

Quantitation and Interpretation of Release of Mercury from Coal Utilization By-Products

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ABSTRACT

Mercury emission control technologies have the potential to impact existing coal utilization by-products (CUBs) produced at coal-fired power plants. The CUBs most likely to be affected are the fly ash or flue gas desulfurization (FGD) materials. The mechanisms that may allow mercury to be released under typical management scenarios are leaching—both direct and microbiologically mediated—and vapor release, ambient-temperature release, elevated-temperature release, and microbiologically mediated release.

In order to evaluate the potential for mercury release from CUBs associated with those mechanisms, the Energy & Environmental Research Center has developed experimental protocols to simulate conditions that would allow mercury releases from CUBs to be measured in a controlled laboratory setting. Release data have been generated on fly ash and FGD material from existing systems and systems where mercury control technologies were being demonstrated. Results to date indicate that direct leaching of mercury is limited regardless of the leaching method used, and no correlation has been noted between the total mercury content of a CUB and the leachate concentrations. Results of ambient-temperature release experiments indicate that most CUBs act as mercury sinks rather than releasing mercury. Results of elevated-temperature release of mercury indicate that at least some mercury remains associated with the CUB even after exposure to temperatures up to 750°C. Preliminary results from microbiologically mediated release experiments indicate that organomercury compounds have been identified and quantitated in both the vapor releases and the leachate.

INTRODUCTION

Mercury and other air toxic elements can be present in fly ash, flue gas desulfurization (FGD) material and, to a lesser extent, bottom ash and boiler slag. The mercury that can associate with coal utilization by-products (CUBs) is a function of the mercury content of the coal used, the coal properties, the combustion technology, and the

emission control technologies at a specific coal-fired power plant. The knowledge base of mercury in emissions from coal-fired power plants has grown significantly in recent years because of the December 2000 U.S. Environmental Protection Agency (EPA) regulatory decision that mercury emissions from coal-fired electric generating plants will be controlled, with full compliance scheduled for December 2007. The studies performed by EPA and others to quantitate mercury emissions from coal-fired power plants have fostered the development of generalizations about mercury emissions that are useful when mercury and CUBs are considered. Mercury is a volatile element with specific chemistry which results in mercury in high-temperature systems, such as power plants, to be present in the vapor phase until temperatures drop significantly.

It is known that mercury can be present in flue gases as both reduced (elemental mercury) and oxidized species (mercury [II] chloride, nitrate, oxide, or other compounds). Generally, combustion of lignite and subbituminous coal results in high percentages of elemental mercury in the flue gas, and combustion of bituminous coal results in high percentages of oxidized mercury in the flue gas. Once the flue gas temperature is reduced, elemental mercury is readily sorbed on unburned carbon that is sometimes present in the coal fly ash and collected by use of electrostatic precipitators (ESPs) or fabric filters. Oxidized mercury can be sorbed on fly ash, carbon, or calcium-based FGD materials.

Mercury emission control technologies are being developed to remove mercury from the flue gases, and in many cases, these technologies are designed to incorporate the mercury removed from the flue gas into the fly ash or FGD material. Significant changes in the chemical composition, physical properties, and morphology of CUBs may occur as a result of the application of new emission controls. The stability of mercury associated with CUBs is currently under investigation at the Energy & Environmental Research Center (EERC). The reasons for evaluating the rerelease of mercury from CUBs are twofold: 1) to determine if mercury captured on CUBs is stable or if it will be rereleased from these materials, thus negating the purpose of the removal of the mercury from the emissions and 2) to aid utilities in determining and understanding changes in CUBs associated with mercury control and associated CUB management.

