

# **SUBTASK 2.9 – SORBENT DEVELOPMENT FOR MERCURY CONTROL**

Final Report

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## **SUBTASK 2.9 – SORBENT DEVELOPMENT FOR MERCURY CONTROL**

### **1.0 INTRODUCTION**

The U.S. Environmental Protection Agency (EPA) draft Mercury Study Report to Congress (1) estimated anthropogenic mercury emissions to be 253 tons/yr in the United States, with the majority (216 tons/yr) from combustion sources. The three main combustion sources listed were coal (72 tons/yr), medical waste incinerators (65 tons/yr), and municipal waste combustors (64 tons/yr). The emissions from both medical waste incinerators and municipal waste combustors were recently regulated, which, together with the reduction of mercury in consumer products such as batteries and fluorescent lights, has already reduced the emissions from these sources, as stated in the final EPA Mercury Report to Congress (2). EPA now estimates total point-source mercury emissions to be 158 tons/yr, with coal remaining at 72 tons/yr, while medical waste incinerators are down to 16 tons/yr and municipal waste combustors are at 30 tons/yr.

Coal is now the primary source of anthropogenic mercury emissions in the United States, accounting for 46%. In addition, the use of coal in the United States has been increasing every year and passed the 1-billion-ton-per-year mark for the first time in 1997 (3). At the current rate of increase, coal consumption would reach 1.4 billion tons annually by the year 2020 (see Figure 1-1). 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 level (see Figure 1-2). 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, much uncertainty remains over the most technically sound and cost-effective approach for reducing mercury emissions from coal-fired boilers, and a number of critical research needs will have to be met to develop better control (2).

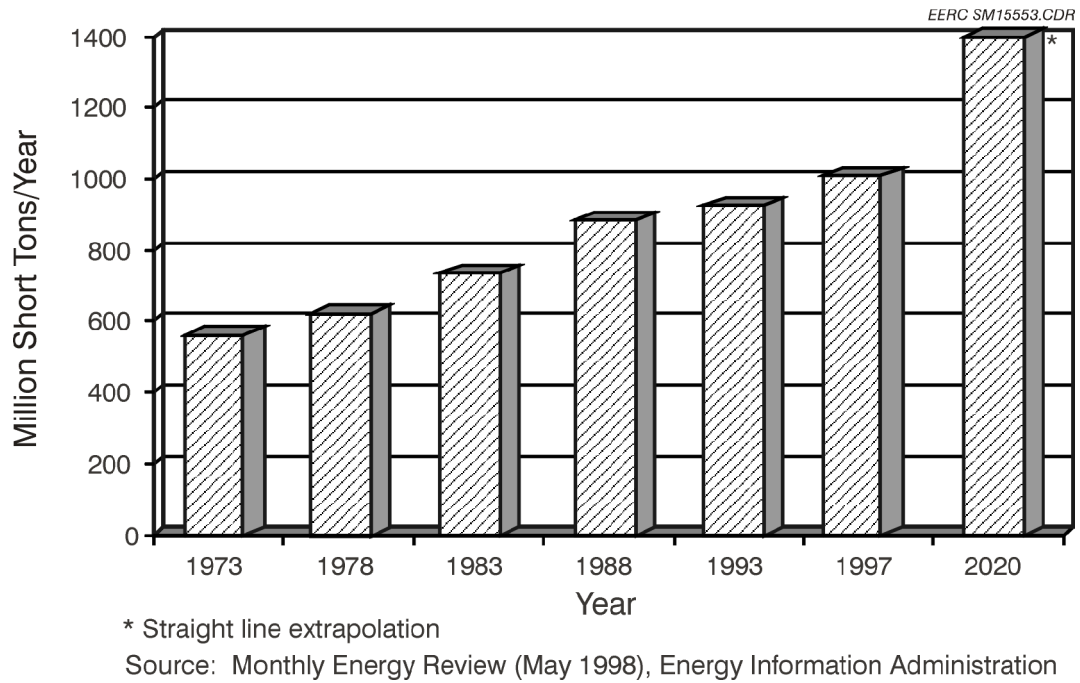


Figure 1-1. U.S. coal consumption.

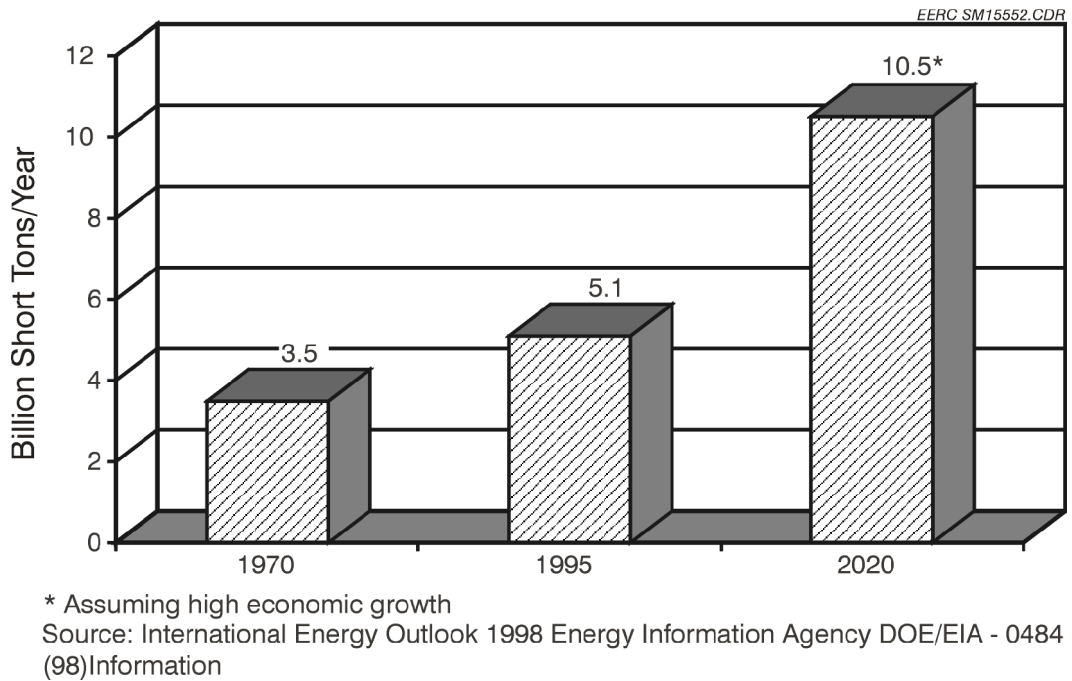


Figure 1-2. World coal consumption.

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 elemental mercury ( $\text{Hg}^0$ ) and mercury in oxidized forms ( $\text{Hg}^{2+}$ ), 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, usually in the range of 5 to 10  $\mu\text{g}/\text{m}^3$  (about 1 ppbv), 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  $\text{mg}/\text{m}^3$ , which is only 0.1% to 0.2% of a typical dust loading of 5–10  $\text{g}/\text{m}^3$  (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:

- 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.
- 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.

- Once the mercury molecules reach the surface of a sorbent particle, they will not be trapped unless sorption occurs at a rate that is greater than or equal to the rate of mass transfer by diffusion to the particle surface. Based on analysis of the pore-size distribution of activated carbons, Rostam-Abadi and others concluded that diffusion within a sorbent is unlikely to be a rate-limiting step and that only a very small surface area would theoretically be required to trap the mercury (4). The implication is that reactive surface sites are much more important than the amount of surface area.
- 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.

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 (5–13). 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. 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. Mercury capture in sorbents is already known to be affected by SO<sub>2</sub>, NO<sub>x</sub>, HCl, and O<sub>2</sub>. In addition, suspicion is that CO, Cl<sub>2</sub>, and HF may also play a role. Until the sorption mechanisms and kinetics of reactions with other gases are known, predicting capacity and reactivity will be very difficult.

Carbon-based sorbents are promising for mercury control in applications where the temperature is less than 225°F (107°C) and where mercury concentrations are high. In coal applications where the air heater outlet temperature is between 275° and 350°F (135° and

177°C), a sorbent has not been found that is effective for various coals and will collect both  $\text{Hg}^0$  and  $\text{Hg}^{2+}$ . A better understanding of the science of sorption of  $\text{Hg}^0$  as well as oxidized species on various surfaces is required to design more effective control technologies. Of particular importance in identifying and elucidating these mercury–surface interactions is to learn the chemisorption as well as desorption mechanisms that apply in the moderate temperature range (225°–600°F [107°C–316°C]). At these temperatures, those materials that depend on physical adsorption for removing mercury species from the gas phase are not suitable, since the physisorption process becomes dramatically less effective with increasing temperature. At elevated temperatures, mercury species are better removed through chemical fixation. However, the mechanism by which  $\text{Hg}^0$ , or even  $\text{Hg}^{2+}$ , becomes chemisorbed to a carbon has not been fully recognized or understood.

## 2.0 OBJECTIVES AND SCOPE OF WORK

The overall project goal is to develop an understanding of sorbent chemistry and capitalize on that development to produce more effective mercury sorbents targeted at specific applications for both coal combustion and incinerators. Specific objectives include the following:

- Understand the mechanism for capture of  $\text{Hg}^0$  by carbon, including carbon-catalyzed oxidation of  $\text{Hg}^0$ .
- Understand capture mechanisms for  $\text{HgCl}_2$ .
- Develop improved mercury sorbents targeted at  $\text{Hg}^0$  and  $\text{HgCl}_2$ .
- Determine the mercury capture effectiveness of newly developed sorbents and commercially available sorbents for both  $\text{Hg}^0$  and  $\text{HgCl}_2$ .
- Determine the stability of the captured mercury for the most promising sorbents.

The scope of work for Task 2.9 included three main activities. The first consisted of bench-scale development of novel sorbents in an attempt to achieve better mercury capture than commercially available carbons. Extensive evaluation of pretreatment with various nitrogen compounds and acids along with thermal processing was completed. The various preparations were then tested for mercury capture in a granular bed with air. These results are presented in Section 3.0.

The second activity also consisted of bench-scale evaluation of commercial and EERC-developed sorbents, but with a different test system that had the capability to more closely simulate real flue gas conditions in terms of the mercury concentration, other gases present, and sorbent-to-mercury ratio. Extensive testing was completed under carefully controlled conditions

where the mercury breakthrough was monitored continuously and sorbents were evaluated for oxidation as well as capture of mercury. Results are presented in Section 4.0.

The third main activity consisted of exploratory methods to test the stability of mercury in spent sorbents. Initial tests were conducted with a thermogravimetric analysis (TGA) system, and later tests were completed with a desorption furnace coupled to a cold-vapor atomic absorption (CVAA) analyzer. Some samples were also evaluated for leaching potential. These results are presented in Section 5.0.

### 3.0 BENCH-SCALE SORBENT DEVELOPMENT

#### 3.1 Novel Catalytic Carbon Sorbents

The Energy & Environmental Research Center (EERC) developed a new mercury vapor carbon sorbent technology in a 1995 U.S. Department of Energy (DOE) Cooperative Agreement project. The goal of the project was to find methods for converting lignite coal to activated carbons with high mercury sorption capability (98% to 100% of the influent mercury concentration at 302°F [150°C]). The mercury sorption activities of catalytic carbons that had been prepared by various techniques in earlier projects were compared with commercial (Centaur) catalytic carbon and other activated carbons. The hypothesis being tested was that the catalytic carbons would catalyze the reaction of mercury with oxygen in the air to form oxidized mercury forms with low vapor pressure that would remain on the carbon sorbent. The mercury sorption studies were performed in an air stream containing mercury vapor using a fixed tubular bed of granular activated carbons or chars, mostly at temperatures of 302°F (150°C). Elemental mercury in the effluent gas was determined by a continuous vapor monitor so that breakthrough curves could be plotted.

In this earlier work, four technologies were discovered for production of exceptionally active nitrogen-containing carbons for mercury sorption. Two of these methods involve washing the coal with an inexpensive reagent prior to carbonization. The reagents are diazabicyclooctane and sulfamic acid. Another method involves addition of amines and sugars to the intermediate char, which is subsequently carbonized. The fourth method involves treating a steam-activated carbon with a nitrogen-containing polymer that forms a highly reactive catalyst when the coated carbon is recarbonized. The treated carbon catalyzes the conversion of  $\text{Hg}^0$  vapor in air to  $\text{Hg}^{2+}$  species that are strongly bound to the carbon. The conversion is promoted by the addition of mineral acid, such as sulfuric acid, to the activated carbon.

To understand the nature of the carbon surface and the remarkable catalytic activity of these nitrogenous carbon sorbents, in the current project we used a set of specific nitrogen heterocyclic

precursors to produce highly active carbons that can substantiate the model or models for the edge structure. Thus a set of nitrogen heterocyclic and acyclic precursors was impregnated and carbonized. In the current project, substantially faster air flow rates were used to better discriminate the activities of the various sorbent preparations. In addition to the studies with the novel granular catalytic carbons, fine particles of the catalytic carbons were prepared by similar methods, and these were tested in a large matrix of gas compositions, including the reactive acidic components of flue gas.

The types of N-carbon precursors selected for the verification program include high-molecular-weight polymers (pitches) prepared by condensation of the following heterocyclic compounds:

- One nitrogen in a six-membered ring (aromatic)
  - Quinoline
  - Isoquinoline
  - Phenanthridine
  
- Two nitrogens in a six-membered ring (aromatic)
  - Quinoxaline (1,4)
  - Phenazine (1,4)
  
- One nitrogen in a five-membered ring (aromatic)
  - Carbazole
  - Indole

The precursor six-membered-ring heterocyclics were converted to polymeric forms by heating with aluminum chloride at 536°F (280°C) for 4 hours. The polymer was extracted with 0.1N hydrochloric acid to remove aluminum chloride and with methanol to remove unreacted starting material. The five-membered-ring heterocyclic (indole) was heated without the aluminum chloride, since the strong Lewis acid is not required for the condensation polymerization of the

more reactive indole. The methanol-insoluble pitches were dried in vacuo and further separated into benzene-soluble and benzene-insoluble fractions or ethylenediamine-soluble and -insoluble fractions. The soluble fractions were impregnated into an inactive carbon support and re-carbonized in nitrogen at 1382°F (750°C). Two different processing methods were investigated for the re-carbonization/activation. The insoluble fractions were also carbonized at 1382°F (750°C). These products were tested for mercury sorption in granular form in a tubular reactor at 302°F (150°C).

Other carbon sorbents were prepared by impregnating various sugar-amine combinations that were likely to yield nitrogenous condensation products on heating. These impregnated carbons were re-carbonized/activated by heating in nitrogen at 1382°F (750°C). Earlier versions of this type of nitrogenous carbon were active in the slow-flow-rate tests performed in earlier projects.

A series of tests were also performed with carbons prepared with nitrogenous polymer coating at different concentrations of coating polymers, different polymer compositions, different re-carbonization methods, and different precursor carbon sizes. These results were compared with those from a commercial nitrogenous carbon (Centaur from Calgon) and an uncoated carbon also available from Calgon (Calgon F400). In this report, the unmodified Calgon F400 carbon is referred to as “Calgon,” and the Calgon Centaur carbon is referred to as “Centaur.”

### ***3.1.1 Preparation of Nitrogen-Containing Pitches***

Nitrogen-containing pitches were prepared according to the procedure reported by Mochida and others (14). Preparations are summarized in Table 3-1. As an example, a mixture of isoquinoline (26 g, 0.2 mole), anhydrous aluminum(III) chloride (13.3 g, 0.25 mole), and nitrobenzene (7.68 g, 0.06 mole) was placed in a two-necked flask equipped with a reflux condenser and a nitrogen inlet tube. The mixture was refluxed at 536°F (280°C) for 4 hours. The residue was extracted with 0.1N hydrochloric acid and filtered, washed with 0.1N hydrochloric acid, and further extracted with methanol to remove any monomer. The methanol-insoluble pitch

was dried in vacuo. The yield of the pitch was 49%. A portion of the N-pitches was carbonized using Procedure A or B in a nitrogen stream, as described in the next section.

TABLE 3-1

Preparation of Nitrogen-Containing Pitches

Substrate (g, mole)	Catalyst (g, mole)	Cocatalyst (g, mole)	Temp., °F (°C)	Time, hr	Yield, g (%)	Soluble (%)
Indole <sup>1</sup> (10, 0.77)	None	None	487 (253)	4	9.6 (96)	Methanol (100)
Quinoxaline <sup>1</sup> (26, 0.2)	AlCl <sub>3</sub> (13.3, 0.1)	Nitrobenzene (0.06)	437 (225)	4	13.5 (52)	EDA <sup>2</sup>
Carbazole (16.7, 0.1)	AlCl <sub>3</sub> (27.7, 0.2)	Nitrobenzene (3.6, 0.03)	77 (25)	12	59.1 (92)	EDA
Isoquinoline (26, 0.2)	AlCl <sub>3</sub> (13.3, 0.1)	Nitrobenzene (7.68, 0.06)	536 (280)	4	6.5 (25)	EDA

<sup>1</sup> Reactions carried out in 300-mL Parr reactor.

<sup>2</sup> Ethylenediamine.

Several modifications of the method were used for the quinoline polymerization. In addition to the flask method, a Parr reactor was used for the reaction, and temperatures and reaction times were varied. The yields are reported in Table 3-2. In this procedure, 64.5 g of

TABLE 3-2

Yields of Nitrogen-Containing Pitches

Quinoline, g	AlCl <sub>3</sub> , g	Temp., °F (°C)	Time, hr	Yield, g (%)	Ethanol-S, g (%)	Ethanol-I, g (%)
64.5	33.25	536 (280)	12	57.7 (89)	—	—
64.5 <sup>1</sup>	33.25	347 (175)	12	0 (0)	—	—
64.5 <sup>1</sup>	33.25	536 (280)	12	59.1 (92)	—	—
64.5 <sup>1</sup>	33.25	536 (280)	4	56.8 (88)	7.3 <sup>2</sup> (73)	2.7 (27)

<sup>1</sup> Reactions carried out in 300-mL Parr reactor.

<sup>2</sup> 10 g of pitch was extracted with ethanol.

quinoline and 33.25 g of aluminum(III) chloride was placed in an 3000-mL Parr autoclave. The reactor was sealed under nitrogen and heated at 536°F (280°C) for 4 hours. The hard black mass was extracted with 0.1N hydrochloric acid followed by extraction with methanol and drying in vacuo. To determine the solubility of the polymer, a 10-g portion of this black mass was extracted with 100 mL of ethanol. Extraction data showed that 27 wt% of the product dissolved in ethanol.

Similar reactions of phenanthridine and phenazine gave viscous liquids, which solidified upon cooling. Extraction with 0.1N hydrochloric acid resulted in complete dissolution of the product. No pitch was formed under these conditions.

### ***3.1.2 Preparation of Nitrogen-Impregnated Carbons***

Granular activated carbon (Calgon F400, 20 × 60) obtained from Calgon Corporation, PO Box 717, Pittsburgh, PA 15230, was impregnated with various nitrogen-containing polymers and pitches using the incipient wetness method. For the fine-particle sorbent studies in flue gas compositions, the Calgon carbon was ground to -400-mesh size prior to impregnation.

The nitrogen polymers (polyvinyl pyrrolidone [PVP], etc.) are the same as those investigated earlier and are commercially available. The impregnations and recarbonizations were repeated to investigate the effects of precursor concentration, activation procedure, and sorbent particle size on the mercury sorption. The alanine–dextrose precursors were also previously studied, and the related piperazine–dextrose and polyethylenimine–dextrose precursors were prepared for comparison.

