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DEVELOPMENT OF NEW SORBENTS TO REMOVE MERCURY AND SELENIUM FROM FLUE GAS

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by

S.Y. Shiao

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Project Manager: S.Y. Shiao, Research Specialist, Babcock & Wilcox Company,
Alliance, OH 44601
(216) 829-7597

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EXECUTIVE SUMMARY

Mercury (Hg) and selenium (Se) are two of the volatile trace metals in coal, which are often not captured by conventional gas clean up devices of coal-fired boilers. An alternative is to use sorbents to capture the volatile components of trace metals after coal combustion.

In this project sorbent screening tests were performed in which ten sorbents were selected to remove metallic mercury in N_2. These sorbents included activated carbon, char prepared from Ohio No. 5 coal, molecular sieves, silica gel, aluminum oxide, hydrated lime, Wyoming bentonite, kaolin, and Amberite IR-120 (an ion-exchanger). The sorbents were selected based on published information and B&W's experience on mercury removal. The promising sorbent was then selected and modified for detailed studies of removal of mercury and selenium compounds.

The sorbents were tested in a bench-scale adsorption facility. A known amount of each sorbent was loaded in the column as a packed bed. A carrier gas was bubbled through the mercury and selenium compounds. The vaporized species were carried by the gas and went through the sorbent beds. The amount of mercury and selenium compounds captured by the sorbents was determined by atomic absorption.

The results of the sorbent screening tests indicated that activated carbon removed 200 μg Hg/gm of sorbent at 100°C and a flow rate of 0.63 liter of N_2/minute in 6 hours. Except for Wyoming bentonite which removed 28.8 μg Hg/gm of sorbent, the other mineral-based sorbents had mercury removal less than 3 μg Hg/gm of sorbent. The activated carbon was the best-performing sorbent for mercury capture among the 10 selected sorbents. Adsorption of metallic mercury on the activated carbon was performed at different reaction times. The results indicated that the reaction still occurred after two days.

The activated carbon was then impregnated with inorganic salts, i.e., KCl, $CaCl_2$, $FeCl_3$, $ZnCl_2$, and K_2S. The activated carbon and its impregnated samples were evaluated by performing bench-scale adsorption tests under different conditions. The test variables included the type of inorganic salt additives, reaction temperature, type of the carrier gas, and the chemical species of mercury and selenium compounds. Two types of carrier gases were used: pure N_2 and a premixed gas of 3000 ppm SO_2 and 10% CO_2 in N_2. Metallic mercury and mercuric chloride ($HgCl_2$) were used as the representatives for mercury compounds. Selenium dioxide was used as the representative for selenium compounds.

Capture of metallic mercury and mercuric chloride by the activated carbon samples was generally higher in the premixed gas than in pure N_2. Adsorption of metallic mercury increased as the reaction temperature was decreased.

Some of the inorganic salts in the impregnated activated carbon enhanced mercury capture. The degree of increasing adsorption of metallic mercury was dependent on temperature, the carrier gas, and other test conditions. Some other impregnated inorganic salts reduced the amount of metallic mercury. The reduction in adsorption might be attributed to plugging the fine pores of the activated carbon by the inorganic salts.

Adsorption of mercuric chloride ($HgCl_2$) on the activated carbon samples was much higher than that for metallic mercury under comparable test conditions. Adsorption of mercuric chloride on the activated carbon was 1546 µg/gm of sorbent at 60°C and 0.63 liter of N_2/min. in 6 hours, as compared to 254 µg/gm of sorbent for mercury under similar conditions. Impregnation of the activated carbon with inorganic salts reduced the amount of adsorption of mercuric chloride.

Although SeO_2 is more volatile than metallic mercury, adsorption of SeO_2 on the activated carbon samples was much less than that for metallic mercury. Adsorption of SeO_2 on the activated carbon was 11 µg/gm of sorbent at 60°C and 0.63 liter/minute of N_2 in 6 hours, as compared to 254 µg/gm of sorbent for mercury under comparable conditions.

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1.0 INTRODUCTION

1.1 Background

Trace elements and their compounds in coal could impose risks to human health and the environment. During coal combustion, trace elements in coal may exit as gases, condense as submicron particles, or condense on the surface of the particulate matter in the combustion gas stream.

Due to potential government regulations on air toxics, removal of trace metals from coal-fired boilers has drawn attention in recent years. Also, because of the development in advanced power generation schemes, such as pressurized fluidized-bed combustion (PFBC) combined-cycle or integrated gasification combined cycle (IGCC), high purity coal-derived gas is needed for gas turbine in the advanced power generation systems. Therefore, removal of particulates elutriated from the gasifier or the combustor, as well as the volatile trace metals of the coal-derived gas, becomes necessary.

For highly volatile trace elements, the elements may exist as gaseous phase and condense very little even when the flue gas cools down. These trace elements can not be removed effectively by the existing particulate removal equipment in coal combustion systems.

