

# **TASK 1.2 – MERCURY STABILITY IN THE ENVIRONMENT**

Final Report

*for the period April 15, 1998, through June 30, 1999*

*Prepared for:*

Mr. Thomas Brown  
Federal Energy Technology Center  
U.S. Department of Energy  
PO Box 10940, MS 921-143  
Pittsburgh, PA 15236

Cooperative Agreement No. DE-FC26-98FT40320--05  
Performance Monitor: Thomas Brown

*Prepared by:*

John H. Pavlish

Energy & Environmental Research Center  
University of North Dakota  
PO Box 9018  
Grand Forks, ND 58202-9018

## TABLE OF CONTENTS

LIST OF FIGURES .....	ii
LIST OF TABLES .....	ii
1.0 INTRODUCTION .....	1
2.0 GOALS AND OBJECTIVES .....	2
3.0 CURRENT UNDERSTANDING OF MERCURY STABILITY IN THE ENVIRONMENT BASED ON REVIEW AND ASSESSMENT OF MOST RECENT REFERENCES .....	2
4.0 EXPERIMENTAL APPROACH – TESTING OF COMBUSTION PROCESS EFFLUENTS .....	6
4.1 Experimental Procedures .....	6
4.2 Leaching Results .....	11
4.3 Thermal Desorption Results .....	12
CONCLUSIONS .....	16
RECOMMENDATIONS FOR FURTHER RESEARCH .....	19
REFERENCES .....	20

## **LIST OF FIGURES**

1	Schematic of the thermal desorption apparatus . . . . .	10
2	Diagram of the thermal desorption section . . . . .	10
3	Thermal desorption curve for Ash 186 . . . . .	13
4	Thermal desorption curve for Ash 186, duplicate . . . . .	13
5	Thermal desorption curve for Ash 189 . . . . .	14
6	Thermal desorption curve for WTE ash . . . . .	14
7	Thermal desorption curve for C-1 mercury . . . . .	15
8	Thermal desorption curve for M-1 mercury . . . . .	15

## **LIST OF TABLES**

1	Samples Screen for Use with the Mercury Stability Study . . . . .	9
2	Leaching Results . . . . .	11
3	Thermal Desorption Information . . . . .	18
4	Mercury Removal Efficiency of Thermal Desorption Procedure . . . . .	18

## **TASK 1.2 – MERCURY STABILITY IN THE ENVIRONMENT**

### **1.0 INTRODUCTION**

The 1990 Clean Air Act Amendments (CAAs) require the U.S. Environmental Protection Agency (EPA) to determine whether the presence of mercury and 188 other trace substances, referred to as air toxics or hazardous air pollutants (HAPs), in the stack emissions from fossil fuel-fired electric utility power plants poses an unacceptable public health risk (1). The EPA's conclusions and recommendations were presented in two reports: *Mercury Study Report to Congress* and *Study of Hazardous Air Pollutant Emissions from Electric Utility Steam Generating Units – Final Report to Congress*. The first congressional report addressed both human health and the environmental effects of anthropogenic mercury emissions, while the second report addressed the risk to public health posed by emissions of HAPs from steam electricity-generating units. The National Institute of Environmental Health Sciences is also required by the CAAs to investigate mercury and determine a safe threshold level of exposure. Recently the National Academy of Sciences has also been commissioned by Congress to complete a report, based the available scientific evidence, regarding safe threshold levels of mercury exposure.

Although the EPA reports did not state that mercury controls on coal-fired electric power stations should be required given the current state of the art, they did indicate that EPA views mercury as a potential threat to human health. It is likely that major sources of mercury emissions, including fossil-fired combustion systems, will be controlled at some point. In fact, municipal waste combustion units are already regulated. In anticipation of additional control measures, much research has been done (and continues) regarding the development of control technologies for mercury emitted from stationary sources to the atmosphere. Most approaches taken to date involve sorbent injection technologies or improve upon removal of mercury using existing technologies such as flue gas desulfurization scrubbers, fabric filters, and electrostatic precipitators. Depending on the fly ash chemistry and the form of mercury present in the flue gas, some of these existing technologies can be effective at capturing vapor-phase mercury from the flue gas stream.

Although much research has been done on enhancing the removal of mercury from flue gas streams, little research has focused on what happens to the mercury when it is captured and converted and/or transferred to a solid or aqueous solution. The stability (or mobility) of mercury in this final process is critical and leads to the questions, What impact will the increased concentration of mercury have on utilization, disposal, and reuse? and Is the mercury removed from the flue gas really removed from the environment or rereleased at a later point? To help answer these questions, the Energy & Environmental Research Center (EERC) as part of the U.S. Department of Energy (DOE) Base Cooperative Agreement did a series of experiments using thermal desorption and leaching techniques. This report presents the results from these tests.

### **2.0 GOALS AND OBJECTIVES**

The overall goal of the project is to determine stability and quantitate mercury release to the environment through vapor- and liquid-phase transport mechanisms in coal or waste combustion by-products. Specific objectives of the project are as follows:

- Conduct a literature search to determine the knowledge base regarding the stability of mercury in sorbents, fly ash, scrubber sludge, and other waste materials.
- Develop protocols for determining the stability of mercury in these materials.
- Perform preliminary analyses that define and test appropriate analytical and stabilization methods.
- Identify processes and issues associated with utilization, disposal, and reuse of highly concentrated mercury effluents from various combustion sources.
- Identify mechanisms by which mercury may be rereleased to the environment.

### **3.0 CURRENT UNDERSTANDING OF MERCURY STABILITY IN THE ENVIRONMENT BASED ON REVIEW AND ASSESSMENT OF MOST RECENT REFERENCES**

In the last few years there has been increased interest in mercury emissions to the atmosphere as the number of lakes and streams that have mercury warnings posted increases. The two most-scrutinized mercury emission sources are waste incinerators and coal-fired utilities. The mercury emissions associated with these two industries present very different situations. These include mercury concentration, species emitted, control, deposition, and mercury stability.

It has been found that some of the fly ashes generated during incineration and coal combustion can remove a substantial amount of the mercury (2, 3). The exact mechanism is still unknown, but more than likely it involves both physical and chemical adsorption. Also, for both industries carbon injection appears to be the most likely method of control. This technology is already being used extensively in the municipal solid waste (MSW) industry where mercury regulations are already in place. The question being asked is whether the mercury that is collected with the fly ash, or on the carbon, will desorb after disposal or from the ash material in utilization applications.

This is a relatively new area of interest with respect to mercury. Although leaching tests on waste materials such as fly ash have been conducted for many years, mercury has generally been overlooked as a problem. When leaching tests have been done in the past, inductively coupled plasma (ICP) analyses of mercury have usually been done using inductively coupled plasma spectrometry (ICAP). The reported results have usually been below the detection limits or they have been very erratic. Since the goal of these analyses was to determine whether concentrations exceeded the Resource Conservation and Recovery Act (RCRA) limit of 0.2 mg/L mercury, this accomplished the characterization goals. However, the data are not useful for the research

purpose of quantifying mercury release to the environment. Although ICP is useful for determination of regulatory status, other techniques such as cold-vapor atomic absorption (CVAAS) and atomic fluorescence spectrometry provide the lower detection limits for mercury that are required to meet research needs. More recent data on fly ash, scrubber sludges, or activated carbon sorbents in reference to mercury are limited.