The rerelease mechanisms for mercury from CUBs have been identified as 1) direct leachability, 2) vapor-phase release at ambient and elevated temperatures, and 3) biologically induced leachability and vapor-phase release. Leaching is the most likely mechanism of transport of constituents from disposed or utilized CUBs contacted by water. Leaching is typically performed on CUBs to characterize them for management purposes. Several issues have been raised by EPA's Office of Research and Development (ORD) and Office of Solid Waste (OSW) related to the best means of evaluating the leaching potential of CUBs. Vapor-phase release, particularly of mercury, is important from the perspective of long-term use, storage, or disposal of CUBs. Although the concentration of mercury in CUBs is relatively low, the large volumes of CUBs produced annually cause concern about potential mercury releases. Ambient, near-ambient, and elevated-temperature studies of mercury release resulted in the development of equipment to determine mercury release in real time from CUBs.

Preliminary EERC results are presented regarding mercury release from CUBs subjected to laboratory tests designed to simulate the identified release mechanisms.

EXPERIMENTAL

Leaching

Project samples were evaluated through the use of the synthetic groundwater leaching procedure (SGLP),¹ 30- and 60-day long-term leaching (LTL) procedure, and toxicity characteristic leaching procedure (TCLP).² The SGLP was selected as the primary leaching procedure applied to characterize release of mercury and other air toxic elements from CUBs. Samples with pH >10 were also leached using LTL because CUBs with pH >10 are typically reactive and the leaching profile may change over time, hence requiring the longer duration leaching data to assess the leaching characteristics of those samples. TCLP was applied to some samples upon request of the sample submitter.

Ambient Temperature Release

A system was devised to collect mercury vapor releases from CUBs at ambient temperature. This system underwent several improvements throughout the duration of the task. The latest setup is described below. A quantity of ash (generally around 150 g) was placed and compacted into 250-mL-tall wide-mouth bottles with bonded Teflon liner caps. The caps were drilled with two holes to accommodate a Teflon outlet bulkhead fitting and a silicone tube for a gas inlet. Samples of CUBs 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 gas chromatography (GC) capillary tubing to each of the individual bottles. The pressure drop across the GC capillary tubing allowed for the regulation of airflow 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 i.d. of 0.25 mm. This length of tubing, when pressurized to 1 to 2 psig through a gas distribution manifold, provided a convenient means of regulating gas flow to approximately 2 cm³/min. The air exiting the GC tubing was given a final scrubbing to remove mercury vapor using another gold-coated quartz trap just prior to entering the bottle containing the CUB. 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 analytical gold-coated quartz nearest the exit bulkhead fitting was analyzed at regular intervals to determine the mass of mercury vapor released from the CUBs while the top guard trap, in the same tube, was present to prevent mercury contamination from atmospheric mercury. This setup is illustrated in Figure 1.

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 mass of released mercury was determined using atomic fluorescence.

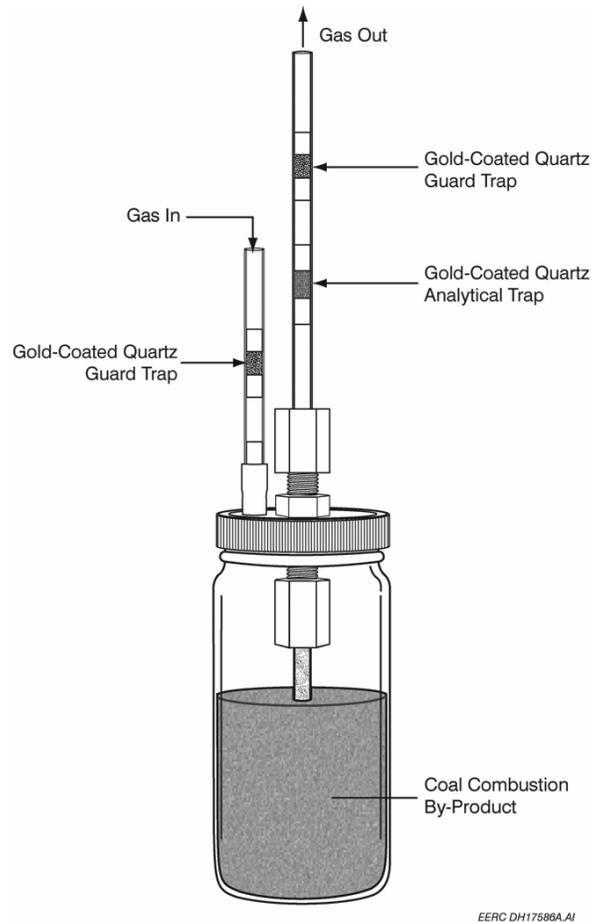


Figure 1. Mercury vapor release collection apparatus.

