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STABILITY OF MERCURY IN COAL COMBUSTION BY-PRODUCTS

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Project Description

This continuing project focused on three primary tasks with the goal of determining the mechanisms of mercury release from coal combustion by-products (CCBs). Each task was designed to address specific objectives. Six CCB samples were selected for use in all tasks. These samples had been analyzed in previous CATM work and were shown to have higher-than-average mercury concentrations. It was deemed necessary to evaluate high-mercury-content samples in these tasks to ensure quality-assured data. Utilizing the same samples for all tasks provided an opportunity to begin a hypothesis on the release of mercury from CCBs over a typical CCB lifecycle.

Work in Task 1 focused on release of mercury from the CCBs in the range of ambient temperature to 600°C. Calibration of the apparatus assembled in previous efforts was completed, and replicate evaluations of six samples were initiated. Results of Task 1 include the temperatures at which mercury (or mercury compounds) are released, relative amounts of mercury released at the varying temperatures, and the amount of mercury remaining on the ash after the desorption. These were interpreted based on the initial total mercury concentrations of samples evaluated as one component describing the stability of mercury sorbed on CCBs. This task provided baseline information on release of mercury from CCBs under utilization scenarios such as use in cement manufacture, gypsum wallboard production, a component of ceramic or brick, and other high-temperature manufacturing processes.

In Task 2, the research was directed toward understanding releases of mercury from microbial activity in fly ash under a disposal setting. Two samples were evaluated under six biological conditions. The releases of elemental and organomercury were evaluated.

Task 3 addressed the question of long-term release of mercury from CCBs at ambient and near-ambient temperatures. Samples were subjected to mercury-free air at ambient and near-ambient temperature for approximately 260 days. Mercury was collected on a gold-coated quartz trap, desorbed, and quantified. Quantification of the released mercury was difficult, as the levels of mercury released from samples were extremely low and nearly equivalent to the experimental blanks. Experimental protocols underwent several iterations to improve the reliability of the results.

Goals

The overall goal of the project was to quantify mercury being released to the environment from CCBs and to determine the mechanism resulting in mercury vapor transport. Supporting objectives were to:

- Evaluate the effect of biota on mercury transformations and subsequent release to the groundwater through leaching or offgassing to the atmosphere.
- Quantify the mercury released by thermal desorption.
- Determine the stability of fly ash collected following selective catalytic reduction.
- Determine the effects of NH_3 (as ammonium sulfate) on mercury stability.

Rationale

Mercury is of great concern because of its potential to bioaccumulate in the environment. The 1990 amendment of the Clean Air Act required the U.S. Environmental Protection Agency (EPA) to submit a study to Congress on atmospheric mercury emissions. The resulting EPA *Mercury Study Report to Congress* identifies the coal-fired electric utility generation industry as the largest anthropogenic mercury emission source in the United States [1]. EPA announced on December 14, 2000, that it would regulate mercury emissions from coal- and oil-fired electric utility steam generating power plants. EPA also announced that mercury controls would be required on coal-fired electric utilities by the year 2007 [2]. As technologies are developed to reduce the air emissions of mercury, the amount of mercury in CCBs will likely increase. Recent studies have indicated that from 0%–70% of the mercury originally in the coal can be associated with the fly ash [3, 4]. This poses a critical question: Will the mercury removed from the flue gas really be removed from the environment or will it be released later and at what rate? Concern that all of the mercury present on any coal ash might potentially be released to the air after a long enough time period was voiced at the EPA Coal Combustion Residues Workshop held January 10–11, 2001, in Research Triangle Park, North Carolina.

Long-term stability experiments were designed to measure mercury release from CCBs at ambient temperature and at temperatures that might be encountered from summer conditions or sunlight warming of an ash deposit. For purposes of this report, this temperature was defined as near-ambient and was set at 37°C (99°F). In an earlier study, thermal desorption indicated no significant mercury peaks at temperatures below 150°C [5]. It was determined that the most likely species of mercury that would be released from CCBs at the conditions chosen would be elemental mercury vapor.

