

# Measurement of mercury flux from coal utilization by-products with a laboratory flux chamber

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## INTRODUCTION

As a result of recent regulations, the emission of mercury in the flue gas of coal-fired power plants will be reduced. This will result in the transfer of mercury to one or more of the coal utilization by-products depending on the mercury control strategy selected by the power plant. Over 40 percent of these coal utilization by-products (CUB), which include fly ash, bottom ash, boiler slag, and flue gas desulphurization (FGD) by-products, are used beneficially to make wallboard, cement, and other products. The remainder is disposed in landfills and other impoundments. The potential release of mercury from CUB is being evaluated to help ensure the environmental acceptability of current disposal practices as well as the continued and expanded commercial use of these materials. While previous studies have shown that mercury in CUB is retained under most conditions, additional research into the potential for atmospheric releases is needed. Most studies have shown that CUB do not emit significant amounts of mercury to the atmosphere. However, the effects of temperature, moisture content, light exposure, and the increased mercury content resulting from mercury controls are not well studied. In response, the Department of Energy/National Energy Technology Laboratory's Office of Research and Development is utilizing an environmental chamber to assess the influence of these factors on mercury flux from a variety of CUB materials.

## EXPERIMENTAL METHODS

### Dynamic Flux Chamber

The chamber was built from a 9.25L Pyrex jar resting on a Teflon base, which had inlet and outlet ports bored through the plate for ambient air to flow through the chamber. A third port allowed a Barnstead RHTEMP101 Humidity and Temperature Recorder (Barnstead International, Dubuque, Iowa) to continuously monitor the relative humidity and temperature inside the chamber in five minute intervals. A Tekran 2537A Mercury Vapor Analyzer (Tekran Inc., Toronto, Ontario) measured the concentration of elemental mercury in the air entering and exiting the chamber. The detection limit of the Tekran is approximately 0.1 ng/m<sup>3</sup>. A Tekran Model 1110 2-Port Sampler with switching valves controlled the influent to the Tekran 2537A. Every ten minutes the influent was switched from ambient air to the air exiting the chamber, thus providing mercury flux measurements every 20 minutes. Flux,  $F$ , in ng/m<sup>2</sup>hr, was calculated as

## Equation 1.

$$F = (C_{outlet} - C_{inlet}) * Q / A$$

where:

$C_{outlet}$  and  $C_{inlet}$  are the concentrations of mercury at the outlet and inlet in ng/m<sup>2</sup>hr,

A is the area of the CUB sample exposed to the air in the flux chamber in m<sup>2</sup>, and

Q is the flow rate of the air through the chamber in m<sup>3</sup>/hr.

An auxiliary pump kept the air flow through the chamber steady at approximately 1 L/min. The experiments conducted in the dark required a cloth cover for the chamber such that light did not enter. To monitor light exposure for the lighted experiments, two sensors, Fisherbrand Traceable Light Meter (400-700 nm) and UV Light Meter (320-390 nm) were placed near the chamber to measure visible and UV light intensity in 20 minute intervals (Thermo Fisher Scientific, Inc., Waltham, Massachusetts). A full spectrum lamp was positioned over the chamber to mimic natural light exposure. Visible light intensity ranged from 480-550 lux and UV light irradiance ranged from 1.8-2.1 W/cm<sup>2</sup>.

## Samples

The mercury flux measurements were conducted on coal fly ash samples produced from both Eastern and Western U.S. coals. Mercury concentration in the coal fly ash samples was measured before and after the experiments using EPA method 7473<sup>1</sup>. Mass balances were performed using the solids analyses and flux measurements. Six samples were selected for long-term (approximately 30-day) experiments. These samples were kept dry and not exposed to light. Two of the samples were from NETL's coal fly ash inventory and the remaining four were paired samples from the U.S. Department of Energy/NETL Mercury Emissions Control Technologies field testing Phase II program. Each sample pair consists of a sample collected before mercury controls were applied to the flue gas and a sample collected while the mercury control technology, such as activated carbon injection (ACI), was applied. Eight Phase II samples have been selected for shorter duration (7-day) experiments conducted under conditions of both wet and dry samples, and dark and lighted chamber conditions. Currently, results are available for only two of these samples, or one sample pair. Wet experiments were conducted by mixing 30mL of deionized water into the sample immediately before placing the sample in the chamber.