Carbon preparations are summarized in Table 3-3. In a typical method, the desired amount of polymer or pitch dissolved in an appropriate solvent was added to the carbon slowly with thorough mixing (incipient wetness method). The paste was dried to remove solvent. The dried product was packed in a stainless steel tube and activated in a gentle flow of nitrogen using one of the following two activation techniques:

TABLE 3-3

Preparation of Nitrogen-Impregnated Carbons						
Carbon (g, size)	N-Precursor (g)	Sugar (g)	Solvent	N-Precursor, wt %	Procedure	Activation Procedure
Calgon (100, 20 × 50)	PVP (5)	–	Methanol	5	Incipient wetness	B
Calgon (10, –400)	PVP (0.5)	–	Methanol	5	Incipient wetness	B
Calgon (25, 20 × 50)	PVP (0.5)	–	Methanol	2	Incipient wetness	B
Calgon (25, 20 × 50)	PVP (2.5)	–	Methanol	10	Incipient wetness	B
Calgon (25, 20 × 50)	PVP (2.5)	–	Methanol	10	Incipient wetness	A
Calgon 25, 20 × 50)	PVPcoVA <sup>1</sup> (1.25)	–	Methanol	5	Incipient wetness	A
Calgon (25, 20 × 50)	PVPcoAA <sup>2</sup> (1.25)	–	Methanol	5	Incipient wetness	A
Calgon (25, 20 × 50)	Piperazine (1.0)	Dextrose (2.0)	Water	4	Incipient wetness	A
Calgon (25, 20 × 50)	Sulfamic acid (1.25)	–	Water	5	Incipient wetness	A
Calgon (25, 20 × 50)	Alanine (1.0)	Dextrose (2.0)	Water	4	Incipient wetness	A
Calgon (5, –400)	Alanine (0.20)	Dextrose (0.4)	Water	4	Incipient wetness	A
Calgon (25, 20 × 50)	Polyethylenimine (1.0)	–	Water	4	Incipient wetness	A
Calgon (25, 20 × 50)	Polyethylenimine (1.0)	Dextrose (2.0)	Water	4	Incipient wetness	A
Calgon (55, 20 × 50)	Quinoline pitch <sup>3</sup> (2.75)	–	Ethanol		Incipient wetness	A
Calgon (5, 20 × 50)	Quinoline pitch <sup>3</sup> (0.25)	–	EDA	5	Incipient wetness	B
Calgon (5, 20 × 50)	Indole pitch (0.25)	–	Methanol	5	Incipient wetness	B
Calgon (5, 20 × 50)	Quinoxaline pitch (0.25)	–	EDA	5	Incipient wetness	B

<sup>1</sup> Poly(1-vinylpyrrolidone-*co*-vinyl acetate).<sup>2</sup> Poly(1-vinylpyrrolidone-*co*-acrylic acid).<sup>3</sup> Pitch was prepared by heating in a Parr reactor. A portion of the activated carbon was ground to –400-mesh particles.

*Procedure A:*

77°–752°F (25°–400°C) @ 10°C/min

Held at 752°F (400°C) for 30 min

752°–1382°F (400°–750°C) @ 20°C/min

Held at 1382°F (750°C) for 4 hr

*Procedure B:*

77°–437°F (25°–225°C) @ 15°C/min

437°–518°F (225°–270°C) @ 1°C/min

Held at 518°F (270°C) for 1 hr

Cooled to room temperature

Heated to 1382°F (750°C) @ 15°C/min

Held at 1382°F (750°C) for 4 hr

### ***3.1.3 Preparation of Nitrogen-Containing Carbons from Insoluble Fractions***

Insoluble fractions of pitches described in Table 3-1 were converted into nitrogen-containing carbons by heating in a gentle flow of nitrogen using Procedure B as described above. The resulting carbons were porous glassy materials, similar to cokes.

### ***3.1.4 Acid Impregnation of Carbons***

Acid impregnation of the nitrogen-containing carbons prepared from carbonization of the nitrogen-containing pitches or nitrogen-containing pitches impregnated on Calgon carbon was accomplished by adding 5 wt% sulfuric acid by the incipient wetness method. The acid-impregnated carbons were dried at 230°F (110°C).

### 3.2 Metal Oxide Sorbents

While much of the focus for mercury sorbent development has been on various forms of carbon, the fact that significant amounts of mercury can be captured by low-carbon fly ash suggests that other ash components may provide active sorption sites for mercury. Owing to the oxidizing activity of transition metal oxides, the metal oxide components in ash were hypothesized to be agents mainly responsible for mercury sorption observed with certain fly ashes. In order to test the hypothesis, a previous project screened a number of metal oxides for mercury vapor sorption at 302°–662°F (150°–350°C) in a fixed-bed tubular reactor. Elemental mercury concentrations of 300 µg/m<sup>3</sup> in an air or nitrogen stream were used at flow rates of 100 cm<sup>3</sup>/min. The gas stream was monitored for mercury breakthrough with an EPM CVAA analyzer. These studies have shown that although transition metal oxides are relatively poor or mediocre sorbents for elemental mercury vapor at ambient temperatures, some are highly effective at temperatures in the range of 302°–662°F (150°–350°C). Since the mercury can be desorbed from the metal oxide at much higher temperatures, this approach provides an ideal mercury sorbent for certain gas treatment systems. The sorption of the mercury on the transition metal oxide was equally effective in both nitrogen and air streams; thus the mercury sorption does not require catalytic activation of oxygen, but rather involves a direct oxidation of mercury to mercury oxides. This contrasts with the behavior of carbon sorbents that use other mechanisms for capturing elemental mercury. The behavior is consistent, however, with the reactive sorption found in the sulfurized and iodized carbons, which also do not require oxygen for sorption to occur. In these sorbents, the mercury reacts with the highly reactive sulfur or iodine complex to form mercury sulfide or iodide, respectively.

Among the transition metal oxides investigated, manganese oxide was found to be most effective. In this project, a number of manganese oxide-based sorbents were prepared and tested both in the granular and powder forms at high flow rates. Of special interest were inexpensive forms such as the naturally occurring ores. Other studies involved evaluation of the effects of supports on the manganese oxides.

Manganese oxide ores (manganite, psilomelane, pyrolusite) were ground to 20- × 50-mesh particle size. Manganese oxide was also generated by heating hydrated manganese nitrate at 392°F (200°C) in air. The calcined oxide was ground to 20- × 50-mesh particle size. These ores were also impregnated with 5% sulfuric or nitric acid as needed using the incipient wetness method. Impregnated ores were dried at 230°F (110°C) to remove solvent (water). These air-dried samples were also calcined in air overnight at 392°F (200°C).

Manganese oxide was impregnated on CaO and sodium montmorillonite (basic supports), acid-washed montmorillonite (K-10, acidic support), and granular silica (neutral support). Impregnation was carried out by adding an aqueous solution of hydrated manganese nitrate to the support. Resulting product was dried at 230°F (110°C) to remove the solvent, calcined at 392°F (200°C) to decompose manganese nitrate, and dried and ground to 20- × 50-mesh particle size.

### **3.3 Test Procedure for Preliminary Screening of Sorbents for Mercury Uptake in Air**

Packed-bed tests in air flow were conducted on the granular carbon products to evaluate the effects of surface modification. The mercury sorption was tested in a flowthrough tubular reactor system equipped with continuous on-line mercury analysis of the effluent from the bed to determine mercury removal rates as a function of time. Integration of breakthrough volumes allows determination of mercury sorption per unit mass carbon (mg/g).

Air with an elemental mercury concentration of 56 or 81  $\mu\text{g}/\text{m}^3$  was passed through the heated (302°F [150°C]) reactor. This concentration was obtained by placing the mercury source in a double-jacketed glass condenser and heating it to the desired temperature by pumping hot oil through the condenser.

A glass tube with constriction and glass wool plug was used as the reactor for the mercury sorption tests. A gas chromatography (GC) oven was used as a constant-temperature (302°F [150°C]) chamber for the reactor. Before the actual test, a blank test was run. The glass tube was

attached to the source and the mercury analyzer by Teflon tubes. Mercury vapors diluted with air (2000–4000 cm<sup>3</sup>/min or 4–8 scfh measured at the detector end) were passed through the tube. The mercury analyzer (EPM continuous vapor monitor) was interfaced to a Hydra and personal computer to record the data.

For the packed-bed tests, impregnated activated carbons (20- × 60-mesh size) were used. In an actual test, about 0.2–0.6 g of sorbent was packed in the glass tube and held by glass wool plugs on both ends. The tests were conducted under the following conditions:

Source temperature = 212°F (100°C)

Oven temperature = 302°F (150°C)

Air flow = 4 or 8 scfh (2000 or 4000 cm<sup>3</sup>/min)

Packed-bed tests were conducted to evaluate the mercuric chloride sorption efficiency of sorbents developed at the EERC. For the packed-bed tests, impregnated activated carbon (20- × 60-mesh size) was used. In an actual test, about 0.2–0.4 g of sorbent was packed in the glass tube and held by glass wool plugs on both ends. The tests were conducted under the following conditions:

Source = mercuric chloride

Source temperature = 212°F (100°C)

Oven temperature = 302°F (150°C)

Air flow = 4 scfh ( 2000 cm<sup>3</sup>/min)

Testing of granular forms of EERC-developed carbon and manganese oxide-based sorbent for activity with mercuric chloride was also performed. Manganese oxide-impregnated gamma-alumina and PVP-impregnated carbon were used as sorbents to investigate sorption of mercury chloride species. Continuous measurements of the mercuric chloride in the gas effluent from the sorbent bed were determined by including a SnCl<sub>2</sub> trap and drying system to convert the mercury chloride in the effluent to elemental mercury so that its UV absorption could be

monitored by the EPM monitor. The conversion was partial at high  $\text{HgCl}_2$  concentrations, but the method was usable for breakthrough determination. At  $302^\circ\text{F}$  ( $150^\circ\text{C}$ ), manganese oxide supported on alumina sorbent in granular form was very effective (100% removal for several hours) for mercury chloride sorption, as it was for the elemental mercury sorption. The nature of the sorption at high temperature is likely to be a chemisorption mechanism, where the mercury bonds to the oxygen atoms on the metal oxide surface to form stable mixed oxide, and chlorine is partially or completely transferred to a metal atom.

The procedure for the mercury chloride sorption tests was similar to that used for elemental mercury sorption tests. The mercury chloride sorption capacity of sorbents was tested in a flowthrough system equipped with continuous on-line mercury analysis. The air, with mercuric chloride (equivalent to elemental mercury) concentration of  $26\ \mu\text{g}/\text{m}^3$ , was analyzed for breakthrough to allow determination of mercury sorption per unit of mass carbon ( $\text{mg}/\text{g}$ ).

For the mercury chloride adsorption tests, a GC oven was used as a constant-temperature chamber. The source was placed in a double-jacketed glass condenser and heated to the desired temperature by pumping hot oil through the condenser. A glass tube with constriction was used for mercury sorption tests. Before the actual tests, a blank test was run. The glass tube was placed in the oven and attached to the mercuric chloride source and the mercury analyzer by Teflon tubes. The glass tube was heated to  $302^\circ\text{F}$  ( $150^\circ\text{C}$ ), and then mercuric chloride vapors diluted with air ( $2000\ \text{cm}^3/\text{min}$  or  $4\ \text{scfh}$  measured at the detector end) were passed through the tube.

The calibration of the mercuric chloride-diluted air was carried out by using EPA Method 101-A. The calibration tests were run in duplicate for 1 hour using 500 mL of potassium permanganate solution. The mean amount of mercury was  $41.3\ \mu\text{g}/\text{hr}$ .

Reduction of mercuric chloride was accomplished by passing the mercuric chloride-containing air through an aqueous solution containing 10% stannous chloride, 10% hydrochloric acid, and a small amount of tin metal to convert the mercury chloride into elemental mercury.

Reduced mercury was passed through drying tubes containing soda-lime and magnesium perchlorate. The dried airstream was passed through the elemental mercury analyzer.

### **3.4 Activity Comparisons for Granular Carbons in Air**

The sorption-testing results are listed in the following tables. The initial mercury concentration in the effluent from the sorbent bed is divided by the concentration of mercury in the blank (no sorbent present), converted to a percentage, and subtracted from 100% to give the percentage of mercury removed. For a good sorbent, the percentage removal decreases very slowly with time. In most tests, the experiment was continued until the percentage removal had decreased to 50%. The times for this 50% breakthrough to occur are listed for each sorbent in the tables. Each test was concluded at a different time or removal percentage (as recorded in the tables).

#### ***3.4.1 Effect of Flow Rate***

Preliminary testing (Table 3-4) was conducted at a gas flow velocity of 2000 cm<sup>3</sup>/min (4 scfh). Results with the sulfuric acid-impregnated commercial N-carbon (Centaur) indicated a fairly long breakthrough time; that is, at 292 min, the sorbent was still removing 97% of the mercury. Similar good results were obtained with the manganese oxide sorbent. Thus at the flow rate used, all of the mercury was reacting, and rate limits could not be determined at the beginning of the experiment. Even at long reaction times, little discrimination between sorbents would have been observed. Thus faster air flow rates are needed to move the sorption off 100%.

Similar tests were then conducted at 4000 cm<sup>3</sup>/min (8 scfh), which gave partial breakthroughs for the sorbents and allowed comparisons in their kinetic activities. Now the acid-impregnated Centaur carbon exhibited 100% mercury removal initially, but decreased to 50% at 305 min. The test was concluded at 306 min. Later repetition of this experiment gave 575 min for

TABLE 3-4

Effect of Flow Rate on Mercury Sorption Reactivity 302°F (150°C)

File Name	Sorbent	Air Flow, scfh	Hg Conc., μg/m <sup>3</sup>	Percent Hg Removed (time, min)		
				Initial	50%	Final
RKS3	None	4 <sup>1</sup>	56	0	<1	–
RKS7	None	8 <sup>2</sup>	77	77	<1	–
RKS4	Centaur 5% H <sub>2</sub> SO <sub>4</sub>	4 <sup>1</sup>	77	100 (0)	50 (<292)	97 (292)
RKS8	Centaur 5% H <sub>2</sub> SO <sub>4</sub>	8 <sup>2</sup>	77	100 (0)	50 (305)	49 (306)
RKS5	Al <sub>2</sub> O <sub>3</sub> /MnO <sub>2</sub>	4 <sup>1</sup>	77	100 (0)	50 (>894)	93 (894)
RKS9	Al <sub>2</sub> O <sub>3</sub> /MnO <sub>2</sub>	8 <sup>2</sup>	77	96 (0)	50 (60)	35 (183)

<sup>1</sup> Air flow = 4 scfh (2000 cm<sup>3</sup>/min), source temperature = 176°F (80°C).

<sup>2</sup> Air flow = 8 scfh (4000 cm<sup>3</sup>/min), source temperature = 212°F (100°C).

50% breakthrough. Extension of the experiment time showed a further decrease to 38% removal after 1221 min. It is likely that at these fast flow rates, channeling could be an important factor and could cause a large variation in the observed rates and capacities. Nevertheless, the initial rates for both of the experiments with this sorbent are 100% removal.

Mercury sorption activity of manganese oxide–alumina sorbent was also determined for the two flow rates (Table 3-4). At the higher flow rate, breakthrough occurred much sooner; however, mercury capture was reasonably good. These data show that acid-impregnated Centaur is a much better sorbent for mercury than manganese oxide–alumina.

### 3.4.2 Effect of Acid Impregnation

Previous data at slow flow rates showed that the commercial Centaur carbon and other catalytic carbons exhibited significantly higher capture rates when 5 wt% sulfuric acid was impregnated into the carbon before testing. Results in the higher flow system in this project confirm the high activity of the acid-impregnated Centaur. The sulfuric acid impregnation also has a considerable beneficial effect on the mercury sorption activity of the unmodified Calgon carbon (Table 3-5). This is an inexpensive noncatalytic carbon with medium surface area. The test conducted without sulfuric acid addition required only 1 min for 50% breakthrough and decreased further to 8% removal at 165 min. The corresponding test with the acid-impregnated Calgon carbon required 171 min for 50% breakthrough and decreased to 38% removal after 304 min.

TABLE 3-5

Effect of Acid Impregnation on Mercury Sorption Reactivity of the Sorbents

File Name	Sorbent (g)	H <sub>2</sub> SO <sub>4</sub> Impreg.	Hg Conc., µg/m <sup>3</sup>	Percent Hg Removed (time, min)		
				Initial	50%	Final
RKS13	Calgon (0.20)	None	77	80 (0)	50 (1)	8 (165)
RKS11	Calgon (0.20)	5%	77	100 (0)	50 (171)	38 (304)
RKS8	Centaur (0.20)	5%	77	100 (0)	50 (305)	49 (306)

<sup>1</sup> Air flow = 8 scfh (4000 cm<sup>3</sup>/min), source temperature = 212°F (100°C), oven temperature = 302°F (150°C).

### 3.4.3 Effect of Nitrogen Precursors in Catalytic Carbons

Numerous tests were performed at 4000 cm<sup>3</sup>/min (8 scfh) with carbons prepared by impregnation of various nitrogen compounds, polymers, and pitches into a base Calgon carbon. These conditions gave partial breakthroughs for the sorbents and allowed comparisons of their kinetic activities.

Carbons prepared by impregnation of sulfamic acid into the Calgon base carbon and recarbonization gave 50% breakthrough at 226 min, decreasing to 39% sorption at 1303 min. These results are significantly better than those observed with the unmodified Calgon carbon but poorer than the Centaur catalytic carbon (see Table 3-6).

TABLE 3-6  
Sorbent Testing of Surface-Treated Carbons for Mercury Removal<sup>1</sup>

File Name	Carbon	Recarb. Method	H <sub>2</sub> SO <sub>4</sub> Impreg.	Hg Conc., µg/m <sup>3</sup>	Percent Hg Removed (time, min)			
					Initial	50%	Final	Breakthrough
RKS32	Blank		–	81	0 (0)	<1	–	bt <sup>1</sup>
RKS11	Calgon		5%	81	100 (0)	50 (171)	38 (304)	bt
RKS8	Centaur		5%	81	100 (0)	50 (305)	49 (306)	bt
RKS17	Centaur		5%	81	100 (0)	50 (575)	38 (1221)	bt
RKS18	Calgon/2% sulfamic acid	A	5%	81	92 (0)	50 (226)	39 (1303)	bt
RKS21	Calgon/5% PVP	A	5%	81	94 (0)	50 (2217)	42 (2574)	bt
RKS20	Calgon/10% PVP	A	5%	81	88 (0)	50 (150)	55 (253)	bt
RKS72	Calgon/10% PVP	B	5%	81	90 (0)	50 (300)	65 (1098)	bt
RKS29a	Calgon/5% PVP	B	5%	81	98 (0)	50 (3315)	43 (4010)	bt
RKS33	Calgon/2% PVP	B	5%	81	79 (0)	50 (312)	49 (320)	bt
RKS34	Calgon/10% PVP	B	5%	81	85 (0)	50 (424)	30 (1114)	bt
RKS12	Calgon/5% PVPcoVA	A	5%	81	90 (0)	50 (84)	39 (180)	bt
RKS14	Calgon/5% PVPcoAA	A	5%	81	90 (0)	50 (76)	29 (362)	bt
RKS28	Calgon/5% PVPcoAA	B	5%	81	98 (0)	50 (223)	50 (223)	bt
RKS25	Calgon/polyethylenimine	A	5%	81	88 (0)	50 (373)	22 (1147)	bt
RKS26	Calgon/dextrose/ polyethylenimine	A	5%	81	88 (0)	50 (51)	35 (350)	bt
RKS27	Calgon/dextrose + polyethylenimine	A	5%	81	78 (0)	50 (28)	9 (1298)	bt
RKS29	Calgon/dextrose + alanine	A	5%	81	88 (0)	50 (76)	42 (216)	bt
RKS36	Calgon/dextrose + piperazine	A	5%	81	65 (0)	50 (35)	25 (942)	bt

<sup>1</sup> Air flow = 8 scfh (4000 cm<sup>3</sup>/min), source temperature = 212°F (100°C), oven temperature = 302°F (150°C).

Carbons prepared by impregnation of a nitrogen-containing polymer were highly active in these tests, as they were in the previous project. The sorbent prepared by impregnation of 5 wt% PVP was activated using Procedure A (fast heating rate) and demonstrated superior activity. The initial removal was 94%, and the decrease to 50% removal required 2217 min. Thus this sorbent retains its high reactivity for longer than the Centaur carbon. The sorbent prepared using 10% PVP (also Procedure A) was less active (initially 88% removal, decreasing to 50% at 150 min). Using Procedure B (slow heating rate) gave more active sorbent at the 10% concentration level. Another set of carbons was prepared with different concentrations using Procedure B. Again, the impregnation with 5% concentration of PVP resulted in high activity (initially 98% removal, decreasing to 50% at 3315 min). The 10% was again less active, and the 2% concentration was the least active. The reason for optimal activity at 5% is not understood presently.