The DOE Federal Energy Technology Center (FETC) has contracted with CONSOL to do experiments to evaluate how readily mercury offgases from scrubber sludges, fly ash from coal-fired boilers, and carbon mercury sorbents (4). To date, the work has been with scrubber sludges. Fly ashes that have been known to adsorb mercury, and spent sorbents are being studied.

CONSOL conducted stability tests on unfixated and fixated wet flue gas desulfurization (FGD) solids from a plant burning a medium-sulfur eastern bituminous coal. The solid samples were subjected to the EPA toxicity characteristic leaching procedure (TCLP), Parts a and b, and a modified leaching protocol. In addition, the samples were heated to determine whether the captured mercury could be desorbed or re-emitted (volatilized). The mercury concentrations of the unfixated and fixated wet FGD samples were  $0.70 \pm 0.03$  ppmw and  $0.39 \pm 0.03$  ppmw, respectively. The concentrations of mercury found in the leachate samples for all three extraction solutions (acetic acid buffered to pH 2.8, acetic acid buffered to pH 4.9, and distilled deionized [DI] water) were below CONSOL's reporting limit of 0.01 mg/L. On the basis of the RCRA 0.20- mg/L limit for mercury, both wet FGD materials would be classified as nonhazardous. Mercury analysis conducted on the unfixated filtered solids ranged from  $0.68 \pm 0.03$  ppmw to  $0.73 \pm 0.03$ , which is statistically the same as the starting material. The mercury concentration determined on the weighed, fixated, filtered solids was  $0.39 \pm 0.03$  ppmw, which is the same as the starting material. On the basis of the leaching results, researchers at CONSOL concluded that the mercury contained in the solids was in a nonleachable form. They hypothesized that the mercury might be chemically bound with the  $\text{CaSO}_4$ .

During the volatilization tests, both of the wet FGD wastes were exposed to elevated temperatures for 11 weeks, with the most stringent case at  $140^\circ\text{F}$  ( $60^\circ\text{C}$ ). Analyses conducted at the end of the exposure period showed no loss of mercury. It was concluded from these tests that mercury did not revolatilize when exposed to temperatures of up to  $140^\circ\text{F}$ .

Recently, the EERC completed mercury sampling at a power plant in North Dakota. As part of this test, scrubber samples were taken and analyzed to determine where the mercury that was absorbed by the scrubber ended up. This plant was unusual, in that the fly ash, which is inherently high in calcium, was used to remove the  $\text{SO}_2$  in the scrubber. About 10% of the mercury was absorbed by the fly ash prior to being utilized in the scrubber. An additional 10% of the mercury in the flue gas was in the oxidized form and therefore, removed by the wet scrubber. The analysis of these slurries did give interesting results. Prior to entering the scrubber, the fly ash is mixed with water from the ash pond. In this reaction tank, the pH is very basic ( $>9$ ) because of the ash alkali content. Yet after mixing, the concentration of mercury in solution was less than the reporting limit of CVAAS. The scrubber slurry (after coming into contact with the  $\text{SO}_2$ -containing flue gas) is a highly acidic system, pH  $\sim 4.5$ . In this case also, the slurry water contained little or no mercury. The results from these tests appear to indicate that once mercury is absorbed by fly

ash (or fly ash slurry), it does not again become mobile. These results were in agreement with the work published by CONSOL and Breit et al. (4, 5). They also found that the mercury was almost exclusively found in the solid portion of an FGD slurry and tended to stay there.

However, it has been found that if scrubber sludge from this plant undergoes a forced oxidation process, some of the mercury is released into the aqueous phase (6). The increase in mercury concentration in the aqueous phase may be a concern, depending upon the fate of this liquid. The solid resulting from the oxidation process was subjected to leaching. The results of the leaching test indicated that the mercury in the solid was not leachable.

Under the EERC's Center for Air Toxic Metals (CATM) program, thermal stability experiments were then carried out on unoxidized sludge solids. On the basis of the initial experiments, it appears that if the temperature is high enough to desorb all the mercury, the desorbed mercury is in the oxidized form. Stepwise thermal stability experiments showed that the mercury in the FGD solids is stable up to 100°C, with desorption occurring at higher temperatures.

At the 1997 Ash Utilization Symposium in Lexington, Kentucky, several papers dealing with the leachability of mercury from coal fly ash or combustion by-products were presented. Nathan et al. (7) evaluated several coal fly ashes generated from combustors located in Israel. The fly ashes came from South African and Colombian coals. Fly ashes were leached according to various regulatory procedures, including EPA TCLP and the European proposed E-CEN/TC192/WG2 method. Leaching solutions included water and dilute acetic acid or acetate buffer, and leaching durations ranged from 18 to 48 hours. The researchers reported that the amount of mercury leached from 1 kg of ash ranged from not detected (less than 1.8 µg) to 23 µg.

At the same conference, by-products from three different clean coal technologies were similarly tested (8). These materials were the solids collected following dry scrubbing of SO<sub>2</sub>, the bed material from a pressurized fluid-bed combustor (PFBC), and the bed material from a circulating fluid-bed combustor (CFBC) burning a mixture of coal and MSW. Of these three materials, the CFBC waste had the highest concentration of mercury at 1.1 ppm, with the PFBC being the lowest (<0.1 ppm). In all cases, the TCLP results indicated that the mercury was not mobile. The measured mercury in the leachate was less than the detection limits of the instrument, which again was ICP with mass spectrometry (MS). For comparison purposes, the established mercury level for a mercury hazardous material is 3.2 mg/kg or 3.2 ppm of waste. As described in a 1994 *EPRI Journal* article (9), soils containing tar that was contaminated with mercury were burned in an incinerator. Leaching tests of these soils also showed no movement of mercury.

Somewhat contradictory results as to the ability of mercury to offgas were reported in an article by Hamilton and Bowers (10), although with a different material. In their tests, they evaluated a solidified and stabilized portland cement. Their article stated that when a stabilized cement was placed in a batch reactor, a small amount of elemental mercury (Hg<sup>0</sup>) was detected in the headspace of the reactor. When the cement was doped with either HgO or Hg<sup>0</sup> prior to being stabilized, the headspace of the reactor of the HgO containing cement was saturated in about

1 hour. The cement containing  $\text{Hg}^0$  was about 20% saturated in 2 hours. As was expected, the rate of offgassing of mercury increased with temperature. However, when the cement was doped with  $\text{HgS}$ , there was no offgassing. This appears to show that the amount of offgassing was directly related to the volatility of the mercury species, which should come as no surprise.

In a study completed by Carpi et al. (11) at a sewage sludge disposal site, a significant elevation of  $\text{Hg}^0$  was measured at the air–solid interface compared to the background level. In fact, the flux rate of  $\text{Hg}^0$  was more than one order of magnitude higher than background. In addition, they found that methylmercury emissions were also significantly elevated at the disposal level. The mercury concentration in the sludge was  $\sim 7000 \text{ }\mu\text{g/kg}$ , which is just slightly higher than most of these types of materials. About 0.5% of the mercury in the sewage sludge was in the form of monomethyl mercury.

It is also well known that there is a fairly substantial mercury flux at municipal landfills. For example, a landfill in Florida emitted 80–100 g/y of mercury (12). Most of these emissions occur during routine waste handling at the surface of the landfill and may be caused by disturbing things like fluorescent bulbs that contain mercury.

