Long-Term Mercury Release from CCBs

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ABSTRACT

The release of mercury vapor from coal combustion ash was tested over a time period of 264 days. Six ashes with atypically high levels of total mercury content were selected as having potential for releasing measurable amounts of mercury vapor. The ashes selected included two eastern bituminous fly ashes, two South African fly ashes, one Powder River Basin (PRB) fly ash, and one PRB flue gas desulfurization material.

Air was passed through compacted 150-gram aliquots of each sample at 2 mL/min and vented to a gold-coated quartz trap to collect the mercury vapor. The samples were at ambient temperature. In initial experiments, all samples indicated the release of low picogram levels of mercury after 90 days. No pattern was evident to link the total mercury content to the release of mercury vapor. When the total apparent release of mercury was equated to what would be expected of a full-scale coal-burning power plant ash quantity, the release that would be expected per year equated to less than 1 gram of mercury. Follow-on investigation has indicated that the mercury measured was likely experimental blank and that the coal combustion by-products (CCBs) were acting as mercury sinks rather than release agents.

INTRODUCTION

The Energy & Environmental Research Center (EERC) is currently investigating the release of mercury from coal combustion by-products (CCBs) under a variety of conditions including ambient temperature, thermal release up to 700°C, biologically mediated release, and leaching. Ambient, near-ambient, and thermal release experiments have been ongoing for over 3 years while biologically mediated release experiments have been ongoing for just over 2 years. Leaching studies have been ongoing for over 25 years. During the course of this diverse research, much has been learned about the various CCBs, especially regarding hydration reactions. This knowledge has been used in the development of a number of tests for determining the release of major, minor, and trace constituents from CCBs. These tests include methods for determining mercury release through leaching and mercury release through long-term ambient, thermal, biologically mediated release mechanisms.[1–5]

The EERC has recently completed a set of experiments to determine the gaseous release of mercury from a set of six relatively high mercury concentration CCBs. The materials selected were tested for two separate timed-release experiments of

263 days[1–3] and 264 days followed by a 180-day blank determination. The results of the recently completed blank determination have confirmed what had been previously suspected; the CCBs selected for this research were acting, for the most part, as mercury sinks rather than as mercury sources.

EXPERIMENTAL

Six CCBs were selected from among a large number of archived samples at the EERC acquired through the Coal Ash Resources Research Consortium℠ (CARRC℠; pronounced “cars”). The samples selected are summarized in Table 1.

Table 1. CCB Description and Bulk Mercury Content

Ash Sample	Description	Total Hg Content, µg/g
99-188	PRB[1] subbituminous fly ash + FGD[2] material	0.112
99-189	PRB subbituminous + petcoke blend fly ash	0.736
99-692	Eastern bituminous fly ash	0.140
99-693	Eastern bituminous fly ash	0.268
99-722	South African fly ash	0.638
99-724	South African fly ash	0.555

[1] Powder River Basin.
[2] Flue gas desulfurization.

The apparatus that was used in the study of these six CCB samples has been greatly improved over the last few years. This has resulted in a considerable reduction of blank concentrations. In this report, only details of the second set of experiments (Test 2) are given. Details of Test 1 are reported elsewhere.[1]

A 150-gram aliquot of ash was placed into 250-mL tall, wide-mouth bottles with bonded Teflon liner caps. The caps were drilled with two holes to accommodate a silicone tube for gas inlet and a Teflon outlet bulkhead fitting (see Figure 1). Two samples of each CCB were set up for duplicate analyses. Breathing-quality air from a cylinder was passed through several sets of gold-coated quartz traps for mercury removal and admitted to each of the bottles through a gas distribution manifold that routed the gas through 0.23-mm-ID gas chromatography (GC) capillary tubing to each of the individual bottles. The pressure drop across the GC capillary tubing allowed for the regulation of air flow through each bottle by simply adjusting the length of tubing to each bottle. The length of tubing was a nominal 65 cm. This length of tubing, when pressurized to between 1 and 2 psig through a gas distribution manifold, provided a convenient means of regulating gas flow to approximately 2 cm^3/min. Because of the variability of particle sizes between different ash samples, the sample with the initial highest gas flow was left with a 65-cm length of GC tubing, and other samples had their tubing lengths shortened until all samples had approximately the same flow rate. The air exiting the GC tubing was given a final scrubbing to remove mercury vapor using gold-coated quartz just prior to entering the bottle containing the CCB. After entering the bottles, the air passed through the ash and exited to a central mercury collection tube containing two separate gold-coated quartz traps. The gold-coated quartz nearest the exit bulkhead fitting was analyzed at regular intervals to determine the mass of mercury vapor released from the

