TASK 2.1 – VALUE-ADDED SORBENT DEVELOPMENT

Final Report

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TABLE OF CONTENTS

LIST OF FIGURES	ii
LIST OF TABLES	iv
INTRODUCTION	1
BACKGROUND	2
RESULTS	8
Effects of SO ₂ and NO ₂ Concentration	8
Potential Oxidation Mechanisms	13
Effects of O ₂ and H ₂ O	15
Evaluation of Alternative Sorbents	21
Removal of Inorganic Material from Activated Carbons	29
Desorption of Mercury from the LAC Sorbent in Flue Gas	35
CONCLUSIONS AND RECOMMENDATIONS	37
REFERENCES	38
PROPRIETARY INFORMATION	Appendix A

LIST OF FIGURES

1	Schematic diagram of the mercury bench-scale system	3
2	Outlet mercury concentration as a function of time for a baseline test using three mercury CEMs	5
3	Outlet mercury concentration as a function of time for runs with 10 mg of an IAC at 325°F (163°C)	5
4	Outlet mercury concentration as a function of time and SO ₂ concentration	9
5	Relationship between adsorption capacity at 100% breakthrough and SO ₂ concentration	9
6	Outlet mercury as a function of time with intermittent SO ₂ injection	10
7	Outlet mercury concentration as a function of time and NO ₂ concentration	11
8	Relationship between adsorption capacity at 100% breakthrough and NO ₂ concentration	12
9	Outlet mercury as a function of time, with intermittent NO ₂ injection	13
10	Outlet mercury concentration as a function of time, without O ₂ in the simulated flue gas	16
11	Outlet mercury concentration as a function of time, without O ₂ or HCl in the simulated flue gas	16
12	Outlet mercury concentration as a function of time, with HF instead of HCl in the simulated flue gas	17
13	Outlet mercury concentration as a function of time, without H ₂ O in the simulated flue gas at 225°F	18
14	Outlet mercury concentration as a function of time, without H ₂ O in the simulated flue gas at 225°F	19
15	Outlet mercury concentration as a function of time, without H ₂ O in the simulated flue gas at 225°F	19
16	Outlet mercury as a function of time, with intermittent H ₂ O injection	20

LIST OF FIGURES (continued)

17	Outlet mercury concentration as a function of time, without H ₂ O in the simulated flue gas at 225°F	20
18	Outlet mercury, SO ₂ , and NO concentrations as a function of time	21
19	Outlet mercury and NO ₂ concentrations as a function of time	22
20	Outlet mercury concentration as a function of time for EERC SFS soot at 225°F	23
21	Outlet mercury concentration as a function of time for EERC SFS soot at 225°F	23
22	Outlet mercury concentration as a function of time for carbon black at 225°F	24
23	Outlet mercury concentration as a function of time for carbon black at 325°F	24
24	Outlet mercury concentration as a function of time for acetylene soot at 225°F	25
25	Outlet mercury concentration as a function of time for methane soot at 225°F	26
26	Outlet mercury concentration as a function of time for a gold-coated quartz filter at 225°F	26
27	Outlet mercury concentration as a function of time for a gold-coated quartz filter at 225°F with N ₂ carrier gas	27
28	Outlet mercury concentration as a function of time for a gold-coated quartz filter at 225°F with N ₂ carrier gas	27
29	Outlet mercury concentration as a function of time for a gold-coated quartz filter at 225°F with N ₂ carrier gas and HCl added later	28
30	Outlet mercury concentration as a function of time for EERC Sorbent 147-2 at 225°F	29
31	Outlet mercury concentration as a function of time for EERC Sorbent 149-1 at 225°F	30
32	Outlet mercury concentration as a function of time for the DI water-leached LAC carbon at 225°F	34
33	Outlet mercury concentration as a function of time for the DI water-, AA-, and HCl-leached LAC carbon at 225°F	34

LIST OF FIGURES (continued)

34	Outlet mercury concentration as a function of time for the DI water-, AA-, HCl-, HF-, and HNO ₃ -leached LAC carbon at 225°F	35
35	Total and elemental outlet mercury concentrations as a function of time, with elemental mercury injection later in the test	36
36	Total and elemental outlet mercury concentrations as a function of time	36
37	Outlet mercury concentration as a function of time, with Hg ⁰ injection discontinued	37

LIST OF TABLES

1	Baseline Flue Gas	4
2	XRF Analysis of the Baseline LAC Sorbent	32
3	XRF Analysis of the DI Water-, AA-, HCl-, and HF-Leached LAC Sorbent	32
4	Chemical Fractionation Results	33

TASK 2.1 – VALUE-ADDED SORBENT DEVELOPMENT

INTRODUCTION

Coal is now the primary source of anthropogenic mercury emissions in the United States, accounting for 46%, or 72 tons/year, of the total U.S. Environmental Protection Agency (EPA) estimated 158 tons/year.¹ Development of cost-effective mercury control for coal-fired boilers is a primary research need identified in the EPA Mercury Study Report to Congress.¹ During combustion of mercury-containing fuels such as coal, the mercury is completely volatilized and is not controlled by conventional particulate control devices unless the solid material effectively traps the mercury through sorption mechanisms. Typically, this does not occur naturally to a significant degree by the collected ash material. However, a promising approach for mercury control is the injection of an effective sorbent upstream of the particulate control device. Since the amount of mercury in the gas stream from coal combustion is usually in the range of 5 to 10 $\mu\text{g}/\text{m}^3$ (about 1 ppbv), only very small amounts of a sorbent may be necessary. A requirement is that the mercury be tightly bound in the sorbent, not desorbing upon exposure to ambient air or leaching under wet disposal conditions.

On a worldwide basis, the projected increase in coal usage over the next two decades in China, India, and Indonesia will dwarf the current U.S. coal consumption of 1 billion tons/year.² Therefore, in the United States, coal will be the dominant source of mercury emissions, and worldwide, coal may be the cause of significantly increased mercury emissions unless an effective control strategy is implemented. However, there is much uncertainty over the most technically sound and cost-effective approach for reducing mercury emissions from coal-fired boilers.

Several approaches are suggested for mercury control from coal-fired boilers, including enhancing the ability of wet scrubbers to retain mercury. However, many coal-fired boilers are not equipped with wet scrubbers. On the other hand, since almost all coal-fired boilers are equipped with either an electrostatic precipitator (ESP) or a baghouse, sorbent injection upstream of either an ESP or baghouse appears attractive, because it has the potential to control both Hg^0 and Hg^{2+} , would appear to be easy to retrofit, and would be applicable to both industrial and utility boilers.

Since mercury in the gas stream from coal combustion is present in only trace quantities, only very small amounts of sorbent may be necessary. If we assume a mercury concentration of 10 $\mu\text{g}/\text{m}^3$ and a sorbent-to-mercury mass ratio of 1000:1, the required sorbent loading is 10 mg/m^3 , which is only 0.1% to 0.2% of a typical dust loading of 5–10 g/m^3 (2.2–4.4 grains/scf). This amount of additional sorbent material in the ash would appear to be negligible and would not be expected to have an impact on control device performance or ash utilization.

Accomplishing effective mercury control with sorbent injection upstream of a particulate control device requires several critical steps:

1. Dispersion of the small sorbent particles and mixing with the flue gas must be adequate to ensure that all of the gas is effectively treated in the short residence time (typically a few seconds) between sorbent injection and particle collection.

