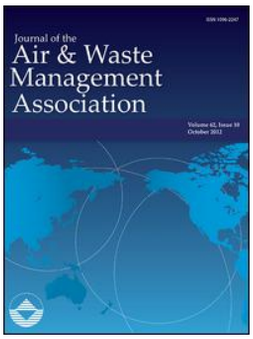

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Factors Affecting Mercury Control in Utility Flue Gas Using Activated Carbon

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ABSTRACT

The Electric Power Research Institute (EPRI) is conducting research to investigate mercury removal in utility flue gas using sorbents. Bench-scale and pilot-scale tests have been conducted to determine the abilities of different sorbents to remove mercury in simulated and actual flue gas streams. Bench-scale tests have investigated the effects of various sorbent and flue gas parameters on sorbent performance. These data are being used to develop a theoretical model for predicting mercury removal by sorbents at different conditions. This paper describes the results of parametric bench-scale tests investigating the removal of mercuric chloride and elemental mercury by activated carbon.

Results obtained to date indicate that the adsorption capacity of a given sorbent is dependent on many factors, including the type of mercury being adsorbed, flue gas composition, and adsorption temperature. These data provide insight into potential mercury adsorption mechanisms and suggest that the removal of mercury involves both physical and chemical mechanisms. Understanding these effects is important since the performance of a given sorbent could vary significantly from site to site depending on the coal- or gas-matrix composition.

IMPLICATIONS

Mercury continues to be considered for possible regulation in the electric power industry under Title III of the 1990 Clean Air Act Amendments. This possibility has generated interest in assessing whether cost-effective technologies exist for removing mercury from fossil-fired flue gas. One promising approach involves the direct injection of activated carbon into the flue gas. This paper describes the results of parametric bench-scale tests investigating the adsorption of mercuric chloride and elemental mercury from utility flue gas by activated carbon. This information is important for determining mercury removal using activated carbon injection under different flue gas conditions.

INTRODUCTION

The Clean Air Act Amendments of 1990 listed 189 substances as hazardous air pollutants. Thirty-seven of these substances have been detected in power plant emissions with eleven being trace metal species. Mercury is the trace metal species of greatest concern because of perceived risks from its environmental release.[1] Most of the trace metal species are efficiently removed in properly operated particulate removal systems. Mercury, however, is present mainly in the vapor form and is not captured effectively by existing particulate removal systems.

Injection of activated carbon or other sorbents upstream of a particulate control device is one potential method for controlling mercury emissions from utility boilers. Carbon-based and other sorbents have been developed for control of mercury emissions from municipal- and hazardous-waste incinerators. Existing data from the incinerators provide some insight into mercury control, but these data cannot be used directly for coal-fired utilities because mercury concentrations, species, and process conditions differ greatly.[2] For example, mercury concentrations (200 to 1,000 $\mu g/m^3$) from municipal solid waste (MSW) are 1 to 2 orders of magnitude higher than those from coal combustion sources (5 to 20 $\mu g/m^3$). The relatively high mercury concentrations in MSW systems and other differences in process conditions generally result in relatively low carbon injection rates. Tests have shown that the carbon-to-mercury ratio in MSW incinerators is more than an order of magnitude lower than

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that necessary to achieve similar mercury removal in coal combustors.

Several bench-,[3-5] pilot-,[6-9] and full-scale[10,11] tests have examined the influence of carbon type, carbon structure, carbon surface chemistry, injection method (dry or wet), amount of carbon injected, and flue gas temperature on mercury removal. Inconsistencies in the data suggest that a wide variety of factors may influence the mercury removal obtained when injecting sorbents into flue gas upstream of an electrostatic precipitator (ESP) or a baghouse. These factors potentially include the mercury species being removed (oxidized vs. elemental), the flue gas composition, process conditions (e.g., temperature), sorbent characteristics, and the presence of other active surfaces (e.g., fly ash). Many of the earlier tests did not consider or measure all of these variables. Thus, data have been difficult to compare.

Mercury speciation in the flue gas, flue gas composition, and process operating conditions are all important factors in determining mercury removal. Current mercury measurement methods indicate the presence of both elemental and ionic forms of mercury in flue gas. The ionic mercury is usually assumed to be a chloride or oxide, and mercuric chloride is normally used in bench experiments to simulate oxidized mercury species. Results presented later in this paper show that sorption behavior is dependent on mercury type. In addition, gas components such as sulfur oxides, nitrogen oxides, water, and chlorine compounds can affect adsorption. These variables make data interpretation difficult since the flue gas composition can vary widely from one boiler to another or even test to test. Other process conditions, such as temperature, sorbent dispersion uniformity, and sorbent residence time, can also be difficult to maintain or determine in large-scale systems. For example, sorbent residence times in an electrostatic precipitator are difficult to quantify since many of the particles are collected in the first field. Also, particle migration will skew sorbent distribution. In a baghouse, the residence time between the baghouse inlet and the filter bags is difficult to determine, and dustcake thickness will vary with time in operation, pressure drop, and cleaning frequency.