Thermal desorption of mercury and mercury compounds from CCBs was studied at temperatures from between ambient and 600°C. These data gave indications of the bond strength of sorbed species and also provided information for determining long-term stability of CCBs.

The effect of biologic activity, although not of immediate interest in many disposal and use scenarios, will eventually become important as aging materials are infiltrated with water and become sites where microbes can live. The ability of mercury and mercury compounds to be methylated, becoming more toxic and likely to bioaccumulate, necessitated the study of microbial impacts on mercury in CCBs.

The CCBs used in this project were chosen from ashes from the United States, South Africa, and South America having total mercury contents ranging from <0.002 to 1.240 $\mu\text{g/g}$, with an average of 0.244 $\mu\text{g/g}$. Other reported mean values of mercury in fly ash are 0.500 $\mu\text{g/g}$ based on historical data from the EPRI PISCES (Power Plant Integrated Systems: Chemical Emissions Studies) database [6] and 0.395 $\mu\text{g/g}$ based on 1998 mass balance calculations [7].

Approach

Ash Samples

Six ashes consisting of five fly ashes and one flue gas desulfurization (FGD) material were chosen from CCBs that had been analyzed in a previous study at the EERC. The total mercury content in the ashes chosen ranged from 0.112 to 0.736 $\mu\text{g/g}$, as determined by cold-vapor generation atomic absorption spectrophotometry. These values are not typical of CCBs but were selected as having the greatest potential for releasing measurable amounts of mercury vapor. With samples containing these levels of bulk mercury, even minute percentage releases would be measurable. Table 1 provides a description of each sample.

Table 1. Ash Sample Total Mercury Content

Ash Sample	Coal/Ash Description	Total Mercury Content, $\mu\text{g/g}$
99-188	PRB* subbituminous fly ash + FGD material	0.112
99-189	PRB subbituminous + petroleum coke fly ash	0.736
99-692	Eastern bituminous fly ash	0.14
99-693	Eastern bituminous fly ash	0.268
99-722	South African fly ash	0.638
99-724	South African fly ash	0.555

* Powder River Basin.

Long-Term Release

A 100-gram aliquot of each ash sample was placed and compacted into glass containers (see Figure 1). Two sets of samples were set up to compare the release of mercury at both the ambient and near-ambient temperatures. Air from a cylinder was introduced at the top of the container through a gas inlet in the cap. This caused the container to become slightly pressurized and forced air through the ash. The air that passed through the ash was collected by an outlet tube located at the center of the sample several millimeters from the bottom of the container and vented to a gold-coated sand trap to collect any mercury released. To prevent ash from escaping with the air, glass wool and a 0.45- μm Teflon filter were used. Mercury released from the ash into the air was trapped on a gold-coated quartz analytical trap. A coarse, second gold-coated quartz guard trap was present to prevent any mercury in the surroundings from entering the system. The traps were heated prior to use to ensure there was no mercury contamination.

A flow rate of 1 mL/min of air was the target gas flow; however, actual flow rates ranged from 1 to about 4 mL/min. The difficulty of accurately setting low flow rates has been overcome through recent experiments being conducted at the EERC by changing from a system using gas flow restriction valves and clamps to a system utilizing lengths of capillary gas chromatography columns. Assuming the gas pressure to the manifold is held at a constant pressure, increasing or decreasing the lengths of capillary tubing connected to each individual container can provide accurate flow control.

