



David J. Hassett
Principal Investigator

STABILITY OF MERCURY IN COAL COMBUSTION BY-PRODUCTS AND SORBENTS

Key Personnel: David J. Hassett (EERC), Loreal V. Heebink (EERC), John R. Gallagher (EERC), Debra F. Pflughoeft-Hassett (EERC), and Dennis L. Laudal (EERC)

Student Personnel: Amy L. Gieske (EERC), Linnea M. Schluessler (EERC), Robert J. Ducioame (EERC), and Eric J. Zacher (EERC)

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.

In Task 1, the research was directed toward understanding releases of mercury from microbial activity in fly ash in a disposal setting. One ash sample was evaluated in triplicate under aerobic and anaerobic conditions. Elemental mercury (Hg^0) releases were evaluated.

Task 2 involved leaching samples for mercury. The samples included fly ash, bottom ash, slag, gypsum, coal fines, atmospheric fluidized-bed combustion (AFBC) spent bed material, AFBC char, and fly ash with sorbent.

Task 3 addressed thermal effects on mercury vapor release. Tests included long-term ambient mercury release from six ash samples previously studied under CATM and on the effect of temperature on the release of mercury from CCBs, from ambient temperature to 650°C. The apparatus for long-term ambient mercury release was improved for more reliable results. Samples were subjected to mercury-free air for approximately 260 days. Mercury was collected on a gold-coated quartz trap, desorbed, and quantified. Thermal desorption was performed on a number of samples, and attempts were made to determine if speciation of mercury forms would be possible.

Goal

The overall goal of the project was to determine the amount of mercury released from CCBs under specific environmentally related conditions and to compile a database of information on mercury release from CCBs for use in regulating and managing disposal and beneficial reuse applications. Supporting objectives were to:

- Determine the amount and forms of mercury released from fly ash and other CCBs into air due to microbial action.
- Determine the leachability of mercury from conventional fly ash samples, ammoniated fly ash, high-carbon fly ash, and dry flue gas desulfurization (FGD) materials.

- Develop more reliable and reproducible data on mercury release through offgassing.
- Identify mercury compounds present on CCBs using thermal desorption.
- Obtain data for a wider range of CCBs.

Rationale

Mercury, known to be present in CCBs, including primarily fly ash and FGD materials, presents a potential environmental problem depending on the stability of the mercury under a variety of reuse or disposal conditions. The U.S. Environmental Protection Agency (EPA) announced on December 14, 2000, that it would regulate mercury emissions from coal- and oil-fired electric utility steam-generating power plants. EPA plans to issue final regulations by December 2004 and is expected to require compliance by December 2007 [1]. 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% to 70% of the mercury originally in the coal can be associated with the fly ash [2, 3].

Biological activity, groundwater leaching, and thermal offgassing are potential mechanisms for the release of mercury from CCBs into the environment. 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 effects of microbial action, such as changing redox conditions, methylation and demethylation, production of chelators, and changing pH, among others, can influence the mobility of metals such as mercury. The long-term potential of these changes to mobilize and release mercury from combustion residues and other solids necessitated the study of microbial impacts on mercury in CCBs.

Last year's CATM results on high-mercury CCBs showed an average release of mercury at ambient temperature equivalent to 2.2×10^{18} lb Hg/ton CCB/yr, which is a very small mass of mercury. To put this into context, a coal-fired power plant with an annual production of 200,000 tons of ash per year would potentially release 0.0044 pounds (2.0 grams) of mercury per year because of offgassing from ash [4]. An improved apparatus was designed to further study this.

Early CATM tests on thermal desorption for a limited number of samples indicate that some mercury remains on the CCB at temperatures up to 600°C [5]. Temperature profiles for mercury release showed one to five peaks, but could not be related to known mercury compounds. Thermal desorption of mercury and mercury compounds from CCBs was studied at temperatures from ambient to 650°C.

Approach

Effect of Biological Activity

One previously tested fly ash sample, a Powder River Basin (PRB) subbituminous plus petroleum coke fly ash, was evaluated in triplicate under aerobic and anaerobic conditions. The experiment was set up as follows. A 250-mL Erlenmeyer flask was fitted with an impinger inlet/outlet tube with the inlet side extending to just below the surface of a slurry or buffer. The slurry in the flask consisted of 80 grams of fly ash suspended in 100 mL of phosphate buffer or buffer plus glucose with the entire apparatus held in a wrist-action shaker. A 100-: L aliquot of mixed bacterial culture was added to each flask. The outlet side of the impinger insert was fitted with two mercury traps, which consisted of a gold-coated quartz trap followed by a carbon trap. The theory behind this setup was that the first gold trap would capture Hg^0 while any organomercury compounds would be captured on the carbon trap.

