EVALUATION OF COAL COMBUSTION BY-PRODUCT MERCURY RERELEASE POTENTIAL

Loreal V. Heebink and David J. Hassett

University of North Dakota
Energy & Environmental Research Center
15 North 23rd Street
Grand Forks, ND 58203

Introduction

Mercury, known to be present in coal combustion by-products (CCBs) including primarily fly ash and flue gas desulfurization (FGD) materials, presents a potential environmental problem depending on the stability of the mercury under a variety of reuse of disposal conditions. The U.S. Environmental Protection Agency (EPA) announced on December 14, 2000, that it would regulate Hg emissions from coal- and oil-fired electric utility steam-generating power plants. EPA plans to issue final regulation by December 2004 and is expected to require compliance by December 2007.[1] As technologies are developed to reduce the air emissions of Hg, the amount of Hg in CCBs will likely increase. Recent studies have indicated that from 0% to 70% of the Hg originally in the coal can be associated with the fly ash.[2,3]

The Energy & Environmental Research Center (EERC) has investigated the potential for the rerelease of Hg from CCBs under a variety of conditions in an effort to address various ash management scenarios. Four conditions that have been examined are leaching, long-term ambient-temperature vapor release, microbiologically mediated vapor release, and high-temperature thermal release.[4,5] Leaching of CCBs has been ongoing at the EERC for over 25 years and vapor and thermal release methods have been investigated for the last several years.

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. Recently, EPA proposed a leaching method for evaluating CCBs based on its interest in CCBs that may be affected by Hg emission controls. These recommendations do not adequately address some typical long-term behaviors of reactive alkaline 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 Hg release. Ambient, near-ambient, and elevated-temperature studies of Hg release have resulted in the development of apparatuses to determine Hg 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 Hg 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

Work is ongoing at the EERC to examine the rerelease of Hg from CCBs under four conditions including leaching, long-term ambient-temperature vapor release, microbiologically mediated vapor release, and high-temperature thermal release up to 700°C. CCBs with atypically high levels of total Hg content were selected as having a significant potential for releasing measurable amounts of Hg vapor for use in the long-term ambient-temperature and microbiologically mediated vapor-release experiments.

Leaching. Leaching of CCBs using various batch laboratory methods has been ongoing at the EERC for over 27 years. It became apparent early in EERC work that the methods being advocated and used were generating scientifically invalid and often misleading data. The EERC identified the inappropriate use of acetic acid in leaching solutions for CCBs understanding that CCBs would be unlikely to contact acetic acid under typical management conditions. Agreement by numerous research groups and government agencies that the use of acetic acid-based leaching solution is not appropriate for CCBs has led to many questions regarding what leaching methods are appropriate. Work at the EERC identified formation of secondary hydrated phases in alkaline CCBs, and it was determined that formation of these hydrated phases had a demonstrated influence on concentrations of certain trace elements in leachate. As a result of these observation, the EERC developed the SGLP (synthetic groundwater leaching procedure), including long-term leaching (LTL), to address discrepancies with existing methods.[6]

The SGLP batch-leaching procedure is a relatively simple test that follows many of the conditions of the toxicity characteristic leaching procedure (TCLP), EPA Method 1311.[7] The test utilizes a 20:1 liquid-to-solid ratio, end-over-end agitation at approximately 30 rpm, and usually employs a leaching solution consisting of water from the site, water that has been prepared in the lab similar to water likely to contact the ash, or distilled deionized water. For the long-term component of this procedure, multiple bottles are set up and analyzed at different time intervals. A typical SGLP and LTL test might consist of 18-hour, 30-day, and 60-day equilibration times. Although 60 days is often not long enough to have achieved complete equilibrium, it is generally long enough to determine the concentration evolution of individual parameters. The most important factor when performing LTL is to have at least three equilibration times to determine a true trend.

