

POTENTIAL FOR MERCURY RELEASE FROM COAL COMBUSTION BY-PRODUCTS

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ABSTRACT

Determination of the mechanisms of mercury release from coal combustion by-products (CCBs) is one area of research at the Energy & Environmental Research Center (EERC). Two of the tasks of this research are as follows:

- Determine the level of mercury that would offgas from various CCBs.
- Examine the potential for biological activity to further mobilize mercury in CCBs.

In these experiments, six CCB samples were tested for mercury vapor release at ambient and near-ambient temperatures. The results have shown no clear evidence that the rate of mercury release is related to the bulk mercury concentration. The six samples are being retested for ambient temperature release. These new experiments are being done in duplicate in an improved version of the apparatus to verify previous results. Because of improved methods, results indicate that the vapor release of mercury is an order of magnitude lower than previously thought.

Microbiological experiments were also performed on two of the CCB samples. Results for biological release were scattered and difficult to evaluate because of experimental difficulties. Mercury release was increased, and some evidence was found for the formation of organomercury compounds. Microbial activity was evident.

INTRODUCTION

The Energy & Environmental Research Center (EERC) is currently investigating leaching, ambient-temperature Hg release from coal combustion by-products (CCBs), thermal release of Hg from CCBs at temperatures from ambient to 650 °C, and the effects of microbial action on release of Hg and organomercury compounds from CCBs.^{1,2} The EERC has been conducting leaching studies on CCBs and other materials for over 20 years.⁵⁻⁷ Studies on ambient, near-ambient, and thermal release of mercury have been ongoing for approximately 3 years. Studies to evaluate the impact of biological activity on leaching and vapor transport have been ongoing for approximately 1 year.²

During these experiments, methods for leaching and thermal desorption have been developed. In particular, a leaching method called the synthetic groundwater leaching procedure (SGLP) was developed for use in determining potential for environmental impacts by CCBs. In the coming years, mercury emissions from coal-fired power plants will be regulated, potentially increasing the amount of mercury present in CCBs. Therefore, the transport of mercury from CCBs must be understood.

Leaching is the most likely mechanism of transport of constituents from disposed or utilized CCBs contacted by water. Leaching is typically performed on CCBs to characterize them for management purposes. Several issues have been raised by the U.S. Environmental Protection Agency's (EPA) Office of Research and Development and Office of Solid Waste related to the best means of evaluating the leaching potential of CCBs. EPA has made preliminary recommendations for leaching methodologies to be used to evaluate mercury release from CCBs. These recommendations do not adequately address some typical long-term behaviors of reactive CCBs under hydration conditions.

Thermal release, particularly of Hg, is important for long-term utilization, storage, and disposal of CCBs. Although the concentration of Hg in CCBs is relatively low, the large volumes of CCBs produced annually cause concern about potential mercury release. Ambient, near-ambient, and elevated-temperature studies of Hg release have resulted in the development of apparatuses to determine mercury release from CCBs. Vapor transport experiments evaluate Hg release from a bed of CCBs at ambient and near-ambient temperatures with constant airflow through the bed. The design of these and future experiments is critical to produce laboratory results that can be compared to field experiments at CCB management sites.

The wide distribution and variety of microorganisms in the environment indicate that microbiological mercury release needs to be investigated. A wide variety of specific microbe interactions can affect key elements associated with CCBs, including oxidation/reduction and alkylation/dealkylation reactions. In order for microbes to be metabolically active, a few constraints must be satisfied. In some CCB management options, these criteria are unlikely to be met, but for options where they can be met, laboratory experiments will simulate appropriate scenarios.

EXPERIMENTAL

Six coal ashes were chosen from ashes in a collection of CCBs analyzed in a previous study at the EERC. Table 1 shows that the total mercury content in the ash samples ranged from 0.112 to 0.736 $\mu\text{g/g}$, determined by cold-vapor atomic absorption spectrophotometry. These values are not all typical of CCBs and 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 release would be measurable.

Table 1. Ash sample total mercury content.