While the above factors influence mercury adsorption and removal, the most important factor is probably the sorbent type and its associated properties. However, sorbent properties that allow a given sorbent to effectively adsorb mercury are not well understood. Specific functional groups present on the good mercury sorbents are not known, and the mercury adsorption mechanisms are not well understood. Variations in the physical properties of a given sorbent such as size, shape, effective surface area, and porosity can affect adsorption effectiveness. Because of these factors, particles already present in flue gas such as fly ash or calcium sorbents injected for sulfur oxide control can be quite active for mercury adsorption under some conditions. This activity can make interpretation of sorbent effectiveness difficult.

To develop a better understanding of how the above parameters affect mercury adsorption and sorbent effectiveness, EPRI has developed a systematic approach for evaluating potential sorbents and developing a theoretical model to predict performance. This approach and the theoretical model have been discussed in more detail previously.[12,13] Laboratory tests are used to characterize the physical and chemical properties of a given sorbent such as size, shape, surface area, porosity, and chemical composition. Bench-scale, fixed-bed tests are then conducted to determine the equilibrium adsorption capacity and breakthrough characteristics. These tests are conducted under simulated flue gas conditions, and results using different sorbents can be compared to provide relative indicators of performance. The sorbent properties and adsorption equilibrium data are then used in the theoretical model that incorporates mass transfer considerations to predict mercury removal during sorbent injection. This model will be refined as bench-scale and pilot-scale injection test data are collected. Tests upstream of both electrostatic precipitators and baghouses are needed to account for differences in residence time and physical configuration.

This paper discusses recent bench-scale, fixed-bed adsorption results using both elemental mercury and mercuric chloride under simulated flue gas conditions. A lignite-based activated carbon obtained from Norit Americas (commercial name, Darco FGD carbon) has been tested under a wide variety of mercury concentrations and flue gas conditions. This work is significantly different than the work of others since the majority of previous work has been done in nitrogen. Before discussion of the mercury adsorption results, the bench-scale test equipment and procedures are described.

TEST METHODS AND PROCEDURES

In order to model the performance of a given sorbent, the equilibrium adsorption capacity and characteristics of the sorbent must be known. If a particular sorbent has a low equilibrium capacity for mercury, the mercury removal rate will be adversely affected since equilibrium will be rapidly approached. Sorbent equilibrium data can be generated by conducting fixed-bed, adsorption breakthrough tests. The bench-scale studies presented in this paper have focused on evaluating the breakthrough characteristics of Norit Americas' Darco FGD carbon under a wide variety of test conditions.

Figure 1 shows a schematic diagram of the bench-scale mercury sorbent test apparatus. Two identical test

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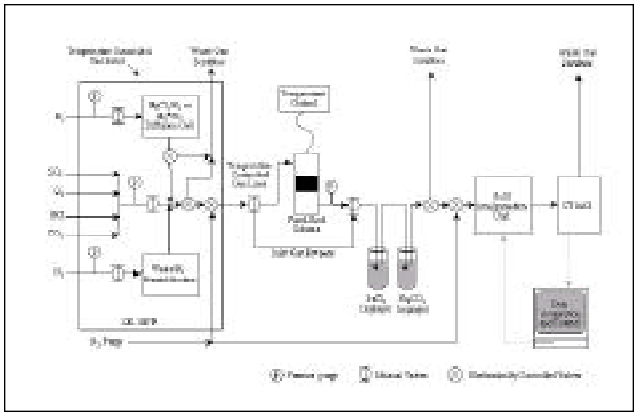

Figure 1. Bench-scale, fixed-bed mercury adsorption apparatus.

units have been constructed. One unit is used to test elemental mercury adsorption while the other is used to test mercuric chloride adsorption. In both systems, a simulated flue gas is prepared by mixing heated, nitrogen gas streams containing SO_2, HC1, CO_2, O_2, NO_x, and water. The gas composition can be varied by appropriately adjusting the various gas rates. Mercury is injected into the gas by contacting nitrogen carrier gas with either recrystallized mercuric chloride solids or with an elemental mercury diffusion tube (VICI Metronics) in a mercury saturation vessel. The mercury concentration is controlled by the temperature of the mercury saturator and the nitrogen flow rate through the saturator. All gas mixing, water saturation, and mercury injection occur within a closed, temperature-controlled box designed to prevent water condensation, which can affect the behavior of mercury and the gas concentrations in the flow lines.

The reaction gas flows at about 1 standard L/min through heated (225°F) Teflon lines to a temperature-controlled column (0.5-in. i.d.) containing the sorbent to be studied. The sorbent is mixed in a sand diluent prior to being packed in the reaction column. A ratio of 20 mg carbon to 10 g of sand was used in all tests reported in this paper. In the column, the gas is heated to the reaction temperature before contacting the sorbent by passing it across a bed of pyrex spheres designed to enhance heat exchange. The column temperature is controlled using an internally mounted thermocouple shielded from the gas with a glass sheath. The reaction gas flows downward through the column to minimize the chance of selective flow or channeling through the bed. The bed material is supported by a fritted glass disk and packed with quartz wool. The linear gas velocity through the empty column is approximately 36 ft/min at 275°F.