Blank value determination was an important issue in this task. The method developed involved determining the mercury vapor release from the CUB and then determining the blank value contribution. After mercury vapor release was measured for a desired time period, the CUBs were emptied from the bottles and gas was allowed to continue to flow through the empty bottles for a given time period. This yielded a separate blank value for each sample container.

The ambient-temperature release of mercury was evaluated for twelve CUBs in duplicate (see Table 1). The mercury released from the samples was analyzed after one 7-day period and two 90-day periods. The CUBs used did not have total mercury contents typical of CUBs but 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 releases were most likely measurable.

Table 1. Samples Included in Long-Term Ambient Temperature Mercury Release Experiment

ID No.	Sample Type	Total Hg, $\mu\text{g/g}$
99-188	Fly ash + FGD	0.112
99-456	Fly ash	1.24
00-048	Fly ash + FGD	0.361
01-002	Fly ash	0.187
01-008	Fly ash	1.22
01-011	Fly ash + FGD	2.55
03-006	Fly ash	0.194
03-017	Fly ash + FGD	0.225
03-018	Fly ash + FGD	0.289
03-060	Fly ash	1.86
03-061	Fly ash	0.578
03-062	Fly ash + FGD	0.490

Elevated Temperature Release

The release of mercury and mercury compounds at elevated temperatures was evaluated by heating a sample in a temperature-controlled tube furnace and detecting the emitted mercury or mercury compounds with atomic absorption (AA) spectrometry in a quartz t-cell heated to 800°C. A schematic of the apparatus is shown in Figure 2. The use of a heated cell allowed detection of mercury compounds by thermally decomposing compounds to form elemental mercury, which can be detected by AA spectrometry. A mass flow controller was used to maintain a nitrogen flow of 5 cm³/min. The temperature controller was ramped from ambient temperature to 750°C at a rate of 25°C per minute to heat the sample. The AA was calibrated for the amount of mercury thermally desorbed from the CUBs tested. This was done by injecting a known amount of mercury, from air saturated with elemental mercury, onto a gold-coated quartz trap and thermally desorbing the mercury in the same manner as samples. A more complete description along with a description of the experimental protocol can be found elsewhere.³

Additional elevated temperature release experiments were also performed on CUB samples spiked with mercury. The experimental design focused on the use of analytical spikes using mercuric chloride and elemental mercury. The base samples for spike additions were CUB samples, quartz sand, or quartz powder. The CUB base samples were fly ash, some of which contained activated carbon from mercury emission control demonstrations. Mercuric chloride was dissolved in ether and then added to the base samples. Elemental mercury was added in a gaseous form to CUB samples.