On the basis of a literature review of the data, it appears that the mercury contained in scrubber sludges tends to be quite stable. It is clear, however, that longer-term tests need to be conducted under simulated landfill conditions. In addition, field testing at wet FGD waste landfills needs to be conducted to determine whether mercury vapor is being released. Overall, the data are preliminary and not extensive and, for fly ashes and mercury sorbents, do not exist. This is an area that does need to be researched for three major reasons:

- The extent of the ability of mercury in these materials to contaminate groundwater must be determined.
- Because mercury is persistent, bioaccumulative, and potentially toxic at high exposures, removing the mercury from the flue gas and capturing it in a solid material must render the mercury as a fully sequestered analyte. If the mercury is not stable in the wastes and by-products, it will eventually become part of the global mercury cycle.
- Many plants sell their fly ash. They may not be able to continue this practice if the fly ash includes mercury sorbents if the mercury is at all mobile.

## 4.0 EXPERIMENTAL APPROACH – TESTING OF COMBUSTION PROCESS EFFLUENTS

Waste disposal presents special environmental problems, especially in cases where leachates contain potentially problematic elements. The term “potentially problematic elements” is in itself nebulous, since with only a few exceptions trace elements have been shown to play a part in the metabolic pathways of various life forms, thus often making toxicity a factor of dose rather than of identity. Mercury, however, is one of the exceptions with no known essential metabolic function and with a propensity to bioaccumulate to concentrations that can cause chronic or acute toxicity.

This section details experiments in Subtask 1.2, performed to gain an understanding of the environmental fate of mercury sorbed onto coal fly ash, MSW fly ash, and sorbents used for mercury removal. Leaching characterization and thermal desorption were utilized during the course of this study. Leaching was carried out using DI water. Because the fly ash samples studied were highly alkaline, it was assumed that biotransformation of mercury and mercury compounds to methylated species was unlikely because of the high pH of the solution that forms upon contact of ash with DI water (pH 11–12.5). Thus the issue of biotransformation was not incorporated into this research. It is recognized, however, that long-term storage of ash containing sorbed or bound mercury might eventually become host to bio-organisms that could form methylated mercury species or that could cause reduction of mercury compounds to elemental mercury. This could enhance vapor transport and some forms of liquid mobility such as transport with colloids.

Both short-term (18-hour) and long-term leaching, with 2- and 4-week equilibration times, were used in this study. Long-term leaching was carried out to determine the evolution of leachate concentrations of mercury. Since the alkaline ash types included in this study undergo mineralogical transformations upon contact with water, the normal assumption of trace concentrations increasing to a point of equilibration is not always valid. Some ash samples have been known to exhibit increasing concentrations of trace elements during short-term leaching and upon long-term equilibration concentrations of select trace elements, have been seen to decrease. These phenomena are referred to as normal and anomalous leaching, respectively.

### 4.1 Experimental Procedures

*Selection of Samples.* Samples of coal fly ash, municipal waste incinerator (waste-to-energy [WTE]) ash, and sorbents were collected for use in this study. Ash samples were studied as received; however, the sorbents, initially containing no mercury, were loaded with  $\text{Hg}^0$  and mercury(II) chloride ( $\text{HgCl}_2$ ) in the laboratory using mercury-containing gas streams.  $\text{Hg}^0$  and  $\text{HgCl}_2$  vapor were added to a nitrogen gas stream using permeation tubes. This gas was then passed through a bed of the appropriate sorbent until breakthrough occurred (breakthrough was determined using a mercury continuous emission monitor). All samples were analyzed for total mercury content as an initial screening to determine which samples would be included in the complete testing protocol.

One of the sorbents that was tested was prepared from MnO<sub>2</sub>. This sorbent was prepared as follows: Approximately 100 g of gamma Al<sub>2</sub>O<sub>3</sub> was crushed to -18 +50 mesh. 20.1 grams of Mn(NO<sub>3</sub>)<sub>2</sub> · 6H<sub>2</sub>O was weighed under nitrogen and dissolved in 60 mL of DI water. The resulting solution was added to the alumina and placed into a 250-mL round-bottom flask. The water was removed using moderate heat (<100°) under vacuum with a rotary vacuum evaporator. The dry mixture was placed into an evaporating dish and heated in an oven at 200° C for 2 hours to decompose the Mn(NO<sub>3</sub>)<sub>2</sub> into MnO<sub>2</sub>, with the evolution of red fumes of NO<sub>2</sub>.

Table 1 lists the samples tested and their mercury concentration. Analysis for total mercury was done using CVAAS. As shown in Table 1, the tests focused on four fly ash samples, two WTE ash samples, one dry FGD ash, and four sorbents each loaded with either Hg<sup>0</sup> or HgCl<sub>2</sub>, totaling 15 samples.

*Leaching Protocols.* The stability of mercury on these materials with respect to potential long-term environmental impact was studied using two techniques, leaching and thermal desorption. Leaching was carried out using a leaching protocol called the synthetic groundwater leaching procedure (SGLP) with DI water as the leaching solution. The SGLP was developed at the EERC (13) as a result of research conducted on coal conversion solid wastes (6, 14). The test, which is a generic leaching procedure designed for simulation of leaching under environmental conditions, was initially developed for use in the characterization of highly alkaline coal conversion solid residues, primarily fly ash produced from the combustion of low-rank lignitic or subbituminous coals. The test, modeled after the TCLP (15) with modifications to allow for numerous disposal scenarios, is primarily for use with reactive materials such as low-rank coal ash that will undergo hydration reactions upon contact with water.

Further testing with more site-specific leaching solutions would be required for determination of environmental mobility under field conditions and would be different for varying sites. For many of the materials studied, it can be assumed that the material being leached would have a major influence over leaching solution chemistry. This is especially true of some of the more alkaline coal ash samples where relatively high solubility of ash constituents is likely to be the major determining factor on leachate chemistry composition where ash is infiltrated by rainwater or groundwater. The effects of biological activity would be an additional determining factor, especially with some of the less-alkaline samples. Samples with leachate pH values above 11.5 would be expected to support minimal biological activity.

The SGLP leaching for this study utilized DI water as a first-cut screening method. The use of DI water as the leaching solution makes this form of the SGLP very similar to the ASTM shake extraction test (16). End-over-end agitation was used with sampling times of 18 hours, 2 weeks, and 4 weeks. The extended leaching times were included to allow a determination of changes in the rate of mercury leaching and to allow reactive ash samples time to equilibrate and form secondary hydrated phases. It has been shown that the formation of secondary hydrated phases can exert a substantial effect on leachate chemistry. Normally, solid-to-liquid ratios of 20:1 are used for SGLP evaluation (as is used in the TCLP protocol). However, in this study, the ash samples, which had a lower mercury concentration than the load sorbents, were leached at a solid-to-liquid ratio of 10:1 in an effort to obtain more statistically significant analytical data. The

sorbents were leached at the normal 20:1 liquid-to-solid ratio. These leaching tests were not intended to produce leachate concentrations that would be expected under field conditions. It may not be possible to accurately reproduce field leaching conditions in the laboratory except in isolated and specific cases, as discussed in *The Compendium of Waste Leaching Tests* (17). It may be possible, however, to calculate the field conditions using a modeling scenario based on the amount of easily released analyte and rate of leachate formation.