Ash Sample	Coal/Ash Description	Total Mercury Content ($\mu\text{g/g}$)
99-188	PRB ^a subbituminous fly ash + FGD ^b material	0.112
99-189	PRB subbituminous + petroleum coke 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

^a Power River Basin.

^b Flue gas desulfurization.

Two sets of samples were set up to compare and contrast the release of mercury at ambient and near-ambient temperatures. The near-ambient sample set was placed in a 37 °C heated sand bath. Both sample sets shared a gas stream from a common gas manifold. The same ash samples are being retested at ambient temperature. The mercury collection setup is described below.

An aliquot of each ash sample was compacted into tall, wide-mouth 250-mL bottles with bonded Teflon liner caps (see Figure 1). Breathing-quality 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. A flow rate of 1–2 mL/min of air was the target gas flow. All gas was scrubbed through a gold-coated sand trap for mercury removal. In addition to scrubbing the common gas stream, each container had an individual gold-coated sand trap connected directly to the inlet tube for additional mercury removal. These precautions were found to be necessary because of the extremely low levels of mercury being determined. The air that passed through the ash was collected by an outlet tube and vented to a trap to collect any mercury released. The outlet of the container was a glass tube in the center of the sample that terminated several millimeters from the bottom of the container. In the first set of experiments, glass wool and a 0.45- μm Teflon filter were used to prevent ash from escaping with the air. It was determined that the glass wool and filter were not needed.

Mercury released from the ash was trapped on the gold-coated quartz analytical trap. A second gold-coated quartz guard trap prevented any mercury in the surroundings from entering the system. The collection system, consisting of the two gold-coated quartz traps in one tube, was blanked by heating to 500 °C, driving off all mercury before being placed on the ash containers.

After mercury vapor collection, the analytical gold-coated quartz trap on each tube was heated to 500 °C to desorb mercury, and the amount released was detected with atomic fluorescence. The tubes were desorbed several times for the capture of mercury vapor. In the first experiment, mercury vapor was captured from the ambient sample set for 263 days and from the near-ambient sample set for 216 days. Containers with no ash (blanks) were added to the sample sets in the middle of the first experiment to potentially determine the amount of mercury contributed by the containers and the airstream.

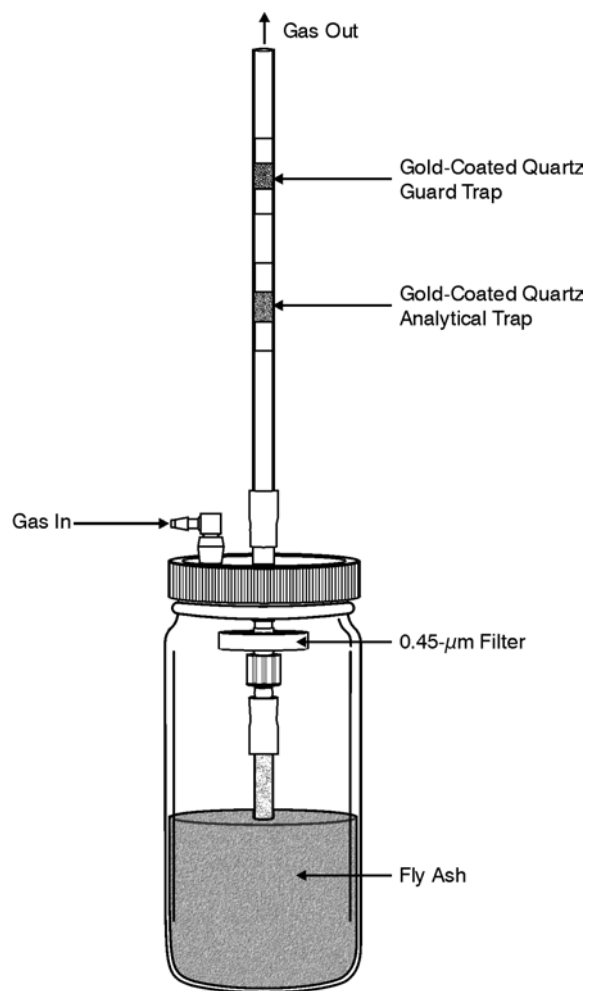


Figure 1. Mercury collection system.

