

Factors Controlling the Solubility of Mercury Adsorbed on Fly Ash

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ABSTRACT

It is expected that increased controls on Hg emissions will shift the environmental burden from the flue gas to the solid coal utilization by-products (CUB), such as fly ash and flue-gas desulfurization residues. If Hg can be leached from fly ash, it will have an impact on utilization, particularly for those uses that may allow for transport of the mercury into surface or ground water. Assuming that powdered activated carbon (PAC) injection will be the dominant control technology, researchers at NETL have compared the stability of Hg on fly ash samples containing PAC to samples containing unburned carbon. Column leaching studies of nine high mercury fly ash samples (3 from high mercury coal, 3 from pilot scale studies of PAC injection, and 3 from full scale PAC injection tests), indicated that mercury on both types of fly ash is only slightly soluble. The cumulative amount of mercury leached was less than 1 % of the amount present in the fly ash sample. However, unlike other metals, the dominant control on Hg stability does not appear to be pH. Although in different samples Hg was most soluble in alkaline or acidic solutions, it was more soluble in acetic acid (pH 2.9) than in sulfuric acid (pH 1.2). Also, acetic acid soluble Hg continues to be released at a low but constant rate. Comparing samples with similar C concentrations, lower Hg release was more frequently associated with samples containing PAC rather than unburned carbon.

INTRODUCTION

Approximately one billion tons of coal is consumed in utility boilers each year to generate electric power in the United States¹. During combustion, mercury (Hg), both elemental (Hg^0) and oxidized (Hg^{+1} and Hg^{+2}) is vaporized and emitted in the flue gas. According to the Environmental Protection Agency (EPA), almost 1/3 of anthropogenic Hg released to the environment in the U.S. is emitted from this source². It is expected that increased controls on Hg emissions will shift the environmental burden from the flue gas to the solid combustion by-products, fly ash and flue-gas desulfurization residues. If Hg can be leached from the CUB, the beneficial uses of CUB may be in jeopardy. This is particularly true for those uses that may allow for transport of the mercury into surface or ground water.

To predict the environmental fate of the CUB-bound Hg, it is important determine the magnitude of and conditions for its release. Adsorption on the carbon phase is the primary mechanism for the removal of mercury from flue gas in all three of its oxidation states ($\text{Hg}_{\text{TOT}} = \text{Hg}^0 + \text{Hg}^{+1} + \text{Hg}^{+2}$)³⁻⁵. It is assumed that the small fraction of Hg^0 that is directly captured is contained primarily in the carbon phase of the CUB⁶⁻⁷. Elemental Hg adsorption increases with increasing surface area of the carbon phase⁶.

The adsorption of both Hg^0 ¹⁴ and Hg_{TOT} ^{3-5,7} increases as temperature decreases. The extent of Hg_{TOT} adsorption increases as residence time increases¹³. Because Hg is captured at temperatures below 175 °C (350 °F)^{3,7}, solidification of the ash particles can be considered complete, and no encapsulation of the Hg within mineral particles would be expected. This indicates that Hg is captured on the surfaces, or within the pores, of existing particles, probably unburnt carbon (UBC) or injected powdered activated carbon (PAC) through a surface adsorption or pore-filling mechanism.

The adsorption of Hg by fly ash is viewed as a simple surface-coverage or pore-filling of an ionic mercuric compound on a carbonaceous substrate. Since physical adsorption provides a weak bond, Hg^0 on the ash will volatilize relatively quickly. The persistent Hg in fly ash is Hg^{+2} in the pores of the carbon phase, most likely HgCl_2 , HgO , or HgSO_4 .

The extent to which adsorbed Hg^{+2} can be extracted from fly ash into an aqueous environment is a potential constraint on utilization and disposal. Fly ash bound Hg^{+2} can be released by partitioning between adsorbed and dissolved phases. Understanding the conditions which enhance or retard mercury release from fly ash may provide confidence in estimates of the long-term immobility under environmental conditions. Since currently available data are not adequate for estimating potential release of adsorbed Hg from CUB, we have used a column leaching method to determine the magnitude and conditions of aqueous release of Hg from fly ash.