2. Assuming the sorbent particles can be injected and dispersed adequately, a second critical step is the mass transfer by diffusion of the mercury from the bulk flue gas to the particle surface within the available residence time. The ideal case would be to achieve sufficient mass transfer in the duct and not depend on additional transfer within the collection device.
3. Once the mercury molecules reach the surface of a sorbent particle, they will not be trapped unless sorption can occur at a rate equal to the rate of mass transfer by diffusion to the particle surface. Analysis by Rostam-Abadi and others concluded that only a very small surface area would theoretically be required to trap the mercury.³ The implication is that reactive surface sites are much more important than the amount of surface area.
4. Assuming the sorbent has the capacity and reactivity to trap the mercury that reaches the sorbent particles, the final critical step is long-term stability of the sorbed mercury.

BACKGROUND

Extensive pilot-scale testing of carbon-based sorbents has previously been reported.^{4,5} Greater than 90% mercury capture was achieved under some conditions, but the level of control was found to be highly dependent on coal type and temperature. In addition, interference of the capture of some of the mercury by fly ash made interpretation of results difficult. While these coal combustion pilot-scale tests are probably the best indicator of sorbent performance in larger boilers because of the large number of independent variables, they do not lead to a good understanding of mechanisms. Therefore, a bench-scale test system was developed where independent control over parameters such as temperature, sorbent type, flue gas species, mercury species, and mercury concentration could be achieved. Figure 1 is a schematic of the bench-scale system which is composed of three subsystems: the mercury/gas delivery system, the fixed-bed system, and the mercury measurement system. Mass flow controllers are used to maintain constant gas flow for most of the flue gas constituents, and flowmeters are used for flow verification. The mercury and mercuric chloride permeation tubes are maintained at a constant temperature and continuously purged with nitrogen to ensure constant outlet mercury concentrations. The output from each of the permeation tubes is periodically verified by taking EPA Method 101A samples at the inlet of the fixed-bed system. A simulated flue gas was used for all tests, and the baseline gas mixture is presented in Table 1. The fixed bed is a Teflon-coated 2.5-inch-diameter EPA Method 5 dust-loading filter holder. A quartz filter loaded with sorbent makes up the actual fixed bed. The filters are uniformly coated with the sorbents by pulling a vacuum on the outlet side of the filter holder and feeding the sorbent at the inlet side. The fixed-bed assembly is maintained at the desired temperature inside an oven which can be controlled to $\pm 1^\circ\text{F}$. A slipstream of the flue gas can be taken at the inlet of the filter holder or after it passes through the fixed bed and is sent to the mercury continuous emission monitors (CEMs). The remainder of the flue gas is vented.

Figure 1. Schematic diagram of the mercury bench-scale system.

TABLE 1

Baseline Flue Gas, dry basis	
Gas Component	Concentrations
O ₂	6%
CO ₂	12%
SO ₂	1600 ppm
HCl	50 ppm
Hg ⁰ or HgCl ₂	15 µg/m ³
NO	300 pm
NO ₂	20 ppm
N ₂	Balance
H ₂ O	8%

The mercury measurement system consists of a conditioning/conversion system and several mercury CEMs. The system conditions the sample gas by removing moisture and acid gases. In order to speciate between elemental and oxidized forms of mercury, the system either reduces all forms of mercury to elemental mercury for a measurement of total mercury concentration, or removes the oxidized forms of mercury from the flue gas stream for a measurement of elemental mercury concentration. The oxidized forms are reduced by passing the flue gas through a SnCl₂ solution. The difference between the total mercury and Hg⁰ is assumed to be some form of Hg²⁺. Three different CEMs have been used to measure outlet mercury concentrations from the bench-scale system: a Semtech 2000, a PS Analytical Sir Galahad, and a Tekran Model Tekran 2537A. The Semtech 2000 mercury analyzer continuously measures the elemental mercury concentration and utilizes a Zeeman shift in the light source to eliminate interferences from SO₂, water vapor, and particulate. Both the PSA and Tekran measure mercury based on atomic fluorescence. Figure 2 is a plot of the outlet mercury concentration as a function of time, from one run where all three instruments were being used to measure the mercury concentration. The agreement between the instruments is very good. For most of the tests under this task, the results will be presented as mercury concentration (normalized to a percent of the inlet mercury concentration) as a function of time. Normalizing the data to the inlet concentration removed any variations in mercury concentration due to temperature swings or mass flow controller calibration drift. In addition to demonstrating the repeatability of the results, it is also important to establish that they are not mass transfer-limited. This is reflected either by an initial period of 100% capture for a given test or by 100% capture demonstrated with a more reactive sorbent, but with the same particle size and mass. Since the results shown in Figure 3 with an iodine-impregnated activated carbon (IAC) were repeatable and clearly demonstrated a time of 100% capture, we can conclude that for sorbent mass of 10 mg or greater with a similar particle-size distribution, the capture

Figure 2. Outlet mercury concentration as a function of time for a baseline test using three mercury CEMs.

Figure 3. Outlet mercury concentration (as a percentage of inlet mercury concentration) as a function of time for runs with 10 mg of an IAC at 325°F (163°F).

is not mass transfer-limited. Any breakthrough observed then is the result of a reactivity or capacity limit, which allows a relative comparison to be made for differing sorbents or gas composition. The comparative tests presented in this paper, using a commercially available lignite-based activated carbon (LAC) (Norit FGD, labeled LAC in figures), were performed with a sorbent mass of 150 mg, which is well beyond the range where mass transfer might be a concern. The LAC sorbent had a mass median diameter of 9 μm as measured by a Coulter counter.

The fixed-bed tests are not intended to simulate the conditions where a sorbent is injected continuously upstream of a particulate control device but they give a good indication of sorbent effectiveness, provided the exposure conditions are similar. For the test flow rate of 0.9 m^3/hr and a mercury concentration of 15 $\mu\text{g}/\text{m}^3$, 150 mg of sorbent would correspond to a sorbent-to-mercury ratio of 3700 at the end of 3 hours. This carbon-to-mercury ratio would be reasonable to use in a large boiler, although the goal would be to achieve effective mercury control with less carbon, in the range of 1000:1. If the mercury capture at the end of 3 hours is at least 80%, it is an indication that the sorbent would provide good mercury capture at a reasonable carbon-to-mercury ratio. However, if significant breakthrough is seen before 3 hours, the implication is that the sorbent would not provide good mercury capture at reasonable carbon-to-mercury ratios.

A critical factor for evaluating bench-scale sorbent tests is the composition and concentration of various flue gas components. Previous results⁵ indicate that the initial breakthrough capacity increases linearly with respect to mercury concentration. This may explain why under high mercury concentrations and long exposure times, very high capacities (in the 3% to 7% range) have been observed. It also suggests caution interpreting capacity data when mercury concentrations are significantly higher than the conditions for which the sorbent is targeted. To alleviate this concern, all of the simulated flue gas tests with the LAC were with a fairly low mercury concentration of approximately 15 $\mu\text{g}/\text{m}^3$, which is within the range observed for coal-fired boilers.

Recent results from bench-scale tests from several different groups indicate that sorbent capacity is highly dependent on temperature, mercury species, mercury concentration, and other flue gas constituents.⁴⁻¹⁵ The sorbent reactivity to mercury is also likely to be highly dependent on these variables, but may not be directly predictable from the capacity data. A logical starting point for sorbent development is to perform sorption experiments under simple conditions to provide insight as to the sorbent-mercury chemistry. This is the case for much of the sorbent capacity data in the literature that were generated with higher mercury concentrations than flue gas from coal combustion and over very long exposure times. In addition, when conditions do not include the reactive gases present in flue gas, the results may not be good indicators of the performance under real process conditions. Since complex interactions can occur at the sorbent surface between the mercury and various flue gas components, a safer approach is to test sorbents under realistic conditions that include all of the reactive gases known to be present in coal combustion flue gas.

