

Mercury Release from Coal Combustion By-Products to the Environment

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ABSTRACT

Mercury emissions from coal-fired power plants and options that may be used to effectively and economically control these emissions have been the topic of numerous research projects. The Energy & Environmental Research Center (EERC) has performed evaluations of the potential for mercury control technologies to impact the character of coal combustion by-products (CCBs). Other questions related to mercury and CCBs are also being investigated: 1) how is mercury associated with typical CCBs and 2) how readily will the mercury be released into the environment under traditional management options. There are two primary means for mercury to be released from CCBs into the environment, aqueous transport and vapor-phase transport; but understanding these potential release mechanisms is complicated by the different mercury species that may be inherent in the CCB, the current emission control technologies being employed at a power plant, the CCB handling methods, and, finally, the broad variety of management options employed for CCBs nationwide.

Learning more about the mercury present on CCBs currently being generated using no mercury control technologies and comparing that information with laboratory-generated data on proposed mercury sorbents and CCBs that have been subjected to additional mercury constitute the approach used by the EERC to determine the potential for mercury release from CCBs. The study was initiated by determining the mercury content of a large number of coal combustion fly ash samples submitted by industry. These samples represent coal of various types from different coal mining areas in the United States. Several samples will be selected for evaluation by leaching and desorption at a variety of temperatures and simulated atmospheric conditions. These samples will also be subjected to mercury-laden gas streams in an attempt to load higher concentrations of mercury on various fly ash samples. These loaded samples will be reevaluated for leaching and vapor-phase mercury release.

INTRODUCTION

The 1990 Clean Air Act Amendments (CAAA) require the U.S. Environmental Protection Agency (EPA) to determine whether the presence of mercury and 188 other trace substances, referred to as air toxics or hazardous air pollutants (HAPs), in the stack emissions from fossil fuel-fired electric utility power plants poses an unacceptable public health risk.¹ EPA's

conclusions and recommendations were presented in two reports: "Mercury Study Report to Congress" and "Utility Air Toxics Report to Congress." The first congressional report addressed both human health and the environmental effects of anthropogenic mercury emissions, while the second report addressed the risk to public health posed by emissions of HAPs from steam-electric-generating units. The National Institute of Environmental Health Sciences is also required by the CAAAs to investigate mercury and determine a safe threshold level of exposure. Recently the National Academy of Sciences has also been commissioned by Congress to complete a report, based on the available scientific evidence, as to the safe threshold levels of mercury exposure. A goal of this study is to establish a threshold for mercury concentrations in the tissue of fish that may be consumed (including consumption by sensitive populations), without adverse effects to public health.

Although EPA reports did not state that mercury controls on coal-fired electric power stations should be required given the current state of the art, they did indicate that EPA views mercury as a potential threat to human health. It is likely that major sources of mercury emissions, including fossil-fired combustion systems, will be controlled at some point. In fact, municipal waste combustion units are already regulated. In anticipation of additional control measures, much research has been done (and continues) regarding the development of control technologies for mercury emitted from stationary sources to the atmosphere. Most approaches taken to date involve sorbent injection technologies or improve upon removal of mercury using existing technologies such as flue gas desulfurization scrubbers, fabric filters, and electrostatic precipitators. Depending on the fly ash chemistry and the form of mercury present in the flue gas, some of these existing technologies can be effective at capturing vapor-phase mercury from the flue gas stream.

Although, much research has been done on enhancing the removal of mercury from flue gas streams, little research has focused on what happens to the mercury when it is captured and converted and/or transferred to a solid or aqueous solution. The stability (or mobility) of mercury in this final process is critical and leads to the questions, What impact will the increased concentration of mercury have on utilization, disposal, and reuse? and, Is the mercury removed from the flue gas really removed from the environment or released at a later point? To help answer these questions, the EERC, as part of a U.S. Department of Energy Base Cooperative Agreement, did a series of experiments using thermal desorption and leaching techniques. This paper presents the results from these tests.

EXPERIMENTAL

Selection of Samples

All samples collected were analyzed for total mercury content as an initial screening to determine which samples would be included in the complete testing protocol. Table 1 lists the samples tested and their mercury concentration. Analysis for total mercury was done using cold-vapor generation atomic absorption spectrophotometry.

