

# MECHANISMS OF MERCURY CAPTURE AND BREAKTHROUGH ON ACTIVATED CARBON SORBENTS

Edwin S. Olson, Grant E. Dunham, Ramesh K. Sharma, Stanley J. Miller

Energy & Environmental Research Center, University of North Dakota

Grand Forks, ND 58202

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## ABSTRACT

An extensive series of studies was performed at the Energy & Environmental Research Center with mercury ( $Hg^0$ ) sorbents in a thin bed using combinations of various flue gas constituents. This work determined that all the sorbents exhibited breakthrough in about 1 hour in the full flue gas mixture, and the mercury emitted after breakthrough is an oxidized mercury species. Trapping of the oxidized species and identification by mass spectrometry demonstrated that both carbon and metal oxide sorbents release the relatively volatile mercuric nitrate hydrate when both  $NO_2$ ,  $SO_2$ , and water vapor are present in the gas phase. Further investigations of treated sorbents allow us to determine the role of oxidation and basic sites on the sorbent in the capture of mercury in  $NO_2$  and  $SO_2$  streams.

## INTRODUCTION

There is currently intense interest in discovering effective sorbents for the control of mercury emissions in flue gas from coal-burning utilities. Extensive factorial evaluations of powdered sorbents were conducted at the Energy & Environmental Research Center in a bench-scale system consisting of a thin fixed-bed reactor in gas streams containing  $15 \mu g/m^3$  of elemental mercury ( $Hg^0$ ) in various flue gas components and simulated mixtures (1). One of the effective sorbents tested was the commercial powdered carbon sorbent Norit FGD, which is a lignite-derived activated carbon (LAC), and this carbon was selected for more extensive testing to determine the critical factors involved in mercury capture. The previous results showed that in an atmosphere containing an acid gas such as HCl or  $NO_2$ , effective capture of  $Hg^0$  from the gas phase occurred on activated carbon sorbents at temperatures of  $100^\circ$  to  $150^\circ C$ . Without either of these acid components in the gas stream, the carbon sorbents are ineffective, and immediate breakthrough occurred.

In tests conducted in the simulated flue gas containing  $NO_2$  but not  $SO_2$ , very little breakthrough was observed over an extended time period, indicating that the bound mercury form is quite stable. The capture is attributed to oxidation of the  $Hg^0$  and concomitant reduction of  $NO_2$  with formation of a low-volatile oxidized mercury species that remains bonded to the sorbent. Reactions of  $Hg^0$  with NO and  $NO_2$  in a glass container were previously reported to form mercuric oxide and mercuric nitrate/nitrite mixtures (2-3).

When  $SO_2$  was added to the gas mixture containing the  $NO_2$ , the mercury sorption rate was initially high (98% of inlet  $Hg^0$  was sorbed); however, breakthrough occurred after 1 hr at the  $225^\circ F$  conditions. The breakthrough curve was relatively steep, increasing to 100% or greater emission after about 2 hr. Not only is mercury no longer sorbed, but mercury sorbed earlier in the experiment is released. Thus there is a significant interaction effect for  $SO_2$  and  $NO_2$  on the sorbent breakthrough time.

The mercury that is emitted from the sorbent after breakthrough is entirely an oxidized mercury species. In reactions conducted with  $NO_2$  and  $SO_2$  and no HCl, this volatile oxidized mercury product was identified as mercuric nitrate hydrate (4). The formation of the mercuric nitrate hydrate from reactions of  $Hg^0$  and  $NO_2$  was not reported in the early literature. It is surprising that  $SO_2$  appears to facilitate the release of the volatile mercuric nitrate hydrate from the sorbent surface. The early breakthrough effect was observed for a number of different sorbents in the flue gas stream containing both  $NO_2$  and  $SO_2$ . This appears to be the controlling element in sorption capacity for mercury in flue gas. Since the effect lowers the capacity and defeats the effectiveness of all the sorbents tested, is important to understand the nature of this interaction and to determine the carbon-related factors that determine the reactivity of the carbon sorbent and its ability to stabilize the oxidized mercury against release as volatile salts. An adequate model for the sorption and breakthrough mechanism is needed to design effective sorbents for mercury control in flue gas.