Results at the EERC and elsewhere indicated that NO_x could have a significant influence on sorbent effectiveness.¹⁴ Subsequently, under Subtask 2.9 of the 1997–1998 U.S. Department of Energy (DOE) Cooperative Agreement, the EERC conducted a full-factorial-design experiment to determine the relative effects of SO_2 , HCl , NO , and NO_2 on the elemental mercury capture ability of a commercially available activated carbon.¹⁶ The following conclusions were made:

1. Without acid gases present, upon exposure to a baseline gas mixture of O₂, CO₂, N₂, and H₂O, the LAC sorbent provided only about 10%–20% mercury capture of Hg⁰ at 225 °F and no capture at 325 °F. Under these conditions, the LAC sorbent was completely ineffective at capturing elemental mercury.
2. When the sorbent was exposed to SO₂ in addition to the baseline gases, LAC sorbent capture improved slightly, but the LAC sorbent was still ineffective at capturing elemental mercury.
3. Upon exposure of the sorbent to HCl, NO, or NO₂ added one at a time to the baseline gases, the mercury capture improved to 90%–100% at 225 °F. Under these conditions, the LAC is a highly effective sorbent for capturing mercury.
4. A highly significant interaction between SO₂ and NO₂ caused a rapid breakthrough of mercury as well as conversion of the elemental mercury to a volatile oxidized form. This effect occurred at both 225 ° and 325 °F and with or without the presence of HCl and NO.
5. A brief test where CO was added to the other gases did not reveal any differences compared to similar conditions without CO.
6. HF alone added to the baseline gases can improve Hg⁰ capture, but when it was added to the other gases, no significant effect was observed.
7. NH₃ added to the other gases appears to delay and reduce the amount of mercury breakthrough.
8. Temperature in the range of 225 °–325 °F did not appear to be a dominant factor in the capture of Hg⁰ when any of the acid gases was present.

The results from these tests identified what appears to be a highly significant interaction between SO₂ and NO₂ that severely impairs the mercury capture ability of several carbon-based sorbents. These previous results are consistent with those reported by Carey and others that the presence of NO_x (when SO₂ and HCl are also present) has a negative effect on the Hg⁰ capture ability of activated carbon.¹⁷ Although Carey and others did not distinguish between the effects of NO and NO₂, since their NO_x consisted of both NO and NO₂, the implication is that a similar condition to that seen in the EERC tests leads to impaired mercury capture. These results also suggest that data collected without SO₂ and NO₂ are likely to be misleading if they are generalized to combustion systems where these gases are almost always present. This discovery may lead to a better explanation for the sporadic results observed in previous sorbent tests in combustion systems.

RESULTS

Effects of SO₂ and NO₂ Concentration

The identification of the interaction between SO₂ and NO₂ led to additional tests to determine the effects of SO₂ and NO₂ concentration on sorbent capacity. Results from these tests indicate the capacity of the sorbent at 100% breakthrough is dependent on the concentration of SO₂ and NO₂. As the concentration of each gas is increased, the capacity decreases. The previous full-factorial-design results with the LAC sorbent were achieved with either 1600 ppm or zero SO₂. These results showed that in all cases which included at least one other acid gas, the presence of SO₂ always had a negative effect on the mercury capture ability of the LAC sorbent compared to the corresponding condition without SO₂. To help understand possible mechanisms, additional tests were run in which the SO₂ concentration was varied from 0 to 3000 ppm, while the other gases were held constant. These included 15 µg/m³ Hg⁰, 50 ppm HCl, 300 ppm NO, 20 ppm NO₂, and the other baseline gases shown in Table 1. In all cases with SO₂ present, the breakthrough curves (Figure 4) indicate a time of nearly 100% capture followed by rapid breakthrough above the inlet concentration. These tests were stopped shortly after reaching the 100% breakthrough point, but from previous test results, we know that much of the mercury captured before breakthrough will desorb upon continued exposure to the flue gases and that the desorbed mercury is in oxidized form. Therefore, even though the mercury capacity increases with decreasing SO₂ concentration, this mercury may not be permanently retained unless the sorbent is removed from flue gas exposure. Since a reduction of SO₂ from 3000 to 100 ppm extended the initial breakthrough time from 1 hour to about 3.3 hours, a clear effect of SO₂ concentration is obvious. Figure 5 shows the relationship between adsorption capacity at 100% breakthrough and SO₂ concentration. The data show that even small amounts of SO₂ can significantly impair sorbent performance. Note that the capacity at 100% breakthrough is sometimes referred to as equilibrium capacity. However, in this case, equilibrium capacity is not an appropriate term since data show that the capacity will decrease upon further exposure to the flue gases. The test with no SO₂ (shown in Figure 4) indicates the contrasting excellent sorbent performance compared to the tests in which SO₂ was present. The test without SO₂ was continued for 29 hours with still no sign of breakthrough. This corresponds to a sorbent capacity of at least 2600 µg of Hg/g sorbent compared to 370 µg of Hg/g sorbent when only 100 ppm of SO₂ was present. Comparing mercury analysis of the spent sorbent after the 29 hours of exposure with the indicated mercury capture from the continuous analyzer resulted in a mass balance closure of 99% and provided independent verification of the high mercury capture for the condition without SO₂.

While the data show a clear, well-behaved dependence of the breakthrough curves on SO₂ concentration, they do not indicate the mechanism by which SO₂ affects sorbent performance. To help ascertain possible mechanisms, a test was conducted in which the SO₂ was turned off and on intermittently (Figure 6). At the start of this run, the sorbent on the filter was slightly disturbed as indicated by a somewhat lower pressure drop than normal. With HCl, NO, NO₂, and the baseline gases, the capture should have been nearly 100% early in the test compared to the approximately 85% capture observed. However, since the capture was steady for the first 2 hours, the decision was made to proceed, and the SO₂ was started at the 2-hour mark of the test. The immediate

Figure 4. Outlet mercury concentration as a function of time and SO₂ concentration.

Figure 5. Relationship between adsorption capacity at 100% breakthrough and SO₂ concentration.

Figure 6. Outlet mercury as a function of time with intermittent SO_2 injection.

result was an increase in mercury breakthrough to about 40% after 25 minutes of SO_2 injection. At this point, the SO_2 was again shut off, and the breakthrough decreased to about 30% and then remained constant for 2.5 hours while the SO_2 was off. At the 5-hour mark of the test, the SO_2 was started again, which resulted in breakthrough up to 50%. After 15 minutes of SO_2 addition, the SO_2 was again shut off, and the breakthrough dropped to 40% and remained constant while the SO_2 was off. At the 5.8-hour mark, starting the SO_2 again for about 40 minutes resulted in breakthrough up to 80%. Shutting the SO_2 off again for 40 minutes resulted in a reduction of the breakthrough to 65%, where it appeared to be steady. Finally, at the 7-hour mark, starting the SO_2 again for an hour resulted in breakthrough to 150% of the inlet level, indicating desorption of previously captured mercury. Similar to previous tests, the breakthrough mercury appeared to be predominantly in oxidized form.