RESULTS AND DISCUSSION

Experiment Set 1

A 100-g aliquot of ash was used in the initial experiments. A flow rate of 1 mL/min was the target gas flow; however, 1 to 4 mL/min was actually achieved in the initial part of the experiment. In the last 90-day period, average airflow rates through the ash were maintained at approximately 1 mL/min by adjusting the flow to each container inlet every few days using clamps.

The results of all desorption tests are shown in Tables 2a and 2b. 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 estimated.

Table 2a. Mercury vapor desorption results of ambient sample set (pg/g).

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	4.120
A99-693	< 0.001	0.648	< 0.001	< 0.001	4.980	5.628
A99-722	< 0.001	1.619	0.033	< 0.001	6.878	8.530
A99-724	< 0.001	0.240	0.007	< 0.001	6.071	6.318

Table 2b. Mercury vapor desorption results of near-ambient sample set (pg/g).

Sample	90 days	10 days	26 days	90 days	Total (216 days)
N99-188	26.369*	0.840	< 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.

It is thought that the higher values of emitted mercury for the last equilibration period were due to saturation of the inlet mercury traps with accumulation of a large blank from the gas stream. The desorbed tubes from the blank containers yielded the highest concentration of mercury.

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 calculated value could not be confirmed.

Table 3 shows the amount of mercury released as a percentage of the total mercury content of the sample. The average amount of mercury released from all samples excluding N99-188 is 0.0038% of the total mercury.

Table 3. Percentage of total mercury released.

Ambient Sample	Percentage	Near-Ambient Sample	Percentage
A99-188	0.0048	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

Experiment Set 2

Current long-term mercury release experiments are being conducted on the same ash samples that were used in the previous test. In the new set of experiments, gas flow is being controlled using varying lengths of capillary tubing. The amount of ash placed in the containers has been increased to 150 g. The use of higher-capacity scrubbing traps, which are desorbed occasionally, on the inlet side of the bottles has lowered the blank considerably. Results from this currently ongoing study are presented in Table 4.

Table 4. Mercury levels for each sample period (pg).

Sample	17 days	13 days	30 days	24 days	90 days	Total 174 days	Average
99-188a	99.8	10.3	18.8	10.5	25.9	165	
99-188b	90.0	11.0	50.1	38.2	364	554	360
99-189a	7.2	1.6	5.9	2.8	3.3	20.8	
99-189b	2.9	1.4	4.5	2.6	4.1	15.5	18.1
99-692a	1.8	1.4	7.1	4.9	6.4	21.6	
99-692b	3.9	1.5	4.5	2.4	3.0	15.3	18.4
99-693a	1.7	1.2	8.6	3.3	5.0	19.9	
99-693b	2.7	1.5	5.5	2.2	4.0	15.9	17.9
99-722a	8.6	15.8	40.2	26.7	67.1	158	
99-722b	12.4	14.3	37.5	30.9	50.0	145	152
99-724a	3.8	3.2	8.3	5.7	19.2	40.2	
99-724b	4.8	5.5	24.8	18.8	69.7	123	81.6

Comparison of Ambient Experiment Sets

Table 5 compares the results of the ambient-temperature mercury release in Experiment Sets 1 and 2. It is evident that the measured mercury release has decreased considerably with the use of an improved apparatus. No blanks have been subtracted from the data in Table 5.

Table 5. Comparison of ambient temperature experiments.