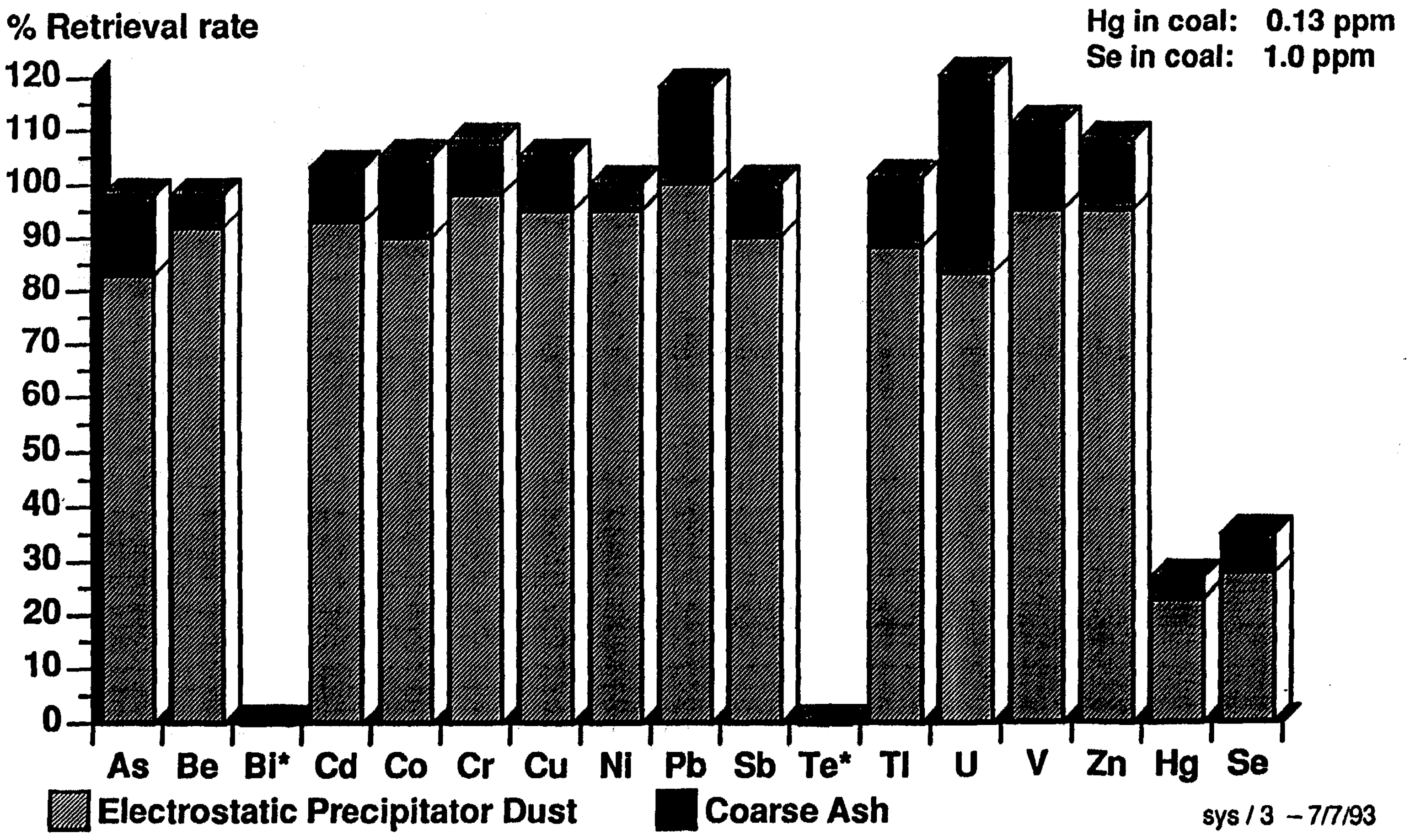
For example, an electrostatic precipitator (ESP) is the most common control device used to remove particulate matter/fly ash from the combustion gases[1]. Current ESPs are highly efficient and can operate in +99% collection efficiency. The overall ESP collection efficiency depends on particle size, ash resistivity, flue gas temperature, moisture content, and presence of conditioning agents[2]. The ESP efficiency is generally lowest in the particle size range of 0.1 to 1.5 micron. This fine material may be enriched in trace elements.

A report on equilibrium calculations of the volatile and the condensed phases of trace elements under fluidized-bed combustion at 1200°K and 10 atm showed that mercury (Hg), selenium (Se), Lead (Pb), and zinc (Zn) were least removed by a high-efficiency ESP and therefore, were discharged to the atmosphere[3].

A recent study of trace metal removal by a flue gas desulfurization process was performed at Scholven F of VEBA Kraftwerke Ruhr AG, Gelsenkirchen[4]. The mass balances of the trace elements were evaluated taking into account the concentrations in coal, electrostatic precipitator ash and coarse ash. Except for mercury (Hg) and selenium (Se), all other thirteen analyzed trace elements had almost 100% mass balance (Figure 1). This indicated that Hg and Se likely exit in the flue gas as gaseous phase. Also, in a study of emissions of trace metals from lignite-fired plants, it was reported that Hg and Se were the extremely volatile trace metals in coal[5].

Figure 1. The Mass Balance of Trace Elements of the 740 MW Unit, Scholven F of VEBA Kraftwerke Rujr AG, Glesenkirchen)

Retrieval Rates, Balancing of Coal, Electrostatic Precipiator Dust and Coarse Ash



Hg in coal: 0.13 ppm
Se in coal: 1.0 ppm

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Conventional gas cleanup devices, such as ESP, cyclone, and bag filter did not have the capability to remove fine/ultrafine particulates. Also, these purification devices are not generally designed to remove the gaseous species. An alternative is to use a sorbent bed to filter trace metal bearing fine particulates and to adsorb gaseous species of volatile trace metals.