The carbons prepared from the copolymers of PVP were also prepared and evaluated. The copolymer with vinyl acetate (PVPcoVA) impregnated at 5% concentration (Procedure A) gave a sorbent with relatively low activity. The poly(1-vinylpyrrolidone-*co*-acrylic acid) (PVPcoAA) at 5% also gave a low-activity sorbent. Using Procedure B for activation improved the activity slightly.

Another type of N-polymer-impregnated carbon was prepared using polyethylenimine. This polymer precursor contains nitrogen in the polymer backbone, in contrast to the PVP where the nitrogen is attached to the carbon chain backbone. The activity was similar to that of the 10% PVP polymers.

Several carbons were prepared by impregnating mixtures of dextrose and amines. None of these exhibited high activities in these tests. Previous tests showed that the dextrose + alanine-impregnated carbon (Procedure B) was fairly active. Since Procedure A was used in the present study, the poor results can be attributed to the fast heating rate used. It may be extremely important to perform the reaction slowly in preparing sorbents from these precursors.

The sorbents prepared by impregnation of the nitrogenous pitches prepared by polymerization of various heterocyclics were all fairly active (Table 3-7). As hoped, significant differences in activity were observed. The N-carbon prepared from impregnation of quinoxaline pitch was 2–3 times more active than the quinoline-derived N-carbon. This result is consistent with the hypothesis that carbons prepared from precursors having two carbons in a ring will be more active. Nevertheless, the results are not definitive, since we really do not know the details of the edge structures of the carbons. More precursor work is needed, as well as structural work.

TABLE 3-7

Sorbent Testing of Nitrogenous Pitch-Impregnated Carbons for Mercury Capture<sup>1</sup>

File Name	Sorbent	H <sub>2</sub> SO <sub>4</sub> , %	Hg Conc., µg/m <sup>3</sup>	Percent Hg Removed (time, min)		
				Initial	50%	Final
RKS32	None	–	81	–	50	–
RKS35	Calgon/5% quinoline polymer <sup>2</sup>	5	81	89 (0)	50 (306)	49 (308)
RKS23	Calgon/5% quinoline polymer <sup>3</sup>	5	81	91 (0)	50 (204)	46 (292)
RKS37	Calgon/5% quinoxaline	5	81	90 (0)	50 (632)	25 (1300)
RKS31	Calgon isoquinoline	5	81	90 (0)	54 (584)	34 (1214)
RKS75	Calgon/5% indole polymer	5	81	98 (0)	50 (1403)	49 (1473)

<sup>1</sup> Recarbonization Procedure B used for all samples; sorbent = 0.20 g, particle size = 20 × 50 mesh, air flow = 8 scfh (4000 mL/min), source temperature = 302°F (150°C), oven temperature = 302°F (150°C).

<sup>2</sup> Pitch obtained from heating quinoline and aluminum(III) chloride in Parr reactor was dissolved in ethanol and impregnated on Calgon carbon.

<sup>3</sup> Pitch obtained from refluxing of quinoline with aluminum(III) chloride was dissolved in EDA and impregnated on Calgon carbon.

The activity of the isoquinoline-derived carbon was also very high. We had postulated earlier that the precursors with two nitrogens would be highly active; now we must consider other structure–activity models that involve the position of the nitrogen in the precursor and final edge structure. More information is needed on the details of the edge structures.

The high activity of the indole-derived carbon was also of great interest. Nothing is known about the structure of the indole-derived carbons, even whether nitrogen is still present in five-membered rings. It is an important lead, however, since indoles are more readily available than the quinoxaline precursors. The activity of the carbazole-derived carbon has not been determined.

Testing was also conducted on the carbonized pitches (Table 3-8) prepared from the insoluble fractions of the nitrogenous pitches. The activities of the carbonized pitches were very poor. Initial breakthrough was substantial, with percent removals of 21% to 54%. The reason for this is believed to be the glassy nature of the carbonized pitches. Although the surface areas were not determined, they are probably very low, since the materials did not resemble activated carbons, but rather cokes.

#### **3.4.4     *Manganese Oxides***

Table 3-9 shows the results from a series of manganese oxide ores compared with synthetic manganese oxide prepared from the decomposition of hydrated manganese nitrate. Among the ores studied, pyrolusite showed the most activity for mercury sorption. In order to boost the mercury sorption activity of these ores, sulfuric or nitric acids were impregnated on these ores. Sulfuric acid resulted in a significant increase in the mercury sorption activity of these ores, but nitric acid significantly reduced their mercury sorption activity (Table 3-10).

Calcination of the acid-impregnated pyrolusite was carried out to convert the manganese nitrate or sulfate formed on the surface into active metal oxide. This treatment resulted in a

TABLE 3-8

Activated Nitrogenous Pitch-Derived Sorbents for Mercury Capture<sup>1</sup>

File Name	Sorbent	H <sub>2</sub> SO <sub>4</sub> , %	Hg Conc., µg/m <sup>3</sup>	Percent Hg Removed (time, min)		
				Initial	50%	Final
RKS7	None	–	81	–	50 (<1)	–
RKS79	Quinoline pitch <sup>2</sup>	–	81	34 (0)	50 (<1)	22 (6)
RKS86	Quinoline pitch <sup>2</sup>	5	81	45 (0)	50 (<1)	33 (9)
RKS80	Quinoline pitch <sup>3</sup>	–	81	21 (0)	50 (<1)	22 (6)
RKS87	Quinoline pitch <sup>3</sup>	5	81	25 (0)	50 (<1)	26 (21)
RKS85	Quinoline pitch <sup>4</sup>	5	81	60 (0)	50 (<1)	30 (14)
RKS84	Quinoline pitch <sup>5</sup>	5	81	18 (0)	50 (<1)	18 (110)
RKS83	Isoquinoline pitch	5	81	54 (0)	50 (4)	41 (176)

<sup>1</sup> Sorbent = 0.20 g, oven temperature = 302°F (150°C), air flow = 8 scfh (4000 cm<sup>3</sup>/min).

<sup>2</sup> Quinoline pitch was prepared by refluxing a mixture of quinoline and aluminum(III) chloride at 536°F (280°C) for 4 hr in a gentle flow of nitrogen. The pitch was carbonized by heating in nitrogen flow using Procedure B.

<sup>3</sup> Quinoline pitch was prepared by heating in a Parr reactor at 536°F (280°C) for 4 hr in 1 atm of nitrogen. The pitch was carbonized by heating in nitrogen using Procedure B.

<sup>4</sup> Quinoline pitch from Procedure B was extracted with ethanol. Ethanol-insoluble pitch was carbonized in nitrogen by using Procedure B.

<sup>5</sup> Quinoline pitch was prepared by heating quinoline and aluminum(III) chloride in a Parr reactor at 536°F (280°C) for 16 hr in 1 atm of nitrogen. The pitch was carbonized using Procedure B.

TABLE 3-9

Mercury Sorption Activity of Manganese Oxide Ores<sup>1</sup>

Sorbent	Hg Conc., µg/m <sup>3</sup>	Percent Hg Removed, (time min)		
		Initial	50%	Final
None	81	0	50 (<1)	–
MnO <sub>2</sub> <sup>2</sup>	81	66 (0)	50 (3)	23 (33)
Manganite	81	30 (0)	50 (<1)	40 (40)
Psilomelane	81	63 (0)	50 (3)	29 (58)
Pyrolusite	81	97 (0)	50 (187)	46 (236)

<sup>1</sup> Sorbent = 0.2 g, particle size = 20 × 50 mesh, air flow = 8 scfh (4000 cm<sup>3</sup>/min) oven temperature = 302°F (150°C).

<sup>2</sup> MnO<sub>2</sub> was obtained by calcining manganese nitrate at 392°F (200°C) overnight.

TABLE 3-10

Effect of Acid Impregnation on the Mercury Sorption Activity of Manganese Oxide Ores<sup>1</sup>

File Name	Sorbent	Acid Impreg.	Hg Conc., $\mu\text{g}/\text{m}^3$	Percent Hg Removed (time, min)		
				Initial	50%	Final
RKS7	None	None	81	0	50 ( $<1$ )	–
RKS77	Pyrolusite	5% $\text{H}_2\text{SO}_4$	81	95 (0)	50 (279)	34 (1062)
RKS78	Pyrolusite	5% $\text{HNO}_3$	81	76 (0)	50 (26)	43 (68)
RKS71	Psilomelane	5% $\text{H}_2\text{SO}_4$	81	58 (0)	50 (35)	28 (219)

<sup>1</sup> Sorbent = 0.2 g, particle size =  $20 \times 50$  mesh, air flow = 8 scfh ( $4000 \text{ cm}^3/\text{min}$ ) oven temperature =  $302^\circ\text{F}$  ( $150^\circ\text{C}$ ).

further increase in the activity of the sulfuric acid-treated pyrolusite (Table 3-11). The 50% breakthrough time was extended significantly compared with the original as well as the sulfuric acid-treated ore (Table 3-12). In contrast, calcining the nitric acid-treated ore improved the mercury capture compared with the nitric acid-treated ore (Table 3-10), but did not restore the activity of the original ore (Table 3-9).

Much of the previous work was carried out with manganese oxide supported on an alumina bead. A set of experiments was performed to determine the effect of support on the activity. Manganese nitrate was impregnated on a variety of supports ranging from basic to neutral to acid, followed by decomposition by heating at  $392^\circ\text{F}$  ( $200^\circ\text{C}$ ) to convert the nitrate into oxide. The set of supports included calcium oxide, sodium montmorillonite clay, acid-washed montmorillonite (K10), and the alumina. The K10 is highly acidic (mainly Brønsted) and is an excellent acid catalyst for many reactions.

The results obtained with these supported sorbents are given in Table 3-12. Manganese oxide formed by thermal decomposition on a basic support had no activity for mercury removal.

TABLE 3-11

Effect of Calcination on Acid-Impregnated Manganese Oxide Ores<sup>1</sup>

File Name	Sorbent	Acid Impreg.	Hg Conc., $\mu\text{g}/\text{m}^3$	Percent Hg Removed (time, min)		
				Initial	50%	Final
RKS7	None	None	81	0	50 (<1)	–
RKS77	Pyrolusite	5% $\text{H}_2\text{SO}_4^1$	81	100 (0)	50 (366)	40 (943)
RKS78	Pyrolusite	5% $\text{HNO}_3^1$	81	99 (0)	50 (127)	49 (130)

<sup>1</sup> Sorbent = 0.2 g, particle size = 20 × 50 mesh, air flow = 8 scfh (4000 cm<sup>3</sup>/min), oven temperature = 302°F (150°C).

TABLE 3-12

Effect of Support on the Mercury Sorption Activity of Supported Manganese Oxide Sorbents<sup>1</sup>

File Name	Sorbent (g)	$\text{H}_2\text{SO}_4$ Impreg.	Hg Conc., $\mu\text{g}/\text{m}^3$	% Hg Removed (time, min)		
				Initial	50%	Final
RKS7	None	None	81	0	50 (<1)	–
RKS67	$\text{MnO}_2$	None	81	66 (0)	50 (3)	23 (33)
RKS70	$\text{CaO}/\text{MnO}_2$ (0.20)	None	81	10 (0)	50 (<1)	10 (25)
RKS68	$\text{Na-Mont}/\text{MnO}_2$ (0.20)	None	81	84 (0)	50 (21)	38 (39)
RKS69	$\text{K10}/\text{MnO}_2$ (0.20)	None	81	100 (0)	50 (91)	95 (91)
RKS9	$\text{Al}_2\text{O}_3/\text{MnO}_2$ (0.20)	None	81	96 (0)	50 (60)	35 (183)

<sup>1</sup> Sorbent = 0.2 g, particle size = 20 × 50 mesh, air flow = 8 scfh (4000cm<sup>3</sup>/min), oven temperature = 302°F (150°C).

However, as the acidity of the support increased, the mercury sorption activity increased considerably.

### 3.4.5 Mercuric Chloride Sorption

Results for the sorption mercuric chloride experiments with two sorbents are presented in Table 3-13. These data show that the manganese oxide is an excellent sorbent for the mercuric chloride. Good results were also obtained for the catalytic carbon. Unfortunately, the activity of the alumina support was not determined, nor was the activity of the base Calgon carbon.

TABLE 3-13

Sorbents for Mercuric Chloride Removal<sup>1</sup>

File Name	Sorbent (g)	H <sub>2</sub> SO <sub>4</sub> , wt%	HgCl <sub>2</sub> Conc., µg/m <sup>3</sup>	Percent HgCl <sub>2</sub> Removal (time, min)		
				Initial	50%	Final
RKS62	Blank	–	26		–	
RKS63	Calgon/5% PVP/5% sulfuric acid (0.43)	5	26	100 (0)	50 (>229)	70 (229)
RKS61	Al <sub>2</sub> O <sub>3</sub> /MnO <sub>2</sub> (0.50)	–	26	100 (0)	50 (>4013)	96 (4013)

<sup>1</sup>Air flow = 4 scfh (2000 cm<sup>3</sup>/min), source temperature = 212°F (100°C), oven temperature = 302°F (150°C).

## 3.5 Conclusions from Bench-Scale Sorbent Development Tests

### 3.5.1 Granular Sorbents – Air Test Results

#### 3.5.1.1 Catalytic Carbons

- Testing of granular activated carbons in air (8 scfh) at 302°F (150°C) verified high mercury capture activities for N-containing carbons, owing to their ability to catalyze the reaction of mercury with oxygen to form less volatile oxides.
- The highest kinetic activities were obtained for carbons derived by impregnation of N-polymer precursors and subsequent recarbonization.

- Optimum activities for the N-polymer-derived carbons were obtained with PVP at 5 wt% incorporation and carbonization using a slow, programmed heating scheme.
- A first attempt at establishing a structure–sorption activity relationship was conducted using carbons resulting from carbonization of impregnated pitches derived from N-heterocyclic precursors. Carbons prepared from N-heterocyclics showed good activity, with precursors containing two nitrogens in a six-membered ring and one nitrogen in a five-membered ring possessing highest activities, which suggests that the carbon edge structures may incorporate these features that confer higher radical ion stabilities, and these stabilities are important in the mercury oxidation mechanism.
- Cokes prepared from insoluble pitches derived from N-heterocyclics were relatively inactive, owing to the low surface areas.

#### 3.5.1.2 Manganese Oxides

- Supported  $\text{MnO}_2$  prepared by calcining  $\text{Mn}(\text{NO}_3)_2$  impregnated on alumina was demonstrated to be less active than the N-carbons for mercury vapor sorption in air at 302°F (150°C).
- Unsupported  $\text{MnO}_2$  prepared by calcining  $\text{Mn}(\text{NO}_3)_2$  was inactive.
- A study of the effects of supports on the activity of  $\text{MnO}_2$  sorbents showed a direct relationship of acidity to sorption activity, with the most acidic support (acid-washed clay [K10]) giving the highest activity and the most basic (calcium oxide) giving the lowest activity.
- The manganese ore, pyrolusite, was more active than the supported  $\text{MnO}_2$ , but other ores, manganite and psilomelane, were much less active.

- The activity of pyrolusite was improved significantly by adding sulfuric acid. The activity improved further on calcining. Other combinations of acids with ores were less reactive for mercury capture.

### ***3.5.2 Granular Sorbents – Mercuric Chloride in Air Results***

- The catalytic carbon prepared from PVP precursor exhibited good activity for sorption of HgCl<sub>2</sub> vapor in air at 302°F (150°C).
- The Al<sub>2</sub>O<sub>3</sub>-supported MnO<sub>2</sub> sorbent exhibited very high sorption reactivity and capacity for HgCl<sub>2</sub>.

## 4.0 BENCH-SCALE SORBENT SCREENING WITH FLUE GAS MATRIX

### 4.1 Bench-Scale Test Protocol

Extensive pilot-scale testing of carbon-based sorbents has previously been reported (12). 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. Initial results with the system, developed under funding from EPRI and DOE, have previously been reported (13).

The fixed-bed contactor consists of a Teflon-coated, 2.5-in.-diameter 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 process is very repeatable for mass loadings down to 10 mg. The fixed-bed assembly is maintained at the desired temperature inside an oven that can be controlled to  $\pm 1^\circ\text{C}$ . A Semtech 2000 mercury analyzer continuously measures the elemental mercury concentration and utilizes a Zeeman shift in the light source to eliminate interferences from  $\text{SO}_2$ , water vapor, and particulate. In order to monitor oxidized forms of mercury, a  $\text{SnCl}_2$  reduction cell is used prior to the analyzer to convert all forms of mercury for analysis. Breakthrough curves generated with this system are highly repeatable, as shown in Figure 4-1, which illustrates the results generated with 10 mg of iodine-impregnated activated carbon (IAC). The spent sorbent is analyzed for mercury to determine a mass balance. The area under the breakthrough curve in Figure 4-1 is integrated to determine the mercury not captured by the sorbent. These results are compared with the permeation rate of inlet mercury to determine the

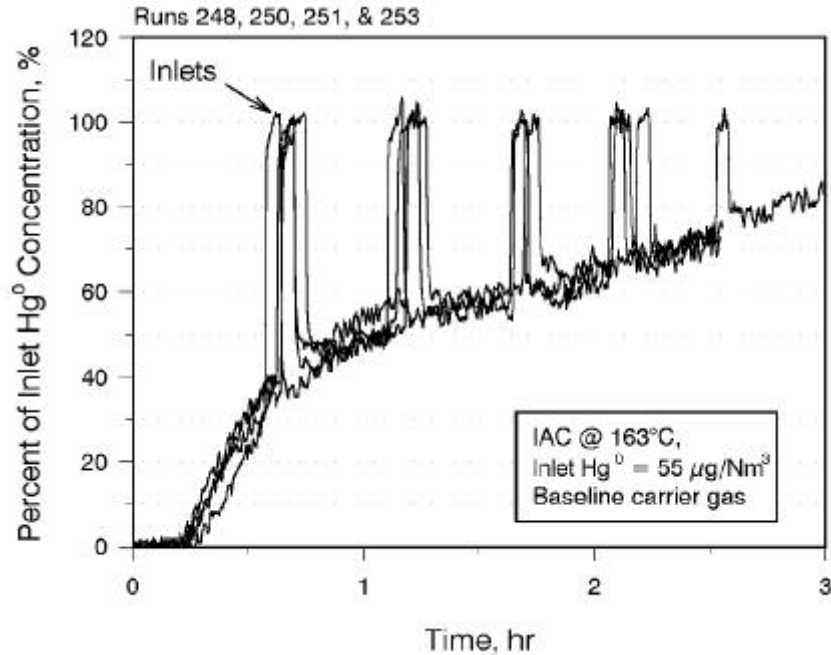


Figure 4-1. Outlet mercury concentration (as a percentage of the inlet mercury concentration) as a function of time for runs with 10 mg of an IAC at 325°F (163°C).

mass balance. Typically, good mass balance closures in the range of 80% to 120% are achieved, as detailed in the final project report (15).

The first step to interpretation of breakthrough tests is 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 4-1 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 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. Most of the comparative tests, using a lignite-based activated carbon (Norit FGD, labeled LAC in figures), Calgon, or EERC developmental sorbents, were performed with a sorbent mass of 100–150 mg, which is well beyond the range where mass transfer might be a concern.

A second critical factor for evaluating bench-scale sorbent tests is the composition and concentration of various flue gas components. Previous results (15) 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 reported in this section were with a fairly low mercury concentration of approximately  $15 \mu\text{g}/\text{m}^3$ , which is in the range observed for coal-fired boilers. The actual gas exposure conditions during the test are also critical to interpreting data. A number of reactive components of flue gas are known to affect the behavior of mercury sorbents, but the mechanisms are undefined. Exposure to a stream of mercury in nitrogen or air may provide insight to mercury sorbent chemistry, but it is not likely indicative of sorbent performance under real process conditions.