*Thermal Desorption Apparatus.* An apparatus for the controlled thermal desorption of mercury and mercury compounds was assembled and is shown schematically in Figures 1 and 2. The apparatus was constructed using a Varian 1475 atomic absorption (AA) spectrophotometer for mercury detection and includes a small tube furnace and temperature controller for thermal desorption. A Hewlett Packard 3393A integrator was used for data collection. The AA was operated using a mercury hollow cathode lamp as the spectral source with detection at 253.7 nm. Detection of thermally desorbed mercury and mercury compounds was done in an electrically heated quartz cell operated at 800°C. The use of a heated cell allowed detection of mercury compounds by thermally decomposing compounds to form  $\text{Hg}^0$ , which can be detected by AA. The heated quartz cell assembly consists of a quartz cell, the heater, and an ETC-50 electrothermal temperature controller that can be heated to a maximum temperature of approximately 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 75° and 80°C using a heating tape. 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 dimples pressed into the tubes 5 cm from the exit end held the sample and quartz plugs in place once the tube had been placed into the tube furnace and connected to the heated quartz absorption cell, and gas flow was initiated.

*Thermal Desorption Protocol.* Samples for thermal desorption were placed into quartz tubes (20 cm × 4.8 mm with a wall thickness of 1 mm) with minimal packing to avoid excessive pressure drops across the sample mass. On the basis of the mercury concentration in the sample, the mass of sample used for each test was sufficient to provide between 100 and 250 nanograms of mercury. This typically required less than 1-gram samples for the ash samples and less than 10 mg for the highly loaded sorbents. The samples were held in the quartz tubes with small plugs of quartz wool. Three indentations pressed into the exit end of the tube held the sample in place and assured that the sample was centered in the tube furnace. Gas flow was 20 mL per minute of nitrogen. The temperature controller was ramped from ambient to 500°C at a rate of 20°C a minute. Replicate samples were run because it was often necessary to make adjustments on sample mass and sensitivity settings to obtain statistically significant thermal desorption results.

TABLE 1

## Samples Screen for Use with the Mercury Stability Study

ID No.	Fuel Type	Plant Configuration	Comments	Hg Conc., µg/g
185	Western bit.	pc-fired boiler, low-NO <sub>x</sub> burners, and fabric filter		0.461
186	Western bit.	pc-fired boiler, low-NO <sub>x</sub> burners, dry FGD, and fabric		0.565
187	ND lignite	pc-fired EERC pilot-scale combustor and fabric filter		0.677
188	PRB subbit.	Dry FGD and fabric filter	Ash contains lime from dry FGD	0.112
189	Blended PRB subbit. and pet coke	Cyclone boiler and ESP		0.736
190*	PRB subbit.	pc-fired boiler, fabric filter, duct injection FGD using Trona	Ash contains Na <sub>2</sub> CO <sub>3</sub> from Trona	<0.002
191*	Blended PRB subbit. and eastern bit.	pc-fired boiler with ESP		0.008
192*	PRB subbit.	pc-fired boiler with ESP		0.026
193*	PRB subbit.	pc-fired boiler with ESP		<0.002
194*	PRB subbit.	PRB sub.-pc fly ash-ESP		0.059
195*	ND lignite	pc-fired boiler, ESP, and wet FGD		0.002
263*	Eastern bit.	pc-fired boiler and ESP		0.004
266*	Eastern bit.	pc-fired boiler and ESP		0.138
267*	Eastern bit.	pc-fired boiler with multiclones and ESP		0.191
264	MSW	WTE system with fabric filter		3.52
265	MSW	WTE system with fabric filter		75.4
C-1	Loaded sorbent	Centaur activated carbon with added Hg <sup>0</sup>		54.4
C-2	Loaded sorbent	9041AC iodated activated carbon with added Hg <sup>0</sup>		180
C-3	Loaded sorbent	Darco FGD activated carbon with added Hg <sup>0</sup>		80.3
M-1	Loaded sorbent	MnO <sub>2</sub> on Al <sub>2</sub> O <sub>3</sub> with added Hg <sup>0</sup>	Prepared in the laboratory	92.6
C-1	Loaded sorbent	Centaur activated carbon with added HgCl <sub>2</sub>		0.590
C-2*	Loaded sorbent	9041AC iodated activated carbon with added HgCl <sub>2</sub>		<0.03
C-3	Loaded sorbent	Darco FGD activated carbon with added HgCl <sub>2</sub>		0.41
M-1	Loaded sorbent	MnO <sub>2</sub> on Al <sub>2</sub> O <sub>3</sub> with added HgCl <sub>2</sub>	Prepared in the laboratory	0.44

\* Eliminated from testing because of low mercury concentration.

pc = pulverized coal.

ESP = electrostatic precipitator.

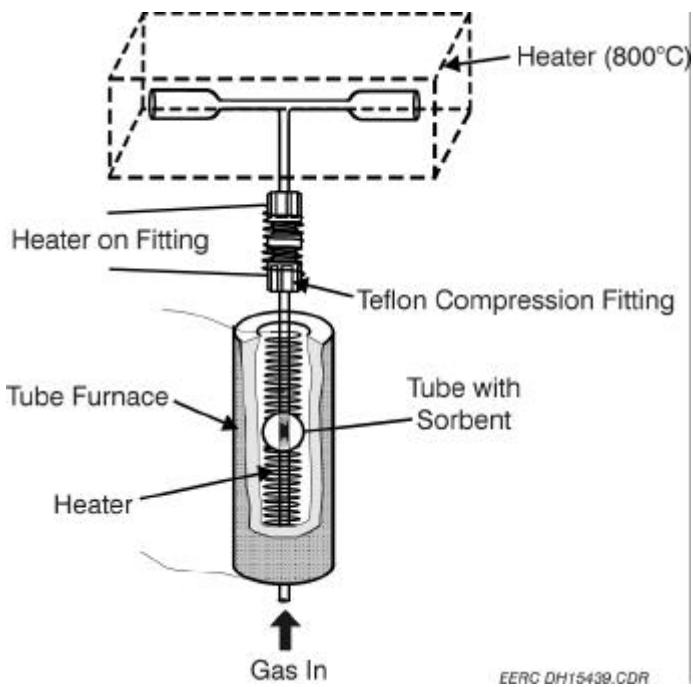


Figure 1. Schematic of the thermal desorption apparatus.