During each test, the sorbent-sand mixture is equilibrated at the desired adsorption temperature for at least one hour before contacting gas. During this time, the inlet gas bypasses the sorbent column and passes to the analytical system to determine the inlet mercury concentration. The analytical system (described below) consists of a gold amalgamation unit and a cold-vapor atomic absorption (CVAA) spectrophotometer. After the inlet mercury concentration is established, the adsorption test is initiated by diverting the reaction gas through the sorbent column. The amount of mercury exiting the column is measured on a semi-continuous basis until 100% of the inlet mercury is detected at the outlet (100% breakthrough). The reaction gas continuously passes through the sorbent column during each test by sending the effluent gas to a waste scrubber during the analysis step.

During normal operation of a test, the effluent gas from the fixed-bed column flows through heated lines to an impinger containing $SnCl_2$ solution, which reduces any oxidized mercury compounds to elemental mercury. After passing through the $SnCl_2$ impinger, the gas flows through a buffer solution (Na_2CO_3) to remove the SO_2 and HCl from the gas, thus protecting the downstream, analytical gold surface. Gas exiting the impinger solutions flows through a gold amalgamation column housed in a tubular furnace where the mercury in the gas is adsorbed (<100 °C). After adsorbing mercury onto the gold for a fixed period of time (typically 6 minutes), the mercury concentrated on the gold is thermally desorbed (>750 °C) in nitrogen and sent as a concentrated mercury stream to the CVAA spectrophotometer for analysis. Therefore, the total effluent mercury concentration is measured semi-continuously with a 6-min sample time followed by a six-minute analytical period.

The gold amalgamation/CVAA system is calibrated by withdrawing a known volume of vapor from a mercury saturation vessel and injecting this vapor upstream of the gold. The mass of elemental mercury injected is calculated based on the vapor volume and mercury saturation temperature and is correlated to the CVAA response. This method of determining the elemental mercury mass has been verified by injecting the mercury vapor into an EPA Method 101A sample train and analyzing the impinger solutions. Calibration of the system is verified periodically by injecting a known mass of elemental mercury into the simulated flue gas and measuring the spike recovery. Spike recoveries are generally between 90% and 110%.

When testing elemental mercury adsorption, the effluent mercury can be fully or partially oxidized due to reactions between the inlet elemental mercury, activated carbon, and flue gas components. The percentage of inlet elemental mercury oxidized across the sorbent is determined by replacing the $SnCl_2$ impinger with an impinger containing tris(hydroxymethyl)aminomethane (tris) solution. The tris solution has been shown in other EPRI studies to capture oxidized mercury while allowing elemental mercury to pass through without being altered.[14] Therefore, with the tris impinger in place, any effluent

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oxidized mercury is captured by the tris impinger, and only elemental mercury is detected by the downstream analytical system. The difference between the total measured effluent mercury ($SnCl_2$ impinger) and the effluent elemental mercury represents the amount of elemental mercury oxidized across the sorbent bed.

Using the apparatus described above, mercury adsorption breakthrough curves using FGD carbon were generated at various operating conditions. Typical breakthrough curves are shown in Figure 2. The percent breakthrough is determined as a function of time by normalizing the measured mercury concentration at the outlet of the sorbent bed to the inlet mercury concentration. The area between the breakthrough curve and 100% breakthrough represents the total mass of mercury adsorbed as a function of time. The adsorption capacity of the sorbent (µg Hg adsorbed/g carbon) at time *t* is determined by summing the total mass of mercury adsorbed through time *t* (area above the breakthrough curve) and dividing by the carbon mass. The initial breakthrough capacity is defined at the time when mercury is first detected at the outlet. The 100% breakthrough (equilibrium) capacity is defined at the time when the outlet mercury concentration is first equal to the inlet concentration.

MERCURY ADSORPTION TEST RESULTS

Although the bench-scale test apparatus is capable of testing nearly any sorbent type, results in this paper focus only on Darco FGD carbon. This activated carbon is lignite-based and was obtained from Norit Americas Incorporated. It is a commercial product primarily sold as a sorbent for heavy metal species in incinerator flue gas streams. Table 1 summarizes the FGD carbon physical and chemical properties measured in the lab. The chemical composition was obtained using energy dispersive x-ray analysis (EDX). The particle size distribution was determined using both a scanning electron microscope method and Microtrac analysis (laser scattering method). Typical product properties obtained from a Norit Americas datasheet are included for comparison. The analytical methods used to make these measurements were not specified.

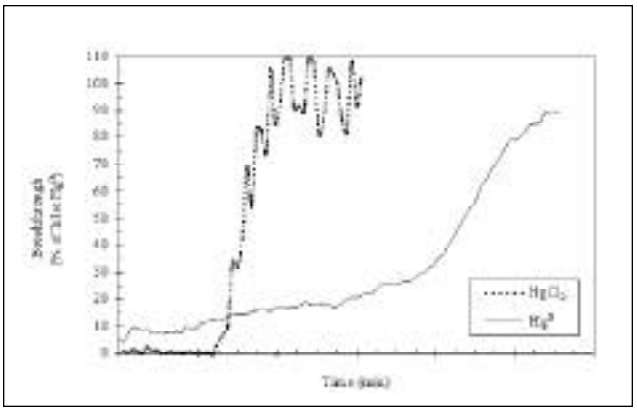

Figure 2. Typical $HgCl_2$ and Hg^0 breakthrough curves.

Table 1. Properties of Darco FGD powdered activated carbon.