These results along with previous observations shed some light as to possible mechanisms of the SO_2 interaction. Since SO_2 alone added to the baseline gases provided poor mercury capture and did not cause oxidation, it does not appear that SO_2 and mercury react directly together. Rather, since SO_2 addition to HCl , NO , or NO_2 to varying degrees always impaired mercury capture, the data suggest that the role of SO_2 may be to either occupy or poison active Hg(II) sorption sites, making them ineffective. The intermittent SO_2 injection data also support this mechanism, because in every case, adding more SO_2 resulted in immediate increased breakthrough, and shutting the SO_2 off again slightly increased capture but did not restore it to previous levels. This suggests that SO_2 has the effect of permanently destroying the mercury capture ability of the sorbent. However, the SO_2 also apparently has the ability to release previously captured mercury and cause desorption. If we assume that the mercury is initially captured through a chemisorption process, then the mercury must both be oxidized and bound to

the surface (as some unknown oxidized species). The role of the SO_2 then appears to be an effect on the binding site rather than impairing the oxidation of the mercury, since the oxidation occurs whether the mercury is captured or released and whether or not SO_2 is present. The possibility exists that the released form of mercury is a different oxidized species than the captured form and that SO_2 may play a role in the conversion of one oxidized form to another and subsequent release, but the SO_2 does not appear to cause the initial oxidation of the mercury.

Tests were run in which NO_2 was varied from 0 to 37 ppm, while the other gases were held constant at the same concentrations previously stated. The breakthrough graphs for these tests are shown in Figure 7. For the case without any NO_2 , capture was nearly 100% for up to 20 hours. However, with only 2.5 ppm NO_2 , initial breakthrough occurred at approximately 3.5 hours into the test and rapidly reached 100% breakthrough by 4.5 hours. Increasing the NO_2 up to 37 ppm resulted in 100% breakthrough after 1.5 hours of testing. All of the tests were stopped shortly after reaching 100% breakthrough, but the data clearly show that breakthrough occurred above the 100% mark, which indicates desorption of previously captured mercury. Figure 8 shows the relationship between the capacity at 100% breakthrough and the NO_2 concentration and clearly demonstrates that even very small amounts of NO_2 can significantly impair mercury capture compared to the case without any NO_2 . At 2.5 ppm, however, the NO_2 is still over 1000 times more concentrated than the approximately 2 ppb ($15 \mu\text{g}/\text{m}^3$) of mercury. The roles of NO_2 and SO_2 leading to the observed breakthrough phenomenon would appear to be very different. Where SO_2 by itself (added to the baseline gases) does not produce good mercury capture, NO_2 alone (added to the baseline gases) produces excellent capture, as shown in Figure 4. This suggests that the Hg^0 and NO_2 react heterogeneously to form a mercury–nitrogen compound that is retained by the sorbent. The high reactivity of Hg^0 with NO_2 on the carbon sorbent is consistent with earlier studies of Pierce and Noyes on glass surfaces.¹⁸

Figure 7. Outlet mercury concentration as a function of time and NO_2 concentration.

Figure 8. Relationship between adsorption capacity at 100% breakthrough and NO₂ concentration.

To further evaluate the interactions among Hg⁰, NO₂, and SO₂, tests were conducted with intermittent NO₂ addition and without HCl, but with constant NO and SO₂ (see Figure 9). Initially, 80% breakthrough was observed at the start of the test with only NO and SO₂. This is similar to results with NO and SO₂ that indicated high initial breakthrough and then better capture with time. After an initial 20 minutes, the NO₂ was started, which resulted in immediate improvement in mercury capture (from 20% capture at 20 minutes to over 90% capture at 40 minutes). At the 40-minute mark, the NO₂ was shut off again, and the capture decreased to 60% at 60 minutes into the test. Turning the NO₂ on again for another 20 minutes improved the capture to about 90%. At the 80-minute mark, the NO₂ was again shut off for 20 minutes, and capture decreased to 70%. Turning the NO₂ on at this point resulted in momentarily improved capture followed by a significant decrease in capture down to 50%. At 2 hours into the test, the NO₂ was again shut off which resulted in improved capture to about 75%. At 140 minutes into the test, turning on the NO₂ resulted in immediate decrease in mercury capture down to 20%, and the breakthrough mercury was in an oxidized form. These results suggest that the role of NO₂ is complex and can either enhance or impair mercury capture, depending on exposure time. Early in the test, the NO₂ clearly enhanced capture, but after about 1.5 hours of total exposure time to NO₂, the NO₂ caused rapid breakthrough.

The results reported here offer further evidence of the significant interaction between SO₂ and NO₂ that leads to rapid breakthrough of mercury from a carbon-based sorbent, desorption of previously captured mercury, and oxidation of the breakthrough mercury. The desorption of previously captured mercury is especially troublesome because it indicates that longer-term

Figure 9. Outlet mercury as a function of time, with intermittent NO_2 injection.

exposure of the sorbent to flue gas will not be acceptable whether the sorbent is in a separate fixed bed, is present on the residual dust cake of a fabric filter, or is on ESP plate deposits. In many cases with fabric filters, the dust may remain on the bags for several hours. Similarly, with ESPs, much of the dust that is released upon rapping is re-collected many times, and the dust may be exposed to flue gas for several hours before eventually reaching the hopper. Even in the hopper, the dust is continually exposed to flue gas, which could result in further desorption of previously captured mercury. With the given flue gas concentrations, the data indicate that good Hg^0 capture is achieved for about an hour. If the sorbent could then be removed from flue gas exposure, desorption of the captured mercury could possibly be avoided.

The SO_2 -induced release of oxidized mercury 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.

Potential Oxidation Mechanisms

A simple model for the reaction of mercury with the sorbent is that the adsorbed Hg^0 is rapidly oxidized at an oxidation site on the carbon surface to a bound Hg(II) species (Equation 1). In the absence of SO_2 , the major species formed would be mercuric oxide or a basic mercuric nitrate/oxide, which is stable at 150°C , even in the stream containing NO_2 . Oxide could be present

on the sorbent surface initially or could be produced from NO₂ as shown in Reaction. These stable products collect in sites adjacent to the oxidation site, and the activated carbon is able to retain relatively large amounts of these forms.

The role of SO₂ in the breakthrough mechanism is more difficult to understand. Since the oxidation of Hg⁰ is still 100% at breakthrough, it is unlikely that SO₂ is inhibiting the oxidation Reaction 1 and, therefore, the oxidation sites. It must also not inhibit Reactions 2 and 3, since SO₂ does not provide the electron sink for Hg⁰ oxidation and is not normally reduced on a carbon surface. Therefore, SO₂ 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. Being nucleophilic itself (Lewis base), the SO₂ should not interfere directly with nucleophilic sites on the carbon surface that bind Hg(II).

Thus a direct association involving binding of SO₂ to an intermediate-bound Hg(II) species seems more likely. In the presence of adsorbed SO₂, the Hg(II) may react to initially form mercuric sulfite or hydrosulfite (Reaction 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. Over time (1 hour), this form is oxidized to mercury sulfate or bisulfate which results in forming Hg–O bonds. These bonds will be more labile, and interconversion to the volatile mercuric nitrate hydrate occurs. Since no Hg⁰ 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 hour. Thus there seem to be other missing structural or reactivity factors that have not yet been considered. It is also difficult to explain the stepwise “sawtooth” behavior when the SO₂ concentration is intermittent.

