logistical challenges and may increase the cost of an ACI retrofit. Injecting activated carbon upstream of SO_3 has been shown to improve mercury capture in plants using SO_3 flue gas conditioning (*4*), but the mercury capture efficiency in this configuration still lags behind the SO_3-free case. This is due in part to the higher temperature upstream of the SO_3 injection point. The development of alternative fly ash conditioning agents may also merit further research.

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Literature Cited

(1) Sjostrom, S.; Wilson, C.; Bustard, J.; Spitznogle, G.; Toole, A.; O'Palko, A.; Chang, R. Full-scale evaluation of carbon injection for mercury control at a unit firing high sulfur coal. In *Proceedings of the U.S. Environmental Protection Agency - Department of Energy - EPRI Combined Power Plant Air Pollutant Control Symposium: The MEGA Symposium*; U.S. EPA - DOE - EPRI: 2006.

(2) Berry, M.; Semmes, R.; Campbell, T.; Glesman, S.; Glesman, R. Impact of coal blending and SO_3 flue gas conditions on mercury removal with activated carbon injection at Mississippi Power's Plant Daniel. In *Proceedings of the U.S. Environmental Protection Agency - Department of Energy - EPRI Combined Power Plant*

Air Pollutant Control Symposium: The MEGA Symposium; U.S. EPA - DOE - EPRI: 2006.
(3) Nelson, S.; Landreth, R.; Zhou, Q.; Miller, J. Accumulated power-plant mercury-removal experience with brominated PAC injection. In *Proceedings of the U.S. Environmental Protection Agency - Department of Energy - EPRI Combined Power Plant Air Pollutant Control Symposium: The MEGA Symposium*; U.S. EPA - DOE - EPRI: 2004.
(4) Nelson, S. *Brominated sorbents for small cold-side ESPs, hot-side ESPs, and fly ash use in concrete*; Report to U.S. DOE/NETL, Cooperative Agreement No. DE-FC26-05NT42308; Sorbent Technologies Corporation: 2006.
(5) Sjostrom, S. *Evaluation of sorbent injection for mercury control. Topical Report for: Sunflower Electric's Holcomb Station*; Report to U.S. DOE/NETL, Cooperative Agreement No. DE-FC26-03NT41986; ADA-ES: 2005.
(6) Kang, S. *Field demonstration of enhanced sorbent injection for mercury control*; Report to U.S. DOE/NETL, Cooperative Agreement No. DE-FC26-04NT42306; Alstom Power, Inc.: 2006.
(7) Srivastava, R.; Miller, C.; Erickson, C.; Jambhekar, R. Emissions of sulfur trioxide from coal-fired power plants. *J. Air Waste Manage. Assoc.* **2004**, *54*, 750.
(8) Johnstone, H. Reactions of sulfur compounds in boiler furnaces. *Ind. Eng. Chem.* **1931**, *23*, 620.
(9) Moser, R. SO_3's impact on plant O&M: Part I. *Power* **2006**, *150*, 40.
(10) Halstead, J.; Armstrong, R.; Pohlman, B.; Sibley, S.; Maier, R. Nonaqueous heterogeneous oxidation of sulfur dioxide. *J. Phys. Chem.* **1990**, *94*, 3261.
(11) Lizzio, A.; DeBarr, J. Mechanism of SO_2 removal by carbon. *Energy Fuels* **1997**, *11*, 284.
(12) Yang, F.; Yang, R. Ab initio molecular orbital study of the mechanism of SO_2 oxidation catalyzed by carbon. *Carbon* **2003**, *41*, 2149.
(13) Raymundo-Pinero, E.; Cazorla-Amoros, D.; Salinas-Martinez de Lecea, C.; Linares-Solano, A. Factors controlling the SO_2 removal by porous carbons: Relevance of the SO_2 oxidation step. *Carbon* **2000**, *38*, 335.
(14) Davini, P. SO_2 adsorption by activated carbons with various burnoffs obtained from a bituminous coal. *Carbon* **2001**, *39*, 1387.
(15) Qiang, T.; Zhigang, Z.; Wenpei, Z.; Zidong, C. SO_2 and NO selective adsorption properties of coal-based activated carbons. *Fuel* **2005**, *84*, 461.
(16) Ralston, N.; Olson, E.; Wocken, C. *Mercury Information Clearinghouse Quarter 5 - Mercury Fundamentals*; Technical Report; Canadian Electric Association: 2005.
(17) Huggins, F.; Yap, N.; Huffman, G.; Senior, C. XAFS characterization of mercury captured from combustion gases on sorbents at low temperatures. *Fuel Proc. Technol.* **2003**, *82*, 167.
(18) Anurov, S. Physicochemical aspects of the adsorption of sulfur dioxide by carbon adsorbents. *Russ. Chem. Rev.* **1996**, *65*, 663.
(19) Siedlewski, J. The mechanism of catalytic oxidation on activated carbon. The influence of free carbon radicals on the adsorption of SO_2. *Int. Chem. Eng.* **1965**, *5*, 297.
(20) Cicha, W.; Manzer, L. Process for producing oxochlorides of sulfur. U.S. Patent No. 5,879,652, 1999.
(21) Granite, E.; Pennline, H.; Hargis, R. Novel sorbents for mercury removal from flue gas. *Ind. Eng. Chem. Res.* **2000**, *39*, 1020.
(22) Presto, A.; Granite, E.; Karash, A.; Hargis, R.; O'Dowd, W.; Pennline, H. A kinetic approach to the catalytic oxidation of mercury in flue gas. *Energy Fuels* **2006**, *20*, 1941.
(23) Yan, R.; Ng, Y.; Liang, D.; Lim, C.; Tay, J. Bench-scale experimental study on the effect of flue gas composition on mercury removal by activated carbon adsorption. *Energy Fuels* **2003**, *17*, 1528.
(24) Dombrowski, K. Sorbent injection for small ESP mercury control. In *Proceedings of the 2006 Mercury Control Technology Conference*; 2006. www.netl.doe.gov (accessed March 2007).
(25) Dunham, G.; Olson, E.; Miller, S. Impact of flue gas constituents on carbon sorbents. In *Proceedings of the Air Quality II: Mercury, Trace Elements, and Particulate Matter Conference*; 2000.
(26) Olson, E.; Crocker, C.; Benson, S.; Pavlish, J.; Holmes, M. Surface compositions of carbon sorbents exposed to simulated low-rank coal flue gases. *J. Air Waste Manage. Assoc.* **2005**, *55*, 747.
(27) Hatakeyama, S.; Leu, M.-T. Rate constants for reactions between atmospheric reservoir species. 2. H_2O. *J. Phys. Chem.* **1989**, *93*, 5784.
(28) Seinfeld, J. H.; Pandis, S. *Atmospheric Chemistry and Physics*; John Wiley & Sons, Inc.: 1998.
(29) Miller, S.; Dunham, G.; Olson, E.; Brown, T. Flue gas effects on a carbon-based mercury sorbent. *Fuel Proc. Technol.* **2000**, *65–66*, 343.
(30) Laumb, J.; Benson, S.; Olson, E. X-ray photoelectron spectroscopy analysis of mercury sorbent surface chemistry. *Fuel Proc. Technol.* **2004**, *85*, 577.

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