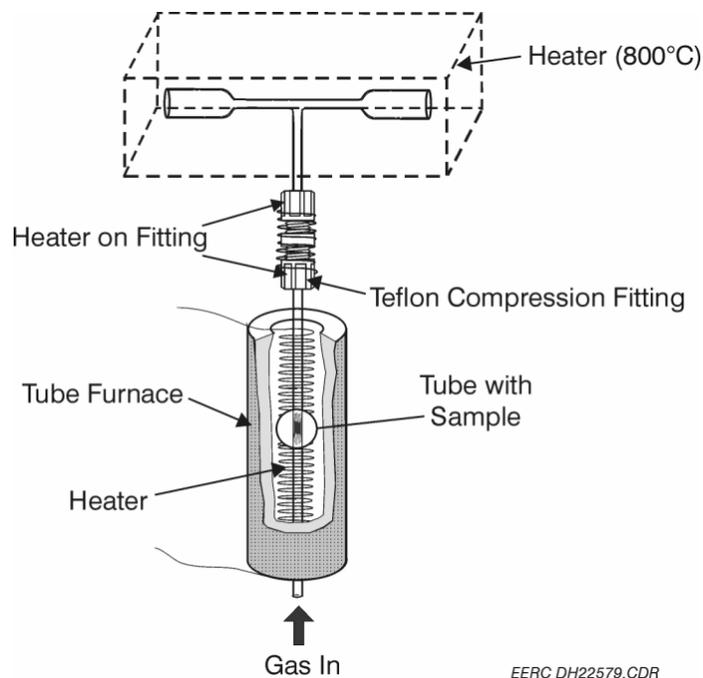


Figure 2. Mercury thermal desorption apparatus.

RESULTS AND DISCUSSION

Leaching

Leachate mercury concentrations have been found to be extremely low regardless of the total mercury content of the sample. Most leachates exhibited mercury concentrations less than the reporting limit of $0.01 \mu\text{g/L}$. All leachate concentrations fell well below the national primary drinking water (PDW) limit of $2.0 \mu\text{g/L}$ for mercury as well as the limit at 30X PDW ($60 \mu\text{g/L}$) and 100X PDW ($200 \mu\text{g/L}$). A comparison of total and leachate mercury concentrations is presented graphically in Figure 3. The figure clearly indicates that the leachable mercury cannot be correlated to the total mercury content of a CUB.

Ambient Temperature Release

Measurements obtained from the release of mercury at ambient temperature from individual sample containers are shown in Figure 4. Over the duration of the entire 187 days of the experiment, five samples showed overall mercury release and seven samples showed overall mercury sorption. The release of mercury, expressed as pg/g/day , was less for most samples in the final 90-day collection period than for the previous 90-day collection period. As evident in Figure 4, the variability of the data is relatively high, averaging -0.0002 pg/g/day . In part, the variability can be attributed to the variability inherent in the analysis of the extremely low concentrations of mercury captured by and desorbed from the gold-coated analytical traps. The samples evaluated

