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PATENT CAUTION

Subtask 2.9 - Sorbent Development for Mercury Control

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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 (January 1995) 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). According to the EPA estimates, all forms of oil combustion account for 13 tons/yr, and sewage sludge incineration releases approximately 2 tons/yr of mercury emissions to the atmosphere.

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. The recently released final EPA Mercury Report to Congress (December 1997) now lists total point-source mercury emissions at 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%. However, on a worldwide basis, the projected increase in coal usage over the next two decades in China, India, and Indonesia will dwarf the current U.S. coal consumption of 900 million tons per year. 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.

During combustion, mercury is completely volatilized as primarily Hg^0 , but as it cools, it may also form HgCl_2 . Both of these species have a high enough vapor pressure to keep them in the vapor form all of the way through a combustion system and stack exit. Neither form will be controlled by conventional particulate control devices unless the solid material effectively traps the mercury through sorption mechanisms. Typically, this does not occur naturally to a significant degree by the collected ash material. However, a promising approach for mercury control is the injection of an effective sorbent upstream of the particulate control device. Since the amount of mercury in the gas stream from coal combustion is usually in the range from 5 to $10 \mu\text{g}/\text{m}^3$ (about 1 ppbv), only very small amounts of a sorbent may be necessary. Assuming 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 only $10 \text{ mg}/\text{m}^3$, which is only 0.1% to 0.2% of a typical dust loading of $5\text{--}10 \text{ g}/\text{m}^3$ (2.2–4.4 grains/scf). This amount of additional sorbent material in the ash is negligible and would not have an impact on control device performance or ash utilization. The only requirement is that the mercury be tightly bound in the sorbent, not desorbing upon exposure to ambient air or leaching under wet disposal conditions. For waste incinerator applications, the flue gas mercury concentrations may be one to two orders of magnitude higher than coal combustion. Under these conditions, the required sorbent-to-mercury ratio is expected to be much lower, on the order of 100:1. Even so, larger amounts of carbon sorbents may be necessary for incinerator applications, which could make the spent sorbent a larger fraction of the total ash produced. However, the concern is more about the stability of the mercury in the spent sorbent than the

actual mass of the sorbent. Since disposal requirements for incinerator ash are already more strict than for coal combustion, the presence of additional spent sorbent in the ash is not expected to adversely affect the disposal approach. Again, as long as the mercury is captured in a stable form, disposal of the spent sorbent along with the ash is an acceptable solution for either incinerator or coal applications.

Wet scrubbers have potential to trap soluble forms of mercury such as HgCl_2 , but they are ineffective for collecting Hg^0 . However, since HgCl_2 is both water-soluble and volatile, the final fate of mercury trapped in scrubber solutions is unclear. Unless it can be bound in a more stable form in the scrubber sludge, it would appear to be highly susceptible to either desorption into the atmosphere or leaching into groundwater. Furthermore, numerous attempts to make scrubbers better at capturing Hg^0 have failed, so an additional approach would be necessary to capture the Hg^0 fraction when both Hg^0 and Hg^{2+} are present. Until these issues are resolved, capture of mercury by wet scrubbers is not the most promising long-term solution to mercury control.

An alternative form of dry mercury capture is to employ a fixed-bed contactor, usually situated downstream of particulate control devices and scrubbers. This approach is attractive because the spent sorbent is not contaminated with particulate matter and acid gases. This system also lends itself to recovery of the mercury and possible regeneration of the sorbent. The main disadvantage is that it requires another add-on control device; for coal applications, the gas volume treated is very large compared to the amount of mercury removed. Therefore, fixed-bed contactors are not considered the most promising approach for coal applications but are more attractive for incinerators.

Carbon-based sorbents are promising for mercury control in applications where the temperature is less than 200°F and where mercury concentrations are high. In coal applications where the air heater outlet temperature is between 275° to 350°F , a sorbent has not been found that is effective for various coals and will collect both Hg^0 and Hg^{2+} . However, recent work at the Energy & Environmental Research Center (EERC) has resulted in a breakthrough in achieving very high rates of elemental mercury vapor sorption as well as high capacities. A better understanding of the science of sorption of 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 (200° – 600°F). At these temperatures, those materials which 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 Hg^0 , or even Hg^{2+} , becomes chemisorbed to a carbon has not been fully recognized or understood.