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.

One hypothesis for the capacity of the LAC to hold mercury is that the basic surface aids in the conversion of the oxidized Hg(II) (Equation 4) to the basic mercuric nitrate oxide that is not volatile. In the flue gas containing SO₂, the basic surface will react not only with the oxidized mercury but also with SO₂ to form sulfite and sulfate. This will continue to occur until the surface is no longer basic, that is, until all the basic oxide binding sites are converted to sulfates. Now the Hg(II) that forms at the oxidation sites can only react with nitrate to form the volatile nitrate hydrate rather than the nonvolatile basic nitrate/oxide (Equation 8). This model predicts a rapid breakthrough when the basic sites are exhausted.

In addition the basic mercuric nitrate/oxide that formed previously will convert to volatile nitrates (Equation 9) because of the acid that accumulates from the hydration of SO₂. Thus even with Hg⁰ influent to the sorbent bed turned off, the previously sorbed mercury will desorb after SO₂ saturation occurs.

This model is also consistent with the experiment where the sorbent is pretreated with SO₂, in which case the basic sites have been all neutralized and are not able to convert Hg(II) to the nonvolatile basic oxide.

Effects of O₂ and H₂O

All of the reported tests so far have included O₂, CO₂, N₂, and H₂O as baseline gases. The possibility exists that one or more of these gases could also play a role in the mechanism. For example O₂ and H₂O may be necessary for the formation of sulfuric or nitric acid, either of which could affect the surface characteristics of the sorbent. O₂ could also be required to form several oxidized forms of mercury such as HgO or Hg₂SO₄. Two hydrate forms of nitrogen–mercury compounds are also possible (Hg[NO₃]₂ · H₂O and Hg[NO₃]₂ · ½H₂O) which may require the presence of both O₂ and H₂O. Since neither the surface-bound mercury species nor the oxidized mercury form that is desorbed is known, the mechanism by which SO₂ and NO₂ interact to produce the observed effects is unclear. Therefore, several tests were completed without O₂ or H₂O present in the flue gas to determine their effects on mercury capture by carbon sorbents.

A test was conducted with the full flue gas with the exception of O₂ at baseline conditions. Figure 10 is a plot of the outlet mercury concentration as a function of time. From the data, it appears there was no effect on reactivity or capacity when O₂ was absent from the flue gas mixture. As with the baseline tests, the elemental mercury was converted to an oxidized form across the sorbent. The test was repeated without HCl in the flue gas to determine if conversion of the elemental mercury to an oxidized form would still occur without the O₂ or HCl present (Figure 11). Initial breakthrough occurred roughly one half hour into each test which is almost an hour sooner than the previous test. As with baseline tests, the elemental mercury was almost all being converted to an oxidized form without O₂ or HCl present. This points to nitrogen–mercury compounds or sulfur–mercury compounds as the forms of oxidized mercury being formed in the

Figure 10. Outlet mercury concentration as a function of time, without O₂ in the simulated flue gas.

Figure 11. Outlet mercury concentration as a function of time, without O₂ or HCl in the simulated flue gas.

presence of SO_2 and NO_2 . of the elemental mercury to an oxidized form would still occur without the O_2 or HCl present (Figure 11). Initial breakthrough occurred roughly one half hour into each test which is almost an hour sooner than the previous test. As with baseline tests, the elemental mercury was almost all being converted to an oxidized form without O_2 or HCl present. This points to nitrogen–mercury compounds or sulfur–mercury compounds as the forms of oxidized mercury being formed in the presence of SO_2 and NO_2 .

One test was completed with 50 ppm HF instead of the normal 50 ppm HCl (Figure 12). Initial breakthrough still occurred a little over an hour into the run, but it continued to over 130% of the inlet concentration. It appears the HF may cause a more rapid desorption of the mercury once breakthrough has been reached.

Several tests were conducted with the full flue gas without moisture addition. The first three tests were conducted at 225°F . During the first test (Figure 13), the moisture was off for the first 6.5 hours, after which moisture (approximately 8%) was added to the flue gas with a corresponding decrease in makeup nitrogen. There was an immediate spike in the outlet mercury concentration which is unexplained at this time. Within 10 minutes, the mercury capture had returned to 90%, and within a half hour of adding moisture, initial breakthrough occurred. Complete breakthrough was reached within 1 hour of starting moisture injection, and the outlet mercury concentration peaked slightly over 120%, which indicates there may have been some offgassing of mercury. Measurement of the elemental mercury indicated most of the injected elemental mercury was converted to an oxidized form. During the second test at these conditions,

Figure 12. Outlet mercury concentration as a function of time, with HF instead of HCl in the simulated flue gas.

Figure 13. Outlet mercury concentration as a function of time, without H₂O in the simulated flue gas at 225°F.

the moisture was off for roughly the first 3 hours (see Figure 14). The mercury capture was essentially 100% over this time period, and after 3 hours, moisture was added to the flue gas.

Again there was an unexplained spike in the mercury concentration when the moisture was turned on. After 1 hour of running with moisture in the flue gas, the mercury removal returned to approximately 100%. After roughly 1.5 hours with moisture, initial breakthrough occurred, and proceeded to 100% in the next hour. The outlet mercury concentration peaked at slightly higher than 100% of the inlet elemental mercury concentration. As with the baseline tests, the mercury was nearly all converted to an oxidized form across the sorbent. The third test was different in that there was no spike in the mercury concentration when the moisture was turned on roughly 2.5 hours into the test (see Figure 15). All three mercury CEMs were used during this test, and none showed a spike in the mercury concentration. Again, there is no explanation for the peak or lack of peak in the mercury concentration. The mercury and flue gases were turned off and the filter sat overnight. The next day, mercury and full flue gas injection was started again (see Figure 16). The mercury capture was 100% for 15 minutes followed by rapid breakthrough to greater than 100% of the inlet concentration. After 1 hour, the moisture was turned off. The outlet mercury concentration dropped to roughly 20% and began to climb. After 2 hours with the moisture off, the outlet concentration had reached 80% of the inlet concentration and appeared to be lining out. Three tests without moisture injection were completed at 325°F (Figure 17). For these tests, there was no need to add moisture to the flue gas because initial breakthrough occurred roughly 3 hours into the test. It took roughly 3 hours to reach 100% breakthrough after initial breakthrough had been observed. Again, almost all of the elemental mercury was converted to an oxidized form across the sorbent bed. From these results, it appears moisture

Figure 14. Outlet mercury concentration as a function of time, without H₂O in the simulated flue gas at 225°F.

Figure 15. Outlet mercury concentration as a function of time, without H₂O in the simulated flue gas at 225°F.

Figure 16. Outlet mercury as a function of time, with intermittent H₂O injection.

Figure 17. Outlet mercury concentration as a function of time, without H₂O in the simulated flue gas at 225°F.

plays an important role in the SO_2 – NO_2 interaction that reduces a sorbent's ability to capture mercury.