METHODS AND MATERIALS

The column leaching system was designed to simulate the reaction of materials during exposure to fluids encountered in nature, such as acid rain or acid mine drainage, and is appropriate for unconsolidated materials with a particle diameter of less than 0.5 cm^8 . The columns are constructed of 1 meter sections of 5 cm ID acrylic pipe with an approximate volume of 2 L. Each column holds a representative 1 kg sample. Threaded PVC pipe caps close each end; 0.635 cm fittings are tapped into the ends for leachant inflow and leachate outflow. Ten g of glass wool is placed in the bottom of the column, then the sample is poured in and another 10 g of glass wool is placed on top of the sample. A cap seals the column, and it is hung on a distillation rack. Four different CUB samples are leached in each test (Fig. 1).

A peristaltic pump delivers leachant solution from a 20 L reservoir to individual delivery lines for each of four columns. The flow rate is approximately 130 mL/d. The leachant solutions are listed in Table 1. Leachate was collected in 1 L volumetric cylinders; pH and leachate volume were measured when samples were taken for analysis at 2 to 3 day intervals.

The concentration of dissolved Hg was determined by cold vapor atomic absorption (CVAA); the detection limit was $0.004 \mu\text{g/L}$. Mercury concentration in the solid samples was determined by Direct Mercury Analyzer (Milestone's DMA-80) with a detection range of 0.02 ng to 600 ng. The carbon content of the fly ash samples is estimated by the loss on ignition (LOI), determined by heating to a constant weight at 750 EC. In conventional ash samples, the LOI is assumed to represent the unburned carbon (UBC). In an ACI test, it is assumed that the LOI represents the

excess activated carbon, since there is no simple technique to differentiate between the two types of carbon particles. The LOI may slightly overestimate the carbon concentration, due to the possible loss of sulfur oxides and carbonates from the sample.

Leaching tests were conducted on 9 fly ash samples (Table 2) that have Hg contents significantly higher than the average (~0.01 - 0.2 mg/kg) for CUB. Samples FA50, FA53, FA56 and FA58 were generated in the NETL 500 pound/hr coal combustion pilot plant that is designed to accurately model the operation of a commercial tube wall boiler. The first three of these samples were collected during a test of Activated Carbon Injection (ACI) upstream of a pulse-jet baghouse. Compared to the Hg concentration of an average PC sample, the Hg concentration of these samples was high, but the LOI seemed low for an ACI test. Sample FA58 was produced from combustion of the same coal under the same conditions but without ACI.

Sample FA52 was produced during a full-scale ACI test at a commercial utility⁹. The Hg concentration of this sample was much higher than the other samples. The LOI was also high, and the concentration of Hg with respect to LOI was 5 to 8 times higher than that from other commercial boilers.

Sample FA55 was also produced in a full scale test at a commercial utility¹⁰. This sample had a high LOI, but a lower Hg concentration; the ratio of Hg to LOI was lower than that of other samples. Sample FA63 was also produced from a full scale ACI test at a plant with a cold side ESP¹¹. This plant also had a urea based selective non-catalytic reduction system (SNCR) to control NO_x. The SNCR was found to have no effect on Hg removal.

Samples FA51, FA57, and FA62 were fly ashes generated in commercial PC boilers from high Hg coals without ACI. Sample FA57 was obtained during the operation of an SCR/SNCR unit. The concentration of Hg relative to LOI was within in the range of the samples from the ACI tests.

RESULTS AND DISCUSSION

The maximum amount of Hg leached from a fly ash sample during the test was 1.6 µg/kg from a sample without ACI and 1.2 µg/kg from an ACI sample (Table 3). For all other samples, the maximum extractable concentration was less than 1µg/kg. The amounts leached in H₂O and SP were of the same order of magnitude for 1/3 of samples, while at least twice as much Hg was leached from the rest of the fly ash samples by H₂O than by the lower pH SP. The effect may not have been related to the acid concentration, since for all but one of the samples, more than twice as much Hg was released in the HAc leachant (pH = 2.9) than in the H₂SO₄ (pH = 1.2). For three of the samples, the maximum amount of Hg was released by the alkaline Na₂CO₃ leachant.