Carbon Property	Lab Data	Norit Americas Datasheet
General Properties:		
Bulk density (g/mL)	—	0.51
Surface area (m^2/g)	—	600
Molasses decolorizing efficiency	—	90
Iodine number	—	600
Particle Size:		
% passing 325 mesh	94	95 minimum
Avg. size from SEM analysis (µm)	15	—
Avg. size from Microtrac analysis (µm)	14	—
Pore Size Distribution (mg/g):		
micro, <20 Å	—	0.18
meso, 20-50 Å	—	0.25
macro, 50-150,000 Å	—	1.06
Chemical Composition (wt%):		
Oxygen	28	—
Carbon	22	—
Silicon	14	—
Calcium	13	—
Iron	7.4	—
Aluminum	7.1	—
Sulfur	3.7	1.8
Magnesium	2.9	—

FGD carbon has been tested over a wide range of test conditions. Table 2 summarizes the baseline test conditions using both elemental mercury and mercuric chloride and the range over which some variables have been tested. The baseline concentrations of SO_2 and HCl are representative of many full-scale utilities burning Eastern U.S. bituminous coals (which contain relatively high sulfur and chloride). However, the flue gas composition can vary dramatically from one full-scale system to another depending on the coal type, operating conditions, and air pollution control technologies used. The range of flue gas concentrations shown in Table 2 was selected to represent this wide range of full-scale gas compositions.

The baseline mercury concentrations in Table 2 are reported as a range because these concentrations can not be precisely controlled from test to test due to the nature of using a mercury saturation vessel. These concentrations (25–45 µg Hg/Nm^3 for $HgCl_2$ and 40–80 µg Hg/Nm^3 for Hg^0) are higher than most full-scale systems (typically 5–20 µg Hg/Nm^3). Higher baseline concentrations were used to decrease the sensitivity of results to variations in the mercury concentration.

FGD carbon is tested at baseline conditions on a regular basis to determine variability in the measurement

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Table 2. Bench-scale test conditions.

Parameter	Baseline Value	Range Tested
Gas Rate (L/min at 75°F)	1.0	—
Gas Composition:		
$HgCl_2$ (µg Hg/Nm^3)	25-45	5-105
Hg^0 (µg Hg/Nm^3)	40-80	5-130
SO_2 (ppmd)	1600	0-3000
HCl (ppmd)	50	0-100
NO_x (ppmd)	0	100, 400
O_2 (%)	6	—
CO_2 (%)	12	—
H_2O (%)	7	0-10
Adsorption Temperature (°F)	275	225-400

methods and to monitor unexpected changes in the results. "Blank" tests conducted with no carbon in the sand bed consistently have shown no mercury adsorption; therefore, all mercury adsorption can be attributed to the carbon during the tests. Generally, the outlet concentration at the end of each test has been between 80% and 120% of the inlet concentration. These data suggest reasonable recovery of mercury through the sorbent bed.

The standard deviation of the adsorption capacity measurements is typically 40–50% of the measured average. This relatively high standard deviation is not surprising since mercury adsorption is dependent on many factors and the mercury concentration is low. Although test conditions are controlled tightly, variations in the inlet mercury concentration, the consistency of FGD carbon surface properties from sample to sample, and the measurement methods contribute to variations in the measured capacity. Given this variability, the adsorption capacities reported for most of the test conditions in this paper have been measured at least three times.

Bench-scale results presented in this paper include the effect of the following variables on the FGD carbon elemental mercury and mercuric chloride adsorption capacities:

- mercury concentration,
- SO_2 concentration,
- HC1 concentration,
- NO_x concentration,
- water concentration, and
- mercury oxidation (elemental mercury only).

The effect of temperature on mercury adsorption has been reported previously.[15] At each set of test conditions, the initial breakthrough capacity and the 100% breakthrough capacity were determined. Changes in these capacities at different conditions provide information about how these variables might affect mercury removal. Changes in the initial breakthrough capacity suggest that the adsorption rate has been affected, while changes in the 100% breakthrough capacity suggest that the equilibrium characteristics have been affected. These results can be combined with the theoretical model to eventually predict changes in mercury removal.

Effect of Mercury Concentration

Figure 3 illustrates the effect of inlet mercuric chloride concentration and elemental mercury concentration on the FGD carbon equilibrium adsorption capacities at baseline conditions (see Table 2). The inlet $HgCl_2$ concentrations and $HgCl_2$ adsorption capacities reported are based on the mass of mercury rather than the mass of $HgCl_2$ so that the comparison is on an equal molar basis. The data in Figure 3 show that the FGD carbon adsorption capacities for mercuric chloride and elemental mercury were equal at baseline conditions when the $HgCl_2$ inlet concentration and capacity were expressed in this way. For both mercury types, the equilibrium adsorption capacity increased as the inlet mercury concentration increased. This effect of concentration is consistent with a physical adsorption mechanism. Data presented in a previous paper showed that the capacity also increased as the temperature decreased for both types of mercury.[15] These data also suggest a physical adsorption mechanism.

FGD carbon had appreciable capacity for mercuric chloride and elemental mercury even at concentrations as low as 5 µg/Nm^3. This result is important since both types of mercury are typically present at 5–20 µg/nm^3 in coal-fired utility flue gases. Preliminary modeling work suggests that a capacity of 500 µg/g should be sufficient to remove mercury from flue gas. The measured capacities at about 10 µg/nm^3 varied from 200 to 1,000 µg/g.