The observed breakthrough results must also be scrutinized for possible misleading interpretation. Some sorbents capture mercury as well as convert it to an oxidized form. Since most mercury analyzers will not detect oxidized mercury, the test system must include a conversion system to ensure that the total breakthrough mercury is measured. Otherwise, results may indicate capture when, in reality, the mercury simply changes form across the sorbent bed. Another approach to check for this possibility is to measure independently the amount of mercury trapped in the spent sorbent. If we compare this with the amount of trapped mercury as indicated by the continuous analyzer, we have an additional quality control check. However, since mercury analyzers are still considered experimental, especially in the range from 1 to  $25 \mu\text{g}/\text{m}^3$ , great care must be taken to ensure that both the inlet and outlet mercury concentrations are known. If both inlet and outlet mercury concentrations were biased low, the results could indicate good capture and 100% mass closure, when in actuality, the capture was only marginal. To prevent this possibility, independent verification should be made of the inlet mercury concentration by calibration of the mercury source with batch testing of the source by EPA Method 101A. Then three independent measurements (inlet concentration, outlet breakthrough data, and mercury in spent sorbent) can be used to calculate a mercury mass balance around the

sorbent bed. If the mass balance closure is within 80%–120% (depending on the experimental precision available), very strong collaborating data support the results. The mercury mass balance data presented in Section 4.2.1 are all calculated on this basis.

#### 4.2 Bench-Scale Sorbent-Screening Results

Initial tests were conducted to compare EERC-developed sorbents under conditions for which protocol was previously developed for screening commercially available sorbents. These tests were conducted using the simulated flue gas concentration shown in Table 4-1. This gas concentration was previously selected based on consultation with several other research groups in an attempt to provide a better basis for comparing results among several different labs.

TABLE 4-1

Baseline Flue Gas

O <sub>2</sub>	6%
CO <sub>2</sub>	12%
SO <sub>2</sub>	1600 ppm
HCl	50 ppm
Hg <sup>0</sup> or HgCl <sub>2</sub>	20 µg/m <sup>3</sup>
N <sub>2</sub>	Balance
H <sub>2</sub> O	8%

Because of concern that NO<sub>x</sub> species may affect mercury sorbent performance, additional tests were completed in which either 300 ppm NO, 20 ppm NO<sub>2</sub>, or both NO and NO<sub>2</sub> were added to the gas concentrations shown in Table 4-1. These tests were at temperatures of 225°F (107°C) and 325°F (163°C). The addition of 300 ppm NO to the matrix gas appeared to have had little effect compared to the baseline gas at either 225°F (107°C) or 325°F (163°C). However, the addition of 20 ppm of NO<sub>2</sub> appeared to have a profound effect. When NO<sub>2</sub> was present, nearly 100% mercury capture was observed for the first hour, followed by fairly rapid breakthrough between the first and second hour. This rapid breakthrough was not observed in the

tests without NO<sub>2</sub>. When both NO and NO<sub>2</sub> were present, the curves more closely resembled the results with just NO<sub>2</sub> added to the other gases. This indicated that NO<sub>2</sub> in the relatively small concentration of 20 ppm could have a significant effect on sorbent performance. Measuring only elemental mercury at the outlet after observing breakthrough and comparing it to the total outlet mercury indicated that the emitted mercury on the outlet side had been converted to an oxidized form. The strong effect of NO<sub>2</sub> appears to be a significant finding, because it indicates that capacity data without NO<sub>2</sub> may suggest much better capture than in real flue gases where a small amount of NO<sub>2</sub> is always present. The data also suggested that a much more thorough investigation must be conducted to understand the interactions between sorbents, mercury, and flue gas components.

Because of the significant effect of NO<sub>2</sub> and question of possible interactions with other flue gases, the decision was made to complete a full factorial design test matrix with four variables (SO<sub>2</sub>, HCl, NO, and NO<sub>2</sub>) with the LAC sorbent at 225°F (107°C). All of these tests included the same concentrations of O<sub>2</sub>, CO<sub>2</sub>, H<sub>2</sub>O, and N<sub>2</sub> listed in Table 4-1. Many of the tests were repeated to evaluate the experimental precision and make sure that the major observations could be duplicated. These tests, along with all of the other simulated flue gas tests, are shown in the order they were completed by run number in Table 4-2. The run number is simply a sequential number assigned to the tests in the order in which they were completed. Only the tests that generated valid results are shown in Table 4-2. Where gaps occur in the run numbers listed, it is either because a test was terminated early because of problems or, after the test, results were invalidated for various reasons such as a disturbed sorbent bed. In addition, a number of the run numbers were assigned to calibration runs, which are not shown in Table 4-2. Breakthrough graphs for all of the tests listed in Table 4-2 are included as Appendix A. Each of these is identified by run number as well as the flue gas conditions and sorbent in the key for each graph. The outlet mercury concentrations are presented on the basis of percent of inlet concentration, but many of these graphs also show a brief check of the inlet mercury concentration. Tables 4-3 through 4-8 organize the runs according to the type of sorbent, temperature, and flue gas

TABLE 4-2

## Simulated Flue Gas Tests

Run No.	Date	Sorbent Type	Sorbent Mass, Temperature,		Flue Gas
			mg	°F (°C)	
686	1-14-98	LAC	150.6	225 (107)	BL + SO <sub>2</sub> + HCl
687	1-14-98	LAC	101.7	225 (107)	BL + SO <sub>2</sub> + HCl
689	1-15-98	LAC	101.7	225 (107)	BL + SO <sub>2</sub> + HCl
690	1-16-98	LAC	102.6	225 (107)	BL + SO <sub>2</sub> + HCl
693	1-20-98	IAC	11.4	225 (107)	BL + SO <sub>2</sub> + HCl
695	1-21-98	EERC 52-1	103.9	225 (107)	BL + SO <sub>2</sub> + HCl
698	1-23-98	EERC 52-1	152.3	225 (107)	BL + SO <sub>2</sub> + HCl
699	1-26-98	EERC 52-1	205.9	225 (107)	BL + SO <sub>2</sub> + HCl
700	1-26-98	EERC 92-4	157.0	225 (107)	BL + SO <sub>2</sub> + HCl
701	1-27-98	EERC 92-4	106.0	225 (107)	BL + SO <sub>2</sub> + HCl
702	1-27-98	EERC 92-5	103.9	225 (107)	BL + SO <sub>2</sub> + HCl
703	1-28-98	EERC 52-1	152.2	325 (163)	BL + SO <sub>2</sub> + HCl
704	1-28-98	EERC 92-4	152.6	325 (163)	BL + SO <sub>2</sub> + HCl
708	1-30-98	LAC	151.5	325 (163)	BL + SO <sub>2</sub> + HCl
709	2-2-98	LAC	151.3	325 (163)	BL + SO <sub>2</sub> + HCl
711	2-6-98	LAC	151.2	225 (107)	BL + SO <sub>2</sub> + HCl + NO
712	2-9-98	LAC	151.4	225 (107)	BL + SO <sub>2</sub> + HCl + NO
713	2-9-29	LAC	151.9	225 (107)	BL + NO
714	2-10-98	LAC	151.0	225 (107)	BL + SO <sub>2</sub> + HCl + NO <sub>2</sub>
715	2-10-98	LAC	151.0	225 (107)	BL + SO <sub>2</sub> + HCl + NO <sub>2</sub>
717	2-13-98	LAC	152.8	225 (107)	BL + SO <sub>2</sub> + HCl + NO <sub>2</sub>
721	2-18-98	LAC	152.9	225 (107)	BL + SO <sub>2</sub> + HCl + NO + NO <sub>2</sub>
723	2-20-98	LAC	153.0	275 (135)	BL + SO <sub>2</sub> + HCl
726	2-23-98	LAC	152.4	325 (163)	BL + SO <sub>2</sub> + HCl + NO <sub>2</sub>
727	2-24-98	LAC	150.9	325 (163)	BL + SO <sub>2</sub> + HCl + NO
729	2-24-98	LAC	150.4	325 (163)	BL + SO <sub>2</sub> + HCl + NO + NO <sub>2</sub>
730	2-25-98	LAC	151.9	325 (163)	BL + SO <sub>2</sub> + HCl + NO + NO <sub>2</sub>
731	2-25-98	LAC	150.8	225 (107)	BL + SO <sub>2</sub> + HCl + NO + NO <sub>2</sub>
734	3-2-98	LAC	151.3	225 (107)	BL
735	3-3-98	LAC	152.6	225 (107)	BL + NO <sub>2</sub>
736	3-4-98	LAC	151.7	225 (107)	BL + NO <sub>2</sub>
737	3-4-98	LAC	152.4	325 (163)	BL + NO <sub>2</sub>
738	3-4-98	LAC	151.0	325 (163)	BL
739	3-6-98	EERC 92-5	151.5	300 (149)	79% N <sub>2</sub> , 21% O <sub>2</sub>
740	3-10-98	LAC	151.1	225 (107)	BL + SO <sub>2</sub> + NO <sub>2</sub>
741	3-10-98	LAC	150.8	225 (107)	BL + HCl + NO <sub>2</sub>
742	3-11-98	LAC	152.6	225 (107)	BL + HCl + NO
743	3-11-98	LAC	151.4	225 (107)	BL + SO <sub>2</sub> + NO

Continued . . .

TABLE 4-2 (continued)

Run No.	Date	Sorbent Type	Sorbent Mass, Temperature,		Flue Gas
			mg	° F	
744	3-12-98	LAC	151.1	225 (107)	BL + HCl
745	3-12-98	LAC	151.3	225 (107)	BL + SO <sub>2</sub>
746	3-13-98	Calgon	151.1	225 (107)	BL + SO <sub>2</sub> + HCl
747	3-13-98	Calgon	153.0	225 (107)	BL + SO <sub>2</sub> + HCl + NO + NO <sub>2</sub>
748	3-30-98	Calgon	150.3	300 (149)	N <sub>2</sub> + O <sub>2</sub>
749	3-30-98	Calgon	151.8	300 (149)	N <sub>2</sub> + O <sub>2</sub>
750	4-2-98	LAC	152.8	225 (107)	BL + SO <sub>2</sub>
751	4-2-98	LAC	153.8	225 (107)	BL + HCl
756	6-16-98	LAC	152.3	225 (107)	79% N <sub>2</sub> , 21% O <sub>2</sub>
757	6-16-98	LAC	151.5	225 (107)	BL + SO <sub>2</sub> + NO + NO <sub>2</sub>
760	6-18-98	LAC	21.6	225 (107)	BL + HCl
761	6-18-98	LAC	153.5	225 (107)	BL + HCl + NO + NO <sub>2</sub>
762	6-19-98	LAC	151.4	225 (107)	BL + NO + NO <sub>2</sub>
763	6-19-98	LAC	151.1	225 (107)	BL + SO <sub>2</sub> + NO + NO <sub>2</sub>
766	6-22-98	LAC	152.5	225 (107)	BL
767	6-22-98	LAC	150.5	225 (107)	BL
768	6-22-98	LAC	153.4	225 (107)	BL + HCl
769	6-23-98	LAC	153.7	225 (107)	BL + NO <sub>2</sub>
770	6-24-98	LAC	151.9	225 (107)	BL + HCl + NO <sub>2</sub> (+SO <sub>2</sub> )
771	6-24-98	EERC 52-1	152.6	225 (107)	BL + SO <sub>2</sub> + HCl + NO + NO <sub>2</sub>
772	6-24-98	EERC 92-5	152.7	225 (107)	BL + SO <sub>2</sub> + HCl + NO + NO <sub>2</sub>
773	6-25-98	EERC 92-4	150.1	225 (107)	BL + SO <sub>2</sub> + HCl + NO + NO <sub>2</sub>
774	6-25-98	EERC 92-5	152.2	225 (107)	BL + SO <sub>2</sub> + HCl + NO + NO <sub>2</sub>
775	6-25-98	EERC 92-4	150.9	300 (149)	79% N <sub>2</sub> , 21% O <sub>2</sub>
776	6-26-98	EERC 52-1	150.4	300 (149)	79% N <sub>2</sub> , 21% O <sub>2</sub>
777	6-26-98	Calgon	150.7	325 (163)	BL + SO <sub>2</sub> + HCl
778	6-26-98	EERC 92-4	144.6	300 (149)	79% N <sub>2</sub> , 21% O <sub>2</sub>
779	6-29-98	LAC	150.9	225 (107)	BL + SO <sub>2</sub> + HCl + NO + NO <sub>2</sub> + HF
781	6-30-98	LAC	150.2	225 (107)	BL + SO <sub>2</sub> + NO + NO <sub>2</sub> + HF
782	6-30-98	LAC	150.8	225 (107)	BL + SO <sub>2</sub> + NO + NO <sub>2</sub> + HF
783	7-1-98	LAC	151.4	225 (107)	BL + HF
784	7-1-98	LAC	153.0	225 (107)	BL + HF
785	7-1-98	LAC	150.5	225 (107)	BL + SO <sub>2</sub> + HCl + NO + NO <sub>2</sub> + CO
786	7-6-98	EERC 92-5	151.0	225 (107)	BL + SO <sub>2</sub> + NO + NO <sub>2</sub>
788	7-7-98	LAC	151.4	225 (107)	BL + SO <sub>2</sub> + HCl + NO + NO <sub>2</sub> + NH <sub>3</sub>
789	7-7-98	EERC 92-5	150.4	225 (107)	BL + SO <sub>2</sub> + HCl + NO + NO <sub>2</sub> + NH <sub>3</sub>

<sup>1</sup> Baseline.

TABLE 4-3

## LAC Sorbent at 225°F (107°C)

Test No.	SO <sub>2</sub> , ppm	HCl, ppm	NO, ppm	NO <sub>2</sub> , ppm	CO, ppm	HF, ppm	NH <sub>3</sub> , ppm	Run No.
1	1600	50	300	0	0	0	0	711, 712
2	1600	50	300	20	0	0	0	721, 731
3	1600	50	0	0	0	0	0	686, 768
4	1600	50	0	20	0	0	0	714, 715
5	1600	0	300	0	0	0	0	743
6	1600	0	300	20	0	0	0	757, 763
7	1600	0	0	0	0	0	0	745, 750
8	1600	0	0	20	0	0	0	740, 769
9	0	50	300	20	0	0	0	761
10	0	50	300	0	0	0	0	742
11	0	50	0	20	0	0	0	741, 770
12	0	50	0	0	0	0	0	744, 751, 768
13	0	0	0	0	0	0	0	734, 766, 767
14	0	0	300	0	0	0	0	713
15	0	0	0	20	0	0	0	735, 765
16	0	0	300	20	0	0	0	762
17	1600	50	300	20	100	0	0	784, 785
18	1600	50	300	20	0	10	0	779
19	1600	0	300	20	0	10	0	782
20	0	0	0	0	0	10	0	783, 784
21	1600	50	300	20	0	0	25	788

TABLE 4-4

## LAC Sorbent at 325°F (163°C)

Test No.	SO <sub>2</sub> , ppm	HCl, ppm	NO, ppm	NO <sub>2</sub> , ppm	CO, ppm	HF, ppm	NH <sub>3</sub> , ppm	Run No.
1	1600	50	300	0	0	0	0	727
2	1600	50	300	20	0	0	0	729, 730
3	1600	50	0	0	0	0	0	709
4	1600	50	0	20	0	0	0	726
5	0	0	300	0	0	0	0	737
6	0	0	0	20	0	0	0	736
7	0	0	0	0	0	0	0	738

TABLE 4-5

## EERC 92-5 Sorbent

Test No.	Temp., °F (°C)	SO <sub>2</sub> , ppm	HCl, ppm	NO, ppm	NO <sub>2</sub> , ppm	CO, ppm	HF, ppm	NH <sub>3</sub> , ppm	Run No.
1	225 (107)	1600	50	0	0	0	0	0	702
2	225 (107)	1600	50	300	20	0	0	0	772, 774
3	225 (107)	1600	0	300	20	0	0	0	786
4	225 (107)	1600	50	300	20	0	0	25	789
5	300 (149)	0	0	0	0	0	0	0	739
6	325 (163)	1600	50	0	0	0	0	0	707

TABLE 4-6

## Calgon Sorbent

Test No.	Temp., °F (°C)	SO <sub>2</sub> , ppm	HCl, ppm	NO, ppm	NO <sub>2</sub> , ppm	CO, ppm	HF, ppm	NH <sub>3</sub> , ppm	Run No.
1	225 (107)	1600	50	0	0	0	0	0	746
2	225 (107)	1600	50	300	20	0	0	0	747
3	300 (149)	0	0	0	0	0	0	0	748, 749
4	325 (163)	1600	50	0	0	0	0	0	777

TABLE 4-7

## EERC 92-4 Sorbent

Test No.	Temp., °F (°C)	SO <sub>2</sub> , ppm	HCl, ppm	NO, ppm	NO <sub>2</sub> , ppm	CO, ppm	HF, ppm	NH <sub>3</sub> , ppm	Run No.
1	225 (107)	1600	50	300	20	0	0	0	773
2	225 (107)	1600	50	0	0	0	0	0	700
3	300 (149)	0	0	0	0	0	0	0	775, 778
4	325 (163)	1600	50	0	0	0	0	0	704

TABLE 4-8

## EERC 52-1 Sorbent

Test No.	Temp., °F (°C)	SO <sub>2</sub> , ppm	HCl, ppm	NO, ppm	NO <sub>2</sub> , ppm	CO, ppm	HF, ppm	NH <sub>3</sub> , ppm	Run No.
1	225 (107)	1600	50	300	20	0	0	0	771
2	225 (107)	1600	50	0	0	0	0	0	698
3	300 (149)	0	0	0	0	0	0	0	776
4	325 (163)	1600	50	0	0	0	0	0	703

conditions. Table 4-9 presents mass balance data for the runs in which the sorbent was analyzed for mercury.

#### 4.2.1 Full Factorial Design with SO<sub>2</sub>, HCl, NO, and NO<sub>2</sub>

All of the tests with the LAC sorbent at 225°F (107°C) are shown in Table 4-3. The first 16 of these tests make up the full factorial design with SO<sub>2</sub>, HCl, NO, and NO<sub>2</sub> as variables and an inlet Hg<sup>0</sup> concentration of 15 µg/m<sup>3</sup>. Tests 17–21 include several additional runs in which CO, HF, and NH<sub>3</sub> were added to the flue gas matrix. Note that many of the tests were repeated and some were done in triplicate as indicated in the last column of Table 4-3. Most of the tests were with a sorbent mass of 150 mg and were run for a period of at least 3 hours. In all of the tests, the Semtech was set up to analyze total mercury so all of the breakthrough graphs represent the total mercury passing through the sorbent bed. For most tests, a determination was also made of the Hg<sup>0</sup> at the outlet for a short time by bypassing the converter system. These intervals are shown on the breakthrough graphs. If a significant fraction of the mercury is oxidized across the bed, this is indicated by a marked decrease in the Hg<sup>0</sup> concentration compared to the total mercury concentration. In cases where little or no difference was observed between the total and Hg<sup>0</sup>, the indication is that the breakthrough mercury species was unchanged from the inlet.

