Further Investigation of the Impact of Sulfur Oxides on Mercury Capture by Activated Carbon[†]

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To gain a more complete understanding of the impact of sulfur oxides on mercury capture by activated carbon, continuous mercury concentration measurements were made downstream of a packed sorbent bed. Previous research from this laboratory, which is presented in a companion study, indicated that the mercury capacity of activated carbon during a 6 h exposure to mercury-laden simulated flue gas was inversely proportional to the S^{6+} content of the carbon. The results presented here indicate that high S^{6+} content limits both the 6-h capacity of activated carbon and the initial mercury removal efficiency. The observed reduction in initial mercury removal efficiency verifies the assumption that the 6-h mercury capacity is indicative of in-flight mercury capture efficiency during activated carbon injection. The activated carbon sample with the highest sulfur content tested here captured a minimal amount of mercury; however, this sample oxidized ∼30% of the incident Hg^0 at 100% breakthrough. This finding suggests that there are multiple available sites for mercury interaction with the sorbent surface, and that capture and oxidation occur at different surface sites.

1. Introduction

Mercury removal from flue gas that contains high concentrations of sulfur oxides, particularly sulfur trioxide (SO_3), has arisen as a key technical hurdle to meeting the mercury emissions requirements that have been set forth by the Clean Air Mercury Rule. Sulfur trioxide enters flue gas via one of three pathways. Coal-S is converted to SO_2 during combustion, and a small fraction is further oxidized to SO_3. The amount of SO_3 formed during combustion is determined, in part, by the sulfur content of the fuel and the excess air level; increasing either of these variables increases the SO_3 concentration in the flue gas.[1] SO_3 can also form from the oxidation of SO_2 across selective catalytic reduction (SCR) catalysts that have been installed for NO_x control. SCR catalysts typically contain vanadium oxides, which are known catalysts for SO_2 oxidation.[1] In some cases, SO_3 is intentionally added to the flue gas as a fly ash conditioning agent and to improve electrostatic precipitator (ESP) performance.

In a companion study, this laboratory recently published experimental results suggesting that SO_3 inhibits mercury adsorption on activated carbon by competing for the same binding sites on the carbon surface.[2] We postulated that the adsorption of SO_3 could be favored both kinetically and thermodynamically. The concentration of SO_3 in flue gas is typically in the range of 1−40 ppm;[3] this is orders of magnitude larger than typical mercury concentrations, which are in the parts per billion (ppb) range. Our previous data also suggested that the bond formed between the S^{6+} species, such as sulfuric acid and sulfates, and the carbon surface is stronger than the bond between mercury and the surface. SO_2 can oxidize to sulfate and form a chemical bond with the carbon surface with a heat of adsorption of >80 kJ/mol.[4] We assume that SO_3 also forms sulfate, with an equally strong bond, on the carbon surface. Previous experiments showed that mercury could not displace

SO_3 from the carbon surface;[2] however, under oxidizing conditions to convert SO_2 to a S^{6+} species, exposure of a mercury-laden activated carbon sample to simulated flue gas caused the mercury to desorb from the surface with a concomitant increase in the surface S^{6+} concentration.[5]

Our companion study of the impact of sulfur oxides on mercury capture by activated carbon relied on analysis of the total mercury content of an activated carbon sample following a 6-h exposure to simulated flue gas in a packed-bed reactor.[2] Packed-bed experiments have been used by many laboratories to test the relative effectiveness of different mercury sorbents. Packed-bed studies offer several advantages over small-scale entrained flow experiments, primarily in simplicity of design and ease of use. The disadvantages of using packed sorbent beds are the long exposure times, which are significantly longer than those encountered during in-duct injection, and the excellent gas−solid contact, which contrasts the potentially poor gas−solid contact present in the duct.

The critical assumption of this experimental method is that the performance of a sorbent over a long exposure time (hours) reflects the in-flight performance during sorbent injection, where the sorbent contacts the flue gas for a few seconds. Therefore, it is preferable to verify this assumption by supplementing the final mercury content data with breakthrough data obtained using a continuous emission monitor (CEM). In this research note, we present CEM data of mercury breakthrough for activated carbon samples with three different sulfur contents. The CEM results echo the findings of our companion paper: mercury and SO_3 compete for the same binding sites on the carbon surface, and higher sulfur loadings lead to lower mercury capture efficiencies.[2] The shorter time scale of the CEM measurements also verify that a high sulfur content on the carbon surface leads to faster mercury breakthrough.