The amount of Hg leached is apparently not directly related to the Hg concentration of the fly ash (Table 4). The samples with the lowest and highest concentrations of Hg released very low amounts of Hg. The amount of Hg released varied by several orders of magnitude for the other samples that had similar Hg concentrations. On a relative basis, the maximum amount of Hg released was 0.70%, and the average amount was less than 0.03% over time periods that varied from 2 months to one year.

Usually, the release of Hg from the fly ash samples occurs over a relatively short time interval. The maximum concentration in a leachant may be 10 to 20 times the average concentration, and only a limited number of samples are much greater than the background level. For these samples even the maximum concentration in any leachant does not represent a hazardous release of Hg (Table 5). The maximum concentration of Hg for all but two leachant /sample combinations was less than 10% of the primary drinking water (PDW) standard of 0.002 µg/L or 2000 ng/L. Both of the higher measured concentrations were leached from the same sample. The Hg released in a H₂O sample was only 11% of the PDW, while the Hg concentration in the high pH Na₂CO₃ for one leachate sample was approximately half of the PDW.

When the amount of Hg leached is compared to the LOI, an approximate measure of the C content, there is also no apparent relationship. One would expect that as the LOI increased, the amount of Hg released would decrease. And Sample FA52, a PC ACI sample that had the highest Hg concentration and also highest LOI, did release the lowest amount of Hg in all

leachants. From the results of these tests, it is not clear if there is a difference between powdered activated carbon (PAC) and unburned carbon (UBC).

The solubility of most metallic elements in fly ash is strongly pH dependent¹² Heavy metals are released when the leachate is acidic, while oxyanions tend to be more soluble at high pH.

Particularly for the acid soluble ions, the soluble concentration is a function of the H⁺ concentration, and apparently is not affected by the acidic cation. The release of Hg does not follow this pattern.

For this group of 9 samples, Hg is most soluble in HAc for five of the samples; two to ten times more soluble than in the more acidic H₂SO₄. This may indicate that Hg released from the CUB reacts with the leachant to form very soluble Hg⁺² acetate. However, it cannot be assumed that the Hg released from the CUB is originally present as HgCl₂ in all samples, since the H₂O soluble Hg shows no correlation to the HAc soluble Hg. Only FA 63, the SNCR ash, is most soluble in H₂SO₄. Hg in three of the other samples is most soluble in the alkaline Na₂CO₃ leachant; in one sample there is less than 10 ng/kg difference in the cumulative amount leached by HAc and Na₂CO₃. The current analysis indicates no obvious factor that distinguishes the samples that were HAc leachable from the Na₂CO₃ leachable.

It does seem that the amount of Hg soluble at high pH is limited. It is released during a relatively short interval; then the slope of the cumulative curve approaches zero as the concentration in the leachate is close to or below the detection level.

For those samples with a higher solubility in HAc, the release of Hg continues for an undetermined time at a relatively low rate (Fig. 2). The slope of the cumulative curve varied between 4 and 30 ng/kg/L for the fly ash samples that exhibited greater Hg solubility in HAc. The magnitude of the rate is not a function of the concentration of Hg in the fly ash.

SUMMARY

Long term leaching tests with several leachant solutions covering a broad pH range indicate that the Hg in flue gas that is captured on fly ash is stable. Less than 1% of the amount of Hg in the

samples tested was extracted, even under acid or basic conditions that exceeded those found in nature. From some samples, Hg was more extractable at high pH. For other samples, HAc extracted more Hg than the more acidic H₂SO₄, probably due to the greater solubility of Hg (II) acetate.

The cumulative release of Hg was not related to the source of the samples or to the concentration of Hg. The amount of carbon, either as unburned carbon from the coal or as activated carbon injected in control tests, could not be directly correlated to the release of Hg. Although the results of these leaching tests did not clarify the factors that control the release of Hg from fly ash, they clearly indicate that Hg in fly ash is very stable.