TABLE 4-9

## Mass Balance Data for Runs in Which Sorbent Was Analyzed for Mercury

Run No.	Sorbent Type	Sorbent Mass, mg	Temp., °F (°C)	Length of Test, hr	Flue Gas Flow Rate, m <sup>3</sup> /hr	Inlet Conc., µg/m <sup>3</sup>	Inlet <sup>1</sup> Hg Generated, µg	Hg Captured on the Sorbent, µg	Capacity at End of Test, µg/g	Integrated Hg Breakthrough, <sup>2</sup> µg	Mass Balance <sup>3</sup> , %
686	LAC	150.6	225 (107)	4.0	1.1	11.7	51.8	37.5	249.0	6.5	85.0
689	LAC	101.7	225 (107)	3.4	1.1	11.7	43.4	35.7	351.0	7.7	100.0
701	EERC 92-4	106.0	225 (107)	3.1	1.1	11.7	40.0	24.4	230.0	22.5	117.0
702	EERC 92-5	103.9	225 (107)	2.5	1.1	11.7	32.2	27.0	260.0	11.6	120.0
704	EERC 92-4	152.6	325 (163)	1.7	1.1	11.7	21.5	3.3	22.0	14.8	84.0
705	EERC 92-5	150.9	325 (163)	1.5	1.1	11.7	19.3	11.6	77.0	5.8	90.0
711	LAC	151.2	225 (107)	2.1	0.9	15.5	27.5	23.1	153.0	3.9	98.0
712	LAC	151.4	225 (107)	3.8	0.9	15.5	48.6	42.5	281.0	4.8	97.0
723	LAC	153.0	275 (135)	3.3	1.0	13.7	42.5	37.2	243.0	13.9	120.0
725	LAC	151.0	325 (163)	2.3	0.9	15.5	29.0	18.7	124.0	11.0	102.0
727	LAC	150.9	325 (163)	3.4	0.9	15.5	43.4	39.2	260.0	6.6	106.0
730	LAC	151.9	325 (163)	2.4	0.9	15.5	30.5	11.6	77.0	11.2	75.0
735	LAC	152.6	225 (107)	8.0	0.9	15.5	103.3	93.7	614.0	6.2	97.0
760	LAC	21.6	225 (107)	4.5	0.9	13.0	58.0	65.6	3037.0	8.6	128.0
761	LAC	153.5	225 (107)	2.7	0.9	14.1	34.2	37.3	243.0	4.7	123.0
762	LAC	151.4	225 (107)	3.9	0.9	15.1	49.8	30.1	199.0	9.5	80.0
763	LAC	151.1	225 (107)	2.9	0.9	15.0	37.2	11.1	73.0	26.2	100.0
768	LAC	153.4	225 (107)	3.1	0.9	14.5	39.5	42.0	274.0	3.1	114.0
769	LAC	153.7	225 (107)	8.2	0.9	14.5	106.1	8.7	57.0	88.2	91.0
770	LAC	151.9	225 (107)	5.6	0.9	12.6	71.7	41.1	271.0	34.6	106.0
773	EERC 92-4	150.1	225 (107)	2.2	0.9	13.6	27.9	14.0	93.0	14.4	101.0
774	EERC 92-5	152.2	225 (107)	2.9	0.9	14.0	37.2	17.4	114.0	22.9	109.0
777	BL Calgon	150.7	325 (163)	4.4	0.9	13.4	56.1	39.2	260.0	20.6	107.0
779	LAC	150.9	225 (107)	3.3	0.9	14.5	42.7	19.2	127.0	21.7	96.0
781	LAC	150.2	225 (107)	2.3	0.9	15.9	29.4	17.2	115.0	11.3	97.0
782	LAC	150.8	225 (107)	2.1	0.9	15.9	27.5	12.3	82.0	13.5	94.0
783	LAC	151.4	225 (107)	3.6	0.9	14.2	46.7	25.2	166.0	18.1	93.0
786	EERC-92-5	151.0	225 (107)	2.2	0.9	14.3	28.4	5.8	38.0	19.1	88.0
788	LAC	151.4	225 (107)	3.5	0.9	14.6	45.1	28.8	190.0	14.0	95.0
789	EERC-92-5	150.4	225 (107)	3.2	0.9	14.4	41.5	29.2	194.0	13.3	102.0

<sup>1</sup> Based on calibrated permeation rates.<sup>2</sup> Based on integrated Semtech values.<sup>3</sup> (Hg captured and breakthrough Hg)/(total Hg generated).

#### 4.2.1.1 Baseline Conditions Without Acid Gases

Three runs were completed, 734, 766, and 767, for this test condition (Test 13 in Table 4-3). Run 734 showed an initial capture of 20%, which improved to 50% after 1 hour; however, this possibly was the result of some zero drift. Repeat Run 766 showed 20% capture with no improvement for the duration of the test, and Run 767 showed only 10% initial capture. Both of these tests were run for an hour or less because of the initial high level of breakthrough observed. Several of the sixteen test conditions were also conducted at an elevated temperature of 325°F (163°C) as listed in Table 4-4. A baseline test at 325°F (163°C) (Run 738) resulted in 100% immediate breakthrough. No conversion of Hg<sup>0</sup> was observed during any of these baseline tests. These results indicate that the LAC is ineffective at capturing Hg<sup>0</sup> in a gas matrix of O<sub>2</sub>, CO<sub>2</sub>, H<sub>2</sub>O, and N<sub>2</sub> within the temperature range of 225°–323°F (107°–162°C). The small amount of capture observed at the lower temperature of 225°F (107°C) is apparently the result of physisorption, because no capture was observed at the higher temperature. Capture by physisorption alone is expected to decrease with an increase in temperature. While the poor capture under the baseline conditions may make the LAC appear ineffective, it facilitates the determination of major effects of other gases when good capture is observed.

#### 4.2.1.2 One-at-a-Time Tests with SO<sub>2</sub>, HCl, NO, and NO<sub>2</sub>

While it is unlikely that flue gas mixes from a real process would contain only one each of SO<sub>2</sub>, HCl, NO, or NO<sub>2</sub> gas, tests were conducted to determine mechanisms. Runs 745 and 750 with 1600 ppm SO<sub>2</sub> alone added to the baseline gases (Test 7 in Table 4-3) showed an initial capture of 30%–50%, which decreased to only 10% capture after 1 hour, and no conversion of Hg<sup>0</sup> was seen. These results indicate that SO<sub>2</sub> alone has a small benefit on Hg<sup>0</sup> capture, but the LAC sorbent would still be considered ineffective at these conditions.

In contrast, the results with 50 ppm HCl alone added to the baseline gases (Test 12, Table 4-3) show nearly 100% capture, indicating that HCl alone has a significant benefit. Run 744 showed 100% capture for 3 hours. A repeat run, 751, showed about 95% capture for 2.5 hours.

The upward trend to 20% breakthrough between 1 and 2 hours was apparently the result of zero drift. A triplicate test, Run 768, also showed at least 95% capture for the first 2 hours, after which  $\text{SO}_2$  was started to see if the additional presence of  $\text{SO}_2$  would cause a deterioration in mercury capture. The presence of  $\text{SO}_2$  appeared to cause a slight upward trend to 15%–20% breakthrough 1 hour after starting the  $\text{SO}_2$ , but no conversion of  $\text{Hg}^0$  was noted. Because of the excellent capture with HCl, another test was conducted in which the sorbent mass was reduced to 22 mg compared to the 150 mg for all of the other tests. As shown in the graph for Run 760 (Appendix A), breakthrough was 15%–20% and held steady for the test duration of 4 hours. At the end of the 4 hours, it appeared that some  $\text{Hg}^0$  was being converted, but this cannot be definitely concluded because of the small amount of mercury breakthrough and instrument variability. At 225°F (107°C), results indicate that HCl in the flue gas can have a profound positive effect on the ability of the LAC sorbent to capture mercury. For Runs 760 and 768, mass balance data indicate that the mercury capture determined by the Semtech analyzer agreed reasonably well with the mercury measured in the spent sorbent. For Run 768 with 153.4 mg of sorbent, the sorbent-to-mercury ratio at the end of the 3.1-hour test period was approximately 4000:1. This is considered on the low side of the amount of sorbent tested in previous pilot-scale work for coal firing and would be quite reasonable.

Achieving 95% capture at a reasonably low sorbent-to-mercury ratio is what must be demonstrated for sorbents to be considered a viable mercury control option. Since the tests were conducted with a low mercury concentration, the good capture cannot be attributed to a kinetic concentration effect resulting from using a very high mercury concentration. For the 22-mg sorbent test, Run 760, the sorbent-to-mercury ratio at the end of the 4.5-hour test was only about 400:1, but still achieved 85% capture. These results shed light on the importance of flue gas chemistry effects and imply that the amount of sorbent needed for effective mercury capture may be very small if the right chemical conditions occur at the sorbent surface.

One test was completed with NO alone added to the baseline gases, Test 14 in Table 4-3 (Run 713). The results indicated an initial capture of 85%–95%, increasing to 100% after

2.5 hours. This is very similar to the results with HCl alone, other than the apparent improvement in capture with time. No repeat tests were conducted, but the improvement in time could possibly be the result of instrument drift and should not be considered a firm conclusion. However, the data show that NO also has a very positive effect on Hg<sup>0</sup> capture compared to the baseline gases and that both high capacity and high capture can be achieved under these conditions.

Two runs were completed for the case with NO<sub>2</sub> alone added to the baseline gases, Test 15 in Table 4-3 (Runs 735 and 765). Run 735 demonstrated from 90% to 100% capture for a period of 8 hours other than some apparent zero-drift occurrences, which were corrected with the auto zero function of the Semtech instrument. The mass balance closure of 97% for Run 735 confirms the excellent capture for the extended period. This condition was also tested at 325 °F (163 °C) as shown in Run 736. Again, other than an apparent zero-drift episode, the capture was nearly 100% and indicates a chemical reaction occurring at the sorbent surface. Interestingly, since excellent capture was seen with HCl or either NO<sub>x</sub> species, the implication is that different mercury-bound species might be formed at the sorbent surface. Because subsequent tests that included both NO<sub>2</sub> and SO<sub>2</sub> showed rapid breakthrough, a repeat run was completed in which SO<sub>2</sub> was started 2.5 hours after starting the test with NO<sub>2</sub> alone (Run 769). Discussion on that effect is given in the next section.

#### 4.2.1.3 Two-at-a-Time Tests with SO<sub>2</sub>, HCl, NO, and NO<sub>2</sub>

The six possible combinations of the four gas variables taken two at a time are part of the full factorial design shown in Table 4-3. The combination of SO<sub>2</sub> and HCl (Test 3 in Table 4-3) is the same as conditions previously tested and reported to provide effective mercury capture (15). Run 686 is an example that indicated 95% capture at the start and about 85% capture at the end of 4 hours. Run 689 was done under similar conditions, but with 102 mg of sorbent instead of 150 mg, so it was not considered to be part of the full factorial design. The breakthrough curve for this run clearly demonstrated nearly 100% capture at the start and slowly decreased to 80% capture by 3.5 hours. From these two tests, along with Run 768, previously discussed, in which SO<sub>2</sub> was started 2 hours after the beginning of the test with HCl alone, it appears that the

combination of HCl and SO<sub>2</sub> gives slightly poorer performance than HCl alone, but much better than SO<sub>2</sub> alone. The primary difference appears to be a slow increase in mercury breakthrough for the combination compared to a fairly flat breakthrough curve with HCl alone. No conversion of Hg<sup>0</sup> was observed in any of the tests with both SO<sub>2</sub> and HCl.

The combination of SO<sub>2</sub> and NO (Test 5 in Table 4-3) was evaluated in only one test, Run 743. At the start of the test, 40% breakthrough was seen, but capture improved to 85% by the end of 3 hours. The improvement in capture with time is similar to that found for the test with NO alone, but the initial and final level of breakthrough is greater with the combination of NO and SO<sub>2</sub>. In addition, with the combination, at the end of the test the 15% breakthrough appears to be oxidized mercury. Based on this one test, it appears that the effect of adding SO<sub>2</sub> to NO is a small decrease in the level of mercury capture and possible oxidation of the mercury that is not captured.

Test 8 in Table 4-3 is for the condition of SO<sub>2</sub> and NO<sub>2</sub>, shown in Runs 740 and 769. From Run 740, the results are significantly different compared to NO<sub>2</sub> alone. An initial period of 90% capture was observed for the first half hour followed by rapid breakthrough above the 100% mark. Furthermore, the breakthrough appears to be almost all oxidized mercury. Since with NO<sub>2</sub> alone, nearly 100% capture was observed for a period of 8 hours (Run 740), these results indicate a significant interaction between the SO<sub>2</sub> and NO<sub>2</sub>. To confirm this effect, a repeat test was conducted in which only NO<sub>2</sub> was added for the first 2.5 hours, after which SO<sub>2</sub> was also added (Run 769). For the first 2.5 hours, the capture was again nearly 100% with one minor and one major zero-drift correction. However, immediately after SO<sub>2</sub> injection was started, the mercury breakthrough increased rapidly and reached a level twice the inlet mercury concentration. This indicated that not only did the SO<sub>2</sub> cause the sorbent to lose its ability to capture mercury, but it also caused the sorbent to desorb the mercury that was captured in the first 2.5 hours. As the test continued for a total of 8 hours, the outlet mercury concentration slowly approached the inlet level. In addition, Hg<sup>0</sup> measurements at 3.5 and 8 hours indicated that almost all of the breakthrough mercury was converted to an oxidized form. Analysis of the sorbent after the test showed that the sorbent retained only 8.7 µg of mercury compared to 106.1 µg injected,

confirming that most of the initially captured mercury was desorbed after starting SO<sub>2</sub>. These results provide very strong evidence of a major interaction between these gases and mercury, but the exact mechanisms by which this occurs remain unclear. Since a volatile oxidized form of mercury is produced under conditions without HCl, there is a question as to the exact mercury species that is desorbed. The possibility exists that traces of chlorine compounds are in the sorbent (since the sorbent is a lignite-based activated carbon) that could serve as a source of chlorine for the production of HgCl<sub>2</sub>. However, that the oxidized mercury desorption is observed only when NO<sub>2</sub> is present suggests that possibly a mercury–nitrogen compound is the initially captured form of mercury, which is then converted to mercuric oxide (HgO) when SO<sub>2</sub> is present. Mercuric oxide would be expected to be stable at 225°F (107°C) and have sufficient vapor pressure to occur in gas phase under these conditions. The identification of this significant interaction that is strong enough to completely dominate the effectiveness of a sorbent is a major finding, but much more work is needed to understand the mechanism.

The combination of NO and NO<sub>2</sub> (Test 16 in Table 4-3) is shown in Run 762. Initially, capture was 80%, but it improved to 95% by 3.5 hours. The result is most similar to those for NO alone, whereby capture improved with time, but is also similar to NO<sub>2</sub> alone, in that excellent capture was observed. Based on this one test, results for the combination of NO and NO<sub>2</sub> are not significantly different from those for either NO or NO<sub>2</sub> alone.

The combination of HCl and NO (Test 10 in Table 4-3) was tested in Run 742. About 95% capture was observed over the entire 4-hour test period. The result is most similar to HCl alone in that capture was constant over the entire test period, while for the test with NO alone capture improved somewhat with time. However, this test indicates that the combination of NO and HCl will produce very similar results to those for either HCl or NO alone for the given conditions.

HCl and NO<sub>2</sub> (Test 11 in Table 4-3) was evaluated in Runs 741 and 770. Close to 100% capture was observed in both of these runs for more than 3 hours, indicating that HCl and NO<sub>2</sub> behave similarly to either gas by itself. In all three cases, close to 100% capture was observed. A change in experimental conditions such as a reduced sorbent mass possibly could reveal

differences, but these tests did not. For Run 770, SO<sub>2</sub> was added after 2.75 hours of testing with HCl and NO<sub>2</sub>. After a period of about 40 minutes, there was rapid breakthrough up to 200% of the inlet mercury concentration, and the breakthrough mercury was all oxidized. This is similar to the result in which SO<sub>2</sub> was added after starting a test with NO<sub>2</sub> alone (Run 769) with one difference. In Run 769 the breakthrough was almost immediate after starting the SO<sub>2</sub>, while in Run 770 there was a distinct delay in the time before breakthrough. This suggests that the combination of SO<sub>2</sub> and NO<sub>2</sub> is dominating the mercury capture, desorption, and oxidation, but that HCl also is playing a role in what is happening at the sorbent surface.

#### 4.2.1.4 Three-at-a-Time Tests with SO<sub>2</sub>, HCl, NO, and NO<sub>2</sub>

The full factorial design of 16 tests includes four possible combinations of these gases taken three at a time. The combination of SO<sub>2</sub>, HCl, and NO (Test 1 in Table 4-3) was evaluated in duplicate tests, Runs 711 and 712. Both of these tests show initially a breakthrough of 10%–25% and then better capture with time, achieving at least 95% capture after 2 hours. This result is similar to a number of the tests with NO (except for the case when both SO<sub>2</sub> and NO<sub>2</sub> are present) that indicate some initial breakthrough and then better capture as the test proceeds. Comparing the results from Runs 711 and 712 with those for Run 742, which included only NO and HCl, suggests that the addition of SO<sub>2</sub> may make the initial breakthrough higher, but after several hours this difference disappears. The net result is that the combination of SO<sub>2</sub>, HCl, and NO still provided good sorbent performance for the given test conditions.

The combination of HCl, NO, and NO<sub>2</sub> (Test 9 in Table 4-3) is represented in the breakthrough graph for Run 761. Initially, 10%–20% breakthrough was observed, which again seemed to improve with time; however, there were some zero-drift problems. Analysis of the sorbent after the run suggests 100% capture, so the data indicate capture in the range from 90% to 100%. This combination of gases also provides excellent capture of Hg<sup>0</sup> for the LAC sorbent at 225°F (107°C).

The combination of HCl, SO<sub>2</sub>, and NO<sub>2</sub> (Test 4 in Table 4-3) was evaluated in duplicate tests, Runs 714 and 715. Results from these duplicate runs are in good agreement and show an initial period of close to 100% capture for 1–1.5 hours, followed by fairly rapid breakthrough above the 100% level. This result is very similar to those for other tests with SO<sub>2</sub> and NO<sub>2</sub> and again demonstrates that the interaction between SO<sub>2</sub> and NO<sub>2</sub> has a profound effect on sorbent performance.

The fourth possible combination, SO<sub>2</sub>, NO, and NO<sub>2</sub> (Test 6 in Table 4-3), was also evaluated in duplicate tests, Runs 757 and 763. A very similar trend of initial good capture followed by rapid breakthrough was seen with this gas mixture. There does appear to be more rapid breakthrough than for the combination of HCl, SO<sub>2</sub>, and NO<sub>2</sub>. This suggests that HCl is also playing a role in the breakthrough phenomenon, possibly delaying the onset. Again, the breakthrough mercury appears to all be oxidized without any HCl present, suggesting a volatile mercury species other than HgCl<sub>2</sub>.

#### 4.2.1.5 All Gases Present, SO<sub>2</sub>, HCl, NO, and NO<sub>2</sub>

The full factorial design includes the condition with all of the variable gases present (Test 2 in Table 4-3), which was tested in duplicate Runs 721 and 731. This combination is the most representative of the possible gas concentrations that are known to be present in real flue gas. Both tests showed the same effect, although Run 731 had more data scatter. An initial period of good mercury capture for 1 hour was followed by a fairly rapid breakthrough up to 100% of the inlet level. The breakthrough did not appear to exceed the inlet level, which occurred in the tests with the combination of SO<sub>2</sub> and NO<sub>2</sub>.

The condition with all four gases was also evaluated at 325°F (163°C) in duplicate tests, Runs 729 and 730. At the higher temperature, the initial capture was somewhat lower, but the same trend occurred, showing significant breakthrough after 1 hour and approaching the inlet concentration by 3 hours. Essentially all of breakthrough mercury was measured as oxidized mercury. These results have significant implications because they show that the interaction

between SO<sub>2</sub> and NO<sub>2</sub> has the potential to dominate Hg<sup>0</sup> capture with this specific activated carbon. Since some SO<sub>2</sub> and NO<sub>2</sub> are always present in coal combustion flue gas, this effect is likely to have an impact on sorbent performance for a variety of coals. In addition, since the effect occurred at both ends of the wide temperature range from 225° to 325°F (107° to 163°C), it cannot be easily avoided by a small change in temperature. The results also imply that previous bench-scale studies of mercury sorbent capacity and reactivity that did not include both SO<sub>2</sub> and NO<sub>2</sub> may provide misleading results.

#### *4.2.2 Effect of CO, HF, and NH<sub>3</sub>*

Because of significant interaction between SO<sub>2</sub> and NO<sub>2</sub>, several additional tests were completed to briefly evaluate whether other reactive gases might also affect mercury capture by sorbents. The effect of CO was tested in Run 785 by adding 100 ppm CO to the other four gases (Test 17 in Table 4-3). Comparing the breakthrough graphs in Appendix A for Run 785 with those for Run 721 (without CO) suggests that CO had no effect on the results. However, further testing would be necessary to show whether CO might affect the results with a different gas matrix.