The work reported in this paper concerns the carbon-related factors that determine the breakthrough behavior in the  $NO_2$ - $SO_2$  stream. Two of these factors are the role of inorganic matter

present in the carbon and the role of catalytic surfaces on the carbon. The hypotheses to be tested are that basic inorganic constituents of the carbons are able to bind mercury by forming relatively stable basic mercury salts and that these basic sites are exhausted by continued exposure to  $\text{SO}_2$ . Release of  $\text{Hg(II)}$  would occur at breakthrough when the basic binding sites are exhausted.

The much higher reactivities observed previously for mercury sorption in air with catalytic carbons compared to noncatalytic carbons lead to the hypothesis that sorption in  $\text{NO}_2$  can also occur at different types of sites and involve formation of different intermediate species. Comparison of the breakthrough curves for the two types of carbons should elucidate these mechanisms.

## RESULTS

To determine whether inorganic sites on the activated carbons are an important factor in mercury sorption in flue gas, carbons with various levels of inorganic constituents were tested. The Norit FGD sorbent that is active for mercury capture in flue gas streams is a finely powdered unwashed LAC. This means that it has a relatively high ash or inorganic content. This carbon is produced from a lignite with high calcium content, so part of the calcium is present in the carbon as the oxide and gives the surface a basic nature. The granular form of the LAC carbon is also available commercially (Norit GAC 1240), but in contrast to the powdered FGD sorbent, the granular lignite-derived carbon is acid-washed to remove some of the inorganic material in the carbon. In previous studies in air, neither the GAC 1240 or the powdered FGD carbon were effective for mercury capture. A ground sample of the GAC 1240 had not been tested for mercury capture in flue gas streams, so it was important to determine if the lower amounts of inorganic constituents on the washed carbon result in shorter breakthrough times owing to a lower capacity for retaining oxidized mercury.

The sorption test performed with the ground sample of commercial acid-washed GAC 1240 in the synthetic flue gas stream showed that the sorption activity was excellent at the start, and breakthrough was not observed for 1.7 hr, compared to 1 hr for LAC. The extended breakthrough results from this experiment are, therefore, not consistent with the concept that basic inorganic material on the surface is required for effective mercury sorption.

To further test the hypothesis that basic surfaces are important for effective mercury control, the Norit FGD carbon was washed with dilute nitric acid to remove basic calcium, iron, and sodium oxides. The demineralized carbon was tested in the synthetic flue gas stream, and results were compared with the initial FGD carbon under the same conditions of temperature, flow rate, and gas composition. The results with the washed FGD (Run 945) were identical to those from the original FGD carbon. Breakthrough occurred at 1 hr and later sampling showed that most of the Hg in the effluent from the sorbent bed was oxidized. Thus removal of basic sites by washing the sorbent with nitric acid did not result in less effective sorption.

Catalytic carbons were previously shown to exhibit very high mercury sorption activities in air streams (5). Not only were high initial kinetics for sorption observed, but the activities decreased only very gradually over several days of testing. But is this higher sorption activity for the catalytic carbons in air also observed in the simulated flue gas system?

The results of testing a catalytic carbon in the bench-scale simulated flue gas showed that the sorption curve is very similar to that of the LAC sorbent and that breakthrough occurred at the same 1-hr point in the experiment as observed for the LAC. Only oxidized mercury is observed in the emission after breakthrough. Thus the catalytic carbon is subject to the same  $\text{NO}_2$ - $\text{SO}_2$  interaction as the LAC.

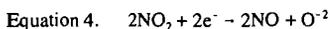
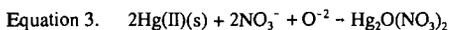
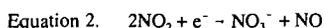
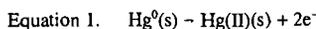
## DISCUSSION

The results with washed carbons do not support the hypothesis that basic inorganic residues in the carbon are involved in binding oxidized mercury, since shorter breakthrough times resulting from failure to bind  $\text{Hg(II)}$  at basic inorganic sites were not observed. The better capacity exhibited by the ground sample of GAC 1240 may be explained by the cleaning effect of the acid in removing basic salts that are plugging the carbon pores and, therefore, improve internal mass transport. Secondly, the removal of inorganic material may expose more carbon surface and, therefore, more oxidation sites, which may overcome the negative effect expected for removal of the basic sites. Thirdly, there may be other binding sites on the carbon structure that would have been exposed by the removal of the basic inorganic sites. It is possible that some residue from the wash solution somehow improved the capacity of the GAC 1240.

