

Development of a Method to Determine Microbiologically Generated Mercury Vapor and Organomercury in CCBs

David J. Hassett, Loreal V. Heebink, Erick J. Zacher, and Debra F. Pflughoeft-Hassett

University of North Dakota (UND) Energy & Environmental Research Center (EERC),
15 North 23rd Street, Stop 9018, Grand Forks, ND 58202-9018

KEYWORDS: Mercury, Methylation, Microbiological Transformation

ABSTRACT

Methods and protocols for determining the effect of microbes on the release of mercury from coal combustion by-products (CCBs) were developed by the Coal Ash Research Group at the EERC. An initial method used the slurry of fly ash with buffer and microbes to determine the inorganic and organomercury releases to the air (vapor-phase release) and to the buffer solution (microbiologically mediated leaching). This wet system was used to successfully assess the mercury releases from fly ash samples from multiple sources including samples from bituminous, subbituminous, and lignite combustion. A limited number of fly ash samples with activated carbon (fly ash + AC) present as a result of activated carbon injection (ACI) were also evaluated. It was determined that this method had limitations for alkaline fly ash samples because they were difficult to buffer to neutral pH to support microbial growth. The use of extensive washing with acid to achieve neutral pH was successful for some alkaline fly ash samples but was not adequate for all alkaline samples, so an alternate dry system method and protocol was developed to determine the microbiologically mediated vapor-phase release of mercury for any CCB sample type.

A complete description of the two methods and protocols is presented, and a discussion of the results for both successful and failed experiments is included.

INTRODUCTION

Laboratory leaching has long been used to evaluate the mobility of various constituents from coal combustion by-products (CCBs), but mercury chemistry and the potential for elevated concentrations of mercury to be present on fly ash and flue gas desulfurization (FGD) materials make it necessary to evaluate other potential mechanisms for mercury to be released from these materials. In several Energy & Environmental Research Center (EERC) studies, leaching, ambient- and elevated-temperature vapor-phase transport, and microbiologically mediated releases of mercury have been investigated. The EERC has worked to develop methods to evaluate the potential for release of mercury from fly ash

and FGD material when they are exposed to microbes and conditions conducive to the growth of those microbes.

Early experiments were designed to measure the release of mercury through leaching and vapor phase from slurries of sample, buffer solution, nutrients, and microbes. While this method was useful for evaluating fly ash samples with near-neutral pH, the method was not well suited for use with alkaline fly ash samples and most FGD materials. It was obvious that microbial growth was being inhibited because of the alkalinity from the high-pH samples under evaluation, so an alternate method was developed to allow the determination of microbiologically mediated vapor-phase releases of mercury. The method development process provided an opportunity to better understand the behavior of reactive fly ash exposed to water and acid solutions and develop hypotheses regarding the impact of fly ash hydration and reactivity related to its buffering capacity.

EXPERIMENTAL

Over the course of 3 years of conducting experiments to evaluate the microbiologically mediated release of mercury from fly ash and FGD materials, several iterations of one wet system apparatus and one dry system apparatus were used. The initial apparatus was designed to measure microbiologically mediated vapor-phase mercury release from a sample subjected to solutions of buffer and microbes with glucose for some vessels to provide a food source for the microbes. Anaerobic conditions (using argon) and aerobic conditions (using breathing-quality air) were maintained in separate sets of experimental vessels. Cylinder gas was scrubbed for mercury through gold-coated quartz traps prior to introduction to the experimental vessels and then the air flushed mercury vapor from the headspace of the flasks to a mercury vapor collection system at the outlet of the flasks, consisting of two traps. A Supelco Carbotrap™ (for collection of organomercury compounds) and a gold-coated quartz trap (for collection of volatile inorganic mercury) were used to collect mercury released in the vapor phase from the flasks. A wrist action shaker was used to agitate the samples. This wet system apparatus underwent several modifications as noted in Table 1.