Gas from a cylinder was passed through each flask; breathing quality air was used for the aerobic gas and argon for the anaerobic gas. Attached to each inlet tube was a gold-coated sand pretrap to capture any

mercury present in the common gas streams. A gas flow rate of 2 mL/min was achieved through a system of varying lengths of capillary gas chromatography (GC) columns. The condition of each flask is shown in Table 1.

Table 1. Biologically Activated Mercury Release Conditions

Anaerobic		Aerobic	
Flask	Contents	Flask	Contents
1	Fly ash + buffer	9	Fly ash + buffer
2	Fly ash + buffer	10	Fly ash + buffer
3	Fly ash + buffer	11	Fly ash + buffer
4	Fly ash + buffer + glucose	12	Fly ash + buffer + glucose
5	Fly ash + buffer + glucose	13	Fly ash + buffer + glucose
6	Fly ash + buffer + glucose	14	Fly ash + buffer + glucose
7	Buffer	15	Buffer
8	Buffer	16	Buffer

The source of bacteria was a mixed bacterial inoculum from a brackish wetland. Bacterial counts were performed on four flasks after a 34-day inoculation period. The four flasks represented the four fly ash conditions. A 1-mL aliquot of solution was taken from each flask. The aqueous supernate was serially diluted in 0.1% sodium pyrophosphate buffer (pH 7.0) and then used to inoculate a series of tubes containing 1% peptone, tryptone, yeast extract, and glucose broth. The tubes were incubated at 30°C, and growth, as turbidity, was monitored over a 3-week period.

After mercury vapor was collected for 34 days, the gold-coated quartz traps were desorbed by heating to approximately 500°C, and the amount of released mercury was measured by atomic fluorescence.

Leaching

CCB samples were received throughout the year, with 47 samples tested for the leachability of mercury. The samples included fly ash, bottom ash, slag, gypsum, coal fines, AFBC spent bed material, AFBC char, and fly ash with sorbent. The leaching tests performed on the samples were the synthetic groundwater leaching procedure (SGLP), 30- and 60-day long-term leaching (LTL), and the toxicity characteristic leaching procedure (TCLP), EPA Method 1311. All tests require a 20:1 liquid-to-solid ratio. Several samples were characterized for mercury using two or more of the above procedures; however, no samples were analyzed using all of the leaching tests. The results were used to increase the database of leaching results.

Thermal Effects and Ambient Release of Mercury Vapor from Ash

Long-Term Ambient Release

Six ash samples previously tested through CATM were evaluated in duplicate using an improved apparatus. A 150-gram aliquot of each ash sample was placed and compacted into glass containers. All samples shared the same gas stream from a common gas manifold. Breathing quality air from a cylinder was first passed through a gold-coated sand trap for mercury removal from the test gas. In addition to scrubbing the common gas stream, each individual container had a gold-coated quartz pretrap connected directly to the inlet tube. Because of the extremely low levels of mercury being measured, these precautions were necessary to achieve low blanks. Air 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 samples several millimeters from the bottom of the container and vented to a gold-coated quartz analytical trap to collect any mercury released.

A coarse, second gold-coated quartz guard trap was present to prevent any mercury in the surroundings from entering the system.

Table 2 provides a description of the six samples evaluated for long-term mercury release. The total mercury content for each sample is also included, 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.

Table 2. CCB Sample Description and Total Mercury Content

CCB Sample	Coal Ash Description	Total Mercury Content, : 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

A flow rate of 2–3 mL/min of air was the target gas flow. This was achieved by using a system of varying lengths of capillary GC 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.

After mercury vapor was collected for a given time interval, the tubes were desorbed by heating the analytical gold-coated quartz trap to approximately 500°C, and the amount of released mercury was measured by atomic fluorescence. Mercury vapor was captured for a total of 264 days.

Thermal Desorption at Elevated Temperatures

Some additional work was done to determine thermal desorption curves for various ash samples as they arrived in the lab. The thermal curves were generated by heating the CCB sample in a tube furnace from ambient temperature to 650°C at 25°C per minute. The release of mercury was detected with a Varian 1474 atomic absorption spectrophotometer. Experimental work was also performed to determine the thermal curve for devolatilization of mercuric chloride from quartz granules.