1.2 Objectives

The overall objective of the project was to study adsorption of gaseous Hg and Se compounds on the selected sorbents. Sorbent screening tests were performed on the selected sorbents for Hg removal using a bench-scale adsorption facility. The results were then used as inputs to develop new sorbents for removal of Hg and Se compounds.

The specific technical objectives were to:

- select sorbents for Hg and Se based on published information and B&W experience;

- perform sorbent screening tests using a bench-scale adsorption facility;

- develop new sorbents to improve mercury and selenium adsorption.

2.0 TECHNICAL DISCUSSION

2.1 Technical Background

Very little information is available about the species of Hg and Se compounds in the emissions. It has generally been assumed that most of the mercury in emissions to air is metallic mercury vapor. From theoretical calculations of equilibrium and mass transfer data, it has been concluded that when burning solid fuels in a furnace, mercury initially exists as mercury vapor. During the cooling of the combustion gases more fraction of mercury vapor reacts to form $HgCl_2$. At about 150°C all mercury vapor becomes $HgCl_2$[6]. However, from the mercury mass balances in coal-fired boilers there are strong indications that the mercury sorption mechanism is influenced by the operation parameters and fly ash properties[6]. In the bench-scale tests of sorption of mercury in flue gas performed by Metzger and Braun[7], they concluded that mainly mercury (II) halogenides and to a lesser extent, mercury (I) halogenides are predominant species in flue gas whereas metallic mercury is insignificant amounts.

In a pilot study of mercury collection in fabric filter of a coal-fired boiler at the Asnaes Power Plant, it was reported that mercury-fly ash bond is of a chemisorption character and the sorption is increased at lower temperature[8].

In a fluidized bed combustor at 1200°K temperature and 10 atm pressure, almost 100% of the mercury is volatile, with possible volatile species being Hg, $HgCl_2$, HgO, Hg_2Cl_2[3]. In a gasifier, more than 90% of the mercury in coal is volatile, with its potentially volatile forms being Hg, HgO, and HgS [3].

The volatile forms of selenium in a gasifier are Se, H_2Se, SeS, and SeS_2[3]. Selenium was measured in coal, slag and flue gas at the Alen steam plant in Memphis, all the Se in the slag and the flue gas exists in the elemental form[3]. Billings et al.,[9] suggested that Se vapor in the stack exists as elemental form. A number of other researchers suggested that the most probable chemical state of Se in vapor state is SeO_2[10,11].

Various sorbents have been used for mercury and other trace metals adsorption. The most common sorbents are activated carbon, silica gel, calcium carbonates, aluminum oxide, and zeolites[12]. Except for activated carbon, all other sorbents are polar, which means that they preferentially adsorb any water vapor that may be present in the gas stream. Because moisture is present in most flue gas streams, it severely limits the use of physical polar sorbents[12].

Adsorption of trace metals on sorbent is largely dependent on the affinities (or reactivity) of the sorbents for various trace metals. The primary adsorption of trace elements on sorbent is chemisorption. For mercury compounds, chemisorption reactions produce stable compounds at temperature below 200 to 300°C[12]. Physical adsorption of mercury on the sorbents is relatively low. Other factors which could affect the adsorption are sorbent surface area, pore volume, pore size, and pore size distribution.

The adsorption capacity of sorbents may be improved by impregnating them with compounds, which may react chemically with mercury and selenium producing stable compounds. Chemisorption is not adversely affected by water vapor, on the contrary, it may in some cases have a favorable effect on the sorption capacity[12].

The sorbent materials which have affinity for trace metals include activated carbon impregnated with sulfur, iodide, and chloride compounds, or oxidized activated carbon, zeolite impregnated with sulfur, etc.[12-15]

The affinity of the sorbents for trace metals in general, and mercury and selenium in particular, may be increased by impregnation of inorganic salts, such as chlorides, iron compounds, sulfides[12-15] and oxides[12,16]. The adsorption can also be increased by preparing sorbents with larger surface area[12].

2.2 Approaches

The project was focused on adsorption of Hg and Se compounds by sorbents. Ten sorbents were selected based on published information and B&W's experience. The sorbent screening tests were performed using a bench-scale adsorption facility. Based on the results from the screening tests, a promising sorbent was selected and was then modified by impregnating with several inorganic salts. The sorbents with the inorganic salts were then evaluated by performing bench-scale adsorption tests.

A photograph of the bench-scale adsorption facility is shown in Figure 2. In this facility, a carrier gas, N_2 or a premixed gas, is supplied by a gas tank. The flow rate is controlled by a flow meter. The carrier gas is preheated in a column which is wrapped by a heating tape. The column is packed with coarse sand to increase the contact time and the surface area for heat transfer. A mercury or selenium compound is added in a bubbler which is maintained at a constant temperature by a heating tape. The gas then flows through the bubbler, vaporizes the mercury or selenium compound, and then flows through a pack bed of a sorbent. The packed bed is placed in the center section of an one-inch diameter glass column. The temperature of the bed is controlled by a Lindberg furnace. A thermocouple is inserted at the bottom of the packed bed to measure the bed temperature.