Evaluation of promising sorbents needs to be conducted in an environment that predicts sorbent performance in larger systems. This means that flue gas component concentrations, including mercury, temperature, sorbent particle size, sorbent-to-mercury ratios, and contact geometry, must be sufficiently simulated so that results indicate sorbent effectiveness for a specific application. The EERC has already developed this expertise in other projects and has a dedicated laboratory available to produce simulated flue gases with known mercury

concentrations for various applications. Since the chemistry of mercury in process streams is highly complex, simulating the exact gas constituents is critical. In addition to the common gases such as nitrogen, oxygen, carbon dioxide, and water vapor, the laboratory has the capability to provide precise mixtures of flue gas containing carbon monoxide, sulfur dioxide, sulfur trioxide, nitric oxide, nitrogen dioxide, hydrogen chloride, chlorine, and hydrogen fluoride. However, even more critical is the ability to provide exact levels of trace mercury species either as elemental metallic mercury vapor or in an oxidized form such as mercuric chloride. This is accomplished by employing precision permeation tubes which not only are factory-calibrated, but also are calibrated on a weekly basis as part of the rigorous quality control program of the laboratory.

The work for this year addresses mercury control only for gas stream applications such as combustion processes. However, much of the work may be generalized to other mercury cleanup needs such as spill cleanup, soil contamination, and water treatment.

2.0 OBJECTIVES

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:

- Understanding the mechanism for capture of Hg^0 by carbon, including carbon-catalyzed oxidation of Hg^0 .
- Understanding capture mechanisms for HgCl_2 .
- Developing improved mercury sorbents targeted at Hg^0 and HgCl_2 .
- Determine the mercury capture effectiveness of newly developed sorbents and commercially available sorbents for both Hg^0 and HgCl_2 .
- Determine the stability of the captured mercury for the most promising sorbents.

3.0 ACCOMPLISHMENTS

3.1 Preparation of Sorbents

The EERC developed a new mercury vapor carbon sorbent technology in a 1995 Department of Energy 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 300°F). 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. These reagents are diazabicyclooctane and sulfamic acid. Another method

involves addition of amines and sugars to the intermediate char that 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 carbons catalyzed the conversion of Hg^0 vapor in air to Hg(II) species that were 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 utilized a set of specific nitrogen heterocyclic precursors which will lead to the preparation of highly active carbons that can substantiate the model or models for the edge structure. Thus a set of nitrogen heterocyclic and acyclic precursors were impregnated and carbonized. Other variables to be examined are the temperature of carbonization and the concentration of precursors.

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:

1) One nitrogen in a six-membered ring (aromatic)

- Quinoline
- Isoquinoline
- Phenanthridine

2) Two nitrogens in a six-membered ring (aromatic)

- Quinoxaline (1,4)
- Phenazine (1,4)

3) 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 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 recarbonized in nitrogen at 750°C . Two different processing methods were investigated for the recarbonization/activation. The insoluble fractions were also carbonized at 750°C . These products were tested for mercury sorption in granular form in a tubular reactor at 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 recarbonized/activated by heating in nitrogen at 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 recarbonization methods, and different precursor carbon sizes. These results were compared with those from a commercial nitrogenous carbon (Centaur) and uncoated Calgon carbon.

3.1.1 Preparation of Nitrogen-Containing Pitch

Nitrogen-containing pitches were prepared according to the procedure reported by Mochida et al. (1). Preparations are summarized in Table 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 280°C for 4 hours. The residue was extracted with 0.1N hydrochloric acid and filtered. The residue was washed with 0.1N hydrochloric acid. The residue was 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 nitrogen stream, as described in the next section.

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. The carbazole preparation had to be repeated because of contamination of the product by mercury from a broken thermometer.

TABLE 1

Preparation of Nitrogen-Containing Pitches

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

* Reactions carried out in 300-mL Parr reactor.

** Ethylenediamine.

3.1.2 Preparation of Nitrogen-Impregnated Carbon

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. Carbon preparations are summarized in Table 2. 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:

Procedure A:

25°–400°C @ 10°C/min
Held at 400°C for 30 min
400°–750°C @ 20°C/min
Held at 750°C for 4 hr

Procedure B:

25°–225°C @ 15°C/min
225°–270°C @ 1°C/min
Held at 270°C for 1 hr
Cooled to room temperature
Heated to 750°C @ 15°C/min
Held at 750°C for 4 hr

3.1.3 Preparation of Nitrogen-Containing Carbons

Insoluble fractions of pitches described in Table 1 were converted into nitrogen-containing activated carbons by carbonizing in a gentle flow of nitrogen using Procedure B as described above.

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 110°C.

3.2 Preliminary Screening of Sorbents for Mercury Uptake

3.2.1 Test Procedure

Packed-bed tests were conducted on the granular carbon products to evaluate the effects of surface modification. The mercury sorption was tested in a flow-through tubular reactor system equipped with continuous in-line mercury analysis of the effluent from the bed to determine

TABLE 3

Sorbent Testing for Mercury Removal at 4 scfh

Air flow = 2000 cm ³ /min (4 scfh), source temperature = 80°C, oven temperature = 150°C							
File Name	Sorbent (g)	H ₂ SO ₄ (wt%)	Hg Conc. (µg/m ³)	% Hg Removed (time, min)			
				Initial	50%	Final	Breakthrough
RKS	Blank	—	56	—	50 (<1)	—	nbt*
RKS4	Centaur (0.43)	5%	—	100 (0)	50 (>292)	97 (292)	nbt
RKS5	Al ₂ O ₃ /MnO ₂ (0.50)	—	—	100 (0)	50 (>894)	93 (894)	nbt

* No breakthrough.