The near-ambient sample set was placed in a 37°C heated sand bath. The ambient and near-ambient samples shared the same gas stream from a common gas manifold. All gas was first passed through a gold-coated sand trap for mercury removal from the test gas. In addition to scrubbing of the common gas stream, each individual container had an individual gold-coated sand trap connected directly to the inlet tube. Because of the extremely low levels of mercury being measured, these precautions were necessary to achieve low-enough blanks. After mercury vapor was collected for a given time interval, the tubes were desorbed by

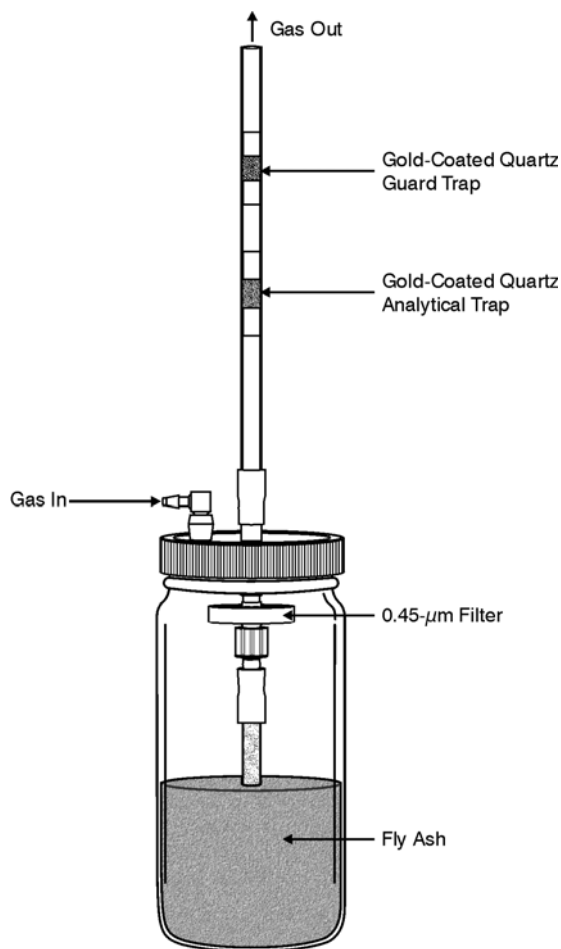


Figure 1. Mercury Collection Apparatus

heating the analytical gold-coated quartz trap to approximately 500°C, and the amount of released mercury was measured by atomic fluorescence.

The mercury was desorbed from the tubes several times with varying durations of time to determine the concentration of mercury vapor. The collection time periods prior to desorption of mercury and reasons for desorption are given below. Mercury vapor was captured for a total of 263 days from the ambient sample set and 216 days from the near-ambient sample set:

- Ambient sample set
 - 2 days: A check for the presence of mercury vapor release
 - 90 days: Desired sample collection time
 - 55 days: Gold-coated quartz pretraps added before each collection apparatus
 - 26 days: Air cylinder ran out during night

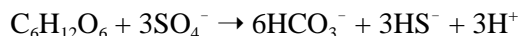
- 90 days: Desired sample collection time
- Near-ambient sample set
 - 90 days: Desired sample collection time
 - 10 days: Gold-coated quartz pretraps added before each collection apparatus
 - 26 days: Air cylinder ran out during night
 - 90 days: Desired sample collection time

Effect of Biological Activity

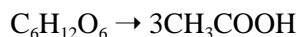
The initial experiments were set up as follows. A 250-mL Erlenmeyer flask was fitted with an impinger inlet/outlet tube with the inlet side extending to below the surface of the slurry. The slurry in the flask consisted of 100 grams of fly ash suspended in 150 mL of buffer with the entire apparatus held in a wrist-action shaker. The outlet side of the impinger insert was fitted with two mercury traps, which consisted of a 7-mm Pyrex tube containing gold-coated quartz followed by a charcoal trap. The theory behind this setup was that the first gold trap would capture elemental mercury while any organomercury compounds would be captured on the carbon trap. Each flask was connected to a gas source, and flow was held between 3 and 5 mL per minute. Severe tube plugging and erratic gas flow were problems during the testing. The gas flow system was changed in the same way as it was for the long-term release system. In addition, shortening the inlet tubing to just above the slurry should eliminate tube-plugging problems.