To help gain an understanding of the interaction between the SO_2 , NO_2 and sorbent, the SO_2 , NO , and NO_2 were measured at the outlet of the fixed bed as a function of time during two baseline tests. The SO_2 concentration was measured with a Dupont Model CD400 SO_2 analyzer. The NO and NO_2 concentrations were measured with a Thermo Electron Model 10 chemiluminescent NO – NO_2 – NO_x analyzer. During the first test (see Figure 18), the SO_2 and NO were continuously measured for the duration of the test. The results indicate no significant change in either the SO_2 or the NO concentration. However, the concentrations of the SO_2 , NO , and NO_2 are all over 10,000 times greater than the Hg^0 concentration, and reactions are most likely taking place in the ppb range which would not be discernible with the instruments being used. For the second test (see Figure 19), the flue gas did not include NO , because the NO_2 concentration is determined by the difference between the NO and NO_x readings on the analyzer, and the high NO concentration would mask any changes in the NO_2 concentration. The results from this test show a steady decrease in the outlet concentration of NO_2 once initial breakthrough of mercury occurred. It is not known what chemistry resulted in a drop in NO_2 concentration, but it appears to be tied in with the mercury breakthrough.

Evaluation of Alternative Sorbents

Another objective of this test program was to test new sorbents that are likely candidates for rapid in-duct sorption of mercury. During a test with the high-temperature slagging furnace system (SFS) at the EERC (under a different program), a gas burner was inadvertently run fuel-rich, which produced high levels of CO and soot. Results from mercury sampling being conducted

Figure 18. Outlet mercury, SO_2 , and NO concentrations as a function of time.

Figure 19. Outlet mercury and NO₂ concentrations as a function of time.

during this time period indicated increased mercury capture across the system baghouse. It was suspected that the soot was acting as a mercury sorbent in the baghouse. Several bench-scale tests were conducted to evaluate the potential of different soots and carbon black for mercury capture. During a subsequent test on the slagging furnace, the burner was run fuel-rich to try to reproduce the previous conditions. Two filters were loaded with soot from this gas stream (similar to an EPA Method 5 sample) and evaluated on the bench-scale unit. Results from these two tests are plotted in Figures 20 and 21 (the appearance of the plot is different because a new data-logging program was used). The full simulated flue gas mix was injected along with elemental mercury. Both soot samples showed little mercury capture, but did show between 65% and 85% oxidation of the elemental mercury. This oxidized form of mercury may have been captured on the fly ash in the baghouse, resulting in the high mercury capture efficiency observed during the previous pilot-scale test. In order to evaluate a “pure” carbon, a sample of carbon black was purchased, and two tests were conducted to evaluate its potential for mercury capture. Carbon black is not an activated carbon and does not have the same surface area or active sites, but it does not contain any inorganic material. The results from the carbon black tests are plotted in Figures 22 and 23. Each sample was exposed to the full flue gas mixture with elemental mercury injection. The first test was conducted at 225 °F. During this test, roughly 20% mercury capture was observed at the beginning of the test. Breakthrough reached 100% in less than 30 minutes. After 1 hour of exposure, the carbon black was oxidizing roughly 50% of the elemental mercury being injected. At 325 °F, the carbon black showed no capacity for elemental mercury capture, but still oxidized roughly 50% of the elemental mercury injected. In addition to these tests, an acetylene soot and a methane soot generated in the lab were evaluated for the potential to capture mercury. The weight of the carbon on each filter was not determined, but the acetylene soot appeared to be at least 150 mg and the methane soot 10 mg. It was difficult to generate a sooty flame with the methane. Both bench-scale tests were run at 225 °F with the full

Figure 20. Outlet mercury concentration as a function of time for EERC SFS soot at 225°F.

Figure 21. Outlet mercury concentration as a function of time for EERC SFS soot at 225°F.

Figure 22. Outlet mercury concentration as a function of time for carbon black at 225°F.

Figure 23. Outlet mercury concentration as a function of time for carbon black at 325°F.

flue gas mixture and elemental mercury injection. Figure 24 plots the results from the test with the acetylene soot, which captured roughly 95% of the mercury at the start of the test, but broke through to 100% of the inlet concentration in less than an hour. The acetylene soot did oxidize almost 60% of the elemental mercury injected. The methane soot showed no capacity for capture or oxidation of the elemental mercury; perhaps a larger quantity is needed (Figure 25).

Several quartz fiber filters were sputter-coated with less than 10 mg of gold and evaluated for their ability to capture mercury in a simulated flue gas. The results from the first test are plotted in Figure 26. The gold showed almost no capacity for mercury capture under full flue gas conditions. It was suspected that the HCl had poisoned the gold. However, the gold did oxidize roughly 95% of the elemental mercury. The same filter was used for the next test with only N₂ and Hg⁰ injection; the results are plotted in Figure 27. Breakthrough was immediate, but only to 50%, and after an hour the gold was oxidizing all of the elemental mercury injected. It was thought that the HCl had permanently poisoned the filter; therefore, a second filter was evaluated with N₂ and Hg⁰ injection at 225°F (see Figure 28). This time, the gold did capture 100% of the mercury for a period of time. After 30 minutes, the mercury began to breakthrough and reached 100% after roughly 45 minutes. However, the gold was still oxidizing the elemental mercury at greater than 95%. The first three tests were completed within 6 hours, and it was thought that there may be enough residual HCl in the lines to poison the second filter. The system was allowed to purge over the weekend with only N₂ injection. In addition, the filters were desorbed in an oven at 400°C over the weekend.

Figure 24. Outlet mercury concentration as a function of time for acetylene soot at 225°F.

Figure 25. Outlet mercury concentration as a function of time for methane soot at 225°F.

Figure 26. Outlet mercury concentration as a function of time for a gold-coated quartz filter at 225°F.

Figure 27. Outlet mercury concentration as a function of time for a gold-coated quartz filter at 225°F with N₂ carrier gas

Figure 28. Outlet mercury concentration as a function of time for a gold-coated quartz filter at 225°F with N₂ carrier gas.

Figure 29 is a plot of the results from the fourth test with the gold filters. With only N_2 and Hg^0 injection, the gold captured 100% of the elemental mercury before initial breakthrough occurred 2 hours into the test. After 4 hours, the elemental mercury concentration at the outlet of the filter was the same as the total concentration, indicating no oxidation across the filter. After briefly measuring the inlet total mercury concentration, HCl injection (@50 ppm) was started, and sampling was switched to elemental mercury at the filter outlet. The effect of the HCl was immediate and dramatic, roughly 95% of the elemental mercury was oxidized across the filter. After injecting HCl for 45 minutes, sampling was switched to the outlet total mercury concentration which spiked to over 200% of the inlet concentration. This indicates that the HCl was also causing the captured mercury to desorb as oxidized mercury. After an hour and fifteen minutes, the HCl injection was discontinued, and sampling was switched to elemental mercury at the outlet of the filter. Two hours after discontinuing the HCl injection, the elemental mercury broke through and continued to climb for the next 2 hours before lining out at roughly 75% of the inlet concentration. After 20 hours, the outlet concentration of elemental mercury had reached roughly 80% of the inlet concentration and appeared to still be climbing. At the end of the test, the inlet and outlet total mercury concentrations were measured and found to be the same. This indicates that the gold was still poisoned and that roughly 20% of the elemental mercury was being oxidized. In general the gold did not work well as a reference sorbent with flue gas injection. However, when only elemental mercury and N_2 were injected, the gold captured a significant amount of mercury. The capacity at initial breakthrough was roughly $12,000 \mu g \text{ Hg/g}$ of gold (assuming 2.5 mg of gold on the filter). This is over 100 times greater than the capacity at initial breakthrough observed for the LAC sorbent under full flue gas conditions. Based on the results, gold should be considered as a potential catalyst for oxidizing elemental mercury, instead of looking at it as a potential sorbent material.

Figure 29. Outlet mercury concentration as a function of time for a gold-coated quartz filter at 225°F with N_2 carrier gas and HCl added later.