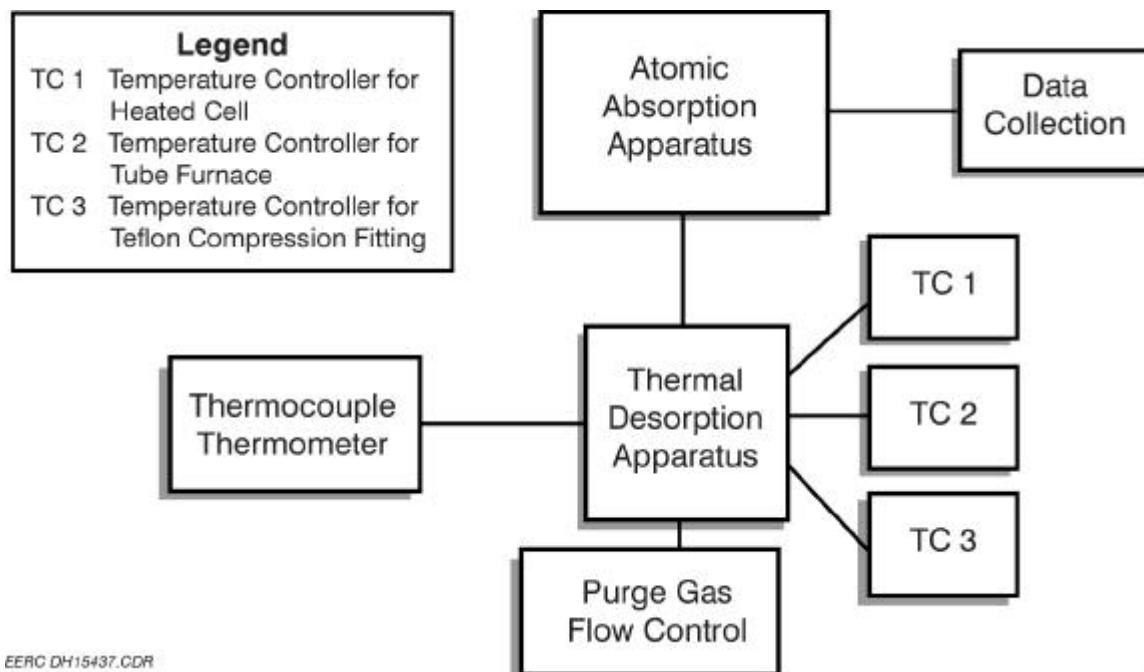


Figure 2. Diagram of the thermal desorption section.

## 4.2 Leaching Results

Leaching results are summarized in Table 2. The calculated maximum mercury is based on the total mercury concentration measured in the solid and the solid-to-liquid ratio used for leaching. It indicates the maximum concentration that could be reached if all of the mercury had dissolved during leaching and represents a calculated worst-case scenario. The table compares the calculated maximum to the leaching results obtained at the 18-hour, 2-week and 4-week equilibration times. In addition to measuring the concentration of mercury in the leachate, the pH was measured on all leachates. The pH levels of the 4-week leachates are listed in Table 2.

As this table shows, with the exception of the two laboratory sorbents (M-1 and C-2), the mercury appears to be very stable in the solids for up to 4 weeks. In almost all cases, less than 1% of the calculated maximum mercury concentration is leached, even up to 4 weeks. This is very much in agreement with the work conducted at CONSOL (4).

Manganese dioxide-coated alumina appeared black before and after loading because of the coating of  $\text{MnO}_2$ . During leaching, the solution also appeared black and remained black. At the end of the leaching experiments, this black suspended material was not removed by filtration through a 0.2- $\mu\text{m}$  membrane filter or centrifugation at nearly 20,000 G. The suspension, which appeared to be colloidal, was either formed from  $\text{MnO}_2$  that came off of the surface of the sorbent during the course of the leaching experiment or from  $\text{MnO}_2$  that was formed in solution during the course of the leaching experiments. It is likely that this suspension, which should contain at least a portion of the sorbed mercury, accounts for the elevated leached mercury in M-1 leachates since mercury in this suspension was included in the final solution in which mercury was determined.

TABLE 2

ID No.	Sample Type	Leaching Results					
		Bulk, $\mu\text{g/g}$	Calc. Max. $\mu\text{g/L}$	18-hr, $\mu\text{g/L}$	2-week, $\mu\text{g/L}$	4-week, $\mu\text{g/L}$	4-week, pH
185	Fly ash	0.461	46.3	<0.05	0.11	<0.05	12.6
186	Fly ash	0.565	56.9	0.24	0.05	<0.05	12.7
187	Fly ash	0.677	67.8	0.12	<0.05	<0.05	12.1
188	FGD ash	0.112	11.2	<0.05	<0.05	<0.05	12.1
189	Fly ash	0.736	73.8	<0.05	<0.05	<0.05	11.3
264	WTE ash	3.52	353	0.14	0.050	0.090	10.7
265	WTE ash	75.4	7540	0.090	0.070	0.090	6.6
C-1	Carbon with $\text{Hg}^0$	54.4	2720	<0.1	0.060	0.24	6.8
C-1	Carbon with $\text{HgCl}_2$	0.590	29.8	<0.1	0.090	0.64	6.8
C-2	Carbon with $\text{Hg}^0$	157	7812	<0.1	<0.05	<0.1	6.2
C-3	Carbon with $\text{Hg}^0$	80.3	4165	<0.1	0.530	0.22	10.1
C-3	Carbon with $\text{HgCl}_2$	0.41	21	ND	ND	ND	ND
M-1	$\text{MnO}_2$ with $\text{Hg}^0$	92.6	4746	646	1380	424	4.6
M-1	$\text{MnO}_2$ $\text{HgCl}_2$	0.44	22	7.52	15.4	11.0	4.6

### 4.3 Thermal Desorption Results

With the exception of two sorbents (C-2 with  $\text{HgCl}_2$  and M-1 with  $\text{HgCl}_2$ ) the same samples were used for the thermal desorption tests as for the leaching tests. The test samples contained nominally 100 to 250 nanograms of mercury where possible. However, some samples comprising fine particles caused a large pressure drop when used in sufficient quantity. For these samples, smaller masses were used, which caused some loss of definition of the desorption curves.

For the C-3 samples with added  $\text{Hg}^0$  and  $\text{HgCl}_2$  and the M-1 sample, no thermal desorption was observed between ambient temperature and 500°C. Representative desorption curves for the other samples are shown in Figures 3 through 8. Figures 3 and 4 are duplicate runs on the same sample. There was a high degree of reproducibility for all the samples. The samples were either tested in duplicate or triplicate.

Although most of the desorption curves are straightforward, containing only one or two major desorption peaks, there were several samples that produced multiple desorption peaks. In addition to the desorption curves on ash and sorbents, two standard samples were also run. These consisted of a fly ash sample initially containing mercury at below the detection limit that was spiked with  $\text{HgCl}_2$  and  $\text{HgO}$ . These samples each presented one thermal desorption peak, with the  $\text{HgCl}_2$  centered at approximately 220°C and the  $\text{HgO}$  peak centered at approximately 355°C. It has been speculated in thermal desorption experiments run by others (18, 19) that there may be a correlation between the temperature of evolution and mercury form. This may not be the case with respect to chemically modified sorbents and ash. Mercury sorbed onto an inert surface would be expected to exhibit reproducible thermal desorption behavior regardless of the mechanism of volatilization. This would be true even for chemical decomposition of sorbed compounds. However, ash and sorbents cannot be thought of as inert. Thus, there may be other factors entering into thermal stability. For example, the same compound sorbed onto different substrates could lead to different thermal desorption profiles. Alternative scenarios that could provide misleading data from thermal desorption experiments include:

- Chemical decomposition of the sorbed mercury compound during the thermal desorption process. This might be the case for sorbed mercuric oxide, which decomposed to form mercury vapor and oxygen upon heating.
- Chemical transformations on ash or sorbent surface that could lead to more or even less volatile mercury compounds.
- Chemically modified carbon sorbents (containing iodine or sulfur) and even some ash could react with the volatile mercury and mercury compounds to form entirely different compounds than were originally in the gas stream during the mercury uptake and finally during the thermal treatment during desorption.

These mercury–sorbent systems must be considered to be dynamic with respect to physical and chemical transforms of initial mercury species and to species released during thermal desorption.