Although the equilibrium adsorption capacity for elemental mercury was equal to that for mercuric chloride at baseline conditions, elemental mercury was not adsorbed as efficiently as mercuric chloride. When testing mercuric chloride, total adsorption (i.e., 100% removal) was generally

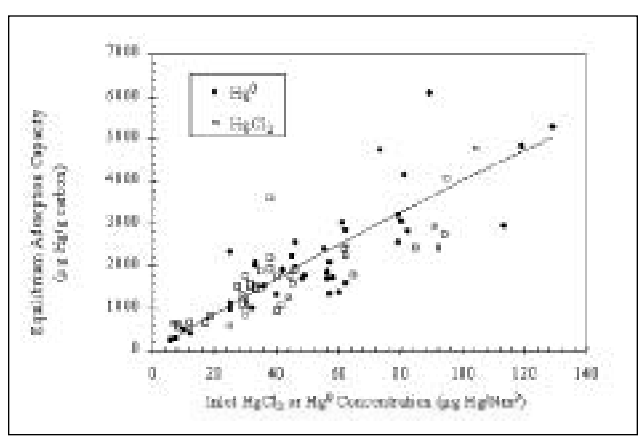

Figure 3. Effect of inlet Hg^0 and $HgCl_2$ concentrations on the FGD carbon adsorption capacity at 275 °F.

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achieved until the carbon was saturated and breakthrough occurred. With elemental mercury, however, typically about 15% breakthrough was observed from the start of the test, when the carbon was "fresh" until breakthrough occurred as the carbon became saturated (see Figure 2). These data suggest that, although FGD carbon has a similar equilibrium capacity for elemental mercury and mercuric chloride, the initial adsorption rate for mercuric chloride is higher, and therefore, this carbon may be more effective at removing mercuric chloride than elemental mercury.

Effect of Flue Gas Composition

The FGD carbon adsorption capacity for elemental mercury and mercuric chloride at 275 °F was determined over a wide range of SO_2, HC1, NO_x, and H_2O concentrations. During most of these parametric tests, the concentration of one gas component was varied while the concentrations of the other flue gas components remained at baseline values (see Table 2). The effect of HCl, however, was also determined over a range of SO_2 and NO_x concentrations.

Effect of SO_2. Figure 4 illustrates the effect of SO_2 on the FGD carbon capacity for elemental mercury and mercuric chloride at 275 °F. The inlet mercury concentration was 60–70 µg Hg/Nm^3 during the elemental mercury tests and 30–45 µg Hg/Nm^3 during the $HgCl_2$ tests. The FGD carbon adsorption capacity for both mercury types decreased as the SO_2 concentration increased from 0 ppm to about 500 ppm. The capacity for elemental mercury increased dramatically when SO_2 was removed entirely from the gas. Above about 500 ppm SO_2, the capacity for both mercury types did not change significantly as the SO_2 concentration increased. Since most full-scale utilities have at least 200 ppm SO_2, the effect of SO_2 on capacity may not be practically important.

Effect of HCl. Figure 5 illustrates the effect of HCl on the FGD carbon capacity for elemental mercury and mercuric chloride at 275 °F with 1,600 ppm SO_2 in the gas. The inlet mercury concentration was 53–61 µg Hg/Nm^3 during the elemental mercury tests and 28–33 µg Hg/Nm^3 during the $HgCl_2$ tests. As the HCl concentration increased from 0 ppm to about 50 ppm, the mercuric chloride capacity increases, with appreciable adsorption at each HCl concentration. However, the effect of HCl on the elemental mercury capacity was more dramatic. Increasing the HCl concentration from 0 ppm to 50 ppm increased the FGD carbon elemental mercury capacity from 0 µg/g to about 2,500 µg/g. Above about 50 ppm HCl, neither the elemental mercury nor $HgCl_2$ capacity changed significantly. The ability of FGD carbon to adsorb elemental mercury was clearly affected by the HCl concentration at baseline gas conditions. At low HCl concentrations, essentially no elemental mercury was adsorbed, and the adsorption capacity for elemental mercury was less than that of mercuric chloride. At high HCl concentrations, the elemental mercury capacity was about equal to the mercuric chloride adsorption capacity (at the same inlet mercury concentration).

Because elemental mercury adsorption is sensitive to both the HCl and SO_2 concentrations, the concentration of both of these species was varied simultaneously. Figure 6 illustrates the effect of HCl on the elemental mercury adsorption capacity at various SO_2 concentrations. The capacity at 0 ppm SO_2 and 50 ppm HCl is not shown since the capacity was so high (see Figure 4). Figure 6 shows that the FGD adsorption capacity for elemental mercury increased as the HCl concentration increased and that the adsorption capacity was 0 µg/g with no HCl in the gas regardless of the SO_2 concentration.