Removal of Inorganic Material from Activated Carbons

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 granular form of the LAC carbon is also available commercially (Norit® granular activated carbon [GAC] 1240), but in contrast to the powdered flue gas desulfurization (FGD) sorbent, it is acid-washed to remove some of the inorganic material in the carbon. In previous studies in air, the GAC 1240 carbon was not 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 lower capacity for retaining oxidized mercury.

The sorption test (see Figure 30) performed with the acid-washed GAC 1240 in a synthetic flue gas stream showed that the activity was excellent at the start, and breakthrough was not observed for 1.7 hours, compared to 1 hour for LAC. The extended breakthrough results from this experiment are, therefore, not consistent with the concept that basic inorganic material on the surface aids in mercury sorption. In fact, the better capacity may be explained by the cleaning effect of the acid in removing basic salts that are plugging the carbon pores or covering active sites on the surface. It is also possible that the washing procedure removed mineral matter only from the mesopores. This should improve the internal mass transfer, but still leave significant amounts of basic sites available on the micropore surface for converting the Hg(II) to nonvolatile basic salts.

Figure 30. Outlet mercury concentration as a function of time for EERC Sorbent 147-2 at 225°F.

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 (see Figure 31) 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 hour, 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.

As in the test with GAC 1240, the positive effect of removal of inorganic material from the pores or carbon surfaces, exposing more surface and, therefore, more oxidation sites, may overcome the negative effect expected for removal of the basic sites. Indeed there may be other binding sites on the carbon surface as well as the basic inorganic sites that would have been removed. The failure of the experiments to demonstrate decreased capacity does not reject basic surface hypothesis.

To further evaluate the role of inorganic material in the capture and oxidation of mercury, a series of carbons (using the base LAC carbon) was prepared using the chemical fractionation method. Chemical fractionation is usually employed as a method of determining the inorganic matter present in coals, chars, or activated carbons as an alternative to the conventional ashing method that concentrates the inorganics and determines the total amounts present. The more informative chemical fractionation method uses a sequential extraction or leaching of the

Figure 31. Outlet mercury concentration as a function of time for EERC Sorbent 149-1 at 225°F.

inorganic components with increasingly severe reagents. Thus the chemical fractionation method yields information on the association of the inorganics with the carbon structure and how easily the inorganics might participate in chemical reactions. Several variations of the fractionation scheme are available, but the one used with the LAC sorbent was a sequence with ammonium acetate, hydrochloric acid, and other reagents.¹⁸ Since it is not possible to selectively remove all of a certain element in each step, this procedure was used to reduce the inorganic species present in each successive sample. The carbon was stirred overnight in each successive reagent solution, filtered, and washed with deionized (DI) water until neutral. A portion of the carbon at each stage was dried and reactivated by heating to 750°C, and the reactivated carbon was submitted for Hg sorption tests. The remaining portion of carbon at each step was continued through the series of treatments. Each of the steps is described in detail below.

Deionized Water – Removes water-soluble salts, including sodium oxide and hydroxide. Sodium and other alkali metals attached to aluminosilicates and organic colloids are not usually removed.

Ammonium Acetate (1 M) – Removes ion-exchangeable cations. This includes ion-exchangeable sodium as well as other alkaline earth metals (Mg, Ca, Sr) that are bonded to carboxylate groups. Some of the ions bonded to aluminosilicates are removed, and some dissolution of carbonates and sulfates may occur.

Hydrochloric Acid (1 M) – Removes a variety of metal ions by digesting oxides and carbonates. Aluminosilicates are partially digested, as are pyrites in coals. Most of the alkaline earth metals are solubilized by HCl. Some of the Al, Fe, and Ti are removed from the lattice structures in aluminosilicates. Silicon, potassium, and titanium are not appreciably removed by HCl.

Hydrofluoric Acid (10%) – Removes Al, Ti, and Fe by digesting silicates and aluminosilicates. Glassy silicates are more easily dissolved, but quartz is not.

Nitric acid (1 M) – Continues digestion of pyrites and some insoluble salts. Pyrites are not likely to be present in activated carbons, so it is not yet clear what residual minerals are removed from activated carbons in this step.

The x-ray fluorescence (XRF) analysis for the baseline LAC is presented in Table 2, and the XRF analysis for the DI water, ammonium acetate, HCL, and HF-leached sample is presented in Table 3. The chemical fractionation results are presented in Table 4. The chemical fractionation results indicate that the deionized water removed some of the calcium, sodium, and sulfur, most likely in the form of salts. The calcium, sodium, and sulfur that remained in the ash were probably tied up in carbonates, silicates, and pyrite. The ammonium acetate removed the remaining ion-exchangeable inorganics which included roughly half of the magnesium. The HCl leaching appeared to remove most of the iron which may have been pyrite, some of the titanium, and the remaining minerals in the form of carbonates. The HF leaching should have removed the remaining inorganic material. However, the ash content of the carbon after this leaching step was still over 13%. The HF removed over 50% of the aluminum, sodium, and potassium, but only 27% of the silicon and 26% of the phosphorus. The majority of the ash remaining at this point is silica and may be in the form of quartz, which the HF would not remove.

TABLE 2

XRF Analysis of the Baseline LAC Sorbent

Oxides, wt%	(a)	(b)	(c)	Elemental, wt%	(d)	(e)
SiO ₂	36.4	36.3	40.3	Si	30.5	32.8
Al ₂ O ₃	15.4	15.3	17.0	Al	14.5	15.7
Fe ₂ O ₃	11.5	11.5	12.7	Fe	14.4	15.5
TiO ₂	1.4	1.4	1.5	Ti	1.5	1.6
P ₂ O ₅	0.1	0.1	0.1	P	0.0	0.1
CaO	19.5	19.5	21.6	Ca	25.0	26.8
MgO	5.0	5.0	5.5	Mg	5.4	5.8
Na ₂ O	0.6	0.6	0.7	Na	0.8	0.9
K ₂ O	0.6	0.6	0.7	K	0.9	1.0
SO ₃	9.9	9.8	—	S	7.1	—

(a) Oxide concentrations (wt%) on an ash basis.

(b) Oxide concentrations normalized to a closure of 100%.

(c) Oxide concentrations renormalized to a SO₃-free basis.

(d) Elemental concentrations (wt%) on an ash basis.

(e) Elemental concentrations renormalized to a S-free basis.

TABLE 3

XRF Analysis of the DI Water-, AA-, HCl-, HF-Leached LAC Sorbent

Oxides, wt%	(a)	(b)	(c)	Elemental wt%	(d)	(e)
SiO ₂	71.4	77.3	77.9	Si	72.6	73.1
Al ₂ O ₃	9.2	10.0	10.0	Al	10.6	10.7
Fe ₂ O ₃	6.4	6.9	7.0	Fe	9.7	9.8
TiO ₂	1.8	1.9	2.0	Ti	2.3	2.4
P ₂ O ₅	0.1	0.1	0.1	P	0.1	0.1
CaO	1.0	1.1	1.1	Ca	1.6	1.6
MgO	1.4	1.5	1.5	Mg	1.9	1.9
Na ₂ O	0.1	0.1	0.1	Na	0.2	0.2
K ₂ O	0.2	0.2	0.2	K	0.4	0.4
SO ₃	0.7	0.8	—	S	0.6	—

(a) Oxide concentrations (wt%) on an ash basis.