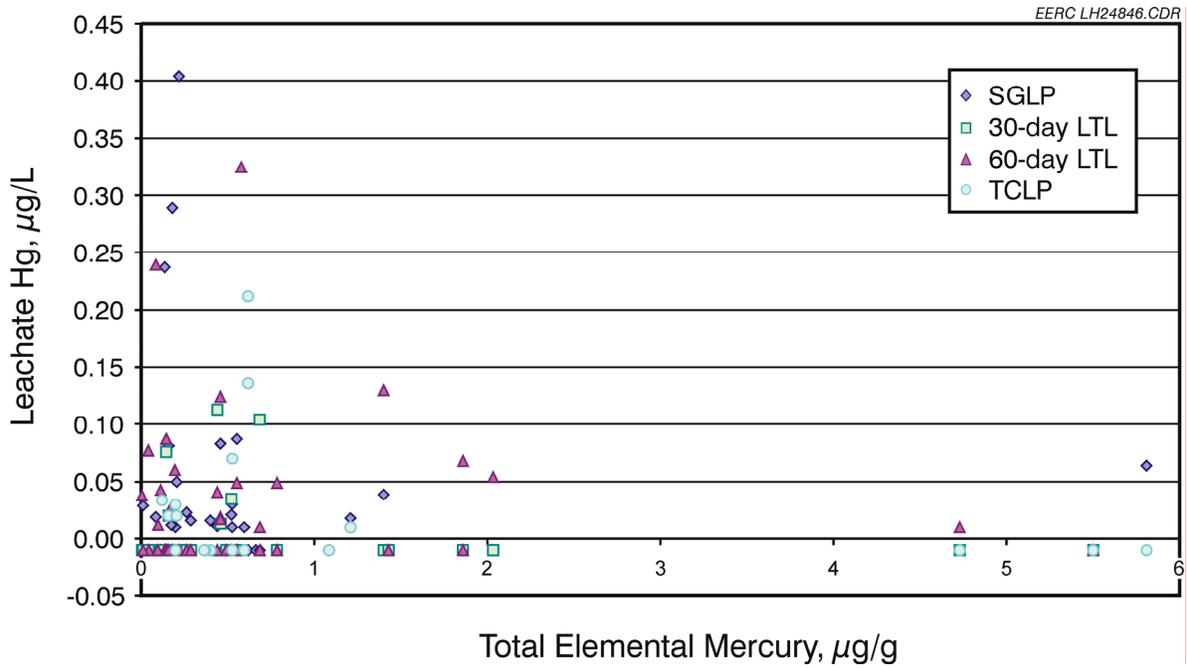


Figure 3. Comparison of total mercury concentrations and leachate concentrations. Negative values indicate less than the reporting limit.

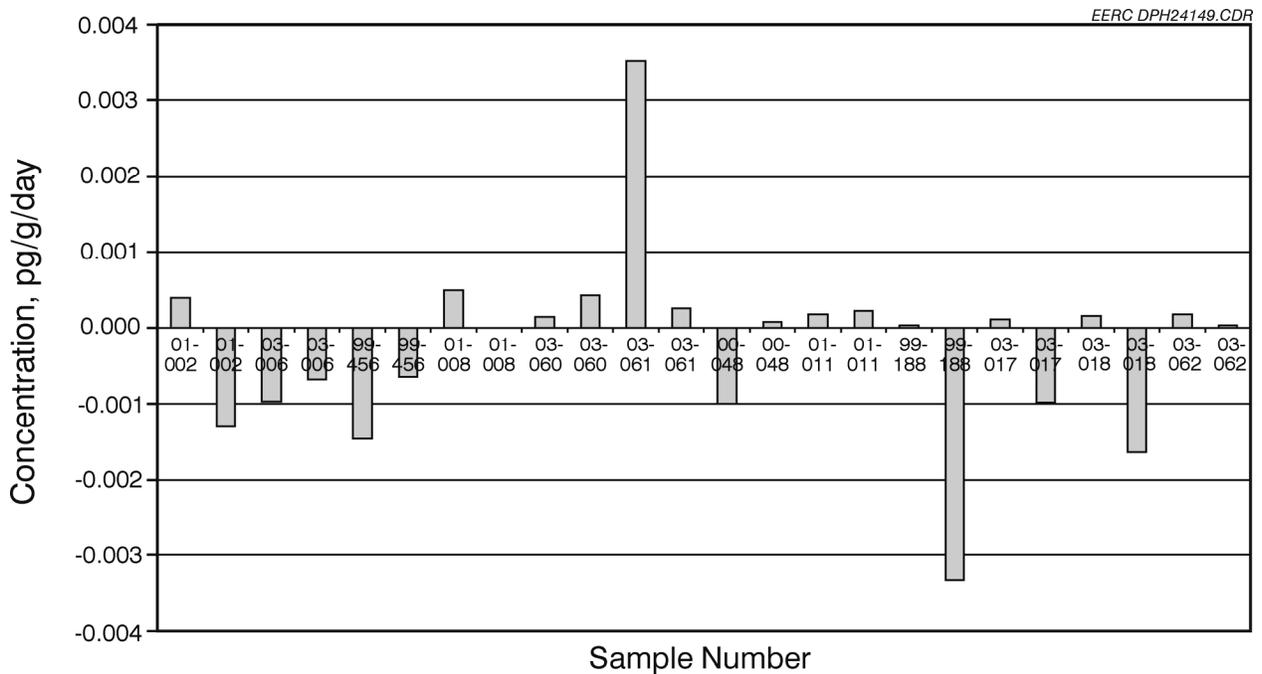


Figure 4. Average total long-term ambient-temperature mercury release or sorption as related to blank values, pg/g/day. Positive values indicate release and negative values indicate sorption of mercury.

were chosen from those having higher mercury content to allow for experimental measurement and any release or sorption of mercury from the samples was extremely low. This is consistent with previous results using this method.^{4, 5}

Elevated Temperature Release

Mercury thermal desorption curves were generated for 57 CUBs including 33 samples without and 24 samples with mercury control. The samples were primarily fly ash but also included various types of FGD materials and a dust collector ash. Most samples generated either one or two mercury peaks with a range of 0–4 peaks. The temperature of the primary mercury peak ranged from 145°C–747°C with an average of 411°C. Some samples actually continued to show increasing mercury release at 750°C so the peak temperature at which the mercury was released could not be determined.