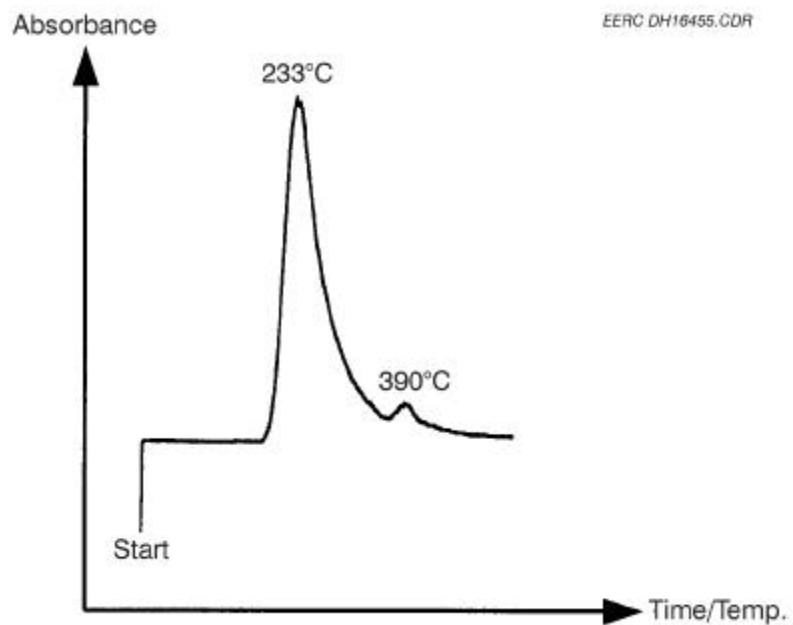


Figure 3. Thermal desorption curve for Ash 186.

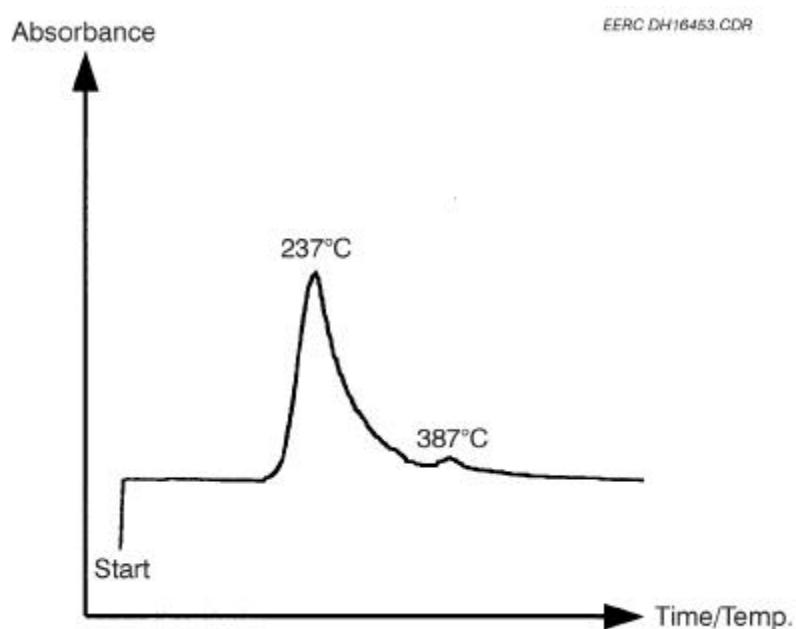


Figure 4. Thermal desorption curve for Ash 186, duplicate.

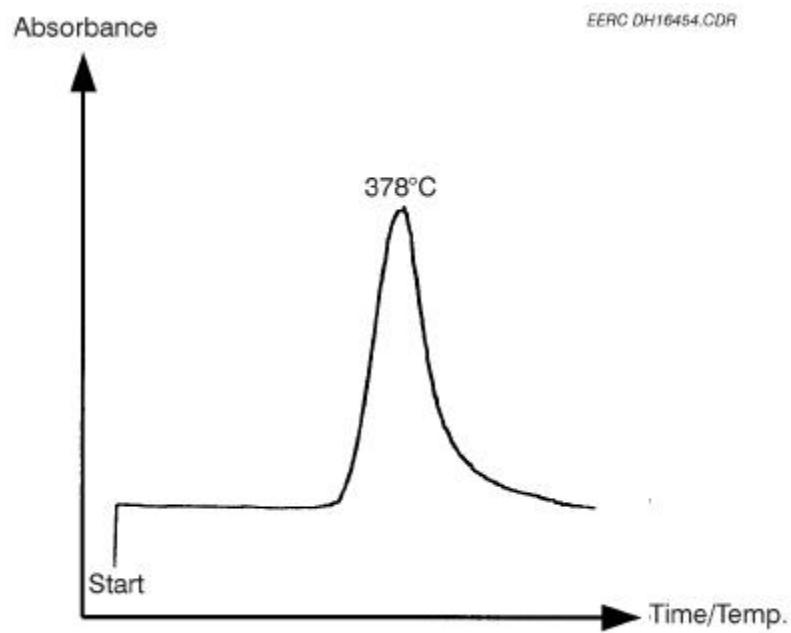


Figure 5. Thermal desorption curve for Ash 189.

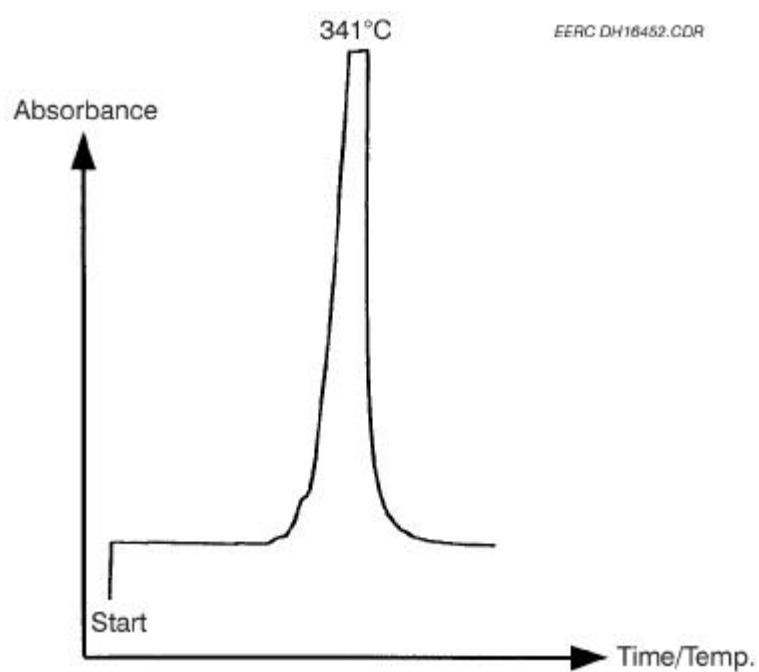


Figure 6. Thermal desorption curve for WTE ash.