Effect of NO_x. Data presented in Figures 4 through 6 were collected with no NO_x in the gas. Figure 7 illustrates the effect of NO_x on the FGD carbon capacity for elemental mercury and mercuric chloride at 275 °F with 0 ppm and 50 ppm HCl in the gas. The total

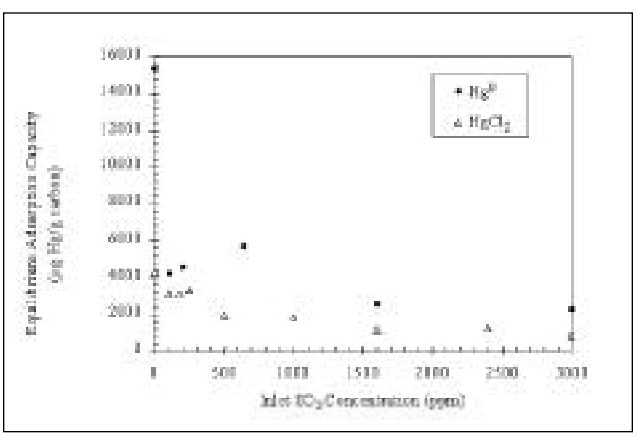

Figure 4. Effect of SO_2 concentration on the FGD carbon Hg^0 and $HgCl_2$ adsorption capacities at 275 °F.

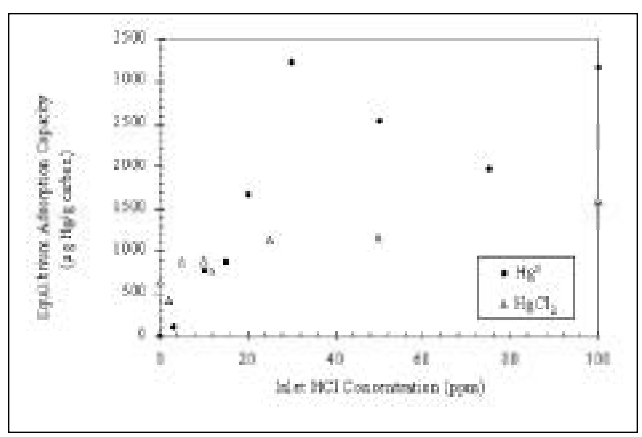

Figure 5. Effect of HCl concentration on the FGD carbon Hg^0 and $HgCl_2$ adsorption capacities at 275 °F.

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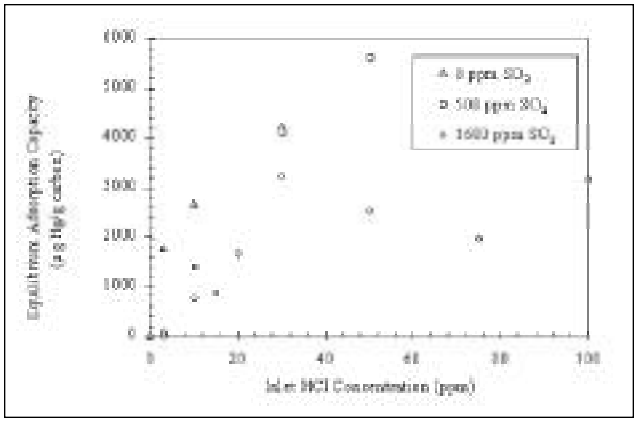

Figure 6. Effect of inlet HCl and SO_2 on the FGD carbon Hg^0 adsorption capacity at 275 °F.

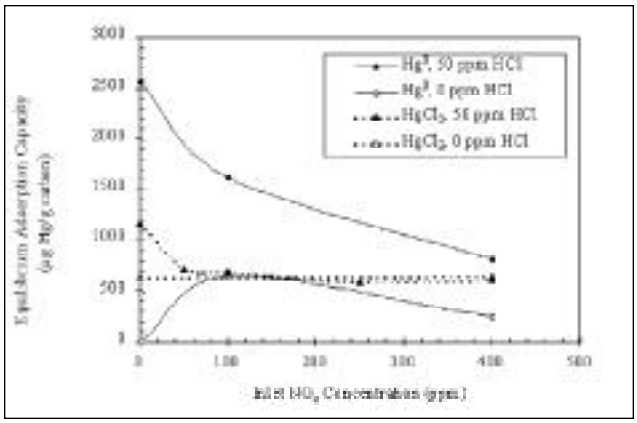

Figure 7. Effect of inlet NO_x and HCl on the FGD carbon Hg^0 and $HgCl_2$ adsorption capacities at 275 °F.

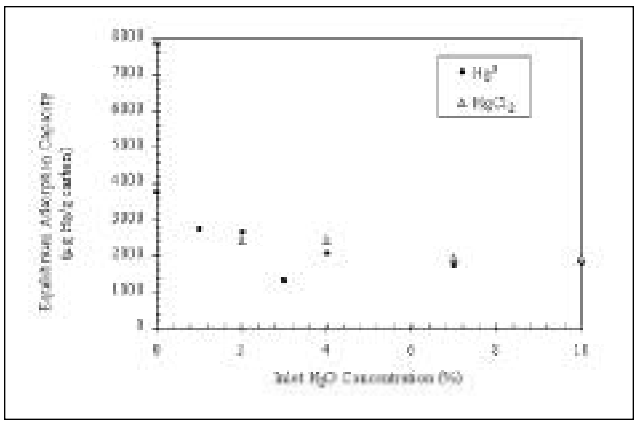

Figure 8. Effect of H_2O concentration on the FGD carbon Hg^0 and $HgCl_2$ adsorption capacities at 275 °F.