The majority of the leachate data on file was generated using leaching procedures with a 20:1 liquid-to-solid ratio with a few 4:1 liquid-to-solid ratio leachings. The 20:1 liquid-to-solid ratio leaching procedures included SGLP, LTL with 30- and 60-day equilibration times, TCLP, synthetic acid leaching (SAL), and synthetic precipitation leaching procedure (SPLP).[8] Distilled deionized water leachings were completed with 18-hour, 2-week, and 4-week equilibration times using a 4:1 liquid-to-solid ratio.

A wide variety of CCBs have been leached at the EERC. Sample types have included atmospheric fluidized-bed combustion (AFBC) char fly ash, AFBC spent bed material, boiler slag, bottom ash, circulating FBC fly ash and bottom ash, coal fines, FBC bottom ash, FBC fly ash, FGD material, and FGD–fly ash mixtures, fly ash, fly ash with Hg sorbent material, and particulate test combustor (PTC) fly ash.

Long-Term Ambient-Temperature Vapor Release. Long-term vapor release of Hg has been investigated utilizing six CCB samples obtained from members of the Coal Ash Resources Research Consortium^{K} (CARRC^{K}). The ashes selected included two eastern bituminous fly ashes, two South African fly ashes, one Powder River Basin (PRB)–pet coke fly ash, and one PRB FGD material.

A 150-gram aliquot of ash was placed and compacted into 250-mL tall wide-mouth bottles with a bonded Teflon liner cap. The cap was drilled with two holes to accommodate a Teflon outlet bulkhead fitting and a silicone tube for gas inlet (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 Hg removal and admitted to each of the bottles through a gas distribution manifold that routed the gas through 0.23-mm 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 using GC tubing with an ID of 0.25 mm. 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 Hg vapor using gold-coated quartz just prior to entering the bottle containing the CCB. After entering the bottle, the air passed through the ash and exited to a central Hg 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 Hg vapor released from the CCBs while the top trap, in the same tube, was present to prevent Hg contamination from atmospheric Hg. This setup is clearly illustrated in Figure 1.

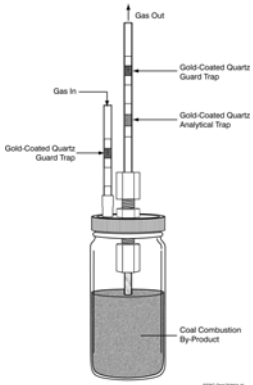

Figure 1. Long-term Hg-vapor release collection apparatus.

The gold-coated quartz collection tubes were desorbed for analysis by heating to approximately 500°C, and the mass of Hg released was determined using atomic fluorescence. The tubes were desorbed several times with varying periods of collection over the length of the experiments. Following the collection of Hg from the CCBs in Test 2, blank values were determined for each separate bottle by emptying the bottles of ash and flowing gas through the empty bottles for two 90-day periods. The gold-coated quartz tubes were analyzed for Hg as described above.

Microbiologically Mediated Vapor Release. Four CCBs have been examined for the microbiologically mediated vapor release of Hg. The tested CCBs have included a neutralized subbituminous FGD material, a hydrated subbituminous fly ash, and two eastern bituminous fly ashes.

The apparatus used for this testing has been improved numerous times over the course of the research; therefore, only the latest setup will be described here. A 250-mL Erlenmeyer flask fitted with an impinger inlet/outlet tube with the inlet center shortened to 6 cm below the standard taper. Gas inlet flow was regulated in the same manner as in the long-term Hg vapor release experiments described above; however, all GC capillary tubing was approximately 60 cm in length. The Hg vapor-collection system differed from the long-term ambient-temperature setup, consisting of two traps. The nearest trap contained Supelco Carbotrap, which collected organomercury compounds. This was followed by a gold-coated quartz trap, which collected Hg^0.