Table 1. Microbiological Release Apparatus Modifications

Original Experiment or Apparatus Component	Difficulty or Unmet Need	Modified Experiment or Apparatus Component
Wrist Action Shaker, Continuous Shaking 50–80-gram Sample Size + ~100-mL Buffer Phosphate Nitrate Buffer Solution	Inadequate suspension of sample. Inadequate volume of liquid to recover for leachate analysis. Interference with the determination of the organomercury compounds in leachate.	Magnetic stir plate, Intermittent stirring. ~20-gram sample + 135–150 mL buffer. Lower concentration of phosphate with potassium glutamate as nitrogen source.
Glucose-Fed and Starved Experiments	Starved experiments did not promote microbial growth so were deemed unnecessary.	All experiments fed with glucose.

The final experimental apparatus used for the majority of the project microbiological experiments is illustrated in Figure 1. This apparatus and experimental setup was used successfully to evaluate the release of mercury (organo- and inorganic mercury) both to the air (vapor-phase release) and to the solution (microbiologically mediated leaching). However, early attempts to use this apparatus and experimental protocol for alkaline fly ash and FGD materials were not successful because the alkalinity released in solution prohibited the growth of the microbes. CCB alkalinity can be attributed to the dissolution of alkaline metal oxides that react with water to generate net alkalinity. Water-soluble calcium content contributes most of a CCB's net alkalinity. This trend can be seen in the classification of fly ashes; Class C fly ash is enriched in Ca and Mg and, subsequently, generates pH values considerably higher than Class F fly ash (e.g., pH >10).



Figure 1. Microbiologically mediated mercury vapor-phase collection apparatus utilizing a stir plate to facilitate mixing.

In order for a CCB, or any material, to support biological activity, it must be near-neutral pH. A pH range of 6.5 to 8.5 was used for optimal microbiological activity, requiring substantial neutralization of some CCBs. Prior to initiation of experiments, buffer was added to sample aliquots, pH of the ash–buffer mixture was measured, and an appropriate volume of acid was added over a period of time to achieve a neutral pH. Sulfuric acid was used for this neutralization procedure. Only limited additions of acid were needed for bituminous fly ash samples in order to produce a neutral pH solution that supported microbial growth. For alkaline fly ash samples, the neutralization process required substantially greater volumes of acid and, in some cases, it was not possible to achieve a neutral pH that could be sustained during the microbiologically mediated experiments. Results were achieved for some alkaline fly ash samples, but for other

alkaline fly ash samples, neutral pH was achieved but not maintained after addition of the microbes. After it became apparent that microbial activity had ceased in the sample system, the pH was measured. The pH had increased to a level (>10) well above that conducive to microbial growth, and on testing, it was determined that the microbes had become inactive. Replicate reaction vessels of fly ash and buffer without microbes present maintained the near-neutral pH over the duration of the experiment.

The difficulty in sample neutralization presented by some alkaline fly ash samples indicated that determination of the microbiologically mediated release of mercury from alkaline fly ash samples was not achievable using the wet system, so an alternate dry method was developed. The new experimental protocol was designed to evaluate the impact of interaction between soil and fly ash on vapor-phase mercury release from fly ash. The interaction of greatest interest was that caused by inherent microbiological organisms typically found in soils. A CCB–soil laboratory experimental apparatus was designed to evaluate microbiologically mediated mercury release from CCB–soil mixtures, analogous to utilization management practices in the field. A schematic of the apparatus is shown in Figure 2. Note that an inverted funnel was placed over the soil–ash bed to facilitate collection of released mercury.

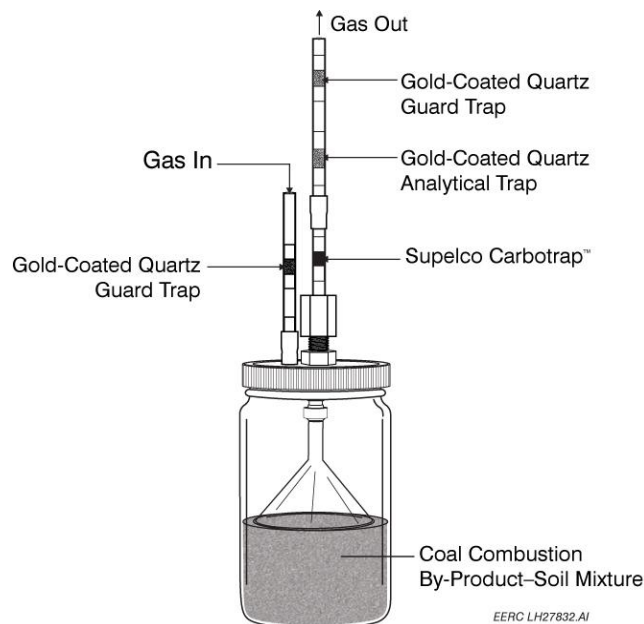


Figure 2. CCB–soil mercury vapor release collection apparatus.