Six conditions of microbial metabolism, shown in Table 2, were examined for two different fly ashes. The first five conditions are different types of anaerobic metabolism, with the sixth being aerobic. These types of microbial metabolism with glucose are described by the following equations:

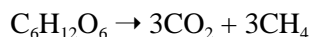
1. Sulfate-reducing conditions



2. Fermentative conditions



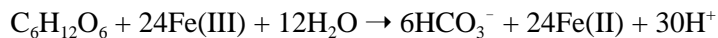
3. Methanogenic conditions



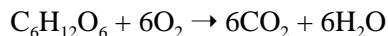
4. Nitrate-reducing conditions



5. Iron-reducing conditions



6. Aerobic conditions



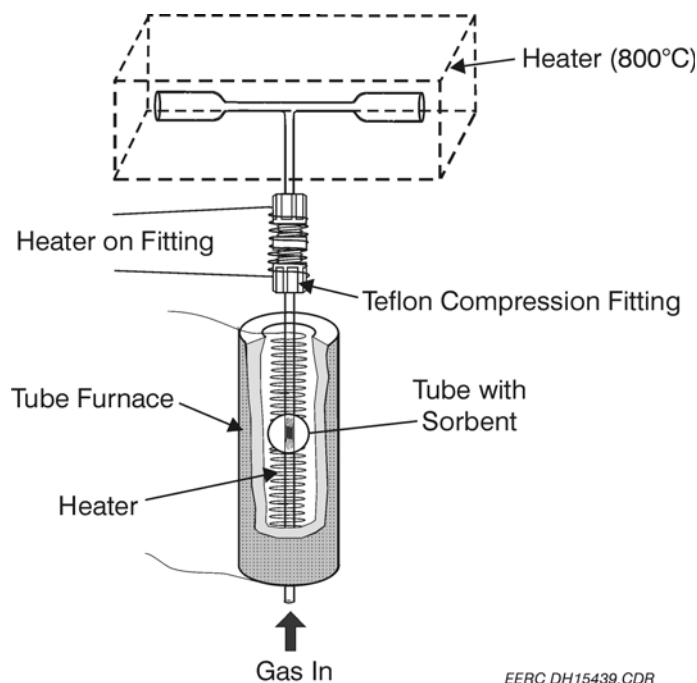
The source of anaerobic inocula was an anaerobic digester. The aerobic seed was obtained from topsoil.

Table 2. Types of Microbial Metabolism, Electron Donors, Electron Acceptors, and Products Evaluated for Potential Mobilization of Mercury

Test	Metabolism	Electron Donor	Electron Acceptor	Product
1	Sulfate reducing	Glucose	Sulfate	Sulfide
2	Fermentative	Glucose	Glucose products	Mixed (acids, alcohols, etc.)
3	Methanogenic	Glucose	Carbonate	Methane
4	Nitrate reducing	Glucose	Nitrate	Nitrogen gas
5	Iron reducing	Glucose	Iron(III)	Iron(II)
6	Aerobic	Glucose	Oxygen	Water

Thermal Desorption Apparatus

An apparatus for the controlled thermal desorption of mercury and mercury compounds from CCBs was assembled and is shown in Figure 2. The apparatus was constructed using a Varian 1475 atomic absorption (AA) spectrophotometer set up for mercury detection and included a small tube furnace and temperature controller for thermal desorption. A Hewlett Packard 3393 A integrator was used for data collection. 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 thermal decomposition to form elemental mercury which can be detected by AA. Gas flow was 20 mL/min of nitrogen. The temperature controller was ramped from ambient to 600°C at a rate of 25°C per minute. A more complete description along with a description of the experimental protocol can be found elsewhere [8].



EERC DH15439.CDR

Figure 2. Thermal Desorption Apparatus

Work has begun on the calibration of this apparatus for the quantitative determination of desorbed mercury peaks. Initial calibration curves have been prepared using 50, 100, and 200 nanogram aliquots of mercury.