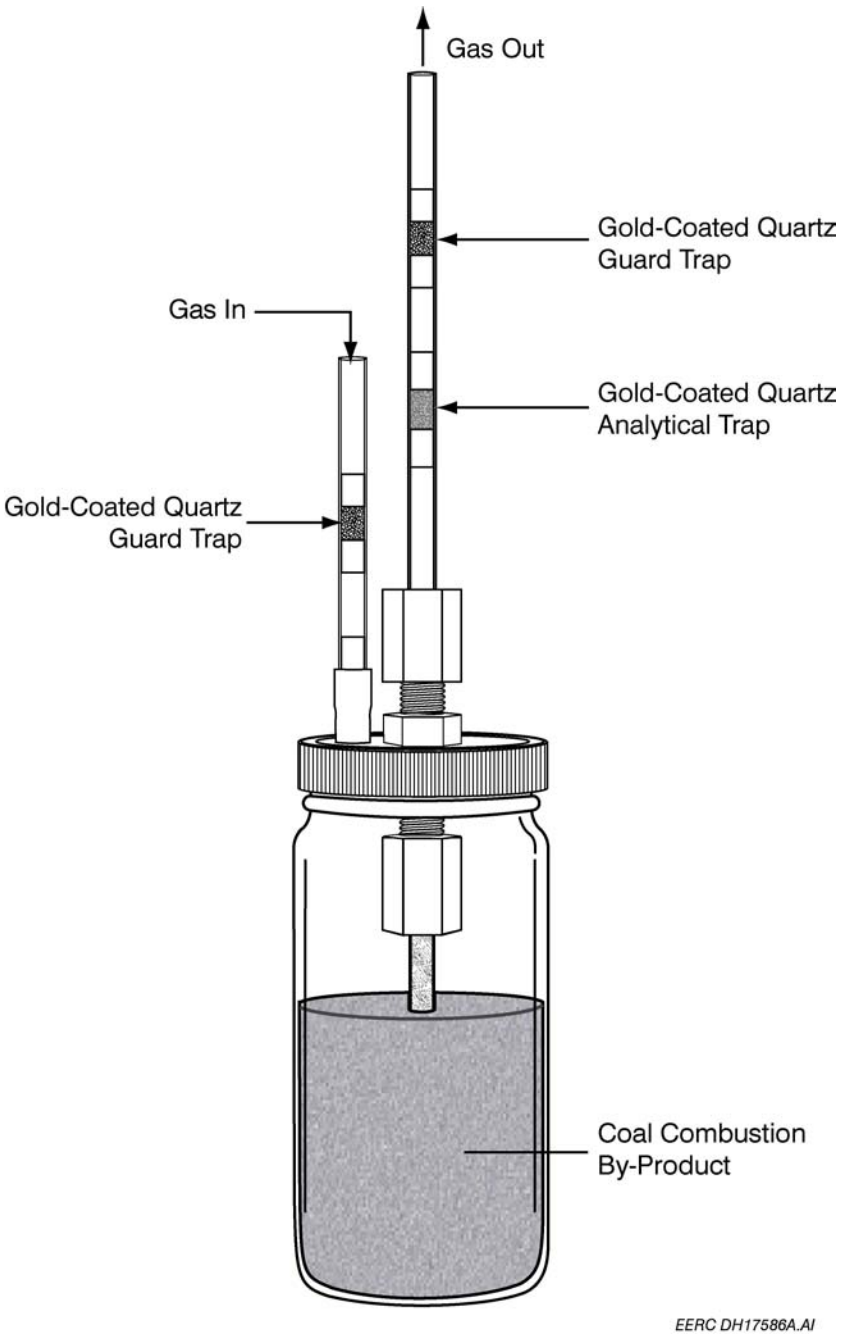

Figure 1. Mercury vapor release collection apparatus.