The flasks were placed on a 16-flask wrist-action shaker. The experimental matrix consisted of eight flasks under aerobic conditions (using breathing-quality air) and eight flasks under anaerobic conditions (using argon). In each set of eight flasks, two contained only buffer, three contained the CCB with buffer, and three contained the CCB with buffer and glucose. An 80-gram aliquot of CCB was placed in the flasks and 100 mL of a phosphate buffer (with or without glucose) was added to create a neutral pH. The ash-containing flasks also had 100 µL of mixed bacterial culture added. The source of bacteria was a mixed bacterial inoculum from a brackish wetland. This apparatus is shown in Figure 2.

Figure 2. Microbiologically mediated Hg vapor-phase collection apparatus.

The experiments were conducted for 30 days. The total mercury collected on the carbon traps was determined. The gold-coated quartz collection tubes were desorbed for analysis by heating to approximately 500°C, and the mass of Hg released was determined using atomic fluorescence. For bacterial counts at the completion of the 30-day period, 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.

High-Temperature Thermal Release. A schematic for the controlled thermal desorption of Hg and Hg compounds was assembled and is shown schematically in Figure 3. The apparatus was constructed using an atomic absorption (AA) spectrophotometer for Hg detection and included a small tube furnace and temperature controller for thermal desorption. A Hewlett Packard 3395 integrator was used for data collection. Detection of thermally desorbed Hg and Hg compounds was done in an electrically heated quartz cell operated at 800°C. The use of a heated cell allowed detection of Hg compounds by thermally decomposing compounds to form Hg^0, which can be detected by AA. Gas flow was 20 cm^3/min of nitrogen. The temperature controller was ramped from ambient temperature to

700°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.[9]

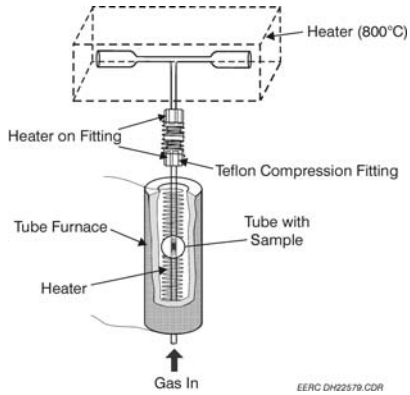

Figure 3. Hg thermal desorption apparatus.

Results and Discussion

An overview of some of the results obtained from the various Hg release techniques is included below.

Leaching. Over the last nearly 28 years, researchers at the EERC have leached a large number of varying CCBs, initially using the more common standard tests.

Data from the past ten years contain 256 Hg leachate values. Only 32 of those values (12%) had detectible Hg values, ranging from 0.01 to 0.39 µg/L. The average is 0.064 µg/L, and the median is 0.02 µg/L. Hg values above the detection limit were obtained in all procedures used except SAL, SPLP, and the 4:1 liquid-to-solid ratio 4-week distilled deionized water. Detectible Hg leachate values resulted from AFBC char fly ash, AFBC spent bed material, boiler slag, bottom ash, fly ash, fly ash with Hg sorbent material, and PTC fly ash.

A total of 38 Hg leaching data points of fly ash resulting from the use of full-scale Hg control technologies are in the current data set. Eleven of the data points are at or above the detection limit of 0.01 µg/L used on those samples.

Long-Term Ambient-Temperature Vapor Release. To date, two complete sets of long-term release experiments have been completed on six CCBs. Tests 1 and 2 were conducted for 263 and 264 days, respectively. The averaged duplicate results from Test 2 are shown in Table 1. It is apparent that all but one of the ash samples appear to be sorbing Hg. The total Hg contents of the ashes had a range of 0.112–0.736 µg/g.

Table 1. 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

Microbiologically Mediated Vapor Release. Two CCB samples with various electron acceptors added were analyzed in the first microbiologically mediated Hg vapor-release experiment. Results from this test were very confusing with the sterile sample releasing the most Hg. It was decided that the CCB would suffice as a source of the various electron acceptors.