Because all coals contain some fluorine as well as chlorine, a trace amount of HF will also be present in the flue gas. For some low-chlorine western coal in the United States, the HF concentration may be several times higher (on a molar basis) than the HCl. Three different test conditions were evaluated in which HF was present (Tests 18–20 in Table 4-3). For Test 18, 10 ppm of HF was added to the other four gases. Run 779 shows that the shape of the breakthrough curve was unchanged from the test without HF other than a somewhat higher initial breakthrough. Whether this was instrument drift or a real effect cannot be determined from this single test. The data suggest that HF at the most has a small effect compared to the similar test without HF. Test 19, Run 782 was similar, except HCl was removed from the gas matrix. Again, the graph indicates very little difference, suggesting that 10 ppm HF did not have a significant effect. In Test 20, all of the other four gases were removed to see if HF alone might have the same effect as HCl alone. Duplicate tests, Runs 783 and 784, indicate that HF alone resulted in

about 45% breakthrough compared to almost 100% capture with HCl alone. This indicates that 10 ppm of HF does not produce the same effect as 50 ppm of HCl. However, compared to the baseline gases alone (O<sub>2</sub>, CO<sub>2</sub>, N<sub>2</sub>, H<sub>2</sub>O), the HF significantly improved the mercury capture, indicating that HF may interact with the mercury or sorbent surface to enhance Hg<sup>0</sup> capture. Another observation with the HF was the much more severe instrument drift, as shown in the graphs. This may have been a result of interaction of HF within the auto-zero carbon trap of the Semtech instrument. This carbon trap contains iodine-impregnated activated carbon (at room temperature) and is intended to serve as a source of mercury-free sample gas for auto-zeroing of the instrument. Analysis of the spent sorbent for Run 783 indicates an average of 54% capture, which is in agreement with the Semtech data after each auto-zero correction. This confirms that the presence of 10 ppm HF does improve mercury capture and suggests that HF should not be ignored when considering possible mechanisms of capture or oxidation.

A test was also conducted with the addition of 25 ppm NH<sub>3</sub> to the other four gases (Test 21 in Table 4-3). Ammonia is not expected in the flue gas from coal combustion but may be present as a result of selective noncatalytic reduction (SNCR) or selective catalytic reduction (SCR) NO<sub>x</sub> control methods. Further, ammonia has the potential to neutralize acid gases and therefore might have an effect on mercury capture with sorbents. The results in Run 788 indicate that the addition of ammonia may increase the time until breakthrough and may reduce the amount of breakthrough, since after 3.5 hours, only up to 60% breakthrough was observed. This indicates that 25 ppm of NH<sub>3</sub> has the potential to affect capture of Hg<sup>0</sup>, but this one test should not be considered definitive as to the effect of ammonia.

#### ***4.2.3 LAC Tests at 325°F (163°C)***

The tests conducted with LAC sorbent at 325°F (163°C) are listed in Table 4-4. Discussion of the comparative results with the corresponding test at 225°F (107°C) is in the previous sections. In summary, all of the tests at 325°F (163°C) (with the exception of the baseline test with no acid gases present) showed similar breakthrough curves to those for the corresponding tests at 225°F (107°C). The most obvious difference was that for some of the tests, the initial

breakthrough level was slightly higher at 325 °F (163 °C). For the baseline condition, 100% breakthrough was observed immediately for the 325 °F (163 °C) test, while at 225 °F (107 °C), the breakthrough was about 80%. This indicates some physisorption at the lower temperature but not at the higher temperature, which is the trend expected. In contrast, with the acid gases present, the fact that excellent capture was observed at both 225 ° and 325 °F (107 ° and 163 °C) indicates that the captured mercury is trapped through chemical bonding. However, several different surface-bound mercury species may be present with differing gas mixtures. The positive identification of these surface-bound species remains a research need. Since excellent mercury capture was observed at 325 °F (163 °C) for the tests without the combination of SO<sub>2</sub> and NO<sub>2</sub>, there is hope that an effective sorbent can be developed if the SO<sub>2</sub>/NO<sub>2</sub> problem can be circumvented.

#### *4.2.4 Conclusions from the LAC Gas Mixture Tests*

- Without acid gases present, upon exposure to a baseline gas mixture of O<sub>2</sub>, CO<sub>2</sub>, N<sub>2</sub>, and H<sub>2</sub>O, the LAC sorbent provided only about 10%–20% mercury capture of Hg<sup>0</sup> at 225 °F (107 °C) and no capture at 325 °F (163 °C). Under these conditions, the LAC sorbent was completely ineffective at capturing elemental mercury.
- When the sorbent was exposed to SO<sub>2</sub> in addition to the baseline gases, LAC sorbent capture improved slightly, but the LAC sorbent was still ineffective at capturing elemental mercury.
- Upon exposure of the sorbent to HCl, NO, or NO<sub>2</sub> added one at a time to the baseline gases, the mercury capture improved to 90%–100% at 225 °F (107 °C). Under these conditions the LAC is a highly effective sorbent for capturing elemental mercury.
- A highly significant interaction between SO<sub>2</sub> and NO<sub>2</sub> caused a rapid breakthrough of mercury as well as conversion of the mercury to a volatile oxidized form. This effect

occurred at both 225° and 325°F (107° and 163°C) and with or without the presence of HCl and NO.

- A brief test where CO was added to the other gases did not reveal any differences compared to similar conditions without CO.
- HF alone added to the baseline gases can improve Hg<sup>0</sup> capture, but when it was added to the other gases no significant effect was observed.
- NH<sub>3</sub> added to the other gases appears to delay and reduce the amount of mercury breakthrough.
- Temperature in the range of 225°–325°F (107°–163°C) did not appear to be a dominant factor in the capture of Hg<sup>0</sup> when any of the acid gases were present.

### **4.3 Fine-Particle Gas Matrix Tests with EERC Sorbents**

The initial development tests with modified carbons were described in detail in Section 3.0. These tests were conducted earlier in the project with a small fixed bed of granular material. The original plan was to also complete fine-particle screening tests with these same materials using simulated flue gases earlier in the project, but the 1997 flood severely damaged the main mercury laboratory so the simulated flue gas tests could not be completed until later. The sorbent development work was conducted in another laboratory at the EERC that was not damaged. Subsequently, the results from the tests using simulated flue gases were not available until later in the project and, therefore, could not be used as a source of information to modify the treatment approach. Tests with four different sorbents were completed.

The purpose of these tests was:

- To compare results with the granular bed experiments.

- To evaluate modified sorbent performance in the presence of acid gases.
- To compare modified sorbent performance with that of the commercial LAC.
- To compare sorbent performance between the baseline Calgon carbon and the EERC-modified Calgon carbon in the presence of acid gases.
- To gain an understanding of the relation between sorbent surface chemistry and mercury capture.

Two catalytic carbons with modified edge structures were tested as fine particles (-400 mesh) in the thin-bed filter apparatus with continuous total mercury monitoring (Semtech). The results were compared with those of the original unmodified Calgon F400 activated carbon. Most tests used 150 mg of the fine sorbent and 2–3 temperatures in a variety of gas mixtures.

Sorbent 92-4 was prepared by impregnating the Calgon carbon with PVP (5 wt%) and recarbonizing. Sorbent 92-5 was prepared by impregnation of the Calgon carbon with the indole pitch and recarbonizing. All carbons were pretreated with 5% sulfuric acid.

The conditions for tests with Sorbents 92-4 and 92-5 are shown in Tables 4-5 and 4-7. The baseline Calgon sorbent tests are listed in Table 4-6. The fourth sorbent tested (Table 4-8) was a manganese oxide sorbent designated 52-1. The breakthrough curves for each run are included in Appendix A.

#### ***4.3.1 Comparative Tests in Air***

To make a direct comparison with the granular-bed tests (which were all conducted in air or nitrogen) several tests were completed in air with each of the four sorbents.

Duplicate runs were conducted with both the PVP carbon (Runs 775, 778) and the unmodified Calgon carbon (Runs 748, 749) in an air flow at 300°F (149°C). Each set of duplicates gave very similar curves and removal rates. Comparison of the sorption curves shows that for both sorbents, the initial removal is high, close to 0% mercury in the effluent. The unmodified carbon broke through fairly rapidly, 50% in 0.5 hr, 67% in 1.25 hr, and 80% in 1.5 hr. For these runs, a second Semtech analyzer was used to provide simultaneous measurement of total and elemental mercury, as shown in the breakthrough graphs. Within the variability of the instruments, the mercury passing through the sorbent was not oxidized, but remained as Hg<sup>0</sup>.

The PVP carbon (92-4) demonstrated significantly better capture, slowly reaching 40% mercury in the effluent after about 1.5 hr. When the converter furnace was switched off, the mercury in the effluent dropped to nearly zero. Thus, in contrast to the unmodified carbon run, the mercury species in the effluent from the PVP carbon was mostly oxidized mercury, presumably HgO. As in the fixed-bed tests, the PVP modified carbon is effective in catalyzing oxidation of the mercury, even to the extent that the mercury that is not captured is also oxidized.

In comparison to the granular catalytic carbon tests at relatively slower flow rates, the capture by the fine-particle catalytic carbons at higher velocity is less effective. Although the surface area is high, the contact time in the thin bed is short. In the granular-bed tests, oxidized mercury in the vapor would pass through several centimeters of carbon before exiting the bed. During this transit, the oxidized mercury may have been captured by the large surface area of the carbon sorbent and was not observed in the effluent.

The results with the indole pitch carbon (92-5) in air (Run 739) show that the carbon is less effective at the start (20% Hg in the effluent), but very little change in the sorption rate occurs over the run time of 3.25 hours (25%). Thus, this carbon has a very high capacity and is clearly superior to the unmodified Calgon carbon. When the converter furnace was switched off, the mercury dropped back only to 20%, indicating little conversion to oxidized mercury in the breakthrough. However, the captured mercury was likely converted to oxide and bound to the sorbent surface.

In the air run with the LAC sorbent (756), the breakthrough was very rapid (5 min) to 80% mercury in the effluent. Compared with the unmodified Calgon carbon with 50% breakthrough at 0.5 hours and 80% at 2.5 hours, the performance is very poor. As with Calgon, the mercury in the effluent is  $\text{Hg}^0$ .

To summarize the results in the air system, the catalytic carbons are far superior to noncatalytic carbons. Additional tests are needed with the catalytic carbons where part of the bed is replaced by another material that could trap the acidic  $\text{HgO}$  or  $\text{HgCl}_2$  that forms in the first part of the bed by the catalytic carbon. This material could be  $\text{CaO}$  or other basic materials or a sulfide. The basic material or sulfide could also reside in the catalytic carbon particles. Runs without the acid promoter are also needed.

#### ***4.3.2 Baseline Gas Tests with HCl and $\text{SO}_2$***

The runs with the baseline gas composition including  $\text{HCl}$  and  $\text{SO}_2$  were conducted at two temperatures, 325° and 225°F (163° and 107°C). The PVP carbon and indole pitch carbon were again compared, with the unmodified Calgon carbon using about 150 mg of sorbent. At 325°F (163°C) (Run 704), the PVP carbon (92-4) showed 10% mercury in the effluent at the start and increased to 50% breakthrough in 1 hour. A slow increase continued for the rest of the test. Unfortunately, the mercury in the effluent was not speciated. The unmodified Calgon run (777) started at 20% mercury in the effluent and increased slowly to 45%. Mercury in the effluent was mostly  $\text{Hg}^0$ . Thus, in the acidic gas composition, the unmodified carbon shows a little better capture. But as in the air tests, the mercury in the effluent from the unmodified carbon is not an oxidized species.

The run with indole pitch carbon (92-5) at 325°F (163°C) (Run 707) started at 12% Hg in the effluent and increased to 30% in 1 hr, and dropped slowly back to 20% by the 4-hour end point. This appears to be a better capturing performance than that of the PVP and Calgon carbons; however, the amount of mercury in the inlet was lower for this test at 7 mg/ $\text{Nm}^3$ .

At 225°F (107°C) in the baseline gas composition with HCl and SO<sub>2</sub>, the PVP carbon (Run 700) gave 10% Hg initially and slowly increased to 27% in 1 hour. So the PVP carbon sorbent was more effective at the lower temperature. The unmodified Calgon was also much more effective at 225°F (107°C) (Run 746), starting at 5% and increasing to 8% Hg in the effluent over the 3.5-hour run. In Run 702, also at 225°F (107°C), the indole pitch carbon was used at lower loading (105 mg) but exhibited good sorption, starting at 15% and increasing slowly to 25% at the 2.5-hour end point.

The LAC sorbent was extensively investigated in the baseline gas composition. At 225°F (107°C) (Run 686), very little mercury (5% to 10%) was in the effluent throughout the 4-hour run. This is better for than the catalytic carbons and similar to the unmodified Calgon. When the HCl was omitted from the baseline composition (Run 750), immediate breakthrough was observed. All of the mercury in the effluent was Hg<sup>0</sup>. Thus HCl is most likely to be the dominant factor in the tests, resulting in greatly enhanced sorption, especially for the LAC and the Calgon carbons. This large positive effect has been previously noted (14).

Why are the catalytic carbons as well as the Calgon more effective at the lower temperature in the acidic gas composition? Previous studies in the air composition showed that the catalytic carbons are more effective at higher temperatures. In the latter (air) case, the kinetics of the mercury oxidation are clearly determining the effectiveness of capture. However, in the acidic gases, other equilibrium effects are important, such as the volatility of the oxidized mercury species. At the higher temperature, less oxidized mercury stays on the sorbent.

#### ***4.3.3 Comparative Tests with HCl, SO<sub>2</sub>, NO, and NO<sub>2</sub>***

In this series of runs, 300 ppm NO and 20 ppm NO<sub>2</sub> were added to the other gases. These runs were all conducted at the lower temperature, 225°F (107°C). The PVP carbon (Run 773) started at 10% Hg in the effluent, showed 50% breakthrough in 1 hour, and increased to 100% in 2 hours. This is a serious negative effect on the capture performance. All the mercury in the effluent was oxidized. The unmodified Calgon (Run 747) started at 12%, showed 50%

breakthrough at 2 hours, and increased to 100% at 2.5 hours. Again, a large negative effect was observed, and again, all of the mercury in the effluent was oxidized. This is an important distinction compared to the test without  $\text{NO}_x$  ( Run 777), where the effluent was  $\text{Hg}^0$ . Thus the two carbons behave similarly in this composition, presumably because of the  $\text{NO}_x$ , which is highly effective at oxidizing  $\text{Hg}^0$  on any surface at temperatures at least as low as ambient. But it is not clear why the ability to capture this oxidized mercury is not retained for a very long time by the carbons.

Duplicate runs (772, 774) with the indole pitch carbon at 225°F (107°C) in the baseline +  $\text{NO}_x$  were conducted. These runs started with 10% Hg in the effluent, showed 50% breakthrough at 1.25 hours, and increased to 100% at 2 hours. This performance was only slightly better than that of the PVP carbon. Again the mercury in the effluent was oxidized.

To determine whether HCl in the baseline composition modifies the negative effect of the  $\text{NO}_x$ , a run was completed without the HCl (Run 786). The 50% breakthrough occurred at 0.7 hours, compared with 1.25 hours in Runs 772 and 774. Thus the HCl in the 772 and 774 runs decreased the negative effect of the  $\text{NO}_x$  on the breakthrough time. This is consistent with the tests without  $\text{NO}_x$ , where the HCl exhibits a positive effect on the breakthrough curve, presumably by oxidizing the mercury.

Comparing the tests of four different sorbents with  $\text{SO}_2$ , HCl, NO, and  $\text{NO}_2$  present indicates that the same interaction between  $\text{NO}_2$  and  $\text{SO}_2$  occurred with the Norit LAC carbon, the Calgon F400 carbon, and the two modified Calgon carbons. In each case, there was an initial period of nearly 100% capture, followed by a rapid and complete breakthrough of an oxidized form of mercury. That it occurred with four different sorbents with differing surface properties and at both 225° and 325°F (107° and 163°C) suggests that this is a dominant effect that needs to be understood to facilitate development of better sorbents.

#### ***4.3.4 Flue Gas Plus NH<sub>3</sub>***

Can a reducing agent like NH<sub>3</sub> lower the effect of NO<sub>x</sub> on capture? When NH<sub>3</sub> was added to the baseline + NO<sub>x</sub> composition (Run 789), the 50% breakthrough was extended to 3 hours. This reduction of the negative NO<sub>x</sub> effect is a significant finding, offering hopes for combined SCR–mercury capture in flue gas treatment. More experiments are required to determine the exact benefit, however. Another significant finding is that the mercury in the effluent at the end of this run was all elemental, in clear distinction from the occurrence of oxidized mercury in previous runs. The NH<sub>3</sub> is therefore affecting the mercury reactions as well as the NO<sub>x</sub> reactions. A similar extension of the breakthrough was observed with the LAC carbon. When NH<sub>3</sub> was added (Run 788), the 50% breakthrough occurred at 2.5 hours compared with 1.3 hours without NH<sub>3</sub> (Runs 729, 730).

#### ***4.3.5 Metal Oxide Sorbent Test with Flue Gas***

Table 4-8 lists the tests completed with a manganese oxide sorbent (52-1), along with the test conditions and specific runs, which are included in the Appendix A. None of these tests resulted in significant mercury capture either with or without acid gases present. Earlier granular-bed tests with a much higher sorbent-to-mercury mass ratio and a much higher mercury concentration showed that this sorbent could effectively trap mercury in nitrogen or air. The much lower mercury capture in these tests may indicate a kinetic limit for the shorter contact time and lower mercury concentration. From the test results with flue gas, this metal oxide sorbent does not appear promising for coal applications.

## 5.0 SORBENT STABILITY

### 5.1 Preliminary Sorbent Stability Tests

Since there is no accepted approach to evaluate the stability of mercury in spent adsorbents, the method evaluated consisted of TGA experiments coupled with the use of a mercury vapor detector to correlate mercury desorption with weight loss upon controlled heating. The procedure used is described below.

The TGA used in laboratory-scale testing is a DuPont Model 951 module interfaced to a DuPont 2100 thermoanalyzer and data processor. The instrument has a 100-mg capacity and a maximum heatup rate of 100°C/min. The sample compartment is a quartz tube through which argon or H<sub>2</sub>/argon is flowed from the balance housing toward the exit port at 275 cm<sup>3</sup>/min. A special quartz tube is also available, which has a sidearm through which a 1/16-in.-OD tube is inserted to allow corrosive gases, simulated combustion or gasification gases, or steam to be introduced to the sample chamber without passing through the balance housing. The small area of metal balance housing exposed to the reaction chamber is bathed in a flow of gas, usually an inert gas such as N<sub>2</sub> or Ar, to minimize backflow of mercury. Typical solid or liquid sample sizes ranged around 50 mg of as-received material, although samples as small as 1 mg or as large as 100 mg may be loaded on a platinum or quartz pan. For the first set of experiments, only platinum pans were available. Real-time weight, time, and temperature were computer-logged for later analysis. Cold-vapor mercury detection was used to detect Hg<sup>0</sup> in the effluent gas stream expelled from the TGA. An EPM mercury analyzer was used to monitor mercury desorption.