Sample	Ambient Test 1		Ambient Test 2		% Decrease
	pg/g for 263 days	fg/g/day	pg/g for 174 days	fg/g/day	
99-188	5.896	22.42	2.400	13.79	39
99-189	5.123	19.48	0.121	0.70	96
99-692	4.120	15.67	0.123	0.71	96
99-693	5.628	21.40	0.119	0.69	97
99-722	8.530	32.43	1.013	5.82	82
99-724	6.318	24.02	0.544	3.13	87

In past experiments, blank values have been calculated from results on separate bottles containing no ash. In this series of experiments, however, blanks will be calculated on an individual basis. At the end of the long-term release experiments, all of the ash will be removed from the bottles. At that time, fresh-blanked tubes will be placed on the bottles, and airflow will be initiated for 90 days. This 90-day blank from each of the bottles will be applied to their appropriate values from the bottles with ash. We feel that this will be more appropriate, since cleaning the bottles as well as the associated mercury collection fittings at these extremely low levels is what caused previous highly variable blanks.

CONCLUSIONS

No pattern was evident to link the total amount of mercury determined through bulk analysis to the release of mercury vapor. This is apparent because Sample 99-188 had the lowest total mercury content of the CCBs used but released the highest amount of mercury vapor over the course of the experiments. 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.⁶ 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 these experiments appear to confirm this hypothesis.

The most important conclusion from these experiments that can be drawn at this time is linked to the extremely low concentrations of mercury being released from these ash samples. An issue exists with blank values that will likely reduce these numbers further. The blanks were variable, however, and work is ongoing to reduce blanks even more.

A parallel project evaluating two of the high-mercury ashes was conducted to determine the effect of biota on mercury release from an ash–water slurry. Initial results are inconclusive, although mercury release appears to have been increased.

Calculations have been used to conclude that improved methods have lowered previous high results by almost an order of magnitude. Conclusions from Experiment Set 2 are contrasted with the conclusions from Experiment Set 1 (in brackets). An average of 0.004 [0.030] pg

Hg/g CCB/day was released from the samples. This equates to 3.0×10^{-9} [2.2×10^{-8}] lb Hg/ton CCB/yr. If this were applied to an annual coal-fired power plant production of 200,000 tons of fly ash a year, there would be a potential release of 0.0006 [0.0044] lb Hg/yr, which is equivalent to 0.27 [2.00] g of mercury.

The most likely species of mercury to be released in the absence of biological activity is elemental mercury. Although other species are likely in CCBs at room temperature, all but the organomercury compounds have extremely low vapor pressures and are unlikely to be released in significant amounts at ambient temperatures. Currently, many CCBs contain relatively little mercury; however, in the future, as mercury emissions are controlled, mercury-containing sorbents in CCBS will likely cause mercury concentrations to increase. The issue of mercury emissions from disposed or utilized CCBs requires additional study.

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REFERENCES

1. CATM Staff. *2000 Annual Report of the Center for Air Toxic Metals*; Energy & Environmental Research Center: Grand Forks, ND, Jan 2001.
2. CATM Staff. *2001 Annual Report of the Center for Air Toxic Metals*; Energy & Environmental Research Center: Grand Forks, ND, Feb 2002.
3. Hassett, D.J.; Henke, K.E.; McCarthy, G.J. Characterization of a Lignite Ash from the METC Gasifier: III. Leaching Behavior. In *Proceedings of Fly Ash and Coal Conversion By-Products: Characterization, Utilization and Disposal I.*; Materials Research Society, 1985; Vol. 44, pp 188–194.
4. Hassett, D.J. A Comprehensive Chemical Characterization to Predict Environmental Impact from Leachate Generation (abs.). In *Proceedings of Achieving Land Use Potential Through Reclamation, 9th Annual Meeting of the American Society for Surface Mining and Reclamation*; Duluth, MN, 1992; p 548.

5. Pflughoeft-Hassett, D.F.; Dockter, B.A.; Eylands, K.E.; Hassett, D.J.; Pavlish, J.H. Impact of Mercury Emission Control Technologies on Conventional Coal Combustion By-Product Management. Presented at the Air & Waste Management Association 89th Annual Meeting and Exhibition, Nashville, TN, June 23–28, 1996.
6. Hassett, D.J.; Pflughoeft-Hassett, D.F.; Laudal, D.L.; Pavlish, J.H. Mercury Release from Coal Combustion By-Products to the Environment. In *Proceedings of the 1999 International Ash Utilization Symposium*; Lexington, KY, Oct 1999.