Testing of three CCBs has been completed using the matrix described in the experimental section, including one of the fly ash samples from the first experiment. Results have been confusing; however, general trends have emerged. The Hg released from the CCB slurry was generally higher in the samples fed with glucose versus starved samples and in aerobic versus anaerobic conditions. The bacterial count has also generally followed that trend. The Hg^0 vapor captured on the gold-coated quartz traps has been higher than seen in the long-term ambient-temperature vapor-release experiments. The flasks containing buffer only have been treated as blanks.[5,10]

High-Temperature Thermal Release. A large variety of CCBs have been analyzed for the thermal release of Hg. Most of the thermal curves generated were straightforward, containing only one or two major desorption peaks.

Thermal desorption curves were rather difficult to interpret since there is no way, at present, using this apparatus to determine exactly what is happening during the thermal treatment. There are several possible scenarios:

- Hg and Hg compounds, as sorbed, are being released unchanged during the thermal desorption procedure.
- Hg compounds are being desorbed by a mechanism of thermal decomposition whereby sorbed compounds such as HgO are thermally decomposed to Hg and oxygen during the thermal desorption.
- Hg or Hg compounds are chemically reacting with the CCB components then thermally desorbed according to the first or second scenario as described above.

Conclusions

Currently, many CCBs contain relatively little Hg; however, in the future, as Hg emissions are controlled, Hg-containing sorbent in CCBs will likely cause Hg concentrations to increase. The issue of Hg emissions from disposed or utilized CCBs requires additional study.

A variety of CCBs have been leached using a variety of batch-leaching procedures. In the overall data set over the past 10 years, 12% of the leachate values were above the detection limit and 29% of the leachings from full-scale Hg control technology CCBs yielded detectible Hg values. That number of samples is low; therefore, the effect of Hg control technologies on the leachability of Hg from CCBs is yet to be seen.

Long-term ambient-temperature release experiments have indicated that five of six CCBs analyzed acted as Hg sinks, although these samples were previously reported as having released small amounts of Hg vapor.[11]

The most likely species of Hg to be released in the absence of biological activity is elemental Hg because of its significant vapor pressure although other species are likely in CCBs at room temperature. All have extremely low vapor pressures and are unlikely to be released in significant amounts at ambient temperatures.

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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) CATM Staff. *2000 Annual Report of the Center for Air Toxic Metals*; Energy & Environmental Research Center: Grand Forks, ND, Jan 2001.
(5) CATM Staff. *2001 Annual Report of the Center for Air Toxic Metals*; Energy & Environmental Research Center: Grand Forks, ND, Feb 2002.
(6) Hassett, D. J. Synthetic Groundwater Leaching Procedure, Encyclopedia of Environmental Analysis and Remediation, pp 4797–4803, John Wyley & Sons, Inc., 1998.
(7) U.S. Environmental Protection Agency. Toxicity Characteristic Leaching Procedure. Method 1311, Test Methods for Evaluating Solid Waste: Physical/Chemical Methods (SW-846), 1992, 35 pp.
(8) U.S. Environmental Protection Agency. Method 1312: Synthetic Precipitation Leaching Procedure (SPLP), Test Methods for Evaluating Solid Waste: Physical/Chemical Methods (SW846), Vol. 1C, 3rd Ed. 1990.
(9) Pavlish, J. H. *Mercury Stability in the Environment.* Final Topical Report (April 15, 1998 – June 30, 1999) for U.S. Department of Energy Cooperative Agreement No. DE-FC26-98FT40320; EERC Publication 99-EERC-09-03; Energy & Environmental Research Center: Grand Forks, ND, Sept 1999.
(10) CATM Staff. *2002 Annual Report of the Center for Air Toxic Metals*; Energy & Environmental Research Center: Grand Forks, ND, 2003.
(11) Hassett, D. J.; Heebink, L. V.; Pflughoeft-Hassett, D. F. Potential for Mercury Release from Coal Combustion By-Products. In *Proceedings of the Air Quality III: Mercury, Trace Elements, and Particulate Matter Conference*; Arlington, VA, Sept 10–12, 2002; Energy & Environmental Research Center: Grand Forks, ND, 2002.