Progress

Long-Term Release

The results of all desorption tests are shown in Tables 3a and 3b. The letter 'A' indicates ambient samples, and the letter 'N' indicates near-ambient samples. The N99-188 initial 90-day desorption value was over the instrument range; however, a value was calculated for comparison.

Table 3a. Mercury Vapor Desorption, pg/g at ambient temperature (37°C)

Sample	2 days	90 days	55 days	26 days	90 days	Total (263 days)
A99-188	0.059	1.439	0.142	0.011	4.245	5.896
A99-189	<0.001	0.489	0.133	<0.001	4.501	5.123
A99-692	<0.001	0.953	<0.001	<0.001	3.167	4.12
A99-693	<0.001	0.648	<0.001	<0.001	4.98	5.628
A99-722	<0.001	1.619	0.033	<0.001	6.878	8.53
A99-724	<0.001	0.24	0.007	<.001	6.071	6.318

Table 3b. Mercury Vapor Desorption, pg/g at near ambient temperature (150°C)

Sample	90 days	10 days	26 days	90 days	Total (216 days)
N99-188	26.369*	0.84	<0.001	3.542	30.751*
N99-189	0.024	<0.001	<0.001	9.307	9.331
N99-692	0.142	<0.001	<0.001	11.191	11.333
N99-693	0.855	<0.001	<0.001	3.448	4.303
N99-722	0.003	<0.001	<0.001	5.636	5.639
N99-724	2.059	<0.001	<0.001	5.852	7.911

* Over instrument range.

The average release of mercury from the ambient samples was 5.936 pg/g or 0.023 pg/g/day. The average release of mercury from the near-ambient samples was 7.703 pg/g or 0.036 pg/g/day. The near-ambient average does not include the value for N99-188 because the value has not been confirmed.

It was found that the guard traps on the inlets of the ash containers contained considerable concentrations of mercury and may have been saturated by the end of the overall experiment. This would explain the higher values during the last 90-day interval.

Table 4 shows the total amount of mercury released as a percentage of the total mercury content of the sample. The average amount of mercury released from all samples except N99-188 is 0.0038% of the total mercury.

Table 4. Percentage of Total Mercury Released

Sample	Percentage	Sample	Percentage
A99-188	0.0052	N99-188	0.0275
A99-189	0.0007	N99-189	0.0013
A99-692	0.0029	N99-692	0.0081
A99-693	0.0021	N99-693	0.0016
A99-722	0.0013	N99-722	0.0009
A99-724	0.0011	N99-724	0.0014

Sample 99-188 has the lowest total mercury content of the CCBs used in the project. Although the fly ash sample included FGD material, unlike the other samples, it was included in the experiment because of thermal desorption results from a previous study [5]. That study showed that the bulk of the mercury thermally desorbed from the sample occurred at a temperature of 250°C and had a different pattern than the other samples. Thermal desorption of mercury from the other samples in that study occurred above 300°C. Therefore, Sample 99-188 was hypothesized to have a greater potential for release of mercury vapor. The results obtained in this experiment appear to confirm this hypothesis.

The average release of 0.023 pg Hg/g CCB/day and 0.036 pg Hg/g CCB/day would equate to 1.8×10^{-8} lb Hg/ton CCB/yr and 2.6×10^{-8} lb Hg/ton CCB/yr, respectively. In either case, the mass of mercury desorbed was minute. An average of 0.030 pg Hg/g CCB/day was released from the samples, which equates to 2.2×10^{-8} lb Hg/ton CCB/yr. To put this in perspective, if this were applied to an annual coal-fired power plant production of 200,000 tons of fly ash per year, there would be a potential release of 0.0044 pounds (2.0 grams) of mercury released per year.

Effects of Biologic Activity

The samples for the biologic experiments have the same sample numbers as samples used in vapor release experiments. However, Sample 99-189, a highly alkaline ash, was hydrated for several weeks prior to use in these biologic activity experiments. This reduced the bulk concentration of mercury from 0.736 to 0.609 micrograms per gram because of leaching.