Progress

Effect of Biological Activity

The results of Hg⁰ release from the biological experiments are shown in Table 3. Corresponding mercury release values from the flasks containing buffer only were treated as blanks.

Table 3. Elemental Mercury Release from Biological Experiments, pg Hg/g ash

Flask	Anaerobic	pg/g	Flask	Aerobic	pg/g
1	Starved	2.19	9	Starved	2.01
2	Starved	0.4	10	Starved	1.03
3	Starved	0.59	11	Starved	2.18
4	Glucose	1.17	12	Glucose	7.41
5	Glucose	4	13	Glucose	12.2
6	Glucose	5.44	14	Glucose	34.2

Bacterial counts were performed on four flasks. These flasks represented each of the four conditions to which the fly ash was exposed. The results are shown in Table 4. After the 34-day inoculation period, bacteria were present under all four conditions. The bacterial count was higher in the samples fed with glucose versus starved samples and in aerobic versus anaerobic conditions.

Table 4. Bacterial Count for Biological Experiments

Flask Condition	Bacterial Count	Flask Condition	Bacterial Count
Anaerobic Starved	$9.0 \times 10^1/\text{mL}$	Aerobic starved	$1.5 \times 10^3/\text{mL}$
Anaerobic Glucose	$7.5 \times 10^2/\text{mL}$	Aerobic glucose	$2.4 \times 10^5/\text{mL}$

Leaching

The results of leaching tests performed on CCBs are shown in Table 5. The detection limit on all samples tested was 0.01 : g/L. Two-thirds of the results were below the detection limit.

Table 5. CCB Mercury Leachate Results

Test	Samples Tested	No. Detected Values	Detected Value Range, : g/L	Sample Types with Detected Values
SGLP	45	13	0.01–0.39	Fly ash, bottom ash, AFBC spent bed material, AFBC char, fly ash with sorbent
30-day LTL	3	1	0.02	Fly ash
60-day LTL	2	2	0.01	Fly ash with sorbent
TCLP	12	5	0.01–0.07	Fly ash with sorbent

Thermal Effects and Ambient Release of Mercury Vapor from Ash

Long-Term Ambient Release

Results from the long-term release of mercury vapor at ambient temperature are shown in Figure 1. The values in the figure are averages for duplicate samples.

The average release of mercury was 1.05 pg Hg/g CCB or 0.004 pg Hg/g CCB/day. This would equate to 2.9×10^9 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 CCB per year, there would be a potential release of 0.0006 pounds (0.26 grams) of mercury released per year if air was passed through the CCB.

Thermal Desorption at Elevated Temperatures

It appears that the thermal maximum for mercuric chloride occurred near 300°C. This is close to reported temperatures for volatilization of mercuric chloride. In previous work utilizing coal fly ash, mercuric chloride came off at 220°C. More work is required to understand the cause of this difference.

Status

Experiments are continuing in all of the areas described in the report. Long-term release experiments for the determination of blank values are in progress. Biota tests are just beginning again on a second ash in triplicate, as described in the progress section.

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 actions toward regulation of 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 the 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 FGD wallboard and fly ash-containing concrete and to regulatory agencies, municipalities, landfill owners and operators, and mercury sorbent vendors and users.

The results of these tasks were published and presented to various audiences [6–11].

References

1. U.S. Environmental Protection Agency. <http://www.epa.gov/mercury/actions.htm> (accessed Nov 26, 2002).
2. Laudal, D.L.; Heidt, M.K. *Evaluation of Flue Gas Mercury Speciation Methods*; EPRI Report No. TR-108988; Dec 1997.
3. Carey, T.R.; Hargrove, O.W., Jr.; Richardson, C.F.; Chang, R.; Meserole, F.B. Factors Affecting Mercury Control in Utility Flue Gas Using Sorbent Injection. Presented at the Air & Waste Management Association 90th Annual Meeting & Exhibition, Toronto, ON, Canada, June 1997; Paper No. 97-WA72A.05.
4. Heebink, L.V.; Hassett, D.J. Release of Mercury Vapor from Coal Combustion Ash. Presented at the U.S. EPA/DOE/EPRI Combined Power Plants Control Symposium: The Mega Symposium, Chicago, IL, Aug 21–23, 2001.