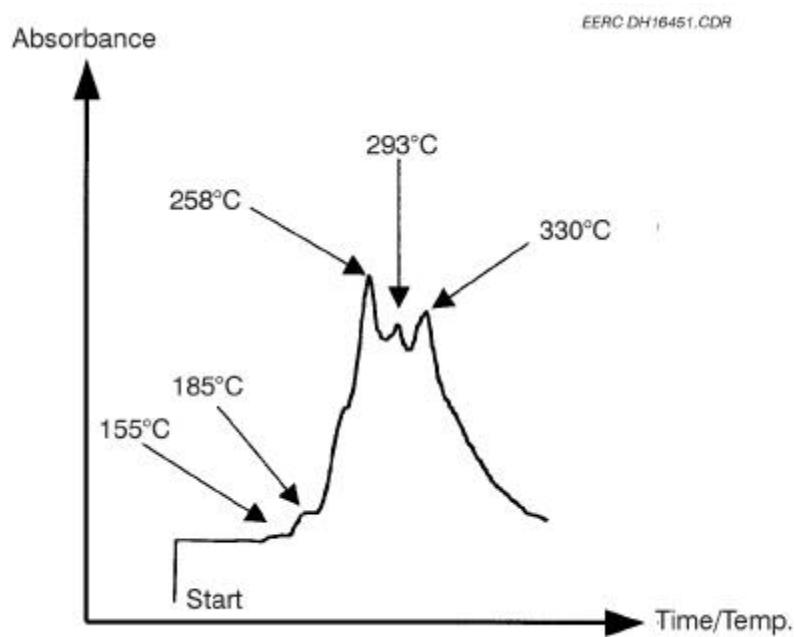


Figure 7. Thermal desorption curve for C-1 mercury.

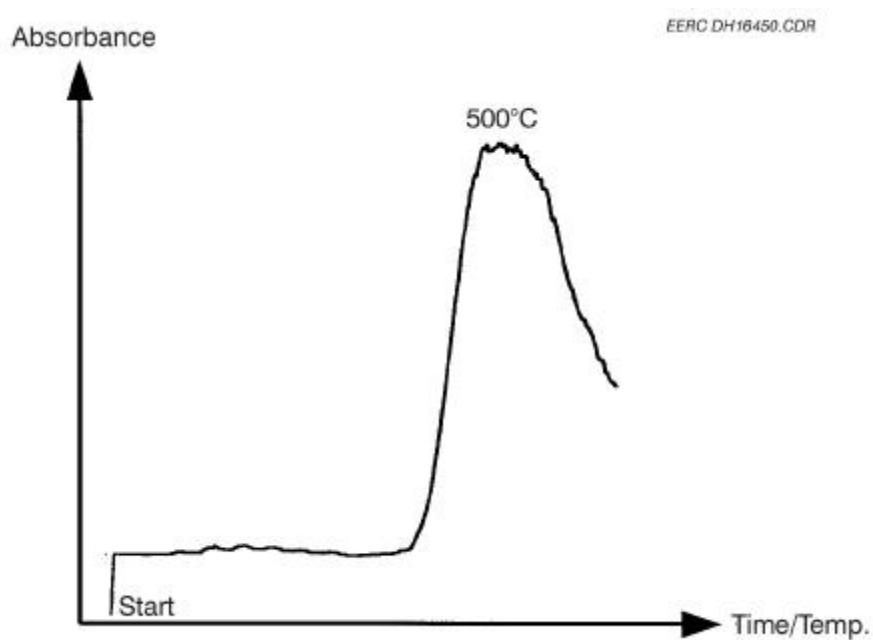


Figure 8. Thermal desorption curve for M-1 mercury.

From the samples tests (as shown in Figures 3–8) there were four representative thermal desorption curves. These are:

- A single predominant peak
- Two or more predominant peaks
- One major and one minor peak
- Numerous small and large peaks

Regardless of the number of peaks, all observed peaks were what are known as tailing peaks, with a somewhat symmetrical rise and a more protracted decrease, sometimes not returning to baseline during the course of the timed run. Additionally, in multiple-peak samples, the peaks were not usually completely resolved. It is likely that some of this peak asymmetry can be corrected by optimization of flow rates and heating rates to take advantage of chromatographic properties of the system.

The thermal desorption information for all of the samples that were thermally desorbed is shown in Table 3. Sample information is given, as well as the temperature or temperatures of maximum absorbance (labeled  $T_{A\ max}$ ) and the percent of total absorbance (the percent each peak represents of total absorbance). The temperature of maximum absorbance was calculated by multiplying the time of the peak maxima shown on the chromatograms by 20, the ramp rate in °C per minute, and adding the starting temperature, which was usually near ambient (between 20° and 35°C). Because it has been shown that not all of the mercury in each sample was thermally desorbed during the course of these experiments, the percent for each peak should not be taken to be in reference to the total measured mercury, but of the total mercury that was thermally desorbed.

In the case of four of the ashes, enough sample was collected after desorption experiments to determine the amount of mercury not remaining on the sample after thermal desorption. The results are shown in Table 4. Because of the rather poor completeness of removal, there was no attempt made to correlate peak areas with quantitation of total mercury. Future experiments with longer desorption times and higher maximum temperatures may make this technique quantitative.

It can be seen from Table 4 that recoveries range from a satisfactory 91% to a low of 46%. If thermal desorption had been complete, the final mercury concentration would have been close to or at zero. It is likely that thermal efficiency can be improved by developing an apparatus that can be operated to above 500°C. This improved apparatus is being developed.

## CONCLUSIONS

- Coal ash samples did not leach mercury above detection limits at the 4-week equilibration period. Some ash samples leached minute amounts of mercury before the 4-week equilibration was reached. This may have been a result of the formation of secondary hydration products, which would be expected to form at the pH levels seen in these samples. However, the amount of mercury leached was only slightly above the detection limit of the instrument.

- The WTE and FGD ash samples leached mercury only near detection limits at the 4-week equilibration time. A comparison of calculated maximum concentrations in 4-week fly ash samples with actual leachate concentrations shows that less than 0.1% of the mercury was leached for both types of ash samples.
- The only sample tested that may present a potential leaching problem was the Centaur activated carbon loaded with  $\text{HgCl}_2$ . In this case, 2.1% of the total available mercury leached out after 4 weeks. All the other carbons leached less than 0.1% of the maximum mercury. Even for the Centaur carbon, the potential for adverse environmental impact through leaching mechanisms may be misleading, since under use conditions, the sorbents, if injected into flue gas streams, would be present along with fly ash and would have a much lower loading. However, if this type of sorbent is used in packed beds, it is possible that leaching may be an issue.
- Sorbents M-1 and M-2 appear to have leached high concentrations of mercury. However, these samples contained black solids that were not removed by centrifugation at 15,000 G or by filtration through a 0.2- $\mu\text{m}$  filter. It is likely that the mercury detected was associated with the particles, but given the experimental approach, this could not be absolutely established.
- Thermal desorption indicated little potential for environmental impact through devolatilization because no significant mercury peaks were detected at temperatures below 150°C. Future experiments using integrated collection of mercury vapor from ash and sorbents over long time periods at low temperatures may help to answer this question more completely. Integrated collection on gold traps with subsequent atomic fluorescent detection will allow detection down to 50 picograms or lower, as opposed to 100 nanograms required using AA.
- The use of a thermal approach to the determination of mercury forms and/or stability has only recently begun to be fully explored. Although initial trials have been promising, more work is needed before detailed conclusions on limitations and uses can be made.
- On the basis of a review of the literature and the project completed by the EERC, it is clear that substantial work needs to be done to determine the stability of mercury in combustion by-products. Although the preliminary data appear to be encouraging, there is contradictory information. In addition, almost nothing is known as to the leachability or offgassing potential of the different mercury sorbents that are being tested as possible control strategies for fossil fuel-fired combustors.