TABLE 1

Samples Screened for Use with the Mercury Stability Study

ID No.	Fuel Type	Plant Configuration	Comments	Hg Conc. µg/g
185	Western bituminous	pc ¹ -fired boiler, low-NO _x burners, and fabric filter		0.461
186	Western bituminous	pc-fired boiler, low-NO _x burners, dry FGD, ² and fabric filter		0.565
187	ND lignite	pc-fired EERC pilot-scale combustor and fabric filter		0.677
188	PRB ³ subbituminous	Dry FGD and fabric filter	Ash contained lime from dry FGD	0.112
189	Blended PRB subbit. and pet. coke	Cyclone boiler and ESP ⁴		0.736
190 ⁵	PRB subbituminous	pc-fired boiler, a fabric filter, duct injection FGD using trona	Ash contained Na ₂ CO ₃ from trona	<0.002
191 ⁵	Blended PRB subbit. and eastern bit.	pc-fired boiler with an ESP		0.008
192 ⁵	PRB subbituminous	pc-fired boiler with an ESP		0.026
193 ⁵	PRB subbituminous	pc-fired boiler with an ESP		<0.002
194 ⁵	PRB subbituminous	PRB subbituminous/pc fly ash/ESP		0.059
195 ⁵	ND lignite	pc-fired boiler, ESP, and wet FGD		0.002
263 ⁵	Eastern bituminous	pc-fired boiler and ESP		0.004
266 ⁵	Eastern bituminous	pc-fired boiler and ESP		0.138
267 ⁵	Eastern bituminous	pc-fired boiler with multicyclones and ESP		0.191

¹ Pulverized coal.

² Flue gas desulfurization.

³ Powder River Basin.

⁴ Electrostatic precipitator.

⁵ Eliminated from testing because of low mercury concentration.

Leaching Protocols

The stability of mercury on these materials with respect to potential long-term environmental impact was studied using two techniques, leaching and thermal desorption. Leaching was carried out using a leaching protocol called the synthetic groundwater leaching procedure (SGLP) using distilled deionized water as the leaching solution. The SGLP was developed at the EERC² as a result of research conducted on coal conversion solid wastes.^{3,4} The test, which is a generic leaching procedure designed for simulation of leaching under environmental conditions, was initially developed for use in the characterization of highly alkaline coal conversion solid residues, primarily fly ash produced from the combustion of low-rank lignitic or subbituminous coals. The test was modeled after the toxicity characteristic leaching procedure (TCLP),⁵ with modifications to allow for numerous disposal scenarios primarily for use with reactive materials such as low-rank coal ash that will undergo hydration reactions upon contact with water.

The SGLP leaching for this study utilized distilled, deionized water as a first-cut screening method. The use of distilled, deionized water as the leaching solution makes this form of the SGLP very similar to the American Society for Testing and Materials (ASTM) shake extraction test.⁶ End-over-end agitation was used, with sampling times of 18 hours, 2 weeks, and 4 weeks. The extended leaching times were included to allow a determination of changes of rate of leaching of mercury and to allow reactive ash samples time to equilibrate and form secondary hydrated phases. It has been shown that the formation of secondary hydrated phases can exert a substantial effect on leachate chemistry. Normally, solid-to-liquid ratios of 20:1 are used for SGLP evaluation (as is used in the TCLP protocol); however, in this study the ash samples, which had a lower mercury concentration than the load sorbents, were leached at a solid-to-liquid ratio of 10:1 in an effort to obtain more statistically significant analytical data. The sorbents were leached at the normal 20:1 liquid-to-solid ratio. These leaching tests were not intended to produce leachate concentrations that would be expected under field conditions. It may not be possible to accurately reproduce field leaching conditions in the laboratory except in isolated and specific cases as is discussed in *The Compendia of Leaching Tests*.⁷ It may be possible, however, to calculate the field conditions using a modeling scenario based on the amount of easily released analyte and rate of leachate formation.