NO_x concentration consisted of about 10% NO_2 and 90% NO. The inlet mercury concentration was 55–70 µg Hg/Nm^3 during the elemental mercury tests and 33–41 µg Hg/Nm^3 during the $HgCl_2$ tests. With 50 ppm HCl in the gas, the FGD carbon capacity for both mercuric chloride and elemental mercury appeared to decrease after NO_x was added to the gas. For mercuric chloride, the capacity decreased after adding just 50 ppm NO_x and then remained constant as the NO_x concentration was further increased. For elemental mercury, the capacity appeared to decrease as the NO_x concentration increased from 0 ppm to 400 ppm. The effect of NO_x on elemental mercury adsorption was more dramatic.

With 0 ppm HCl in the gas, adsorption of mercuric chloride was not affected after adding 400 ppm NO_x to the gas. However, adsorption of elemental mercury increased from 0 µg/g with no HCl or NO_x in the gas to about 640 µg/g with 100 ppm NO_x and 250 µg/g with 400 ppm NO_x. This result is significant because FGD carbon was able to remove elemental mercury with no HCl in the gas, provided NO_x was present. In addition, the effect of NO_x on capacity with no HCl in the flue gas appears to be opposite of that observed with 50 ppm HCl in the flue gas. Both HCl and NO_x clearly affected elemental mercury adsorption.

Effect of H_2O. Figure 8 illustrates the effect of water on the FGD carbon capacity for elemental mercury and mercuric chloride at 275 °F. The inlet mercury concentration was 35–60 µg Hg/Nm^3 during the elemental mercury tests and 26–41 µg Hg/Nm^3 during the $HgCl_2$ tests. The FGD carbon adsorption capacity for mercuric chloride increased significantly after water was removed from the flue gas; however, since full-scale flue gas streams always contain at least some water, this result is not practically important. Neither mercuric chloride nor elemental mercury adsorption was significantly affected by variations in water concentration from 1% to 10%.

Results shown in Figures 4 through 8 clearly indicate that flue gas composition affects carbon performance and that performing adsorption tests under realistic operating conditions is important. The effect of flue gas composition on adsorption capacity suggests that the mercury adsorption mechanism is not purely physical. Interactions between mercury and flue gas components on the carbon surface may be important. Other researchers have generally done bench-scale mercury adsorption tests in nitrogen.[3-5] The results discussed above indicate that tests conducted in nitrogen will probably produce different results than tests conducted in simulated flue gas. However, the effect of SO_2, HCl, and NO_x on adsorption capacity is probably sorbent dependent. Other sorbents may not be affected by these variables if the mercury adsorption mechanism is different.

Effect of Mercury Oxidation on Elemental Mercury Adsorption

During most of the elemental mercury adsorption tests, the percentage of inlet elemental mercury oxidized across the sorbent bed was determined at 100% breakthrough. The percent oxidation was determined using

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the tris solution method described earlier. The inlet elemental mercury stream was also checked with tris solution to verify that the inlet mercury was elemental mercury and not partially oxidized before contacting the sorbent. These measurements showed that the inlet mercury was generally less than 5% oxidized. Oxidation of elemental mercury across FGD carbon appears to be important to elemental mercury adsorption.

Figure 9 illustrates the elemental mercury adsorption capacity of the FGD carbon at 275 °F as a function of mercury oxidation across the carbon. Data are shown for baseline tests, variable SO_2 tests, and variable HCl tests. None of the data shown were collected with NO_x in the gas. The data indicate that as oxidation of elemental mercury across the carbon increased, the adsorption capacity increased. These data follow a relatively tight trend, considering the wide range of test conditions included.

As presented previously, HCl and SO_2 affect the equilibrium adsorption capacity for elemental mercury. The mechanism by which flue gas HCl and SO_2 affect mercury adsorption is not known; however, the effect of these flue gas components on elemental mercury adsorption appears to be related to changes in mercury oxidation. Figure 10 shows that as the flue gas HCl concentration increased (and to a lesser extent as the SO_2 concentration decreased), mercury oxidation across the carbon increased. These data and the data in Figure 9 suggest that the observed effect of HCl and SO_2 on the adsorption of elemental mercury was a result of changes in mercury oxidation.

The data in Figures 9 and 10 were obtained with no NO_x in the gas. Figure 10 shows that with no NO_x or HCl in the gas, no elemental mercury was oxidized. Tests in which NO_x was added to the gas resulted in nearly 100% oxidation, even with no HCl in the gas. Therefore, NO_x significantly affects oxidation of elemental mercury and appears to eliminate the dependence of oxidation on HCl. Since oxidation was close to 100% during each test with NO_x in the gas, Figure 9 suggests that the elemental mercury adsorption capacity should be very high (greater than 3,000 µg/g). However, as shown in Figure 7, the elemental mercury adsorption capacity varied from 250 µg/g to over 1,500 µg/g with NO_x in the gas. Therefore, NO_x appears to alter the effect of oxidation on elemental mercury adsorption capacity.