A 20% addition of CCB was combined with the soil and mixed thoroughly. The soil consisted of a mixture of top soil, potting soil, and peat moss, which had moisture added to increase existing microbial activity. Approximately 200 grams of this mixture was placed in sample containers. Mercury-free air entered the sample container, swept over the sample, and exited through an inverted glass funnel. Organomercury compounds were captured on a collection trap containing Supelco Carbotrap™, and volatile

inorganic mercury was captured on gold-coated quartz. Six fly ash–soil mixtures, one FGD material–soil mixture, and soil alone were set up in duplicate.

After a period of mercury collection, the Supelco Carbotrap™ and gold-coated quartz analytical traps were analyzed for captured mercury as noted previously. All sample containers were subjected to a blanking process to account for elemental mercury present in the empty container and the scrubbed air entering the system. This method was used to determine the microbiologically mediated release of mercury from a limited number of alkaline fly ash samples.

RESULTS AND DISCUSSION

Summaries of vapor-phase release information from the wet experimental system are included in Table 2 for bituminous fly ash samples and in Table 3 for lignite and subbituminous fly ash samples.

Several observations were made based on the results from the samples evaluated using the wet system.

- Aerobic conditions resulted in increased vapor-phase mercury releases for both volatile inorganic mercury and organomercury for all samples evaluated.
- The mercury released from the CCB slurry was generally higher in the samples fed with glucose versus starved samples. The final experiments only included “fed” systems.

Table 2. Summary of Vapor-Phase Mercury Releases from Microbiologically Mediated Experiments on Bituminous Fly Ash Samples in the Wet System

Sample No.	Description	Total Hg, $\mu\text{g/g}$	Vapor-Phase Hg Releases, pg/g/day			
			Anaerobic		Aerobic	
			Elemental Hg	Organo-Hg	Elemental Hg	Organo-Hg
01-002	Bit. FA	0.785	0.1 – 0.24	0.008 – 0.009	0.09 – 1.1	0.008 – 0.032
03-006	Bit. FA	0.685	0.13 – 0.25	0.07 – 0.16	5.36 – 17.9	0.52 – 1.91
03-007	Bit. FA	0.123	0.25 – 6.17	0.05 – 0.18	1.11 – 13.6	0.21 – 1.51
04-003	Bit. FA	0.234	0.07 – 0.28	0.04 – 0.06	4.17 – 15.6	0.04 – 0.17
05-018	Bit. FA	1.86	0.80 – 12.1	0.12 – 0.76	17.7 – 34.9	0.72 – 3.24

Table 3. Summary of Vapor-Phase Mercury Releases from Microbiologically Mediated Experiments on Fly Ash Samples in the Wet System

Sample No.	Description	Total Hg, µg/g	Vapor-Phase Hg Releases, pg/g/day			
			Anaerobic		Aerobic	
			Elemental Hg	Organo-Hg	Elemental Hg	Organo-Hg
03-060	Sub. FA + AC	0.689	0.03 – 0.09	0.002 – 0.008	0.65 – 1.7	0.007 – 0.010
03-079	Lignite FA	0.160	0.56 – 1.06	1.00 – 1.34	2.26 – 3.96	0.50 – 6.16
04-043	Lignite FA	0.287	0.26 – 0.44	0.12 – 0.22	0.08 – 9.30	0.26 – 0.90
04-035	Lignite FA	0.194	0.03 – 0.04	0.03 – 0.14	0.15 – 0.20	0.02 – 0.11
04-036	Lignite FA + AC	0.41	0.03 – 0.52	0.02 – 0.14	0.26 – 0.45	0.07 – 0.11

Shading indicates a paired sample set where 04-035 was collected at baseline conditions and 04-036 was collected during ACI testing.