The experiments do not, however, rule out the involvement of inorganic matter since it could be argued that the washing procedure removed mineral matter only from the mesopores. This would improve the internal mass transfer, but still leave some basic sites available on the micropore surface for converting the Hg(II) to nonvolatile basic salts. Thus the failure of the experiments to demonstrate decreased capacity does not reject the basic inorganic residue hypothesis, but other experiments must be conducted to determine which effects are occurring. The significantly better performance (longer breakthrough time) of the GAC 1240 cannot be adequately explained until further information on these factors is available.

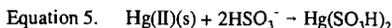
The air oxidation mechanisms of catalytic carbons appear to be quite different than those of noncatalytic carbons. Reactions with NO<sub>2</sub> could also involve different mechanisms and form different intermediate species in the two types of carbons. However, this work shows that the oxidation mechanisms using NO<sub>2</sub> as the primary oxidant (electron sink) may be the same in the catalytic and noncatalytic carbons. The similarity in breakthrough times for the two types of carbons appears to reject the hypothesis that intermediate species are different for the two carbons.

A simple model for the sorption reaction is that the adsorbed Hg<sup>0</sup>(s) is rapidly oxidized at an oxidation site on the carbon surface to a bound Hg(II) species utilizing electrons from the NO<sub>2</sub> (Equations 1-2). This reaction is likely to occur readily on any kind of carbon surface as well as other surfaces. In the absence of SO<sub>2</sub>, the major species formed would be mercuric oxide or a basic mercuric nitrate/oxide (Equation 3), which is stable at 150°C, even in the stream containing NO<sub>2</sub>. Oxide could be present on the sorbent surface initially (such as CaO) or could be produced from NO<sub>2</sub> as shown in Equation 4. The stable basic mercury salts collect in sites adjacent to the oxidation site, and the activated carbon is able to retain relatively large amounts of these forms. Thus this model is consistent with the behavior of both catalytic and LAC carbons.

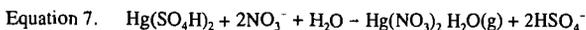
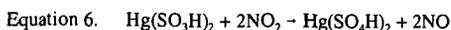


The role of SO<sub>2</sub> in the breakthrough mechanism is more difficult to understand. Since the oxidation of Hg<sup>0</sup> is still 100% at breakthrough, it is unlikely that SO<sub>2</sub> is inhibiting the Oxidation Reaction 1 and, therefore, the oxidation sites. It must also not inhibit Reactions 2 and 4, since SO<sub>2</sub> can not provide the electron sink for Hg<sup>0</sup> oxidation and is not normally reduced on a carbon surface. Therefore, SO<sub>2</sub> must be involved in the reactions leading to mercury stabilization on the sorbent or to bonding of the Hg(II) species formed in or subsequent to the oxidation.

Thus a direct involvement involving binding of SO<sub>2</sub> to an intermediate bound Hg(II) species seems more likely. In the presence of adsorbed SO<sub>2</sub>, the Hg(II) may react to initially form mercuric sulfite or hydrosulfite (Equation 5). These species have Hg-S bonds and are expected to be nonvolatile. This nonvolatile species also collects in sites adjacent to the oxidation site. This form is consistent with the XAFS study (6) that concluded that mercury is bound by either sulfur or chloride on the sorbent.



Over time (1 hr), this form could be oxidized to mercury sulfate or bisulfate which results in forming Hg-O bonds (Equation 6). These bonds will be more labile, and interconversion to the volatile mercuric nitrate hydrate occurs (Equation 7). Since no Hg<sup>0</sup> is emitted, the oxidation sites must still be functioning at breakthrough, only the bonding sites are becoming ineffective. This model is inadequate, however, because it predicts a gradual breakthrough from the start rather than the sudden one that is observed after 1 hr. Thus there seems to be other missing structural or reactivity factors that have not yet been considered.



The original hypothesis was that the LAC uses inorganic CaO sites to aid in the conversion of the oxidized Hg(II) (Equation 4) to the basic mercuric nitrate oxide that is not volatile and these sites are eventually converted to CaSO<sub>3</sub> or CaSO<sub>4</sub> that are inactive for stabilization. But this is not likely since removal of CaO did not shorten breakthrough.

The alternative model we now wish to consider is that SO<sub>2</sub> reacts with oxide at the carbon surface. By complexing these basic sites, this reaction may interfere with the formation of the stable basic mercuric oxide salt, as well as use up SO<sub>2</sub> that would bind directly to the mercury. Further experiments are needed to test this model.

#### ACKNOWLEDGMENTS

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