## RESULTS

For all of the experiments described below, ambient mercury concentrations measured in the influent air tended to range between 2-4 ng/m<sup>3</sup> with higher concentrations at night and early morning, and lower concentrations in the late afternoon. Results for the long-

term dry/dark experiments are given in Table 1. Samples FA-51 and FA-41 are from the DOE-NETL fly ash inventory. Sample FA-51, the class F fly ash sample with higher carbon content, showed absorption of mercury (negative flux) while the sample FA-41, also a class F fly ash but with a low carbon content, showed release (positive flux). Both flux values are relatively small in magnitude and are steady for the entire 30-day experiment duration. For sample FA-51, there was a negative correlation with ambient mercury concentrations: when mercury concentration was high, the flux was more negative, or the sample absorbed more mercury. There was no such correlation for sample FA-41.

Sample pairs 2230-2231 and 2232-2233 are from the Phase II program. The first sample of each pair represents fly ash collected when no Hg controls were applied to the flue gas, while the second represents fly ash collected while the Hg control was applied. In both cases, activated carbon injection (ACI) was employed. For the PRB fly ash sample pair, 2230-2231, a small amount of mercury was released from the baseline sample. The during-control sample clearly showed mercury absorption with a diurnal pattern that paralleled the temperature in the chamber. This diurnal pattern negatively correlated with the ambient mercury concentration: when ambient mercury concentrations were higher, the sample absorbed more mercury. A similar diurnal pattern was obtained for the during-control lignite sample 2233. However, the corresponding baseline sample, 2232, showed neither absorption nor release of mercury.

**Table 1.** Results for 30-day mercury flux experiments.

Sample	Coal Type	Initial Hg Content (µg/kg)*	Final Hg Content (µg/kg)*	Average Hg Flux (ng/m <sup>2</sup> -hr)*	LOI (%)
FA-41	Class F fly ash	1554(14)	1584(17)	-4.18(0.7)	6.96
FA-51	Class F fly ash	251(12)	268(6)	4.35(2.4)	0.10
2230	PRB, no Hg controls	180(2)	191(4)	1.78(4.2)	1.89
2231	PRB, after ACI	1127(39)	1020(76)	-5.63(1.9)	3.32
2232	ND Lignite, no Hg controls	2.46(0.4)	4.55(1.4)	0.50(1.0)	0.97
2233	ND Lignite, after ACI	420(8)	415(4)	-6.82(2.6)	1.21

\*Standard deviation given in parenthesis.

Results for the shorter-term experiments conducted under varying conditions of wet and dry samples and light exposure are given in Table 2. The first sample, 2234, is a baseline sample of a bituminous fly ash, while the second sample, 2235, represents the same fly ash material while mercury controls were applied. For a dry sample 2234, there was only a very small difference in mercury flux when the sample was kept dark or exposed to light, 2234DD and 2234DL respectively. In both cases there was a strong negative correlation with ambient mercury concentration. The wetted sample initially displayed mercury flux values at background levels, but subsequently absorbed mercury in a diurnal pattern similar to the dry sample as the sample dried during the

experiment. Again, there was no difference in flux for the light or dark chamber conditions. Results for the during-control sample, 2235, are very similar. Experiments using the dry sample, 2235DL and 2235DD, show absorption of mercury with a diurnal pattern that is negatively correlated with ambient mercury concentrations. When the sample was wet, there was no release or absorption of mercury initially but, as the sample dried in the chamber, the flux approached the same magnitude and diurnal pattern as seen for the dry samples. There was no difference in flux between the dark and light-exposed dry samples. Results are not yet available for the wet sample/lighted chamber experiment on sample 2235.

**Table 2.** Results for 7-day mercury flux experiments with wet or dry samples and lighted or dark chamber conditions.

Sample*	Coal Type	Initial Hg Content (µg/kg)**	Final Hg Content (µg/kg)**	Average Hg Flux (ng/m <sup>2</sup> -hr)**	LOI (%)
2234 DD	Bituminous, baseline (no Hg controls)	86.2(4.3)	87.5(4.8)	-6.45(2.0)	1.71
2234 DL		86.2(4.3)	87.5(4.8)	-5.30(1.5)	
2234 WD		89.4(5.5)	53.7(1.0)	-2.08(2.7)	
2234 WL		92.6(2.4)	84.1(5.5)	-2.03(3.1)	
2235 DD	Bituminous, controlled (after ACI)	281(31)	287(35)	-4.46(1.2)	1.91
2235 DL		269(43)	184(5.4)	-4.43(1.2)	
2235 WD		181(4.8)	152(6.5)	-2.78(2.2)	

\*First letter refers to a dry (D) or wet (W) sample and second letter refers to a dark (D) or lighted (L) chamber.