CCBs while the top trap, in the same tube, was present to prevent mercury contamination from atmospheric mercury. This setup is illustrated in Figure 1.

Mercury collection was carried out for a total of 264 days in this experiment. The gold-coated quartz collection tubes were desorbed for analysis by heating to approximately 500°C. The mass of mercury released was determined using atomic fluorescence. The

tubes were desorbed several times with varying periods of collection, but only the total results are reported here.

Following the 264-day collection of mercury from the CCBs, blank values were determined for each separate bottle. The bottles were emptied of ash and gas flowed through the empty bottles for two 90-day periods. The gold-coated quartz collection tubes were analyzed for mercury as described above.

RESULTS AND DISCUSSION

Two complete sets of ambient temperature release experiments have been completed to date. Tests 1 and 2 were conducted for 263 and 264 days, respectively. The results of these experiments are summarized below in Table 2. The yearly release using these results is also included in the table to compare and contrast the two tests. The values in this table are averages of duplicate samples and have not been corrected for blanks because blank values were determined differently for the two tests.

Table 2. Results from Two Sets of Ambient Temperature Mercury Release Experiments

	Test 1		Test 2		
Sample	pg/g/263 days	pg/g/year	pg/g/264 days	pg/g/year	% Difference
99-188	5.887	8.170	3.937	5.443	33.3
99-189	5.123	7.110	0.136	0.188	97.4
99-692	4.120	5.718	0.143	0.198	96.5
99-693	5.628	7.811	0.136	0.188	97.6
99-722	8.530	11.838	1.225	1.693	85.7
99-724	6.318	8.768	0.724	1.001	88.6

Modifications to the experimental protocol and an improved apparatus account for the dramatic difference between the two sets of data. Clamps and valves were used to regulate the gas flow in Test 1, which proved to be inconsistent and required constant monitoring. This was modified in Test 2 by using GC capillary tubing sections providing a stable and consistent gas flow. The final scrubbing gold-coated quartz traps in Test 1 were believed to be saturated, admitting mercury from the gas manifold to the samples. These traps were cleaned of mercury during Test 2 in an attempt to prevent saturation.

Blank values were determined differently for Tests 1 and 2. In Test 1, empty bottles were used in an attempt to have a blank to subtract from the individual sample results. In Test 2, the bottles were emptied of ash, and gas was allowed to continue to flow collecting mercury for an additional 180 days. These two 90-day periods were used to derive a separate blank for each sample container.

If one calculates the emission rate in pg/day for the blank on each sample container and compares these values with the emission rate in pg/day for the containers with ash in them from Test 2, it becomes apparent that all but one of the ash samples appear to be sorbing mercury. The ash sample that did not act as a mercury sink was the sample containing a mixture of fly ash and FGD material, which had the lowest bulk

concentration of mercury. These values are presented in Table 3 as averages of the duplicate samples.

Table 3. Comparison of Emission Rates Between the Empty Bottles and the Bottles Containing Ash in Test 2, pg/day

Sample	Bottles with Ash	Bottles Without Ash	Difference
99-188	2.237	2.161	0.076
99-189	0.077	1.127	−1.050
99-692	0.081	2.454	−2.373
99-693	0.077	4.328	−4.251
99-722	0.696	7.165	−6.469
99-724	0.411	4.436	−4.025

CONCLUSIONS

Long-term ambient temperature desorption experiments have indicated that five of the six CCBs analyzed acted as mercury sinks, although these samples were previously reported as having released small amounts of mercury vapor. The previously reported value of a maximum of 0.26 grams of mercury release from 200,000 tons of ash[4] actually becomes a negative number in light of these new data. This does not necessarily mean that no mercury was being released from the CCBs, but in our experiments, eleven of the containers appeared to release more mercury after emptied of ash than while containing ash. The total mercury content of these ashes has not correlated to the apparent amount of mercury released or sorbed.

The sample group evaluated to date has been small, consisting of six well-characterized samples. This series of experiments is being increased through the inclusion of more samples in an attempt to verify the results to date.

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