The gas exiting from the bed flows through three impingers. The first impinger is empty and is used to knock down any moisture in the carrier gas. The second impinger which contains peroxide in nitric acid (HNO_3) is used to catch the water soluble mercury or selenium compound. The third impinger contains permanganate ($KMnO_4$) in sulfuric acid. The metallic compounds are absorbed in the permanganate solution.

The amount of adsorption of the Hg and Se compounds on the sorbents is determined using standard, EPA-approved methods.

In this project, metallic mercury (Hg) and mercuric chloride ($HgCl_2$) were selected as the representative mercury compounds. Selenium oxide (SeO_2) was selected as the representative selenium compound.

There is very limited information about adsorption of selenium compounds. Therefore, the selection of sorbents for removal of selenium compounds was based on the experience of adsorption on mercury compounds. Ten sorbents were selected for evaluation. These sorbents included activated carbon, char prepared from Ohio No. 5 coal, molecular sieves, silica gel, aluminum oxide, hydrated lime, Wyoming bentonite, kaolin, and Amberite IR-120 (an ion-exchanger). The vendors of the sorbents and the sorbent size are shown in Table 1.

Most of the selected sorbents were either purchased or obtained from outside vendors. The activated carbon was an acid-washed lignite. The char sample was prepared from Ohio No. 5 coal using a B&W's 6-inch diameter bench-scale atmospheric fluidized-bed combustor.