The remaining tests (Table 4) were then conducted at 4000 cm³/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% Hg 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 50% breakthrough. Extension of the experiment time showed the 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.

By comparison, an inexpensive Calgon carbon (acid-impregnated) with mediocre surface area also had a high initial removal rate (100%), but required only 171 min for 50% breakthrough and decreased further to 38% removal at 304 min. The corresponding test using the Calgon carbon that was not impregnated with acid required only 1 min for 50% breakthrough and 165 min for 8% removal.

Carbons prepared by impregnation of sulfamic acid in the Calgon carbon and recarbonization gave 50% breakthrough at 226 min, decreasing to 39% at 1303 min. These results are significantly better than that observed with the Calgon carbon precursor (discussed above), but poorer than the Centaur carbon.

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 and activated using Procedure A (fast heating rate) demonstrated superior activity. The initial removal was 94% and the decrease to 50% removal required 2217 min. Thus this sorbent retains its high activity far 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

TABLE 4

Sorbent Testing of Surface-Treated Carbons for Mercury Removal at 8 scfh

Air flow = 4000 cm³/min (8 scfh), source temperature = 100°C, oven temperature = 150°C

File Name	Carbon (g)	Recarb. Method	H ₂ SO ₄ Impreg.	Hg Conc. (µg/m ³)	% Hg Removed (time min)			
					Initial	50%	Final	Breakthrough
RKS32	Blank		—	81	0 (0)	<1	—	bt ¹
RKS13	Calgon (0.20)		—	—	80 (0)	50 (1)	8 (165)	bt
RKS11	Calgon (0.20)		5%	—	100 (0)	50 (171)	38 (304)	bt
RKS8	Centaur (0.20)		5%	—	100 (0)	50 (305)	49 (306)	bt
RKS17	Centaur		5%	—	100 (0)	50 (575)	38 (1221)	bt
RKS18	Calgon/2% sulfamic acid (0.20)	A	5%	—	92 (0)	50 (226)	39 (1303)	bt
RKS21	Calgon/5% PVP	A	5%	—	94 (0)	50 (2217)	42 (2574)	bt
RKS20	Calgon/10% PVP	A	5%	—	88 (0)	50 (150)	55 (253)	bt
RKS72	Calgon/10% PVP	B	5%	—	90 (0)	50 (300)	65 (1098)	bt
RKS29a	Calgon/5% PVP	B	5%	—	98 (0)	50 (3315)	43 (4010)	bt
RKS33	Calgon/2% PVP	B	5%	—	79 (0)	50 (312)	49 (320)	bt
RKS34	Calgon/10% PVP	B	5%	—	85 (0)	50 (424)	30 (1114)	bt
RKS12	Calgon/5% PVPcoVA	A	5%	—	90 (0)	50 (84)	39 (180)	bt
RKS14	Calgon/5% PVPcoAA	A	5%	—	90 (0)	50 (76)	29 (362)	bt
RKS28	Calgon/5% PVPcoAA	B	5%	—	98 (0)	50 (223)	50 (223)	bt
RKS25	Calgon/polyethylenimine (0.20)	A	5%	—	88 (0)	50 (373)	22 (1477)	bt
RKS26	Calgon/dextrose/ polyethylenimine (0.20)	A	5%	—	88 (0)	50 (51)	35 (350)	bt
RKS27	Calgon/dextrose+ polyethylenimine	A	5%	—	78 (0)	50 (28)	9 (1298)	bt
RKS29	Calgon/dextrose+ alanine	A	5%	—	88 (0)	50 (76)	42 (216)	bt
RKS36	Calgon/dextrose+ piperazine	A	5%	—	65 (0)	50 (35)	25 (942)	bt

¹ Breakthrough.

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(vinylpyrrolidone-coacrylic 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 5). 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.

The high activity of the indole-derived carbon was of great interest. Nothing is known about the structure of the indole-derived carbons, even whether nitrogen is still present in 5-membered rings. It is an important lead, however, since indoles are more readily available than the quinoxaline precursors. Further interesting results are expected from the quinazoline and carbazole-derived carbons.

Testing was also conducted on the carbonized pitches (Table 6) 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. The activity of the quinoxaline-derived carbon has not been determined.