Thermal Desorption Apparatus

An apparatus for the controlled thermal desorption of mercury and mercury compounds was assembled and is shown schematically in Figure 1. The apparatus was constructed using a Varian 1475 atomic absorption (AA) spectrophotometer for mercury detection and included a small tube furnace and temperature controller for thermal desorption. A Hewlett Packard 3393A integrator was used for data collection. Detection of thermally desorbed mercury and mercury compounds was done in an electrically heated quartz cell operated at 800°C. The use of a heated cell allowed detection of mercury compounds by thermally decomposing compounds to form Hg⁰ which can be detected by AA. Gas flow was 20 mL per minute of nitrogen. The temperature controller was ramped from ambient to 500°C at a rate of 20°C a minute. A more complete description along with a description of the experimental protocol can be found elsewhere.⁸

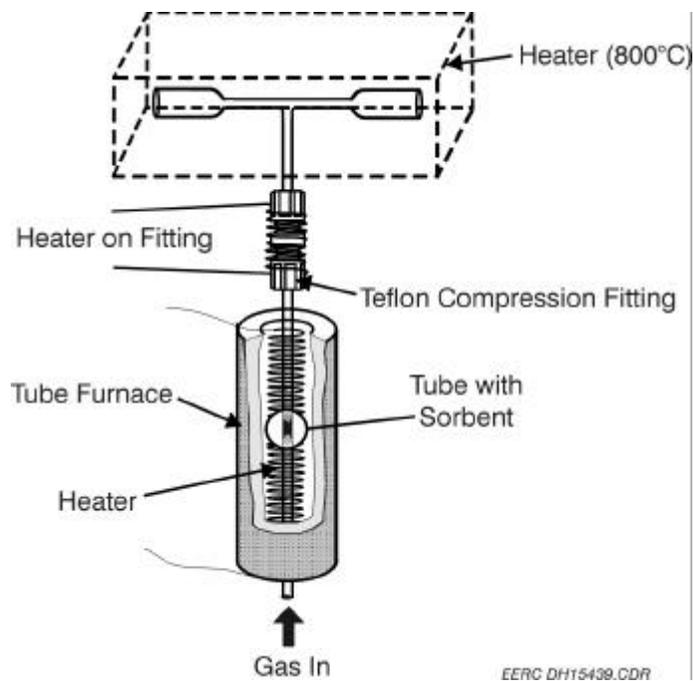


Figure 1. Schematic of the thermal desorption apparatus.

Leaching Results

Leaching results are summarized in Table 2. The calculated maximum mercury indicates the maximum concentration that could be reached if all of the mercury had dissolved during leaching and represents a calculated worst-case scenario.

TABLE 2

Leaching Results

ID No.	Type of Sample	Bulk, $\mu\text{g/g}$	Calc. Max., $\mu\text{g/L}$	18-hr, $\mu\text{g/L}$	2-week, $\mu\text{g/L}$	4-week, $\mu\text{g/L}$	pH
185	Fly ash	0.461	46.3	<0.05	0.11	<0.05	12.6
186	Fly ash	0.565	56.9	0.24	0.05	<0.05	12.7
187	Fly ash	0.677	67.8	0.12	<0.05	–	12.1
188	FGD ash	0.112	11.2	<0.05	<0.05	<0.05	12.1
189	Fly ash	0.736	73.8	<0.05	<0.05	<0.05	11.3

As can be seen from this table, the mercury appears to be very stable in the solids up to 4 weeks, in almost all cases less than 1% of the calculated maximum mercury concentration is leached, even up to 4 weeks.

Thermal Desorption Results

Although most of the desorption curves were straightforward, containing only one or two major desorption peaks, there were several samples that produced multiple desorption peaks. A representative desorption curve is shown in Figure 2. In addition to the desorption curves on ash, two standard samples were also run. These consisted of a fly ash sample, initially containing mercury at below the detection limit, that was spiked with HgCl_2 and HgO . These samples each presented one thermal desorption peak, with the HgCl_2 centered at approximately 220°C and the HgO peak centered at approximately 355°C . It has been speculated in thermal desorption experiments run by others^{9,10} that there may be a correlation between the temperature of evolution and mercury form. This may not be the case with respect to chemically modified sorbents and ash because of the possibility of chemical reactions occurring on the ash surface either after sorption or during thermal desorption.

From the sample tests, there were four representative thermal desorption curves. These are a predominant peak, two or more predominant peaks, one major and one minor peak, and numerous small and large peaks. Regardless of the number of peaks, all observed peaks exhibited tailing. Additionally, in multiple-peak samples, the peaks were not usually completely resolved. It is likely that some of this peak asymmetry can be corrected by optimization of flow rates and heating rates to take advantage of the chromatographic properties of the system.