- Fungi was present in some samples under aerobic conditions and, when fungi was noted, the vapor-phase mercury releases were higher than in replicate sample flasks where no fungi was evident.
- The formation of organomercury compounds was evident in all of the microbiologically mediated experiments. It was observed, however, that organomercury formation appears to be directly related to the amount of fungi present in the flasks at the end of the experiments.

It was also observed that alkaline fly ash samples were difficult to maintain at near neutrality. Experiments performed in the absence of bacteria provide us with a neutralization capacity for acid addition, but in microbiological experiments, these neutralized solutions quickly rose to above pH 10.5, thus inactivating the bacteria. Several attempts were made to neutralize the same highly alkaline fly ash samples using dilute sulfuric acid. For these samples, following addition of the microbes, the pH increased as noted. It was hypothesized that a sulfate coating formed around individual fly ash particles during the addition of the sulfuric acid, resulting in the measured neutral pH. It was further hypothesized that after the microbes were introduced, the microbes acted on the sulfate coating. The result was that the alkaline surfaces of the fly ash particles were reexposed to the solution, allowing release of additional alkalinity.

Results collected from samples subjected to the dry system microbiological experiments are shown in Table 3. The total mercury content of the CCB–soil mixtures was not measured; therefore, a calculation based on the total mercury content of the separate components and the mixture percentage is given in Table 3. Each sample bottle had a blank bottle measurement of elemental mercury prior to introduction of the CCB–soil

mixture. Sorption or release of elemental mercury was determined by subtracting the blank value from the measurements. The calculations in the columns labeled “Cumulative % Elemental Hg Sorption or Release from Mix” and “Years to Release 100% Elemental Hg at Measured Rate” are based on the calculated mixture total mercury content. Paired samples (Samples 05-038 and 05-025) are highlighted; these samples are from the larger sample set of paired lignite fly ash samples.

The results show that the soil mixture (only one data point) used in this task sorbed inorganic mercury. The CCB–soil mixtures exhibited low levels of inorganic mercury release, with the exception of one replicate. On average, over 100,000 years of air movement over the CCB–soil mixtures is required to release all mercury from the system. Samples that had activated carbon (AC) present released lower percentages of volatile inorganic mercury than those without AC present even though the total mercury was higher in the samples with AC, especially those collected after the primary particulate control device (PCD). On average, the samples with AC present released mercury an order of magnitude lower than the sample from a similar coal source without AC. However, the measured volatile inorganic mercury release rate was higher for the fly ash + AC (post-primary PCD) samples. The paired sample set provided a good comparison of a fly ash sample without and with AC present.

Organomercury results are reported in Table 4. No organomercury blank value measurements were performed since preparation of the experimental vessel (heating to >500°C) was expected to eliminate any mercury from the container; additionally, in the absence of contamination from laboratory sources, it is unlikely that organomercury compounds would be present. Therefore, the organomercury collected from the soil-only bottle served as the blank for the experiment. This allowed for a determination of the impact of the CCB in each CCB–soil mixture.

The results indicated that more organomercury was released from four of 13 replicate CCB–soil mixture bottles than from the soil-only bottle. All organomercury releases were low. Again, the samples with AC generally exhibited a lower-percentage release of mercury than those without AC present, although the difference was not as consistent as that observed for inorganic mercury releases. The fly ash alone from the paired sample set released a lower percentage of organomercury by two orders of magnitude when compared to the fly ash + AC in the paired set.

Table 3. Dry System Microbiological Experimental Volatile Inorganic Mercury Release Results for CCB–Soil Mixtures. Positive values indicate release, and negative values indicate sorption of inorganic mercury. Replicates are shown.