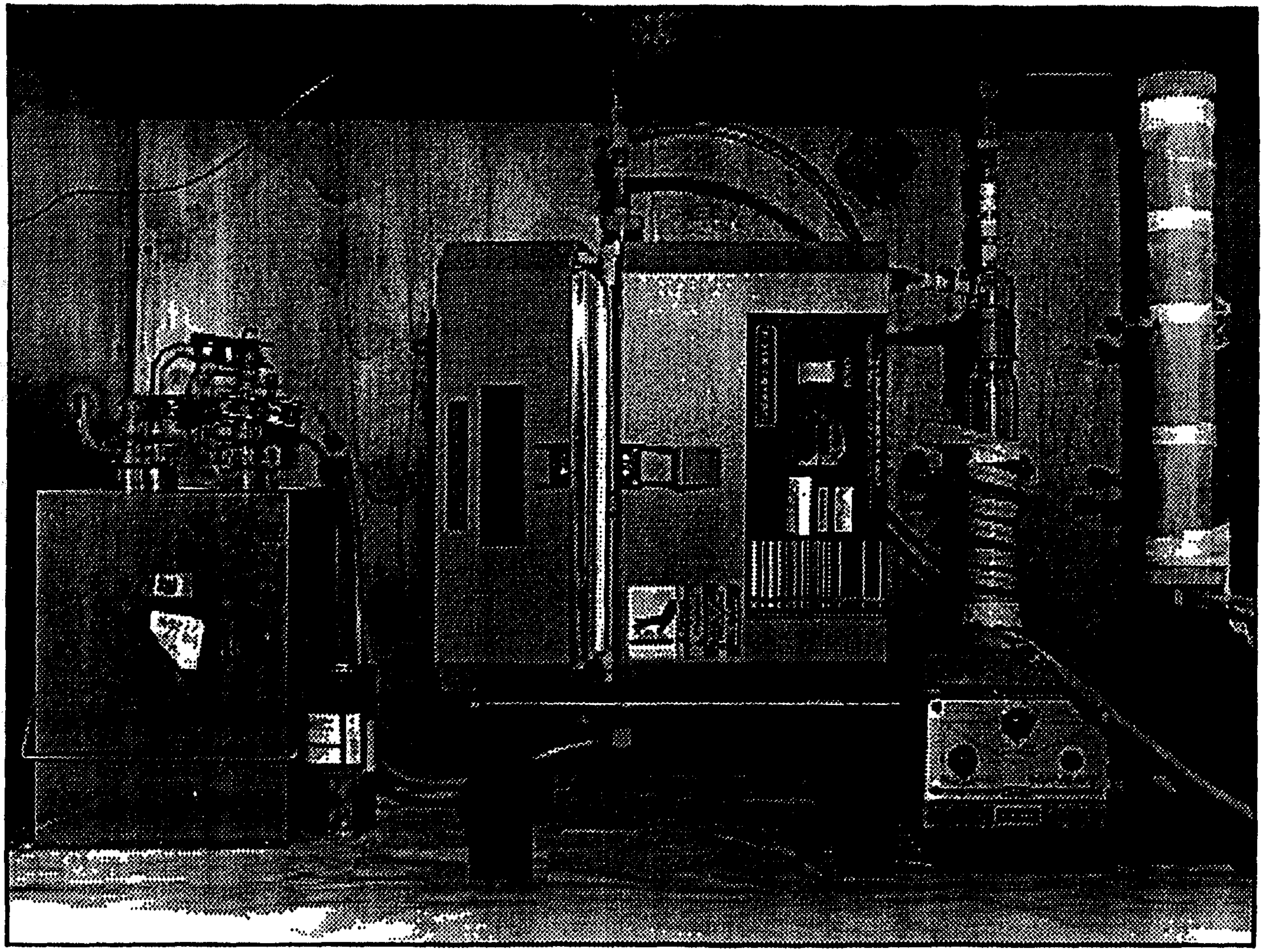

Figure 2. Bench-Scale Testing Facility

Table 1. Selected Sorbents For Bench-Scale Adsorption Tests

Sorbent	Vendor	Size (mesh)
Activated Carbon (Darco)	Aldrich	20 x 40
Char (Ohio No. 5)	Prepared by B&W	16 x 48
Molecular Sieve Type Z (Grade 5A-12)	Sphinx Adsorbents, Inc.	16 x 48*
Molecular Sieve Type Z (Grade 13X-12)	Sphinx Adsorbents, Inc.	16 x 48*
Silica Gel (Grade 15)	Aldrich	30 x 60
Aluminum Oxide (activated, acidic)	Aldrich	150
Hydrated Lime	Dravo Lime Co.	powder
Bentonite	Wyo-Ben, Inc.	16 X 48
Kaolin	Albion Kaolin Co.	powder
Amberite IR-120 (ion-exchange resin)	Aldrich	120

* Obtained as 8 x 12 mesh particles from the vendor.

After procuring the sorbents, some of the sorbents were further ground to finer sizes. This was to reduce the effect of surface area of the sorbents on adsorption of mercury and selenium compounds. Some of the sorbents were received as fine powder, such as hydrated lime and kaolin. The pressure drop of the carrier gas flowing through a packed bed of fine powder was relatively high. Therefore, the powdered sorbents were premixed with silica gel to increase the gas flow rate through the sorbent beds.

The sorbent screening tests were performed in the bench-scale adsorption facility. Nitrogen was used as a carrier gas in the sorbent screening tests.

Before testing, five grams of each sorbent were loaded in an one-inch diameter column as a pack bed. The bed was tapped gently to avoid possible channelling in the bed.

The sorbent screening tests were performed on all the selected sorbents under similar conditions. The most promising sorbent was selected and modified using several inorganic salts as additives.

The best performing sorbent was impregnated with five inorganic salts. In preparation, approximately 20 grams of the activated carbon were soaked in 5 wt% of KCl, $CaCl_2$, $FeCl_3$, $ZnCl_2$, and K_2S solutions overnight. The containers were shaken intermittently. The slurries were then filtered and dried in an air-dry oven at 225°F overnight. The impregnated sorbents were then evaluated by performing bench-scale adsorption tests.

For the most promising sorbent and its modified sorbents, the adsorption tests were performed by changing the following variables.

- Type of Additive
- Hg and Se Compounds
- Sorbent Bed Temperature

Nitrogen and a premixed gas with 3000 ppm SO_2 and 10% CO_2 in N_2 were used as the carrier gases.

The amount of adsorption of Hg and Se compounds on the sorbents was determined by directly measuring the total Hg and Se on the sorbents instead of measuring the concentration difference of Hg and Se in the gaseous phase before and after the adsorption. This minimized the experimental uncertainties caused by adsorption loss on the equipments, gas leakage in the system, and condensation of Hg and Se.

After testing, the sorbent was taken out and digested using the microwave assisted acid digestion method (EPA Method 3051). The slurry was then filtered using 0.45 micron millipore filters. The total Hg in the solution was determined using cold vapor atomic adsorption spectroscopy (EPA Method 7470). Trace amount of Hg will be analyzed using inductively coupled plasma/atomic emission spectroscopy. The total Se was determined using graphite furnace atomic absorption spectroscopy (EPA Method 7740).

The amount of metallic mercury on a few activated carbon samples were determined using X-ray fluorescence. X-ray fluorescence is a nondestructive and nonintrusive method which has the advantage of determine multiple species simultaneously in a short time. However, the disadvantages were; the detection limit was high, and the error in the measurement could be 10% to 15%. All the results reported in this report were determined by atomic absorption.

The performance of different sorbents under different conditions was evaluated and compared. The sorbent which had the most adsorption of Hg and Se was identified.

2.3 Results and Discussion

The sorbent screening tests were performed by adsorption of metallic mercury on the selected sorbents at a temperature of 100°C, a gas flow rate of 0.63 liter of N_2/minute for 6 hours. The results are shown in Table 2. The activated carbon had the highest capture of mercury (200 µg (micro-gram) of Hg/gm [gram] of sorbent). The Ohio No. 5 coal char had 11.4 µg Hg/gm of sorbent. The high capture of mercury by the activated carbon was mainly attributed to its fine pores and the large surface area. The mechanisms of mercury adsorption on the activated carbon were not studied in this project. However, it was speculated that both physical adsorption and trapping of the mercury molecules were the major mechanisms for adsorption of mercury on the activated carbon. Although Ohio No. 5 coal char was porous, the fine pores seemed to be blocked during the process of char preparation.

For mineral-based sorbents, except for Wyoming bentonite, which had 28.8 µg Hg/gm of sorbent, all other sorbents had very little adsorption for mercury (less than 3 µg Hg/gm of sorbent). For the powdered sorbents which were mixed with silica gel to increase the gas flow, the amount of mercury adsorbed on the sorbents was corrected for the amount which was adsorbed on silica gel.

Table 2. Sorbents Screening Tests for Selected Sorbents (100°C, Gas Flow Rate 0.63 liter of N_2/min., 6 hours)	
Sorbents	**Adsorption (μg (micro-gram) Hg/gm of sorbent)**
Activated Carbon (Darco)	200
Char (Ohio No. 5)	11.4
Molecular Sieve Type Z (Grade 5A-12)	0.87
Molecular Sieve Type Z (Grade 13X-12)	0.52
Silica Gel (Grade 15)	0.22
Aluminum Oxide (activated, acidic)	1.33
Hydrated Lime	2.72*
Bentonite	28.8
Kaolin	1.07*
Amberite IR-120 (ion-exchange resin)	0.1
* Was used with silica and the data was corrected for silica.	