The thermal desorption information for all of the samples that were thermally desorbed is shown in Table 3. Sample information is given as well as the temperature or temperatures of maximum absorbance (labeled $T_{A\text{max}}$) and the percentage of total absorbance. The temperature of maximum absorbance was calculated by multiplying the time of the peak maxima shown on the chromatograms by 20, the ramp rate in $^\circ\text{C}$ per minute, and adding the starting temperature which

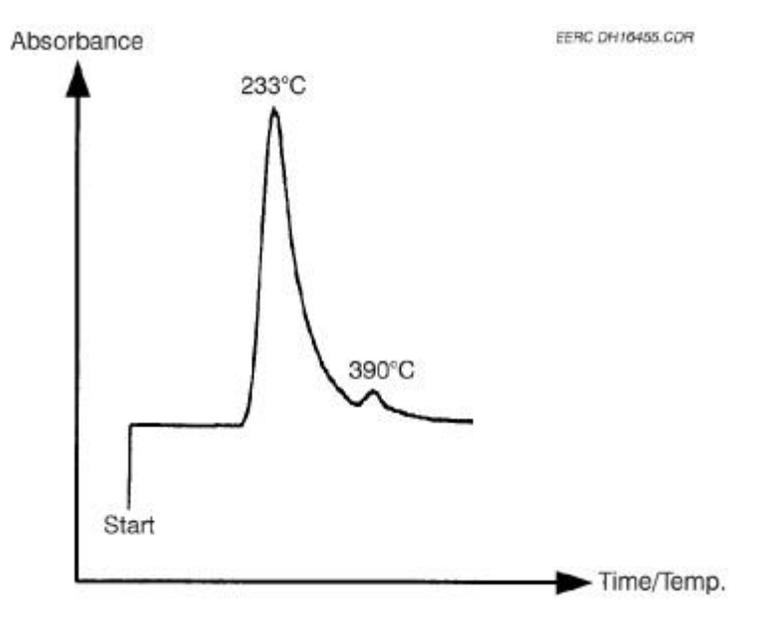


Figure 2. Thermal desorption curve for Ash 186.

TABLE 3

Thermal Desorption Information			
ID No.	Sample Type	T _{A max}	% Total
185	Fly ash	350	100
186	Fly ash	233	91
		390	9
187	Fly ash	317	100
189	Fly ash	378	100
188	FGD ash	250	75
		357	9
		429	12
		454	3

was usually near ambient (between 20° and 35°C). Because it has been shown that not all of the mercury in each sample was thermally desorbed during the course of these experiments, the % absorbance for each peak should not be taken to be in reference to the total mercury measured but equal to the total mercury that was thermally desorbed.

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:

- Mercury and mercury compounds, as sorbed, are being released unchanged during the thermal desorption procedure.
- Mercury compounds are being desorbed by a mechanism of thermal decomposition whereby sorbed compounds such as HgO are thermally decomposed to mercury and oxygen during the thermal desorption.
- Mercury or mercury compounds are chemically reacting with ash or sorbent components and are then thermally desorbed according to the first or second scenario as described above.
- Future experiments may resolve some of this uncertainty.

CONCLUSIONS

Coal ash samples did not leach mercury at above detection limits at the 4-week equilibration period. Some ash samples leached minute amounts of mercury before the 4-week equilibration was reached. This may have been a result of the formation of secondary hydration products which would be expected to form at the pH levels seen in these samples. However, the amount of mercury leached was only slightly above the detection limit of the instrument.

The only sample tested that may present a potential problem was the Centaur activated carbon loaded with HgCl₂. In this case, 2.1% of the total available mercury leached out after 4 weeks. All the other carbons leached less than 0.1% of the maximum mercury. Even for the Centaur carbon, the potential for adverse environmental impact through leaching mechanisms may be misleading since, under use conditions, the sorbents, if injected into flue gas streams, would be present along with fly ash and would have a much lower loading. However, if these types of sorbents are used in packed beds, it is possible that leaching may be an issue.

Thermal desorption has indicated little potential for environmental impact through devolatilization because no significant mercury peaks were detected at temperatures below 150°C. Future experiments using integrated collection of mercury vapor from ash and sorbents over long time periods may help to answer this question more completely. Integrated collection on gold traps with subsequent atomic fluorescent detection will allow detection down to 50 picograms or lower, as opposed to the 100 nanograms required using AA.

Based on a review of the literature and the project completed by the EERC, it is clear that substantial work needs to be done to determine the stability of mercury in combustion by-products. Although the preliminary data appear to be encouraging, there is contradictory information. In addition, almost nothing is known as to the leachability or offgassing potential of the different mercury sorbents that are being tested as possible control strategies for fossil fuel-fired combustors.

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