Mercury desorption from two baseline and three mercury-containing samples was studied:

- Baseline commercial carbon
- Baseline commercial carbon with SO<sub>4</sub><sup>2-</sup> treatment

- Commercial activated carbon doped with  $\text{SO}_4^{2-}$  and containing 0.1% adsorbed mercury
- Commercial activated carbon/quartz sand/ $\text{HgSO}_4$
- 99.73% quartz sand/carbon/ $\text{HgCl}_2$

Initial testing was carried out under an inert atmosphere flowing at  $275 \text{ cm}^3/\text{min}$  using the EPM detector. Tests of thermal evolution of mercury from test equipment and baseline carbon showed a negligible signal, as shown in Figure 5-1. The sulfate-doped baseline carbon showed a significant peak from  $392^\circ$  to  $752^\circ\text{F}$  ( $200^\circ$  to  $400^\circ\text{C}$ ), which was likely the decomposition of sulfate as  $\text{SO}_2$ . The peaks for two tests of the sulfate-containing carbon and adsorbed mercury (Sample 3) showed slightly higher peaks and shifted slightly toward lower temperatures (see Figure 5-1). This is consistent with the desorption of mercury along with sulfate decomposition. The mercury monitor was intended to confirm this, but there was a major interference from  $\text{SO}_2$  absorption of UV frequency with mercury UV absorption, so the mercury desorption could

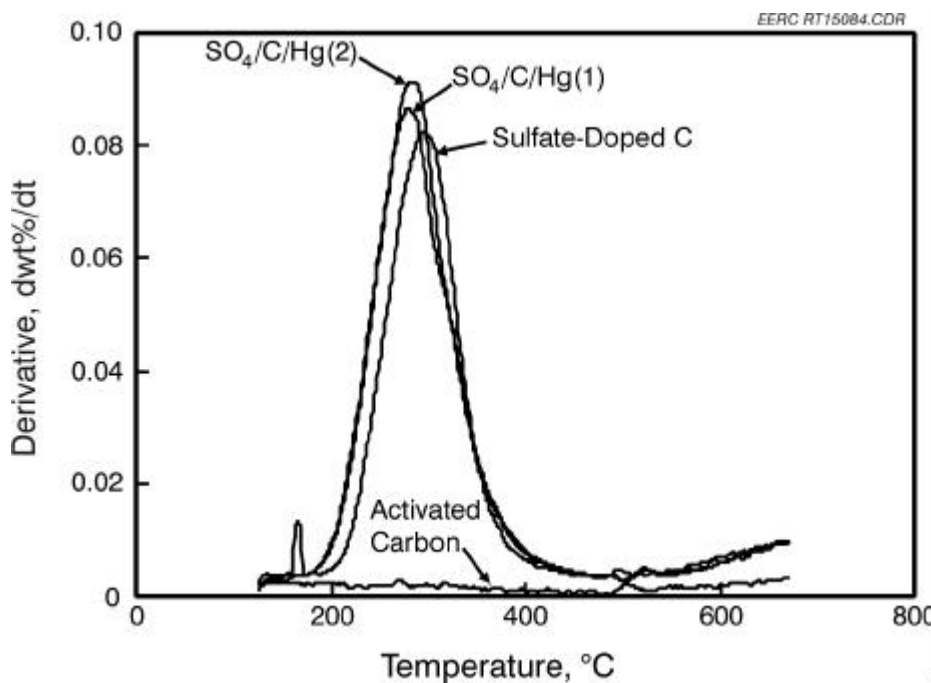


Figure 5-1. TGA results from baseline carbon, sulfate-doped carbon, and mercury-containing carbon.

not be confirmed. There also appeared to be mercury uptake from the platinum pan, most likely the result of mercury amalgamating with the platinum. Heating the pan after the test resulted in a release of mercury beginning at approximately 302°F (150°C), with increasing evolution as the temperature increased. The higher peak for the repeat test of Sample 3 is also an indication that some amalgamation occurred in the first test and was then released again or the sorbent was less effective in capturing mercury in the second test.

Sample 4 was analyzed by TGA to determine the weight loss and reproducibility of the mercury-containing samples with a known amount of mercury mixed with the sample. The mercury analyzer was not used for this test. However, mercury amalgamation was apparent from the duplicate testing on Sample 2. Sample 5 was used to avoid using substrate containing sulfate, so HgCl<sub>2</sub> was mixed with the sand. The quartz sand was analyzed and showed no evolution of UV-absorbing species, indicating the sand had no mercury contamination. Then several tests were conducted with various levels of HgCl<sub>2</sub> added to the sand. Heating the compound with on-line mercury detection was expected to, and did, show a small signal at 302°F (150°C), indicating trace amounts of Hg<sup>0</sup> in the HgCl<sub>2</sub>, and a larger signal at 536°–572°F (280°–300°C), indicating decomposition of the salt. The TGA plot of the sand–HgCl<sub>2</sub> tests is shown in Figure 5-2 and indicates increasing peak heights with higher fractions of HgCl<sub>2</sub>, as would

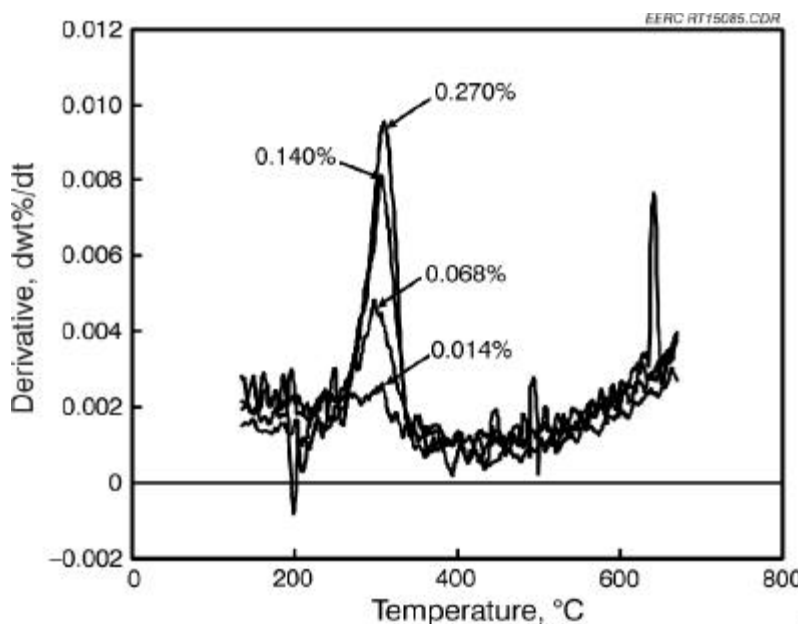


Figure 5-2. TGA results showing mercury desorption from quartz sand, carbon, and HgCl<sub>2</sub> mixture.

be expected; however, some amalgamation was likely occurring so that integrating the peak area would not lead to a mass balance closure. These data indicate that the TGA approach may prove to be a viable method to evaluate desorption, but the two problems of SO<sub>2</sub> interference and platinum amalgamation need to be corrected. Future experiments should be conducted with a quartz pan to prevent any amalgamation interference and with a mercury analyzer that is not susceptible to SO<sub>2</sub> interference. The EERC has a Semtech analyzer that is not as susceptible to SO<sub>2</sub> and will be used for any further work.

The study continued with the Semtech detector replacing the EPM detector. Ideally, entrained SO<sub>2</sub> is transparent to the Semtech detector, and therefore, the SO<sub>2</sub> will not interfere with mercury detection. The same samples listed above were studied under three atmospheres, i.e., argon, H<sub>2</sub> in argon, and simulated flue gas.

A suite of tests was designed to determine the mercury contamination of equipment occurring as a result of mercury vaporization from solid residues. The TGA was interfaced with the Semtech detector. Blank tests were carried out with a new pan, a used (in a mercury test) pan, a used (in a mercury test) tube, sand, and sand spiked with HgCl<sub>2</sub> and HgSO<sub>4</sub>. In all cases, the gaseous atmosphere was H<sub>2</sub>/Ar flowing at 275 cm<sup>3</sup>/min at ambient pressure. The derivative of wt %/t, UV absorbance, time, and temperature were collected, and dwt %/dt and UV absorbance versus temperature were plotted. The results of these tests are shown in Figures 5-3–5-8. Several observations confirmed the need for extreme care in interpreting analytical results for mercury entrained in gas streams:

- The Semtech detector is preferred for mercury detection in a gas stream that may also contain SO<sub>2</sub>.
- Uncontaminated quartz and metal parts, including platinum pan, show measurable mercury desorption when heated (Figure 5-3).

- A once-used platinum pan is contaminated with amalgam, and elemental mercury is present on surfaces of used equipment (Figure 5-4).
- Elemental mercury can be distinguished from amalgamated mercury using thermal desorption (Figure 5-4).
- Fresh sand lost only a very small amount of moisture when heated in a new pan after the instrument had been cleaned. UV absorbance and a small weight loss beginning at about 536°F (280°C) indicated a trace of mercury, probably from the amalgam on the pan support beam (Figure 5-5).
- Although a slight weight loss occurred on heating HgCl<sub>2</sub>/sand, mercury detected was probably not substantially due to decomposition of salt but to amalgam desorption (Figure 5-6).
- Although weight loss from SO<sub>2</sub> evolution occurs in the 400°–600°F (204°–316°C) range, it was transparent to the Semtech instrument (Figure 5-7).
- The HgSO<sub>4</sub>/sand/carbon mixture lost weight in two temperature ranges, and no mercury was detected in the gas stream (Figure 5-7).
- A meticulous cleaning protocol is required to completely remove mercury from all contacted surfaces. Elemental mercury was detected even after exchange of the used quartz vessel and platinum pan for new ones (Figure 5-8).

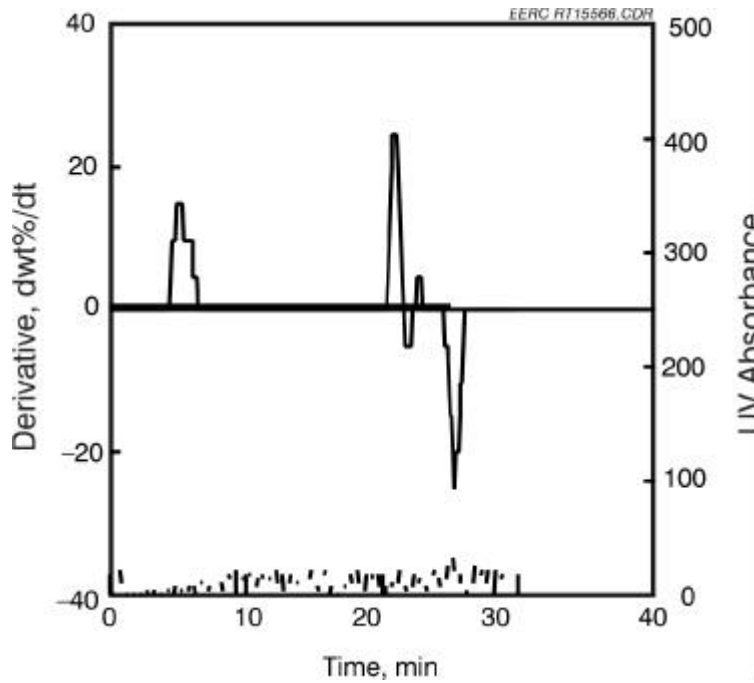


Figure 5-3. TGA instrument without contamination shows no measurable Hg within experimental uncertainty.

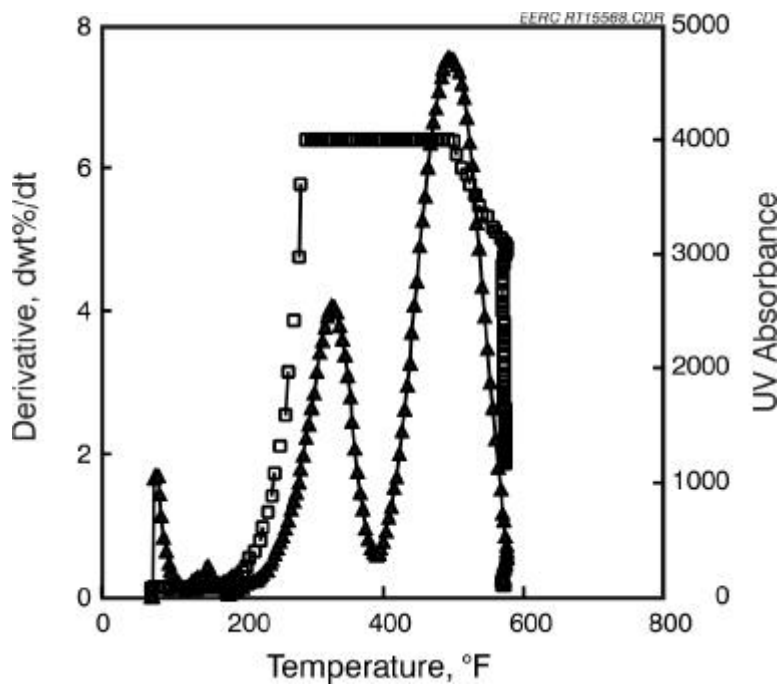


Figure 5-4. Hg desorbed from replaceable and permanent components of TGA sample chamber. Elemental Hg and Hg from amalgam are evident.

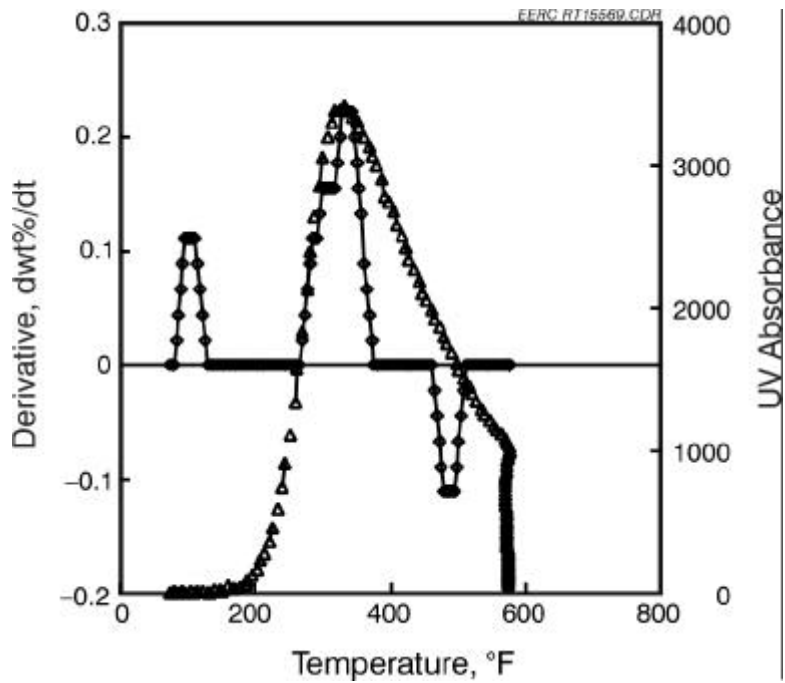


Figure 5-5. Hg desorbed from new sand diluent for Hg salts on unused Pt pan. Hg detected is the result of contamination from previous testing.

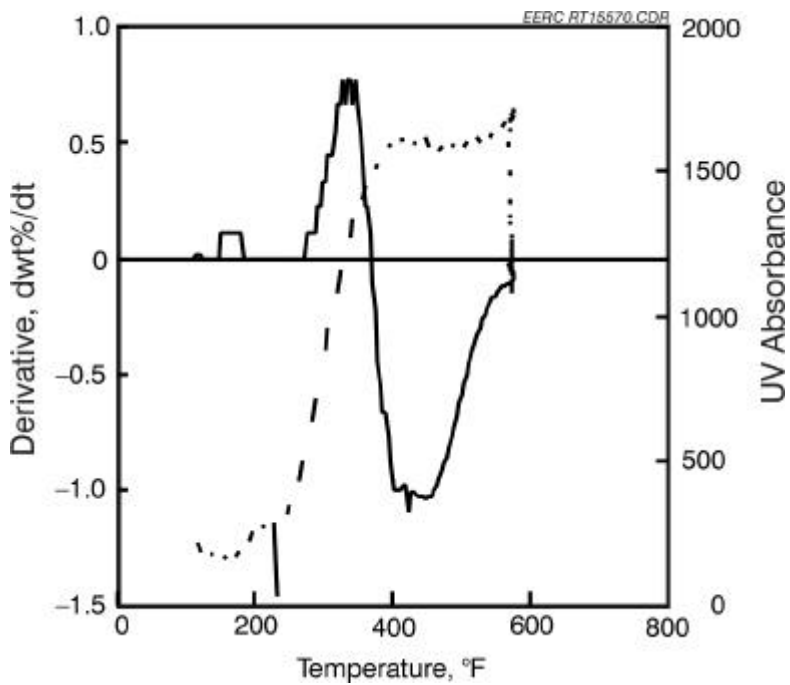


Figure 5-6. Hg desorbed from  $\text{HgCl}_2$  salt diluted with sand and carbon and analyzed on clean unused Pt pan in a reducing atmosphere. The salt appeared to partially decompose.

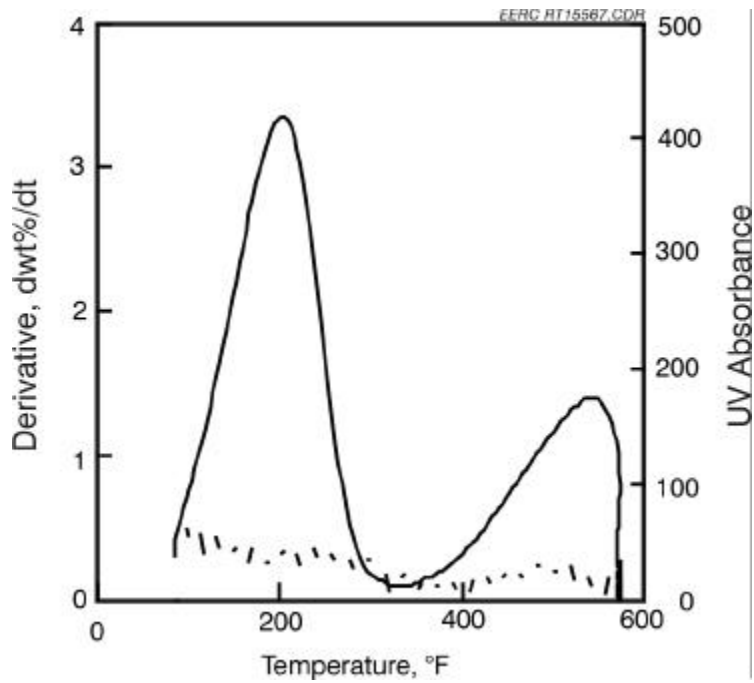


Figure 5-7. Hg desorbed from  $\text{HgSO}_4$  salt diluted with sand and carbon and analyzed on clean unused Pt pan in a reducing atmosphere. The salt did not decompose.

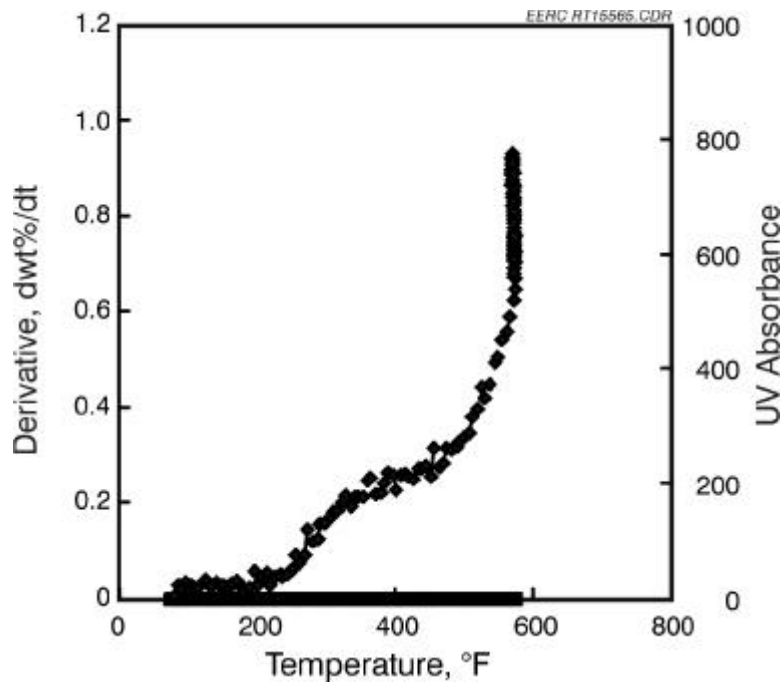


Figure 5-8. New replacement parts (Pt pan and quartz tube) do not eliminate Hg contamination of instrument. Instrument face plate harbors Hg contamination.

## 5.2 Thermal Stability and Leaching Tests

### 5.2.1 Introduction

The use of sorbents to remove mercury from flue gas presents several technical issues relative to the management of the sorbent following use. Whether the mercury control sorbents are collected as a separate stream or commingled with the fly ash, these solid wastes will require management, which will likely include primarily disposal. The behavior of the sorbent and sorbed mercury is an important issue in selection of the type of mercury sorbent that a utility might use and in the method of disposal that is most environmentally sound. Solid materials generated at coal-fired utilities are generally managed by either disposal (70%–80% of the U.S. production is disposed annually) or utilization. In recent years, there has been increased emphasis on the utilization of coal combustion by-products (CCBs) by government agencies and industry because it has been assessed to be an environmentally sound, technically feasible, and economically advantageous method of CCB management. If spent mercury control sorbents are commingled with other CCBs, there may be an impact on the utilization potential of the CCBs. Disposed spent sorbents may require different handling than the CCBs and other low-volume wastes being disposed by utilities. CCBs are typically either handled wet and disposed in ponds or lagoons or handled dry and landfilled. The stability of mercury in spent sorbents needs to be determined for both scenarios.