The activated carbon was then tested at different adsorption times. Table 3 shows the amount of adsorption of metallic mercury at 6, 15, and 48.5 hours was 200, 840, and 1710 μg Hg/gram of sorbent, respectively. The results indicated that adsorption of mercury on the activated carbon sample did not reach saturation even after two days.

Table 3. Adsorption of Metallic Mercury on Activated Carbon (100°C, Gas Flow Rate 0.63 liter of N_2/min)	
Reaction Time (hours)	**Adsorption (μg Hg/gm of sorbent)**
6	200
15	840
48.5	1710

Table 4 shows the results of adsorption of metallic mercury on the activated carbon and the impregnated samples at 100°C and a gas flow rate of 0.63 liter of N_2/minute for 6 hours. The activated carbon impregnated with $ZnCl_2$ showed a significant increase in Hg capture (314 µg Hg/gm of sorbent) as compared to the activated carbon with no additives (200 µg Hg/gm of sorbent).

The other additives, i.e., KCl, $CaCl_2$, $FeCl_3$, K_2S showed some adverse effect on Hg capture. The reduction of Hg capture was probably due to partial blocking of the fine pores of the activated carbon by the additives, which may have overridden the benefits of using the additives.

The results of adsorption of metallic mercury on the impregnated activated carbon samples at 100°C using a premixed gas of 3000 ppm SO_2 and 10% CO_2 in N_2 as a carrier gas, are shown in Table 5. For the activated carbon without additives, Hg capture was 238 µg/gm of sorbent in the premixed gas as compared to 200 µg/gm of sorbent in N_2. For the activated carbon impregnated with KCl and $FeCl_3$, Hg capture increased when the premixed gas was used as a carrier gas as compared to N_2. Changing the carrier gas had little effect on Hg capture when $CaCl_2$ and K_2S were used as the additives in the activated carbon. However, changing the carrier gas from N_2 to the premixed gas reduced the Hg capture when $ZnCl_2$ was used as an additive.

Table 4. Adsorption of Metallic Mercury on Impregnated Activated Carbon (100°C, Gas Flow Rate 0.63 liter of N_2/minute, 6 hours of testing)

Additive	**Adsorption (µg Hg/gm of sorbent)**
No	200
KCl	168
$CaCl_2$	143
$ZnCl_2$	314
$FeCl_3$	136
K_2S	110

Table 5. Adsorption of Metallic Mercury on Impregnated Activated Carbon (100°C, Gas Flow Rate 0.63 liter of 3000 ppm of SO_2 & 10% CO_2 in N_2/minute, 6 hours of testing)

Additive	Adsorption (μg Hg/gm of sorbent)
No	238
KCl	403
$CaCl_2$	143
$ZnCl_2$	215
$FeCl_3$	324
K_2S	106

The results of adsorption of metallic mercury on the impregnated activated carbon performed at 60°C in N_2 are shown in Table 6. Comparing the results in Table 4 (reaction temperature at 100°C) and those in Table 6 (reaction temperature at 60°C), adsorption of metallic mercury was increased as the temperature of the reaction was decreased. For example, the adsorption of metallic mercury was 200 μg/gm of sorbent and 254 μg/gm of sorbent at 100°C and 60°C, respectively. For the activated carbon impregnated with KCl, the adsorption of metallic mercury was 168 μg/gm of sorbent and 256 μg/gm of sorbent at 100°C and 60°C, respectively.

Table 6. Adsorption of Metallic Mercury on Impregnated Activated Carbon (60°C, Gas Flow Rate 0.63 liter of N_2/minute, 6 hours of testing)

Additive	Adsorption (μg Hg/gm of sorbent)
No	254
KCl	256
$CaCl_2$	358
$ZnCl_2$	287
$FeCl_3$	284
K_2S	124

Adsorption of Hg on the activated carbon and the carbon samples impregnated with KCl and $FeCl_3$ were performed at 60°C and used the premixed gas as the carrier gas. The Hg capture was increased substantially at 60°C, as compared to that at 100°C. For example, for the activated carbon with no additive, the Hg capture was 345 μg Hg/gm of sorbent at 60°C in the premixed gas (Table 7) as compared 238 μg of Hg/gm of sorbent at 100°C in the premixed gas (Table 5). However, the activated carbon impregnated with KCl had a reduction in mercury adsorption when the temperature was decreased. The mercury adsorption was 403 μg/gm of sorbent at 100°C versus 320 μg/gm of sorbent at 60°C.

Table 7. Adsorption of Metallic Mercury on Impregnated Activated Carbon (60°C, Gas Flow Rate 0.63 liter of 3000 ppm of SO_2 & 10% CO_2 in N_2/minute, 6 hours of testing)

Additive	Adsorption (μg Hg/gm of sorbent)
No	345
KCl	320
$FeCl_3$	345

The results of adsorption of mercuric chloride on a few selected sorbents at 60°C and a gas flow rate of 0.63 liter of N_2/minute are shown in Table 8. Comparing the data shown in Tables 8 and 6, adsorption of mercuric chloride was much higher than that for metallic mercury under comparable conditions. For example, the removal of mercuric chloride on the activated carbon was 1546 μg/gm of sorbent as compared to 254 μg Hg/gm of sorbent under comparable test conditions.