2. Experimental Procedures

Sorbent samples are exposed to mercury in a bench-scale packed-bed reactor that has been described previously.[2] The assembly consists of a quartz tube reactor, with an inner diameter (ID) of 22 mm and a length of 61 cm, contained in a tube

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[†] References in this paper to any specific commercial product, process, or service is to facilitate understanding and does not necessarily imply its endorsement by the U.S. Department of Energy.

furnace. A 200-mg sorbent bed is placed in the reactor and is supported by ~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) that contains 5.25% O_2, 12.5% CO_2, 50 ppm HCl, 500 ppm SO_2, and $10-12$ μg Nm^{-3} Hg, with N_2 as the balance gas. Previous studies from this laboratory included NO in the simulated flue gas. NO was excluded in this study because its presence interferes with mercury detection by the CEM.

Under typical experimental conditions, the flow rate of the simulated flue gas is 8 slpm and the sorbent bed is held at 149 °C. [The units of standard liters per minutes are abbreviated as slpm.] Mercury is provided by a certified Dynacal permeation tube that is held at constant temperature in a water bath. Although the SFG and mercury feed conditions are held constant for each experiment, the CEM-determined mercury concentration in the SFG exhibits day-to-day variations, of up to 20%. This is consistent with the uncertainty found in this laboratory's previous use of the CEM. 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, and HCl are supplied from certified gas cylinders.

In one experiment, the activated carbon bed was exposed to 100 ppm SO_3 for 2 h at 149 °C prior to mercury exposure. SO_3 is supplied to the system by passing N_2 through a cylindrical saturator[2] that contains SO_3, which is a liquid under ambient conditions. The saturator is constructed of stainless steel and is cooled by a water/propylene glycol mixture that is maintained at subambient temperature 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.

In our companion study, we observed that pre-exposing the sorbent bed to SO_3 had the same effect on mercury capture as including SO_3 in the SFG, and that the S^{6+} content of the sorbent, not the SO_3 concentration in the SFG, governed the final mercury content.[2] We chose to pre-expose the sorbent for this study, to prevent SO_3 or sulfuric acid (H_2SO_4) from condensing downstream in the CEM tubing. The SO_3 concentration used during pre-exposure was higher than concentrations typically observed in real flue gas, and the integrated SO_3 exposure of the activated carbon bed was 200 ppm-h (100 ppm for 2 h). This exposure is equivalent to exposing the carbon sample to 33.3 ppm SO_3 for 6 h. Therefore, the pre-exposure is consistent with our companion investigation that used SFG with typical concentrations of SO_3.[2]

Two different activated carbons were tested in this study: Norit Darco Hg-LH and H_2SO_4-FGD. Norit Americas lists the particle size for both Hg-LH and FGD as 95% <325 mesh (45 μm). Darco Hg-LH, a brominated activated carbon, was 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 concentration and speciation exiting the packed bed are measured using a PS Analytical Sir Galahad CEM. A wet conditioning system with two channels for determining elemental and total mercury is placed upstream of the CEM. The elemental mercury channel uses an impinger filled with KCl solution to remove Hg^{2+} compounds from the sample, and the total mercury channel uses a $SnCl_2$/HCl solution to reduce the Hg^{2+} species to Hg^0. Both the KCl and $SnCl_2$/HCl impingers are followed by impingers that contain $NaHCO_3$ solution that
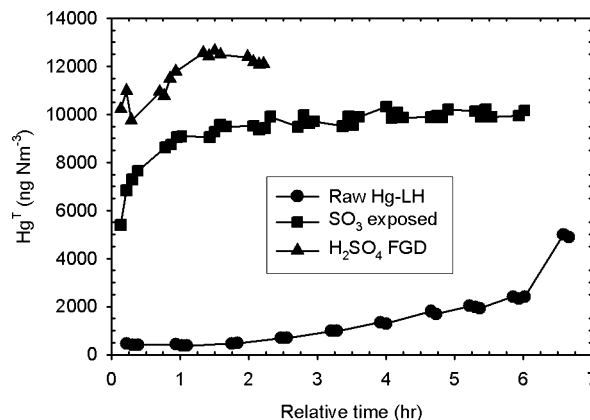

Figure 1. Total mercury concentration (in units of ng/Nm^3) at the exit of the packed-bed reactor, as a function of time from the start of mercury exposure for activated carbon samples with three different sulfur contents. Both the mass of mercury captured and the time to 100% breakthrough decrease as the sulfur content increases for raw Hg-LH (0.7 wt %), Hg-LH that has been exposed to SO_3 (8.4 wt %), and H_2SO_4-FGD (10.6 wt %). The lines that connect the data points are included to guide the eye.

captures the acid gases SO_2 and HCl. The sulfur content of the activated carbon sample exposed to SO_3 is determined by inductively coupled plasma−atomic emission spectroscopy (ICP−AES), following a digestion procedure that was outlined previously.[2]