TABLE 5

Sorbent Testing of Nitrogenous Pitch-Impregnated Carbons for Mercury Capture¹

Sorbent = 0.20 g, particle size = 20 × 50, air flow = 8 scfh (4000 mL/min),
source temperature = 150°C, oven temperature = 150°C

File Name	Sorbent (g)	H ₂ SO ₄	Hg Conc. (μg/m ³)	% Hg Removed (time, min)			
				Initial	50%	Final	Breakthrough
RKS32	None	—	81	—	50 <1	—	bt
RKS35	Calgon/5% quinoline polymer ²	5%	—	89 (0)	50 (306)	49 (308)	bt
RKS23	Calgon/5% quinoline polymer ³	5%	—	91 (0)	50 (204)	46 (292)	bt
RKS37	Calgon/5% quinoxaline	5%	—	90 (0)	50 (632)	25 (1300)	bt
RKS75	Calgon/5% indole polymer	5%	—	98 (0)	50 (1403)	49 (1473)	bt

¹ Recarbonization Procedure B used for all samples.

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

³ Pitch obtained from refluxing of quinoline with aluminum(III) chloride was dissolved in ethylenediamine and impregnated on Calgon carbon.

3.3 Preliminary Sorbent Stability Tests

Since there is no accepted approach to evaluate the stability of mercury in spent adsorbents, the method evaluated consisted of thermogravimetric analysis (TGA) experiments coupled with the use of a mercury vapor detector to correlate mercury desorption with weight loss upon controlled heating. The procedure used was as follows:

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 H₂/argon flowed from the balance housing toward the exit port at 275 cm³/min. (A special quartz tube is also available which has a side-arm 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

TABLE 6

Activated Nitrogenous Pitch-Derived Sorbents for Mercury Capture

Sorbent = 0.20 g, oven temperature = 150°C, air flow = 8 scfh (4000 cm³/min)

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

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

^b Quinoline pitch was prepared by heating in a Parr reactor at 280°C for 4 hr in 1 atm nitrogen. The pitch was carbonized by heating in nitrogen using Procedure B.

^c Quinoline pitch from b was extracted with ethanol. Ethanol-insoluble pitch was carbonized in nitrogen by using Procedure B.

^d Quinoline pitch was prepared by heating quinoline and aluminum(III) chloride in a Parr reactor at 280°C for 16 hr in 1 atm of nitrogen. The pitch was carbonized using Procedure B.

chamber is bathed in a flow of gas, usually an inert gas such as N₂ or Ar to minimize backflow of Hg. 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 Hg detection was used to detect elemental Hg in the effluent gas stream expelled from the TGA. An EPM mercury analyzer was used to monitor mercury desorption.

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

1. Baseline commercial carbon
2. Baseline commercial carbon with SO_4^{2-} treatment
3. Commercial activated carbon which was doped with SO_4^{2-} and contained 0.1% adsorbed Hg
4. Commercial activated carbon/quartz sand/ HgSO_4
5. 99.73% quartz sand/ carbon/ 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 Hg from test equipment and baseline carbon showed a negligible signal, as shown in Figure 1. The sulfate-doped baseline carbon showed a significant peak from 200° to 400°C , which was likely the decomposition of sulfate as 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 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 SO_2 absorption of UV frequency with Hg UV absorption, so the mercury desorption could not be confirmed. There also appeared to be mercury uptake from the Pt pan, most likely the result of Hg amalgamating with the Pt. Heating the pan after the test resulted in a release of Hg beginning at approximately 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 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, Hg amalgamation was apparent from the duplicated testing on Sample 2. Sample 5 was used to avoid using substrate which contained sulfate, so HgCl_2 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_2 added to the sand. Heating the compound with on-line Hg detection was expected to, and did, show a small signal at 150°C , indicating trace amounts of Hg^0 in the HgCl_2 , and a larger signal at 280° – 300°C , indicating decomposition of the salt. The TGA plot of the sand– HgCl_2 tests is shown in Figure 2 and indicates increasing peak heights with higher fractions of HgCl_2 , as would 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_2 interference and Pt 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_2 interference. The EERC has a Semtech analyzer that is not as susceptible to SO_2 and which will be used for any further work.

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

Figure 2. TGA results showing mercury desorption from quartz sand, carbon, and HgCl₂ mixture.

3.4 Testing of Sorbents under Simulated Flue Gas Conditions

Further testing of the most promising sorbents is planned under conditions that more closely simulate flue gas from coal combustion. The primary difference from the prescreening tests will be the presence of SO₂, HCl, NO, NO₂, HCl, CO₂, and H₂O in concentrations typical of combustion conditions. This testing has not been completed yet because of the time required to restore the mercury lab following the 1997 flood. The restoration of the lab is now complete, and this level of testing has started, but the results are not available yet. The project has been extended until June 1998 to accommodate the delay.

4.0 REFERENCES

1. Mochida, I.; An, K.H.; Korai, Y. *Carbon* 1995, 33, 1069.