Metallic mercury has a vapor pressure of 246.8 mm of Hg at 300°C, whereas, the vapor pressure of mercuric chloride was calculated to be about 688.5 mm of Hg at the same temperature[17]. Mercuric chloride is more volatile than metallic mercury. Whether the high adsorption of mercuric chloride on the tested sorbents was attributed to higher volatility of mercuric chloride as compared to metallic mercury or to higher affinity of mercuric chloride to the sorbent was not clear.

Impregnation of the activated carbon with inorganic salts did not improve the capture of mercuric chloride. To the opposite, the additives may have plugged the fine pores of the activated carbon resulting in reducing capture of mercuric chloride.

Adsorption of mercuric chloride on wyoming bentonite was also tested. The capture of mercuric chloride and of metallic mercury was 15.7 μg/gm of sorbent, respectively. Adsorption of mercuric chloride on Wyoming bentonite was much less than that of the activated carbon.

Table 8. Adsorption of Mercuric Chloride ($HgCl_2$) on Sorbents (60°C, Gas Flow Rate 0.63 liter of N_2/minute, 6 hours of testing)

Sorbent	Adsorption (μg Hg/gm of sorbent)
Activated Carbon	1546
Activated Carbon Impregnated with KCl	1113
Activated Carbon Impregnated with $ZnCl_2$	1119
Activated Carbon Impregnated with $FeCl_3$	1175
Wyoming Bentonite	15.7

Table 9 shows the adsorption of mercuric chloride on the activated carbon and Wyoming bentonite at 60°C using the premixed gas as the carrier gas. The capture of mercuric chloride on the activated carbon increased substantially as compared to when N_2 was used as the carrier gas (2745 μg of $HgCl_2$/gm of sorbent in the premixed gas vs. 1546 μg Hg/gm of sorbent in N_2). However, for Wyoming bentonite, adsorption of mercuric chloride was reduced in the premixed gas than in N_2 (7.7 μg/gm of sorbent in the premixed gas vs. 15.7 μg/gm of sorbent in N_2).

Table 9. Adsorption of Mercuric Chloride ($HgCl_2$) on Sorbents (60°C, Gas Flow Rate 0.63 liter of 3000 ppm SO_2, 10% CO_2 in N_2/minute, 6 hours of testing)

Sorbent	Adsorption (μg Hg/gm of sorbent)
Activated Carbon	2745
Wyoming Bentonite	7.7

The results of adsorption of SeO_2 on a few selected sorbents at 60°C and in N_2 are shown in Table 10. The vapor pressure of SeO_2 is 21.28 mm of Hg at 112.5°C as compared to 0.5052 mm of Hg at 112°C for metallic mercury[17]. Therefore, SeO_2 is more volatile than metallic mercury.

Even though SeO_2 is more volatile than metallic mercury, the adsorption of SeO_2 on the activated carbon samples was much less than for metallic mercury under similar test conditions. For example, the amount of adsorption of SeO_2 on the activated carbon was 11 μg/gm of sorbent as compared to 254 μg/gm of sorbent for metallic mercury.

As mentioned earlier, mercury was found to have poorer mass balance than selenium in large-scale demonstration. However, SeO_2 is more volatile than metallic mercury. Much less adsorption of SeO_2 than metallic mercury may imply that only a small portion of Se in the flue gas of the coal-fired boilers exists as SeO_2 .

The additives apparently have an adverse effect on SeO_2 adsorption. For example, adsorption of SeO_2 on the activated carbon impregnated with $ZnCl_2$ was 5 μg/gm of sorbent as compared to 11 μg/gm of sorbent without $ZnCl_2$

Table 10 Adsorption of Selenium Dioxide (SeO_2) on Sorbents (60°C, Gas Flow Rate 0.63 liter of N_2/minute, 6 hours of testing)

Sorbent	Adsorption (μg Se/gm of sorbent)
Activated Carbon	11
Activated Carbon impregnated with KCl	6
Activated Carbon Impregnated with $ZnCl_2$	5
Activated Carbon Impregnated with $FeCl_3$	2
Wyoming Bentonite	<1

In this project, five grams of sorbent were used in each bench-scale testing. The total waste material was less than one pound. These used sorbents were kept for future analysis. Although it was not the objective of this project to study the regeneration of the sorbents, the activated carbon can be regenerated by a thermal method. Basically, the activated carbon can be heated to a certain temperature to vaporize the adsorbed mercury and selenium compounds. The vapor of the mercury and selenium compounds can be condensed and collected for disposal. The activated carbon may be reused for adsorption.

2.4 Conclusions

The conclusions for the project are:

1. Ten sorbents were selected for the screening tests for mercury removal. The activated carbon sample had much greater capture of metallic mercury than other mineral-based sorbents.

2. Capture of metallic mercury and mercuric chloride by the sorbents was generally higher in the premixed gas of 3000 ppm SO_2 and 10% CO_2 in N_2 than in pure N_2.

3. Adsorption of metallic mercury generally increased as the reaction temperature was decreased.

4. Some inorganic salts impregnated in the activated carbon enhanced mercury capture. Some others reduced the mercury capture.