Besides the effect of NO_x, several other aspects of the observed elemental mercury oxidation/adsorption relationship are not understood. First, at constant baseline conditions, oxidation varied from 5% to 100%. No explanation for this variation in oxidation is available. Subtle differences in the carbon surface from test to test may be important. Second, the mercury species resulting from elemental mercury oxidation across the carbon are not known. Since HCl appears to be important to oxidation in the absence of NO_x (i.e., no oxidation occurs with no HCl), the oxidized species was likely mercuric chloride. However, with NO_x in the gas and no HCl, oxidation also occurred, which suggests other oxidized species may have been formed.

Sorbents other than FGD carbon have also been tested. In general, if a sorbent adsorbs a significant amount of elemental mercury, oxidation across the sorbent is high. However, high oxidation does not necessarily mean that adsorption occurs (i.e., some sorbents oxidize mercury without adsorbing it). All of these data suggest that elemental mercury adsorption, and probably mercuric chloride adsorption, occurs through a complex mechanism involving HCl, SO_2, NO_x, and possibly other flue gas components. Since variations in capacity (oxidation) have been observed in the lab while operating at the same conditions with the same sorbent, subtle differences in adsorption conditions and sorbent surface conditions may also be important.

CONCLUSIONS

The adsorption of elemental mercury and mercuric chloride by Norit Americas Darco FGD carbon has been studied

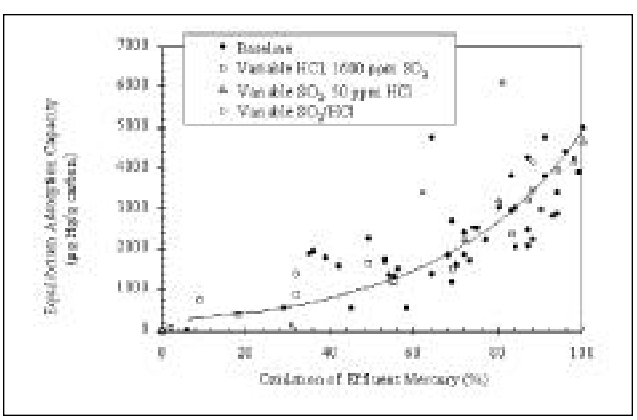

Figure 9. Effect of mercury oxidation on the FGD carbon Hg^0 adsorption capacity at 275 °F and various flue gas conditions.

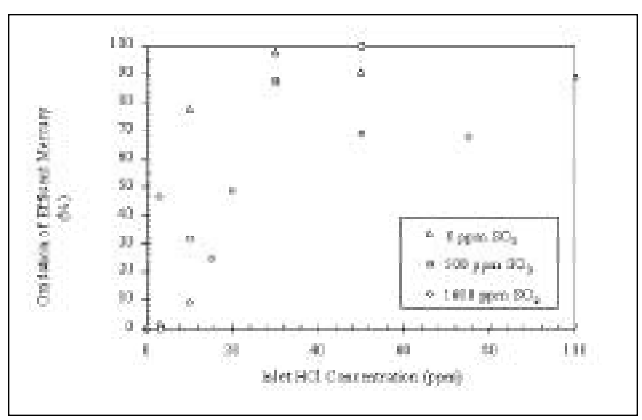

Figure 10. Effect of inlet HCl and SO_2 concentration on elemental mercury oxidation at 275 °F.

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over a wide range of conditions. The adsorption capacities for both types of mercury increased as the temperature decreased and as the inlet mercury concentration increased. These data are consistent with a physical adsorption mechanism. However, the adsorption capacities were also affected by flue gas composition, which suggests the mechanism is not purely physical. The FGD carbon adsorption capacity for both types of mercury increased as the SO_2 concentration decreased. Similarly, the FGD carbon adsorption capacity for both types of mercury increased as the HCl concentration increased; however, elemental mercury adsorption was affected more dramatically by HCl and SO_2 than mercuric chloride adsorption. The elemental mercury adsorption capacity increased from 0 µg/g at 0 ppm HCl to 2500 µg/g at 50 ppm HCl. After NO_x was added to the flue gas, the elemental mercury adsorption capacity decreased with 50 ppm HCl in the gas and increased with 0 ppm HCl in the gas. These results illustrate the importance of testing sorbents under realistic flue gas conditions. In addition, these results suggest that, contrary to previous results obtained in nitrogen,[3,5] activated carbon can remove elemental mercury from flue gas. Oxidation of elemental mercury across the carbon sorbent appears to be important to mercury adsorption, with high levels of oxidation needed to achieve high adsorption capacities. Oxidation, and therefore adsorption, is affected by flue gas composition and may also be affected by unknown factors such as sorbent surface variations.

Overall, the laboratory test results indicate that activated carbon has the potential for removing mercury from flue gas. The actual carbon amount needed for mercury removal via duct injection depends on the process conditions and removal efficiency required. The carbon amount required for a given removal efficiency can be determined directly by conducting injection studies in actual flue gas or estimated by combining laboratory adsorption data with mass transfer models.[16] Although carbon injection has the potential for removing mercury from flue gas, other issues potentially affect the overall effectiveness of this process and must be considered. Two important issues include the stability of mercury adsorbed to the carbon and the impact of carbon injection on operation of the downstream particulate removal device (ESP or baghouse) and on subsequent fly ash disposal.

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