Table 2 breaks down the information on the mercury thermal desorption curves by samples with and without mercury control testing. Samples consisting of or containing FGD material released mercury at a lower temperature than fly ash samples. The lowest mercury release peak temperature for a fly ash sample was 287°C. More samples from mercury control testing continued to release mercury at 750°C than those without mercury control testing. Most samples have not been duplicated but will be to confirm initial results.

It has been hypothesized that the mercury species associated with fly ash, FGD material, or carbon can be identified using thermal desorption techniques. Several experiments were performed in an effort to confirm or refute this hypothesis. The experimental design focused on the use of analytical spikes using mercuric chloride and elemental mercury. The base samples for spike additions were CUB samples, quartz sand, or quartz powder. Mercuric chloride was dissolved in ether and then added to the base samples. Elemental mercury was added in a gaseous form to CUB samples.

In the mercuric chloride experiments, a single sharp peak with an average peak temperature of 266°C was recorded when the mercuric chloride was added to the quartz sand. When mercuric chloride was spiked onto the quartz powder, a double peak with an average peak temperature of 218°C was noted.

Additional elevated-temperature release experiments were also performed on five CUB samples spiked with mercury. All samples used in this experiment were fly ash and three of the samples contained activated carbon from mercury emission control demonstrations. The addition of mercury chloride or elemental mercury to the CUBs

Table 2. Mercury Release at Elevated Temperatures

Sample Type	No. of Samples	No. of Peaks	Peak Temperature (°C)		
			Average	Minimum	Maximum
Without Hg Control	33	0–4	382	145	747
With Hg Control	24	1–3	456	302	740

resulted in a shift of the mercury release peak(s) noted previously from the samples without any added mercury. The peak temperatures measured for spiked CUB samples shifted to higher temperatures for some samples and to lower temperatures for other samples. In one case, the release of mercuric chloride occurred at 260°C, but in all other cases, the release of mercury from mercury spiking was above 300°C or 400°C. These data are under continued review, and additional experiments may be performed in the future. Therefore, speciation of mercury present on CUBs has not been achieved to date.

CONCLUSIONS

While only a limited number of CUBs have been evaluated using the techniques described in this paper with a small subset of the sample set from systems with mercury controls in place, the following preliminary conclusions are presented.

Experiments were performed to evaluate the release of mercury from CUBs by leaching and exposure to ambient and elevated temperatures. Leaching of the CUBs resulted in very low or no release of mercury into the leaching solution. The leachate concentrations did not correlate to the total amount of mercury regardless of the sample source. Leaching data collected to date indicate that CUBs from systems with mercury control are expected to be nonhazardous.

Ambient-temperature exposure experiments showed both release and sorption of mercury; however, all measurements are at extremely low levels (subpg/g/day). If all CUBs produced annually in the United States at coal-fired power plants released these typically low amounts of mercury at ambient temperature, it would likely not make a significant contribution to the overall atmospheric mercury loading.

Elevated-temperature experiments indicated that mercury and mercury compounds are released from CUBs at an average temperature of 411°C; therefore, applications employing high temperature processing could release mercury from the CUB. Speciation of mercury on CUBs has not been achieved to date using the elevated temperature mercury release apparatus.

Additional CUB samples need to be evaluated in order to draw final conclusions about the release of mercury from CUBs by leaching and exposure to ambient and elevated-temperature. Key samples will be those collected from large-scale demonstrations of the various mercury control technologies and the associated baseline samples.

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