3. Results and Discussion

3.1. Mercury Capacity. Figure 1 shows the total mercury concentration exiting the packed-bed reactor, as a function of time from the beginning of mercury exposure, for three different activated carbon samples. Raw Hg-LH was used as-received; it had a sulfur content of 0.7 wt %. A second sample of Hg-LH was exposed to 100 ppm SO_3 for 2 h prior to mercury exposure in an SO_3-free SFG; it had a sulfur content of 8.4 wt %. H_2SO_4-FGD had a sulfur content of 10.6 wt %. Previous tests using H_2SO_4-FGD exhibited almost no capacity for mercury during a 6-h exposure.[2]

Both the mass of mercury captured and the time to 100% mercury breakthrough decreased as the sulfur content increased. The raw Hg-LH captured 125 μg Hg/g sorbent (μg/g) during the first 6 h of exposure and did not reach 100% breakthrough in >6 h of exposure. Mercury breakthrough of 10% was achieved after ~3 h. The CEM data for the raw sample of Hg-LH is qualitatively similar to previous measurements of mercury adsorption by a packed bed of activated carbon,[6] and these data show a long period of slowly increasing outlet mercury concentration, followed by a rapid increase.

The raw Hg-LH captured more mercury than in our companion study, where the mercury content of Hg-LH, following a 6-h exposure to dry SFG, was 53.9 μg/g.[2] The high mercury capacity observed here may be a result of the lack of NO in the SFG used in this study.

The sample of Hg-LH that was exposed to SO_3 exhibited an initial breakthrough of ~55% and reached 100% breakthrough within ~3.5 h. The total mercury captured was 8.4 μg/g. As expected, H_2SO_4-FGD captured very little mercury (<0.5 μg/g). The initial breakthrough was >80%, and 100% breakthough was attained within 1 h.

Please note that the mercury capture listed above is slightly different than the mercury content reported previously by this group.[2] The mercury content determined by digesting the used sorbent after 6 h of mercury exposure includes the native

mercury content of the activated carbon, which is exceedingly small for Hg-LH (0.02 μg/g) but larger for Darco FGD (3.0 μg/g). The mercury capture, as determined by the CEM data, as is the case here, does not include the mercury present in the unexposed activated carbon. Hence, our previous report of a final mercury content for H_2SO_4-FGD of 4.1 μg/g is consistent with the same sample capturing <0.5 μg/g in this study. In each case, the data indicate that H_2SO_4-FGD is a poor mercury sorbent in SFG.

The data presented here serve an important function, with respect to our companion investigation of the impact of sulfur oxides on mercury capture by activated carbons.[2] As noted in the Introduction, a potential shortcoming of packed-bed experiments is the long sampling time. Although it is assumed that poor sorbent performance over the time scale of hours indicates poor performance during in-duct injection, the assumption can only be verified with CEM data. Therefore, the data presented here suggest that the competition for binding sites on the carbon surface between mercury and the S^{6+} species reduce both in-duct mercury capture and the total mass of mercury captured over the course of several hours in a packed-bed experiment. The results presented here are also consistent with observations of poor mercury capture during activated carbon injection into real flue gas that contains high concentrations of SO_3.[7]

3.2. Mercury Oxidation. The presence of oxidized mercury in the packed-bed effluent was observed in all of the experiments conducted for this study. For H_2SO_4-FGD and SO_3-exposed Hg-LH at 100% breakthrough, the fractional conversion of Hg^0 to Hg^{2+} was constant and measurable. The mercury was 30% oxidized downstream of the H_2SO_4-FGD bed, and 60% oxidized downstream of the SO_3-exposed Hg-LH bed. Although this group typically eschews measuring fractional mercury oxidation in favor of a kinetically based reaction rate,[8] we are making an exception in this context, because the experiments in question were performed under identical conditions of temperature, bed size, and SFG composition.

Mercury oxidation across the H_2SO_4-FGD and SO_3-exposed Hg-LH beds may indicate the presence of multiple active sites for mercury interaction with the carbon surface. Previous studies of mercury oxidation catalysts strongly suggest that the conversion of Hg^0 to Hg^{2+} requires surface-bound mercury.[9] Thus, we can assume that the oxidized mercury formed across the H_2SO_4-FGD results from mercury that is interacting with the carbon surface, although this mercury is not permanently captured by the sorbent.

The interaction between SO_2 and activated carbon may provide a clue for mercury, because the two species are known to compete for the same binding sites on the carbon surface.[2] 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 of <50 kJ/mol or a chemical bond with a heat of adsorption of >80 kJ/mol.[4] It is simple to assume that these two bonds describe interactions of SO_2 with a single type of site on the carbon surface; however, a more likely explanation is that SO_2 can bond with multiple types of surface sites. For the example here, one can consider the "weak" and "strong" bonds as occurring at different types of sites on the carbon surface. The same case may be true for mercury.