\*\*Standard deviation given in parenthesis.

## DISCUSSION

In general, mercury flux was constant for the duration of the longer-term experiments, suggesting that experiments could be shortened without loss of information. Under dry conditions, the coal from which the fly ash was produced (lignite, PRB, bituminous, etc.) did not appear to have any bearing on the mercury flux for this small sample set. The mass balance for five of the six samples was 100±10%. Final mercury content for sample 2232 was higher than expected, which may reflect contamination. Mercury content and flux were not correlated: a sample with higher mercury content did not result in higher mercury flux. However, there might be a relationship with carbon content. The samples with a higher LOI tended to absorb mercury under dry conditions.

In comparing Phase II sample pairs, applying mercury controls does increase the mercury content of the fly ash, but the mercury content appears unrelated to the magnitude of mercury flux measured. In all cases, the during-control sample absorbed rather than released mercury. It is likely that the additional carbon contained in the during-control sample is able to absorb additional mercury from the air. The mercury

initially in the fly ash appears to be stable (is not released), regardless of whether the sample is wet or dry or exposed to light. Light exposure at these levels did not impact mercury flux. Wetting the samples had the effect of inhibiting mercury absorption. When samples had a wet surface, no mercury was absorbed, but as the surface dried, absorption increased and approached the same magnitude and diurnal pattern as the corresponding samples that were kept dry for the entire experiment. This made the average flux for the 7-day wet experiments lower than the dry sample flux. If the wet experiments were to continue for longer than seven days it is likely that the average flux would approach the same values as the flux for the dry samples. The mass balance for five of the seven samples was  $100\pm 10\%$ . Further review of the lower than expected final mercury content for samples 2234WD and 2235DL is necessary.

Results presented in this study compare well with previous works. Gustin et al.<sup>2</sup> and Xin et al.<sup>3</sup> found most dry samples were sinks for mercury of similar magnitude as was presented here. Correlations were found with ambient mercury concentrations and/or sample carbon content, but not with sample mercury content. Light exposure did not initiate mercury release, but it did decrease mercury deposition. Hassett and Heebink<sup>4,5</sup> and Hassett et al.<sup>6</sup> found that five of six samples acted as mercury sinks and mercury absorption/release was not correlated with mercury content of the sample. These studies concluded that the small amounts of mercury that could potentially be available for release were so minute that they were insignificant even considering the large volumes of fly ash produced from a commercial-scale power plant. Results from this study suggest that the same conclusion can be made when mercury controls are added to the power plant.

## SUMMARY

A dynamic flux chamber with inlet and outlet ports connected to a Tekran 2537A Mercury Vapor Analyzer allows measurement of very low levels of mercury flux from coal fly ash samples. The use of ACI does result in higher mercury content in the fly ash but based on experiment results presented here, the mercury appears stable and will not be volatilized whether the sample is wet or dry or exposed to light. No relationship was found between the parent coal and potential for mercury release from its ash.

## REFERENCES

1. U. S. EPA (1998). Method 7473, Mercury in solids and solutions by thermal decomposition, amalgamation, and atomic absorption spectrophotometry. January 1998.
2. Gustin, M.S.; Ladwig, K. *J. Air & Waste Manage. Assoc.* **2004**, *54*, 320-330.
3. Xin, M.; Gustin, M.S.; Ladwig, K. *Fuel* **2006**, *85*, 2260-2267.
4. Hassett, D.J.; Heebink, L.V. (2001). Release of mercury vapor from coal

combustion ash. 2001 International Ash Utilization Symposium, Center for Applied Energy Research, University of Kentucky, Paper #65.

5. Hassett, D.J.; Heebink, L.V. (2003). Long-term mercury vapor release from CCBs. 2003 International Ash Utilization Symposium, Center for Applied Energy Research, University of Kentucky, Paper #77.
6. Hassett, D.J.; Heebink, L.V.; Pflughoeft-Hassett, D.F. *Fuel Process. Technol.* **2004**, *85*, 613-620.

## **KEY WORDS**

Mercury, coal fly ash, coal by-products, flux chamber, mercury control technology, Phase II mercury control program