TABLE 3

Thermal Desorption Information				
ID No.	Sample Type	T <sub>A</sub> max	Percent of Total	Starting Temperature, °C
185	Fly ash	350	100	28
186	Fly ash	233	91	22
		390	9	
187	Fly ash	317	100	36
189	Fly ash	378	100	25
188	FGD ash	250	75	22
		357	9	
		429	12	
		454	3	
264	WTE ash	308	100	23
265	WTE ash	341	100	23
C-1	Activated carbon with Hg <sup>0</sup> added	155	0.5	22
		185	2.0	
		258	34.9	
		293	16.8	
		330	45.7	
		364	100	25
C-2	Activated carbon with HgCl <sub>2</sub> added	165	39	22
		266	37	
		360	25	

TABLE 4

Mercury Removal Efficiency of Thermal Desorption Procedure				
ID No.	Sample Type	Initial Hg, µg/g	Final Hg, µg/g	Percent Removed
185	Fly Ash	0.461	0.043	90.7
186	Fly Ash	0.565	0.078	86.2
187	Fly Ash	0.677	0.365	46.1
189	Fly Ash	0.736	0.066	91.0

## RECOMMENDATIONS FOR FURTHER RESEARCH

The results of this preliminary study have provided a sound basis in protocol development and have generated valuable preliminary information. Additional work is needed in the following areas:

- Additional testing to determine leachability or offgassing potential of different mercury sorbents that are being developed and tested as possible control strategies for fossil fuel-fired combustors.
- Additional work to evaluate utilization and disposal under a full range of conditions that would be expected to be used.
- Development of long-term desorption/vapor transport data at near-ambient temperatures and under varying conditions of humidity. These experiments will not all be done in real time because of low concentrations and will be primarily integrated into long-term vapor transport experiments with capture of desorbed mercury on gold or carbon traps.
- Development of additional thermal desorption data going to temperatures higher than 500°C. This will necessitate design changes in the test apparatus. Higher temperatures are needed to desorb all of the mercury in the samples, since in the initial thermal desorption work, recoveries of between 46% and 91% percent were achieved. Although a recovery of 90% may be satisfactory, a recovery of 46% is clearly incomplete, even considering possible experimental and analytical errors.
- Collection of leaching data to incorporate longer equilibration times using site-specific leaching solutions with evaluation of leachate concentrations using lower detection limits. This can be accomplished using atomic fluorescence detection with cold-vapor generation and double gold amalgamation.
- Determination of the form of mercury being desorbed during thermal desorption experiments. Experiments with and without the heated cell could resolve some of the issues associated with the form of mercury being desorbed, since mercury compounds would not be detected by the AA without the heated cell. The form of mercury being desorbed might also be resolved using MS for detection. Additionally, surface techniques, such as Raman and infrared microprobe or even laser desorption mass spectrometry might also aid in discerning mercury forms if mercury concentrations were high enough.
- Thermal desorption experimentation using pure mercury compounds spiked onto inert substrates and onto ash samples that do not contain significant amounts of mercury. This would help answer questions concerning compound transformations and thermal decomposition.

## REFERENCES

1. Provisions for Attainment and Maintenance of National Ambient Air Quality Standards. Public Law 101-549, 1990.
2. Hargrove, O.W.; Richardson, C. Interactions of Flue Gas Constituents and Effects on Mercury Speciation. Presented at the Workshop on Mercury Measurement and Speciation Methods for Stationary Sources, DOE-EPRI-EPA, Research Triangle Park, NC, Jan 29–30, 1997.
3. Laudal, D.L.; Heidt, M.K. *Evaluation of Flue Gas Mercury Speciation Methods*; EPRI TR-108988; Nov 1997.
4. Brown, T.D.; Smith, D.N.; Hargis; R.A. Jr.; O'Dowd, W.J. Mercury Measurement and Its Control: What We Know, Have Learned, and Need to Further Investigate. *Journal of the Air & Waste Management Association* **1999**, 45.
5. Breit, G.; Johnson, R.; Cathcart J.; Bullock, J.; Eble, C. Trace and Minor Element Distribution in a Forced-Oxidation, Limestone-Slurry Flue-Gas-Desulfurization Unit. Presented at the 1997 Ash Utilization Symposium, Lexington, KY, Oct 1997.
6. Hassett, D.J. *Evaluation of the Leaching Potential of Solid Coal Combustion Wastes: Final Report*; prepared for the Indiana Coal Council; Energy & Environmental Research Center: Grand Forks, ND, 1991.
7. Nathan, Y.; Pelly, I.; Mimran, U. Coal Fly Ash in Israel—Characterization and Potential Contamination Resulting from Its Use or Disposal. Presented at the 1997 Ash Utilization Symposium, Lexington, KY, Oct 1997.
8. Cobb, J.T.; Clifford, V.; Neufeld, R.D.; Pritts, J.W.; Beeghly J. H.; Bender, C.F. Laboratory Evaluation and Commercial Demonstration of Hazardous Waste Treatment Using Clean Coal Technology By-Products. Presented at the 1997 Ash Utilization Symposium, Lexington, KY, Oct 1997.
9. Cofiring Tar and Highly Contaminated Soil. *EPRI Journal*, Dec 1994. Also at [http://www.epri.com/EPRI\\_Journal/dec\\_1994/res\\_update.html](http://www.epri.com/EPRI_Journal/dec_1994/res_update.html).
10. Hamilton, W.P.; Bowers, A.R. Determination of Acute Mercury Emissions from Solidified/Stabilized Cement Waste Forms. *Waste Management* **1997**, 17 (1), 25–32.
11. Carpi; Lindberg; Prestbo; Bloom. Methyl Mercury Contamination and Emission to the Atmosphere from Soil Amended with Municipal Sewage Sludge. *Journal of Environmental Quality* **1997**, 26, 1650–1655.
12. Lindberg, S.E.; Price, J.L. A Summary of Measured Mercury Emission from Two Municipal

Landfills in Florida. Presented at the Air & Waste Management Association 91st Annual Meeting & Exhibition, San Diego, CA, June 1998; Paper 98-WP79A.06.

13. Hassett, D.J. Synthetic Groundwater Leaching Procedure. In *Encyclopedia of Environmental Analysis and Remediation*; R. A. Meyers, Ed.; John Wiley and Sons Inc., 1998; pp 4797–4803.
14. Hassett, D.J. Scientifically Valid Leaching of Coal Conversion Solid Residues to Predict Environmental Impact. In *Proceedings of the Trace Element Transformations in Coal-Fired Systems Workshop*, Scottsdale, AZ, April 19–22, 1993; Special Issue of *Fuel Processing Technology* **1994**, 39 (1–3), 445–459.
15. U.S. Environmental Protection Agency. *Federal Register* **1986**, 51 (g), 1750–1758; ISSN 0097-6326.
16. American Society for Testing and Materials. Standard Test Method for Shake Extraction of Solid Wastes with Water. In *Annual Book of ASTM Standards*; Section 11: Water and Environmental Technology, ASTM D3987-85; ASTM: Philadelphia, PA, 1989.
17. Environment Canada. *Compendium of Waste Leaching Tests*; Report EPS 3/HA/7; May 1990.
18. Biester, H.; Nehrke, G. Quantification of Mercury in Soils and Sediments—Acid Digestion Versus Pyrolysis. *Fresenius Journal of Analytical Chemistry* **1997**, 358, 446–452.
19. Biester, H.; Zimmer, H. Solubility and Changes in Mercury Binding Forms in Contaminated Soils After Immobilization Treatment. *Environmental Science and Technology* **1998**, 32, 2755–2762.