Before the carbon traps were analyzed, the carbon granules were dissolved in 6 mL of nitric acid and 3 mL of sulfuric acid. Tables 5 and 6 indicate the amount of mercury released from the biologically active fly ash samples.

Biological activity was evident by effects on the fly ash samples and gold traps for collection of Hg⁰. Both aerobic samples had a musty odor, as well as the iron-reducing and nitrate-reducing samples from Sample 99-692. Mold was noted on the surface of the sulfate-reducing Sample 99-692. The color of the gold-coated quartz traps appeared to be changed on several of the samples. The original color was a brick red. The gold traps on the aerobic samples of both fly ashes were slightly purple; the nitrate-reducing Sample 99-692 was a dull gold; and the sulfate-reducing Sample 99-692 was a silver color. The gold traps returned to the original color upon desorption.

The samples under sterile conditions exhibited larger releases of mercury than many of the other conditions. This will be reevaluated in future work.

Thermal Desorption Apparatus

The calibration results appear to indicate that quantitative determinations can be made, but improvements in the apparatus must be made before this can be done in practice. With the apparatus in its

Table 5. Mercury Release from Fly Ash 99-189

Sample	Conditions	Elemental Mercury, Organomercury,	
		ng	ng
1	Air	81	0.9
2	Fe	103	79
3	NO ₃	95	685
4	Ferm.	99	0.165
5	SO ₄	158	43
6	Sterile	116	1375

Table 6. Mercury Release from Fly Ash 99-692

Sample	Conditions	Elemental Mercury, Organomercury,	
		ng	ng
1	Air	1.4	0.12
2	Fe	1.4	0.3
3	NO ₃	1	0.06
4	Ferm.	0.4	0.11
5	SO ₄	0.4	0.36
6	Sterile	1.2	0.07

current configuration, there has been some variability in sequentially generated calibration curves. The cause for this is not known at this time but is being investigated.

Conclusions

Will the mercury removed from the flue gas really be removed from the environment or will it be released later? Currently, all studies indicate that only a minute amount of mercury vapor will be released into the environment from the disposal of CCBs. As the control of mercury air emissions from coal-fired power plants improves and more mercury is contained in the CCBs, this question will need to be reevaluated.

Status

Experiments are continuing in all of the areas described in this report. Long-term release experiments are being conducted using an improved system of flow through the apparatus as described in the progress section of this report. Flow experiments are initially being conducted only at ambient temperature in duplicate. Thermal desorption experiments are planned using quantitative techniques that were developed as part of this year's research.

Biota tests are just beginning again using an improved apparatus, as described in the progress section of this report. The new set of experiments is being conducted using aerobic and anaerobic conditions as before but without added electron acceptors. It is being assumed that the CCBs being used will supply adequate supplies of these various electron acceptors.

Potential Users/Technology Transfer

The environmental fate and transport of mercury from CCBs is of great concern to coal-fired utilities, regulators, CCB vendors and users, and environmental groups, especially with the EPA announcement of its intent to regulate mercury from coal-fired utilities. For this reason, this project is highly relevant and has relatively high visibility. Regardless of the scientific outcome, this project is extremely important. To date, the results appear to be promising, with releases of mercury at very low levels; however, at this time, the data are very limited and must still be regarded as preliminary. The information from this and other similar studies will be of great importance to users of products containing CCBs such as scrubber sludge wallboard and fly ash-containing concrete as well as to regulatory agencies, municipalities, landfill owners and operators, and mercury sorbent vendors and users.

The results of these tasks were presented to various audiences. One key activity was participation of the EERC researchers in the EPA Office of Research & Development (ORD) effort to determine the impact of mercury emissions from CCBs. Two workshops sponsored by EPA were attended, and EERC research staff made presentations. Researchers also contributed to and commented on the draft EPA ORD report titled *Characterization and Management of Residues from Coal-Fired Power Plants*. The work detailed in this report and proposed for future EERC efforts reflects the preliminary research priorities presented by EPA ORD.

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