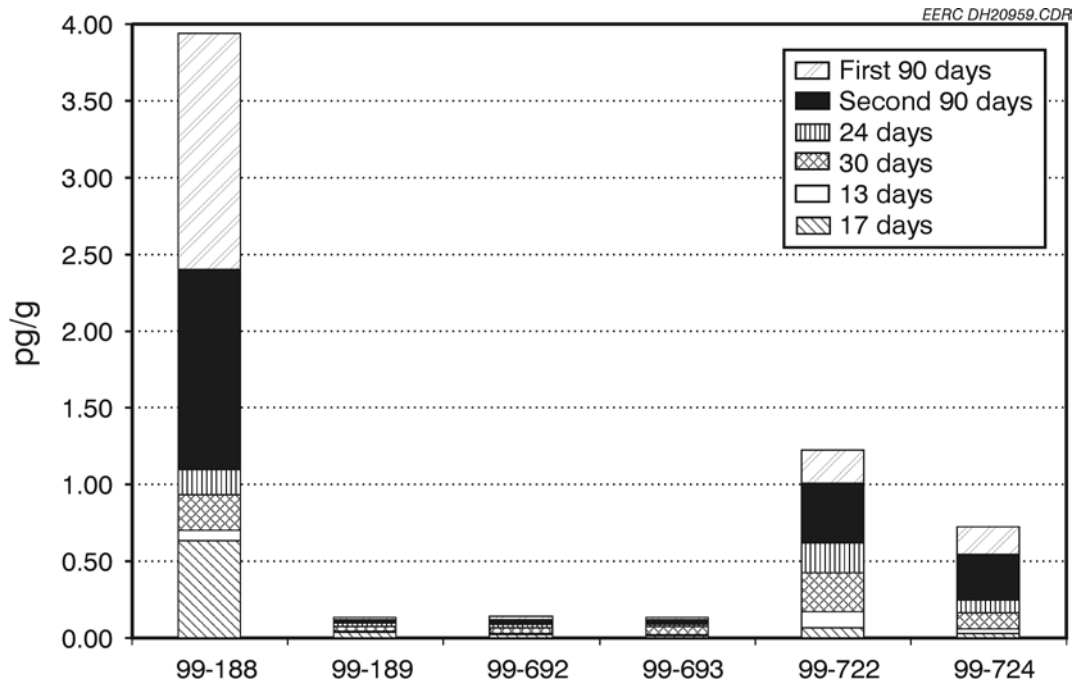


Figure 1. Mercury Vapor Release in 264 days, pg/g

5. Hassett, D.J.; Pflughoeft-Hassett, D.F.; Laudal, D.L.; Pavlish, J.H. Mercury Release from Coal Combustion By-Products to the Environment. Presented at the Air & Waste Management Association Mercury in the Environment Specialty Conference, Minneapolis, MN, Sept 15–17, 1999.
6. Gieske, A.L.; Schluessler, L.M.; Hassett, D.J. Thermal Desorption of Mercury from Coal Fly Ash. Presented at the 94th North Dakota Academy of Science Annual Meeting, Grand Forks, ND, April 25–26, 2002.
7. Hassett, D.J.; Heebink, L.V.; Gallagher, J.R.; Pflughoeft-Hassett, D.F. Microbial Release of Mercury from Coal Combustion By-Products (CCBs). Presented at the USDI Office of Surface Mining Meeting, Denver, CO, April 16–18, 2002.
8. Hassett, D.J.; Pflughoeft-Hassett, D.F. Evaluating Coal Combustion By-Products (CCBs) for Environmental Performance. Presented at the USDI Office of Surface Mining Meeting, Denver, CO, April 16–18, 2002.
9. Heebink, L.V.; Hassett, D.J. Release of Mercury Vapor from Coal Combustion Ash. *J. Air Waste Manage. Assoc.* **2002**, 52 (8), 927–930.
10. Heebink, L.V.; Hassett, D.J. Release of Mercury Vapor from Coal Combustion Ash. Presented at the U.S. EPA/DOE/EPRI Combined Power Plants Control Symposium: The Mega Symposium, Chicago, IL, Aug 21–23, 2001.
11. Heebink, L.V.; Hassett, D.J., Release of Mercury Vapor from Coal Combustion Ash. Presented at the 2001 International Ash Utilization Symposium, Lexington, KY, Oct 22–24, 2001.