ID No.	Sample Type	Coal Type	Calculated Mixture Total Hg, $\mu\text{g/g}$	Cumulative No. Days	Replicate 1		Replicate 2	
					Cumulative % Elemental Hg Sorption or Release from Mix	Years to Release 100% Elemental Hg at Measured Rate	Cumulative % Elemental Hg Sorption or Release from Mix	Years to Release 100% Elemental Hg at Measured Rate
04-003	Fly ash	Eastern bituminous	0.190	167	0.00105	43,693	0.000590	77,517
04-054	Fly ash + AC (post-primary PCD)	Eastern bituminous	3.60	167	0.000288	158,678	0.000295	154,928
04-029	Fly ash	PRB ^a subbituminous	0.106	167	0.00529	8,650	0.00414	11,056
03-060	Fly ash + AC (pre-primary PCD)	PRB subbituminous	0.426	166	-0.000195	NA – sorbing	0.000123	368,455
05-038	Fly ash	Lignite	0.0740	166	0.00266	17,075	NQ ^b	NQ
05-025	Fly ash + AC (post-primary PCD: high ash)	Lignite	2.58	167	0.000205	222,968	0.000266	172,319
06-014	Soil	None	0.0666	166	NQ	NQ	-0.00205	NA – sorbing

^a Powder River Basin.

^b Not quantitated.

∞

Table 4. Dry System Microbiological Experimental Organomercury Vapor-Phase Release Results for CCB-Soil Mixtures. Positive values indicate release, and negative values indicate sorption of organomercury. Replicates are shown.

ID No.	Sample Type	Coal Type	Calculated Mixture Total Hg, $\mu\text{g/g}$	Cumulative No. Days	Replicate 1		Replicate 2	
					Cumulative % Organomercury Sorption or Release from Mixture Compared to Soil	Years to Release 100% Organomercury at Measured Rate Compared to Soil	Cumulative % Organomercury Sorption or Release from Mixture Compared to Soil	Years to Release 100% Organomercury at Measured Rate Compared to Soil
04-003	Fly ash	Eastern bituminous	0.190	168	0.00134	34,465	0.000977	47,396
04-054	Fly ash + AC (post-primary PCD)	Eastern bituminous	3.60	171	-0.0000123	NA – below soil release	-0.0000207	NA – below soil release
04-029	Fly ash	PRB subbituminous	0.106	169	-0.000531	NA – below soil release	-0.000481	NA – below soil release
03-060	Fly ash + AC (pre-primary PCD)	PRB subbituminous	0.426	167	-0.000248	NA – below soil release	-0.000261	NA – below soil release
05-038	Fly ash	Lignite	0.0740	168	-0.00124	NA – below soil release	NQ	NQ
05-025	Fly ash + AC (post-primary PCD: high ash)	Lignite	2.58	172	0.0000297	1,588,470	-0.0000109	NA – below soil release

6

SUMMARY

The evaluation of the impact of microbial action on the release of mercury from fly ash is difficult because the total mercury concentrations in most fly ash samples are low. Even fly ash + AC that exhibits higher total mercury concentrations than fly ash currently produced at coal-fired power plants has relatively low mercury content. The wet experimental system initially developed and used was not well suited for use with alkaline fly ash because the wet system required a neutral pH for the microbes to maintain viability. It was reported previously that the results were also impacted by the incidental introduction of mold into the sample systems, and methylation of mercury appeared to be positively correlated with the growth of a mold tentatively identified as *Scopulariopsis brevicaulis*.

The dry experimental system was developed in an attempt to alleviate the difficulties associated with the alkalinity of some fly ash samples. The dry experimental system was used to evaluate several samples but has not been fully evaluated. In those limited experiments, methylation may not have been a result of microbial action and may have been totally or partly abiotic as a result of the presence of fulvic acids in the soil mixture.^{1,2} Even though the presence of *S. brevicaulis* is likely in soils, the exact mechanism of methylation in these experiments has not been determined.

An important observation in all of these experiments is the extremely low rate of mercury release of both organomercury vapor and elemental mercury vapor. It is assumed that the organomercury vapor released in these experiments is primarily dimethylmercury because of the high water solubility of methylmercury and because of the high volatility of dimethylmercury.

It was shown that pH and buffer capacity of fly ash can impact microbial activity and associated mercury releases, so laboratory work to investigate pH development over time in fly ash and fly ash + AC samples is continuing. Additional laboratory experiments are also planned using the dry experimental system in order to define methylation reaction mechanisms.

REFERENCES

[1] *The Chemistry of the Metal – Carbon Bond, Volume 5*; Hartley, F.R., Ed.; John Wiley & Sons Ltd, 1989; Chapter 10.

[2] www.umd.edu/geosciences/faculty/moore/g431/lectur17.htm (accessed 2007).