Li et al.[10] reported that the mercury capacity of activated carbons is dependent on the relative concentrations of oxygen-containing surface functional groups. Lactone and carbonyl groups seem to provide active sites for mercury capture, whereas phenol groups inhibit mercury adsorption. Padak et al.[11] used density functional theory (DFT) to investigate the binding

energies between mercury and different surface oxygen groups, and they found that the binding energies decrease in the series

$$lactone > carbonyl > phenol > carboxyl$$

Huggins et al.[12] used X-ray absorption fine structure (XAFS) analysis to investigate the bonding of mercury to activated carbon, and they determined that mercury can bind to anionic I, Cl, S, or O present on the surface. Individual sorbents seemed to be dominated by a single interaction (i.e., Hg–I or Hg–O); however, the authors warn that their data reflect an average of the mercury bonding sites for a particular sorbent. The possibility exists for mercury binding to any or all of the available types of sites on a single sorbent sample.

We postulate that mercury binding on the surface of activated carbon can be described by two generalized types of sites: stable sites with a high binding energy and catalytic sites with low binding energy. When a sample of activated carbon is exposed to mercury, the sites with high binding energy are occupied first and are responsible for mercury capture by the sorbent. The abundance of sites with high binding energy determine the mercury capacity of the sorbent. The mercury-site bond is strong, and the mercury is not re-released without a change to the process conditions such as heating. The high concentration of these sites is responsible for the low initial mercury concentration downstream of the raw Hg-LH bed in Figure 1.

The sites with lower binding energy do not retain mercury; they allow mercury to easily adsorb and desorb. These sites serve to catalyze the formation of Hg^{2+}. Huggins et al.[12] showed that mercury bound to the sorbent is chemisorbed as Hg^{2+}; when the bound mercury is released from the surface, it is released as Hg^{2+}.

As noted previously, SO_3 and mercury compete for the same binding sites on the carbon surface. SO_3 also preferentially binds to the sites with higher binding energy to form surface-bound S^{6+} species. The presence of S^{6+} species reduces the mercury capacity of the sorbent, and, as shown in Figure 1, further increasing the S^{6+} concentration consequently reduces the mercury capacity of the sorbent. As the high binding energy sites become filled, SO_3 begins to react with the lower binding energy sites. Thus, as the S^{6+} content increases, the extent of catalytic mercury oxidation across the sorbent bed decreases. Presumably, at sufficiently high S^{6+} loadings, activated carbon could be rendered useless, as either a mercury sorbent or as a catalyst for flue gas applications.

4. Conclusions

The continuous emission monitor (CEM) data presented here verify that the presence of S^{6+} species on the surface of activated carbon inhibits mercury capture at both short and long time scales. The data reinforce our previous finding that S^{6+} species and mercury bind to the same sites on the carbon surface, and that S^{6+} binding is favored over mercury adsorption. The mercury oxidation data obtained for the SO_3-exposed Hg-LH and H_2SO_4-FGD suggest that mercury binding and mercury oxidation occur at different sites on the carbon surface. S^{6+} species initially adsorb onto the sites responsible for binding mercury, thereby reducing the mercury capacity of the sorbent. As the sites with higher binding energy are filled, the S^{6+} species bind to the sites with lower binding energy, which are responsible for mercury oxidation. The data presented here and in our companion study[2] are not sufficient to postulate the chemical structure of the high- and low-energy binding sites. Identifying the chemistry at each of these types of surfaces sites remains an area for future investigation.

The data presented here and in our companion study[2] do not completely explain the interactions between mercury and sulfur. In flue gas environments, the presence of S^{6+} species, as gaseous SO_3 or surface-bound sulfate or sulfuric acid (H_2SO_4), inhibits mercury adsorption onto activated carbon. However, H_2SO_4-impregnated carbons have been successfully used to remove mercury from liquid hydrocarbons.[13] Concentrated sulfuric acid has also been used to scrub mercury from smelter gases via the formation of mercuric sulfate.[14] Previous work from this laboratory also has revealed that H_2SO_4-impregnated activated carbon effectively removes mercury from a stream of nitrogen.[15] Note that, for the hydrocarbon case, mercury capture occurs in a reducing environment, and, for the smelter case, mercuric sulfate precipitates out of a concentrated solution of sulfuric acid. These conditions are significantly different than the flue gas environment. The reasons for the differences in mercury behavior in these environments are unclear at this time and require further investigation.

Acknowledgment

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