5. The degree of increasing adsorption of metallic mercury by the inorganic salts was dependent on temperature, the carrier gas, and other test conditions.

6. Adsorption of mercuric chloride ($HgCl_2$) on the activated carbon samples was much higher than that for metallic mercury under comparable test conditions.

7. Adsorption of selenium dioxide on the activated carbon samples was much less than that for metallic mercury and mercuric chloride.

8. The inorganic salts impregnated in the activated carbon reduced the adsorption of mercuric chloride and selenium dioxide.

3.0 MARKETING/COMMERCIALIZATION DISCUSSIONS

The new amendments to the Federal Clean Air Act have focused attention on 190 substances that the legislation designated as hazardous air pollutants, commonly known as air toxics. Thirty-seven of the compounds have been detected in fossil power plant flue gas[18]. A substantial portion of the air toxics is derived from trace elements in coals. Potential regulations on emissions of some of the trace elements, particularly mercury, could be imposed on coal-fired boilers.

Also, because of the development in advanced power generation schemes, high purity coal-derived gas is needed for gas turbine operation in the advanced power generation systems. Therefore, removal of volatile trace elements from coal-derived gas and the particulates elutriated from the gasifier or the combustor becomes necessary.

Numerous studies indicated that a large portion of mercury and selenium escaped as gaseous phase or with the fine particulates in the flue gas[1,2]. Conventional gas cleanup devices, such as electrostatic precipitators, cyclone, and bag filters are not generally designed to remove gaseous trace element species. An alternative is to use a sorbent bed to filter trace element bearing fine particulates and to adsorb gaseous species of trace elements.

Capture of the volatile mercury compounds by sorbents has been studied. However, the test data, particularly, the information on sorbents, is limited. The chemical forms of mercury in the flue gas conditions are not well known. Also, very little information of selenium capture can be found in the literature.

The project was focused on mercury and selenium capture by the sorbents which have been used previously for mercury capture. Ten sorbents were evaluated for mercury removal under comparable conditions. The best performing sorbent was identified and modified by impregnating with inorganic salts. The most commonly occurred mercury and selenium chemical species in the flue gas were used in the tests.

Table 11 shows the trace elements in Ohio coals[19]. The average concentrations of Hg and Se in Ohio coals are greater than those in U.S. coals. Shaw and Paur[20] investigated the source of high Se concentrating at the Ohio River Valley sites. They suggested that the high Se concentration is primarily associated with coal combustion, which is spread throughout the industrial midwest. Removal of trace elements, particularly the volatile elements, in flue gas from burning Ohio coals will certainly encourage increasing use of Ohio coal.

New sorbents to improve removal Hg and Se compounds from flue gas of coal-fired boilers are needed. The improved sorbents can be used as sorbent beds or injected in the furnace to reduce the emissions of trace elements. Either the sorbent beds or the furnace injection technology can be adaptable to the existing flue gas cleaning systems of coal-fired boilers.

Table 11 Average Concentration (in ppm) of Trace Elements in Ohio Coal Seams

Seam	Be	Cr	Mn	Co	Ni	Cu	Zn	Cd	Hg	Pb	Se	Fe(%)
Bedford	3.03	17.9	33.5	15.9	30.7	16.6	24.1		0.382	19.3	5.31	4.15
Brookville	2.45	14.5	17.8	9.6	18.5	9.1	28.9		0.227	8.9	3.99	2.64
Lower Kittanning	2.71	11.0	25.0	13.4	28.2	10.6	20.0		0.194	10.6	4.46	2.75
Middle Kittanning	2.92	12.9	23.3	8.3	16.5	12.9	28.4	0.73	0.309	12.9	3.90	2.35
Lower Freeport	2.79	15.2	23.1	10.2	24.9	13.1	11.4		0.248	13.0	4.74	2.61
Upper Freeport	1.92	18.2	15.2	6.4	19.0	11.3	9.0	0.99	0.331	16.5	2.99	1.40
Pittsburgh	1.71	13.2	23.6	7.8	12.9	7.4	17.8	1.43	0.130	9.8	2.75	2.26
Redstone	2.01	16.9	27.0	12.0	13.6	9.8	11.0	1.15	0.124	13.0	4.65	4.14
Meigs Creek	2.19	17.0	33.4	10.8	16.8	7.3	12.2	1.00	0.055	9.8	6.27	2.13
All Samples	2.58	14.5	25.5	10.6	18.7	11.9	19.1	0.94	0.215	12.8	4.33	2.49

4.0 FINAL BUDGET REPORT

The total project budget by major category and the contributions of the co-sponsors is shown in the following table.

Table 12. Project Budget

Category	Ohio Coal Research Consortium	Babcock & Wilcox	Total
Total Personnel	17,692	4,159	21,851
Total Supplies	5,180	1,322	6,502
Total Travel	0	357	357
Total Indirect	51,573	13,162	64,735
Total Project Cost	74,445	19,000	93,445

Preliminary expenditures of Ohio Coal Research Consortium (OCRC) funds on this project are shown in the following Table 13.

Table 13. Expenditures of OCRC Funds

Category	Ohio Coal Research Consortium
Total Personnel	17,529
Total Supplies	4,222
Total Travel	0
Total Indirect	50,956
Total Project Cost	72,707

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