The work reported here was designed as a preliminary effort to answer two key questions relative to the management of spent mercury control sorbents: 1) How stable is the sorbed mercury in typical disposal environments? and 2) Will the spent sorbent impact the CCB management strategies if it is commingled with CCBs? Key to answering these questions is the development of methods to evaluate the mercury stability and potential for release into the environment. A significant effort was directed at design of laboratory apparatus and development of test protocols that would provide accurate, scientifically valid, and legally defensible information.

## 5.2.2 *Experimental*

### 5.2.2.1 Selection of Samples

For this project, six samples were selected for characterization by thermal desorption and leaching. Initial selection criteria were that there should be pure sorbents as well as ash containing sorbent and that the sorbents represented were shown to be highly effective in removing mercury and mercury compounds from flue gas. The two major categories of samples were coal fly ash containing sorbent that had been injected into the flue gas stream and pure sorbents prepared in the laboratory. The sorbents were subsequently loaded with mercury or mercuric chloride using bench-scale equipment. There was only approximately 500 mg of each of the pure sorbent samples available for characterization; thus it was decided to use only leaching tests on these samples, since it was known that 100–200 mg of each of the sorbents would be required for bulk chemical analysis. The coal fly ash samples had been collected during combustion tests in a pilot-scale unit at the EERC. These samples, which were several years old, were available in kilogram quantities and had been previously analyzed for mercury. They were used as-received, and any mercury they contained had been sorbed during the combustion run.

The samples included in this project along with descriptions and abbreviated designations are shown in Tables 5-1 and 5-2.

TABLE 5-1

Coal Fly Ash/Sorbent Samples

Initial Sample Designation	Description	Sample Designation Used in This Report
PTC-451-1	Fly ash containing IAC	Ash 451
PTC-454-1	Fly ash containing LAC	Ash 454
PTC-464-1	Fly ash containing LAC	Ash 464

TABLE 5-2

Sorbent Samples

Initial Sample Designation	Description	Sample Designation Used in This Report
1231S-78-1	Manganese oxide sorbent on alumina support	Sorbent 78
1231S-109-1	Manganese oxide sorbent on alumina support	Sorbent 109
1231S-173-1	Activated carbon	Sorbent 173

5.2.2.2 Thermal Desorption Apparatus

An apparatus for the controlled thermal desorption of mercury and mercury compounds was assembled and is shown in Figures 5-9 and 5-10. Figure 5-9 is a block diagram showing the

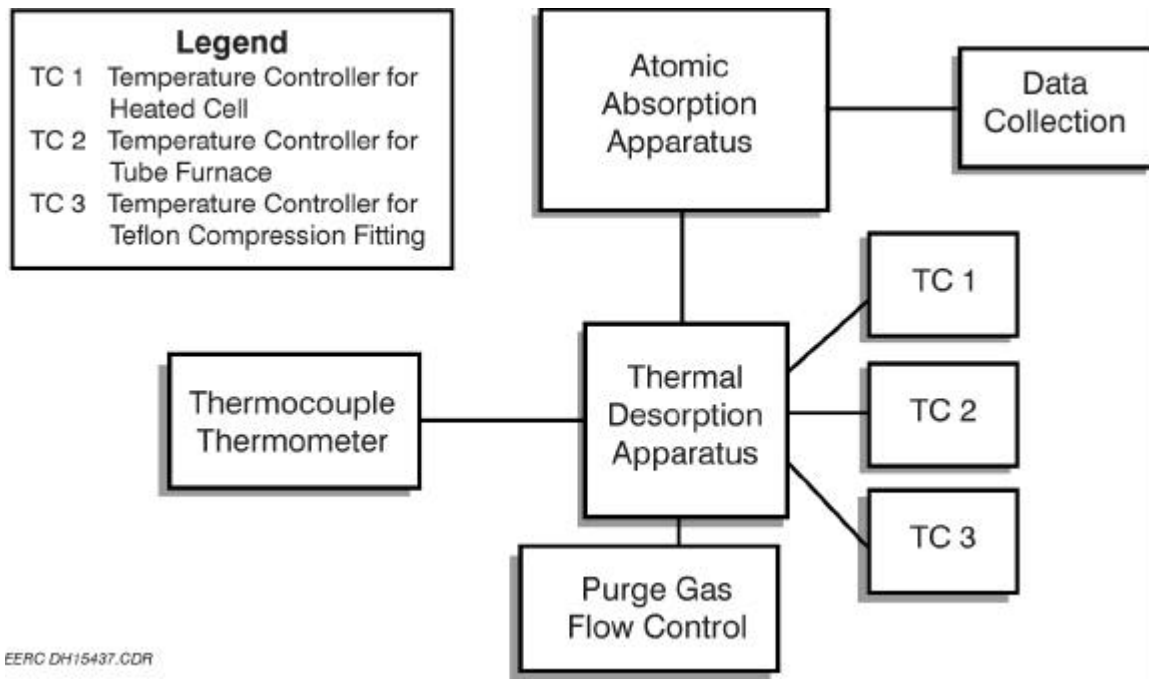


Figure 5-9. Block diagram of the thermal desorption apparatus.

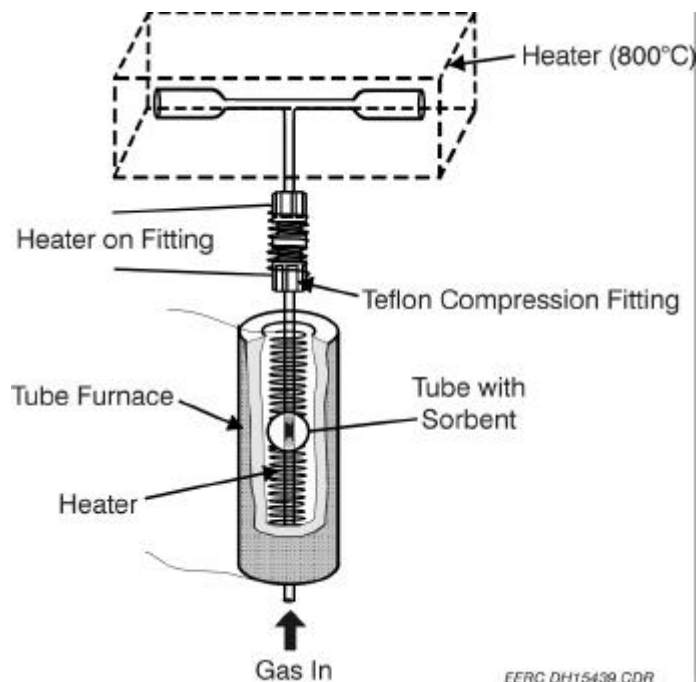


Figure 5-10. Diagram of the thermal desorption section.

major components of the overall system. The apparatus was constructed around a Varian 1475 AA spectrophotometer for mercury detection and included a small tube furnace and temperature controller for thermal desorption. The temperature controller on the tube furnace could either be run to heat ballistically to a given set point or could be programmed to ramp the furnace at a predetermined rate to a set point. A Hewlett Packard 3393A integrator was used for data collection. The AA was operated using a mercury hollow cathode lamp (HCL) as the spectral source, with detection at 253.7 nm. Detection of mercury and mercury compounds thermally desorbed from sorbents was done in an electrically heated quartz cell operated at 1472°F (800°C). The use of a heated cell allowed detection of mercury compounds by thermal reduction. The heated quartz cell assembly (ETC-50, electrothermal temperature controller) is available from Varian and consists of the quartz cell assembly, including the heater and a temperature controller, and can be heated to a maximum temperature of approximately 1832°F (1000°C). The quartz cell has a path length of 17 cm and a diameter of 17 mm at the ends of the tube. The cell is constricted at the center portion to minimize volume and takes advantage of the center-focused optics of the

AA. The inlet capillary of the cell was connected to the quartz tube used for thermal desorption by a Teflon compression fitting. This connection was maintained at between 167° and 176°F (75° and 80°C) using a heating tape. Samples for thermal desorption were packed into quartz tubes that could be inserted into the tube furnace. The plumbing for thermal desorption and transfer of analyte into the heated cell assembly was constructed so that dead space and voids are minimized and the gas stream containing analyte contacts only quartz or Teflon. A complete description of the operation of this apparatus is included below in the thermal desorption experiments section. A detailed diagram of the apparatus is shown in Figure 5-10.

*Thermal Desorption Experimental Protocol.* Samples for thermal desorption were packed into 20-cm × 4.8-mm quartz tubes with a wall thickness of 1 mm. The samples were held in the tubes with a small plug of quartz wool at each end of the specimen. Three indentations pressed into the tubes 5 cm from the exit end held the sample and quartz plugs in place once the tube had been loaded into the tube furnace, the tube connected to the heated quartz absorption cell, and gas flow initiated. Additionally, the placement of the indentations assured that the sample was centered in the tube furnace. Thermal desorption was carried out on samples of between 300 and 500 mg. This gave a packed bed of ash approximately 1 cm in length and produced a minimal pressure drop across the bed at the nominal flow rate of 20 cm<sup>3</sup>/minute of nitrogen purge gas. This sample mass also provided the over 200 ng of mercury needed to produce sufficient absorbance (>0.1 A) to allow recording of signals without noticeable noise and with minimal filtering by the integrator. Since instrument noise amounted to approximately 0.005 A, it would be possible to record thermal desorption curves with considerably smaller samples.

The temperature controller was used with a 10°C per minute ramp from ambient to a final temperature of 932°F (500°C).

#### 5.2.2.3 Leaching Studies

Two leaching tests were used for the evaluation of the potential for environmental release of mercury. These are the toxicity characteristic leaching procedure (TCLP) (16) and the synthetic

groundwater leaching procedure (SGLP) (17). Both tests use similar protocols with a 20:1 liquid-to-solid ratio, end-over-end agitation, and an equilibration time of 18 hours. The TCLP, designed to simulate leaching in a sanitary landfill, uses either an acetate buffer or a dilute acetic acid solution as the leaching fluid, depending on the alkalinity of the sample being evaluated. For this project, it was found that the highly alkaline coal fly ash samples required TCLP leaching solution No. 2 (dilute acetic acid), while the sorbent samples that were essentially neutral required the TCLP leaching solution No. 1 (acetic acid acetate buffer). The test is designed to maintain a pH of approximately 5 with acetic acid as the primary acidulant. This mimics the leaching conditions found in most sanitary landfills. The SGLP, which uses a generic extraction fluid and specifies a leaching solution most like the water likely to contact the waste material, was designed for use in determining potential for environmental impact from materials disposed in monofills. Additionally, because of the reactive nature of alkaline coal ash, the SGLP also incorporates a long-term leaching (LTL) component, which allows secondary hydrated phases to form and exert any influence that they might have on the leachate chemistry. In this project, both tests were extended to 48 hours in addition to the initial 18-hour equilibration time. This was done to determine the continuing trend for leachate evolution. The rationale for the use of long-term leaching with coal ash, particularly lower-rank high-calcium and highly alkaline coal ash, has been described in detail in a previous publication (18).

#### 5.2.2.4 Analysis for Total Mercury

Mercury was determined on all sorbents and leachates. Cold-vapor generation AA was used with stannous chloride reduction. Solid sorbent samples were digested using hot aqua regia for recovery of sorbed mercury and mercury compounds. Liquid samples were preserved by the addition of 2% HCl.

### 5.2.3 *Results and Discussion*

Results of bulk chemical analysis are shown in Table 5-3, and the results for leaching experiments are shown in Table 5-4. Both tables use the abbreviated sample nomenclature shown

in Tables 5-1 and 5-2. Standard units of concentration selected for use were µg/g for solid samples and µg/L for leachates. Table 5-4 contains a column labeled Calculated Maximum Concentration. This represents a calculated maximum mercury concentration if all of the mercury sorbed in the leached sample had become solubilized at a 20:1 liquid-to-solid ratio. This value is useful for comparison with actual leachate concentrations to determine the relative percent of analyte easily mobilized using these leaching protocols.

TABLE 5-3

Bulk Chemical Analysis Results for Total Mercury

Sample	Description	Previous Analysis, µg/g	Current Analysis, µg/g
PTC 451	Ash + IAC	0.70	0.38
PTC 454	Ash + LAC	0.60	0.41
PTC 464	Ash + LAC	1.10	0.76
Sorbent 78	Mn oxide + HgCl <sub>2</sub>	NA <sup>1</sup>	983
Sorbent 109	Mn oxide + Hg	NA	597
Sorbent 173	Carbon + Hg	NA	1645

<sup>1</sup> Data not available.

TABLE 5-4

Results of Mercury Determination in Leachates

Sample	Calculated Maximum Concentration, µg/L	SGLP-18, µg/L	SGLP-48, µg/L	TCLP-18, µg/L	TCLP-48, µg/L
PTC 451	19	<0.1	<0.1	<0.1	<0.1
PTC 454	20	<0.1	<0.1	<0.1	<0.1
PTC 464	38	<0.1	<0.1	<0.1	<0.1
Sorbent 78	49,145	ND <sup>1</sup>	ND	<0.1	ND
Sorbent 109	29,832	ND	ND	<0.1	ND
Sorbent 173	82,258	ND	ND	<0.1	ND

<sup>1</sup> Not done because of lack of sample.

The fly ash samples had been analyzed for mercury at the time of collection, which was several years ago. It can be seen by the comparison of current and previous results that some loss of mercury has occurred. Sorbents used in this project had been loaded with mercury or mercuric chloride vapor to breakthrough. These sorbents are highly efficient, thus the three orders of magnitude higher mercury concentrations compared to the fly ash samples with sorbent was not surprising. Although the fly ash samples contained sorbents that were also highly effective, removing greater than 90% of the mercury in flue gas during the pilot-scale runs, the overall amounts of sorbent, which is assumed to contain the bulk of the sorbed mercury, represent only a small fraction of the sample mass. The lower bulk mercury concentrations compared to those found in the pure sorbents were not unexpected.

Leaching data indicate that less than 0.5% of the mercury may have been leached from the sample containing the least amount by bulk analysis. This assumes that the actual concentration in the leachate was near 0.1 µg/L, the lower level of quantitation and the reporting limit for the laboratory. Data indicate that the actual concentration was closer to 0.01 µg/L, which is the nominal detection limit for mercury. Samples leached for 48 hours did not exhibit any trends in concentration that could be statistically verified. Any changes seen in the raw data were within the range of experimental and analytical variability. The observed concentrations of mercury in leachates were also well below the primary drinking water standard of 2.0 µg/L.

Results for thermal desorption experiments are shown in Figure 5-11. Thermal desorption was done only on the coal fly ash samples because of sample size limitations with pure sorbents. Start is at ambient temperature. Experiments were terminated when the absorbance returned to zero. Temperatures shown on the figures are recorded when the peaks start, at peak maxima, and at maxima for additional unresolved peaks, as shown in the curve for Coal Fly Ash 451. All of the samples were run in triplicate, the first sample being sacrificed in order to determine optimal sample mass and integrator settings. Reproducibility was good. Runs for Fly Ash 464 gave peak maxima at 752°, 759°, 739°, and 815°F (400°, 404°, 393°, and 435°C) in consecutive runs. It is believed that optimization of heating rate and purge gas flow will further improve ramp

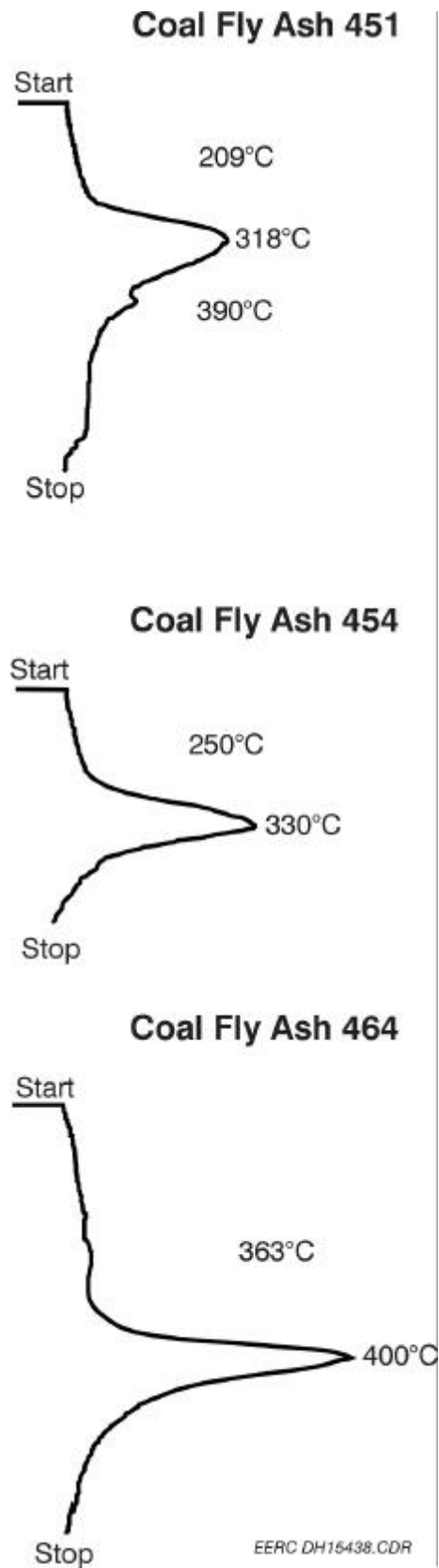


Figure 5-11. Thermal desorption curves.

reproducibility as well as reproducibility of peak appearance and maxima times. The samples characterized for thermal stability of sorbed mercury gave desorption curves with little structure other than a single major peak. Fly Ash 451 gave two easily discernable peaks. It has been speculated that a correlation exists between the temperature required for desorption and inorganic forms of mercury such as various inorganic salts (e.g., oxide, sulfide, chloride) and elemental mercury in thermal desorption experiments (19–21). It is likely, however, that as the matrix on which mercury and mercury compounds are sorbed becomes more complex, these correlations may break down. The possibility that mercury and mercury salts form new compounds on select substrates during the heating necessary to accomplish thermal desorption must be investigated. Sorbents mixed with coal fly ash are excellent candidates to be exceptions to behavior on pure substrates such as quartz, which has been used for initial experimental development (20).

#### *5.2.4 Conclusions on Thermal Stability and Leaching*

- Leaching data indicate that the sorbents evaluated appear to have a low potential for adverse environmental impact and are certainly not considered hazardous under current criteria.
- A reproducible and efficient apparatus has been constructed to study the thermal desorption of mercury and mercury compounds from solid substrates. Further refinement of this apparatus should result in the ability to generate quantitative data as well as the qualitative-type curves shown.
- Thermal desorption curves varied for the three samples characterized using the method described above. That each of the three samples released the mercury sorbed onto its matrix at different temperatures is, of course, indicative of binding energy and volatility. This could be a function of the chemical identity of the sorbed mercury or simply a function of the strength of the sorptive phenomenon. Additionally, in a matrix as complex as coal ash containing a sorbent, it is also possible that the form of sorbed mercury could change as thermal desorption progresses.

### ***5.2.5 Recommendations for Stability Testing***

Additional work is required for the development of a complete understanding of sorptive phenomena associated with mercury in combustion systems. This would be true with or without the use of sorbent materials. Future experiments are planned using background correction to differentiate atomic from nonatomic absorption. Since the thermal desorption experiments are analogous to electrothermal atomization, or furnace AA, it is reasonable to assume that structured background from nonatomic absorption is a possibility. The use of successive runs with and without background correction could answer this question. Deuterium arc background correction will be used in the future experiments. Additionally, to differentiate between elemental mercury and mercury compounds, successive runs are also planned with the heated cell assembly at 1472°F (800°C) and at ambient temperature. With the cell heated, all mercury compounds are detected; with the cell at ambient temperature, only elemental mercury is detected. Optimization of the operating parameters and refinement of the design of the thermal desorption unit will be ongoing.

Leaching studies using extended leaching times of up to 90 days are also planned. These will be primarily using the SGLP, since disposal in a sanitary landfill is unlikely, especially with coal ash from power generation.

### ***5.2.6 Acknowledgment***

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**APPENDIX A**

**RUN DATA**