(b) Oxide concentrations normalized to a closure of 100%.

(c) Oxide concentrations renormalized to a SO₃-free basis.

(d) Elemental concentrations (wt%) on an ash basis.

(e) Elemental concentrations renormalized to a S-free basis.

TABLE 4

Chemical Fractionation Results

Element	Initial, ppm	As Oxides, ppm	Removed by H ₂ O, %	Removed by NH ₄ OAc, %	Removed by HCl, %	Removed by HF, %	Remaining, %
Silicon	62,772	134,273	-0	0	-2	27	76
Aluminum	29,959	56,613	1	-1	24	52	23
Iron	29,606	42,330	6	-1	68	5	21
Titanium	3019	5037	5	6	31	7	51
Phosphorus	100	229	1	-1	17	26	56
Calcium	51,388	71,912	23	22	51	3	2
Magnesium	11,051	18,321	4	47	31	7	11
Sodium	1630	2196	11	-6	33	56	7
Potassium	1902	2292	-6	-49	70	75	10
Sulfur	14,538	36,344	30	10	58	-2	3

The results from the fixed-bed tests with the leached samples are presented in Figures 32–34. The breakthrough curve for the sample leached in DI water and reactivated is similar to the baseline tests with the LAC sorbent with the exception of the level of oxidation of the elemental mercury (see Figure 32). In the baseline tests, roughly 90%–95% of the elemental mercury is oxidized, but the DI-washed carbon only oxidizes 80% of the elemental mercury. When sampling was switched to the inlet at the end of this test, the mercury concentration spiked to almost 200% of the nominal inlet concentration of 15 µg/m³. It may be that a different form of oxidized mercury is being formed and captured somewhere in the sampling system, and when it is exposed to flue gas that has not passed over the sorbent, it desorbs. Results from later tests indicate the spike does eventually decrease to the nominal inlet concentration. At the start of the second test (DI and ammonium acetate-leached sample), the pressure drop across the filter indicated the dust cake may have been disturbed, and the results are not valid. This test was not repeated because of time constraints and the results from the next test. Figure 33 plots the results from the test with the sample leached with DI water, ammonium acetate, and HCl and indicates the only effect of leaching was to prolong breakthrough. Breakthrough did not reach 100% until 4 hours into the test, and roughly 90% of the mercury was being oxidized. Also with this test, the inlet mercury concentration spiked to almost 200% of the nominal inlet concentration. The initial pressure drop across the filter for the test with the DI water-, ammonium acetate- (AA), HCl-, and HF-leached sample indicated the dust cake was disturbed, and the results are not valid. This test was not repeated because of time constraints and the results from the last test which indicate little effect due to the leaching (see Figure 34). The overall results from this series of tests indicate that the ability of a sorbent to capture elemental mercury or oxidize it is not dependent on the mineral matter it contains, but on the active sites on the carbon. Tests with a pure activated carbon such as activated carbon black or an activated carbon derived from a tar pitch would provide important information in this area.

Figure 32. Outlet mercury concentration as a function of time for the DI water-leached LAC carbon at 225°F.

Figure 33. Outlet mercury concentration as a function of time for the DI water-, AA-, and HCl-leached LAC carbon at 225°F.

Figure 34. Outlet mercury concentration as a function of time for the DI water-, AA-, HCl-, HF-, and HNO₃-leached LAC carbon at 225°F.

Desorption of Mercury from the LAC Sorbent in Flue Gas

To help better understand the mechanism of mercury capture and oxidation, three repeats of a test where the LAC was exposed to the simulated flue gas for 2 hours before adding elemental mercury were completed. The tests gave very repeatable results, each showing immediate breakthrough when the mercury injection was initiated. Figure 35 is a plot of the results from one of the tests. Both Semtech CEMs were used during this test, one to measure the total mercury concentration and one to measure the elemental mercury concentration. The plots show that the oxidation of the elemental mercury is immediate, with no breakthrough of the elemental mercury. Figure 36 plots the results from a baseline test (LAC @225°F with full flue gas and Hg⁰ injection) where the total and elemental mercury concentrations were measured with separate Semtech instruments for the duration of the test. The results from this test also indicate that there is no elemental mercury breakthrough, but that it is oxidized once breakthrough occurs.

To demonstrate the desorption of mercury from the sorbent, several tests were completed where a baseline LAC test was started, but the elemental mercury injection was discontinued after roughly 60%–70% breakthrough had been achieved (see Figure 37). Mercury breakthrough had reached slightly more than 60% after 1.5 hours of exposure to the flue gas. At this point, Hg⁰ injection was discontinued. The total outlet concentration continued to decrease for the next hour, reaching roughly 38% of the inlet concentration. At this point, sampling was switched to the outlet elemental mercury, which showed that most of the mercury being desorbed was oxidized. The elemental mercury injection was then restarted to get an inlet concentration reading. The results from these tests confirm the need to remove the sorbent from the gas stream before it begins to desorb mercury.

Figure 35. Total and elemental outlet mercury concentrations as a function of time with elemental mercury injection later in the test.

Figure 36. Total and elemental mercury concentrations as a function of time.

Figure 37. Outlet mercury concentration as a function of time, with Hg^0 injection discontinued.

CONCLUSIONS AND RECOMMENDATIONS

A number of different areas of mercury capture with sorbent were evaluated under this test program, and some significant results were found:

1. The capacity of the LAC sorbent at initial breakthrough is inversely proportional to the concentrations of SO_2 and NO_2 . Concentrations as low as 100 ppm SO_2 and 2.5 ppm NO_2 affected the capacity at breakthrough. When SO_2 and NO concentrations were measured at the outlet of the fixed bed, no change in concentration was observed for the tests. However, when the NO_2 concentration was measured at the outlet of the fixed bed, the concentration began to decrease when initial breakthrough of the mercury occurred.
2. Tests where either the SO_2 or NO_2 were intermittently turned on and off showed that SO_2 always had a negative effect on the ability of the LAC sorbent to capture elemental mercury. However, the NO_2 initially improves the elemental mercury capture, but after roughly 1½ hours, its injection contributed to the breakthrough of mercury.
3. The lack of oxygen in the flue gas stream did not affect the capture of elemental mercury or the conversion to an oxidized form.
4. The capacity of the LAC at initial breakthrough was increased when moisture was not included in the simulated flue gas. At a fixed-bed temperature of 225°F, breakthrough had not occur after 6 hours of exposure to the simulated flue gas (without H_2O) with

elemental mercury. At 325°F, initial breakthrough occurred after 3 hours exposure to the simulated flue gas without H₂O injection.

5. When the HCl in the flue gas was replaced with HF, initial breakthrough was not affected, but the rate of breakthrough was increased.
6. Soots generated under three different conditions showed some reactivity to mercury capture and oxidation.
7. Gold sputtered on quartz filters captured elemental mercury in the presence of nitrogen, but oxidized the elemental mercury in the presence of the simulated flue gas.
8. Tests were conducted where the mercury injection was not initiated until the LAC sorbent had been exposed to the simulated flue gas for 2 hours. Breakthrough was immediate once elemental mercury injection was initiated, indicating the active sites are affected or occupied without mercury present.
9. When mercury injection was discontinued after roughly 60% breakthrough, the mercury already captured desorbed as an oxidized form of mercury.
10. Samples of the baseline LAC sorbent were leached to remove different portions of the inorganic material. Results indicate the inorganic material in the sorbent plays no part in the capacity or the oxidation of elemental mercury.

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