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Table 1. Leachant Solutions In NETL Column Leaching System.

Leachant Solution	pH	ID
Sulfuric Acid	1.2	H ₂ SO ₄
Acetic Acid	2.9	HAc
Synthetic Precipitation ^a	4.2	SP
Deionized (DI) Water	6	H ₂ O
Sodium Carbonate	11.1	Na ₂ CO ₃

^aDI H₂O pH adjusted by drop-wise addition of 60/40 mixture of H₂SO₄ and HNO₃

Table 2. Source, Hg concentration and LOI of fly ash samples.

Sample # ^a	Combuster	Control	Hg, mg/kg	LOI ^b , %
FA50	NETL 500#	ACI	1.096	1.31
FA51	PC	None	1.669	6.46
FA52	PC	ACI	92.067	28.66
FA53	NETL 500#	ACI	1.041	2.45
FA55	PC	ACI	1.380	16.08
FA56	NETL 500#	ACI	1.069	1.89
FA58	NETL 500#	None	0.074	1.79
FA62	PC	None	0.878	2.34
FA63	PC	ACI	0.348	6.83

^aSample # refers to NETL Coal Utilization By-Product Inventory

^bLoss on Ignition (LOI) is assumed to be the equivalent of carbon content, either unburned carbon(UBC) or powdered activated carbon (PAC).

Table 3. Maximum amount of Hg leached from fly ash samples, ng/kg

Sample #	Combuster	Control	H ₂ O	HAc	Na ₂ CO ₃	SP	H ₂ SO ₄
FA50	NETL500#	ACI	108.08	410.14	129.50	94.48	147.69
FA53	NETL500#	ACI	10.17	112.31	8.04	14.51	24.96
FA56	NETL500#	ACI	51.13	145.64	57.62	23.05	42.52
FA52	PC	ACI	2.74	46.54	26.38	2.71	4.15
FA55	PC	ACI	845.79	43.11	1263.06	464.84	83.14
FA63	PC	ACI	29.76	35.48	21.48	4.34	120.63
FA51	PC	None	12.18	1614.78	6.69	9.26	20.18
FA58	NETL500#	None	15.32	44.73	517.04	0.39	12.22
FA62	PC	None	47.77	144.07	153.48	9.34	68.29

Table 4. Cumulative Hg release relative to solid concentration, %

Sample #	Combuster	Control	H2O	HAc	Na2CO3	SP	H2SO4
50	NETL 550#	ACI	0.010	0.037	0.012	0.009	0.013
53	NETL 500#	ACI	0.001	0.011	0.001	0.001	0.002
56	NETL 500#	ACI	0.005	0.014	0.005	0.002	0.004
52	PC	ACI	<0.001	<0.001	<0.001	<0.001	<0.001
55	PC	ACI	0.061	0.003	0.092	0.034	0.006
63	PC	ACI	0.009	0.010	0.006	0.001	0.035
51	PC	None	0.001	0.097	0.000	0.001	0.001
58	NETL 500 #	None	0.021	0.061	0.700	0.001	0.017
62	PC	None	0.005	0.016	0.017	0.001	0.008

Table 5. Maximum sample concentration of Hg leached from CUB samples, ng/L.

Sample #	Combuster	Control	H2O	HAc	Na2CO3	SP	H2SO4
FA50	NETL 500#	ACI	22.80	48.00	56.80	21.20	22.60
FA53	NETL 500#	ACI	4.60	20.10	6.50	17.50	15.70
FA56	NETL 500#	ACI	13.70	22.10	27.10	4.40	8.70
FA52	PC	ACI	4.40	116.00	37.80	6.60	7.80
FA55	PC	ACI	222.00	36.70	1460.00	152.00	39.60
FA63	PC	ACI	20.00	21.70	6.90	2.50	86.30
FA51	PC	None	10.20	112.00	12.80	12.00	33.20
FA58	NETL 500#	None	9.90	13.50	64.40	1.40	4.70
FA62	PC	None	43.20	52.30	168.00	8.40	65.00

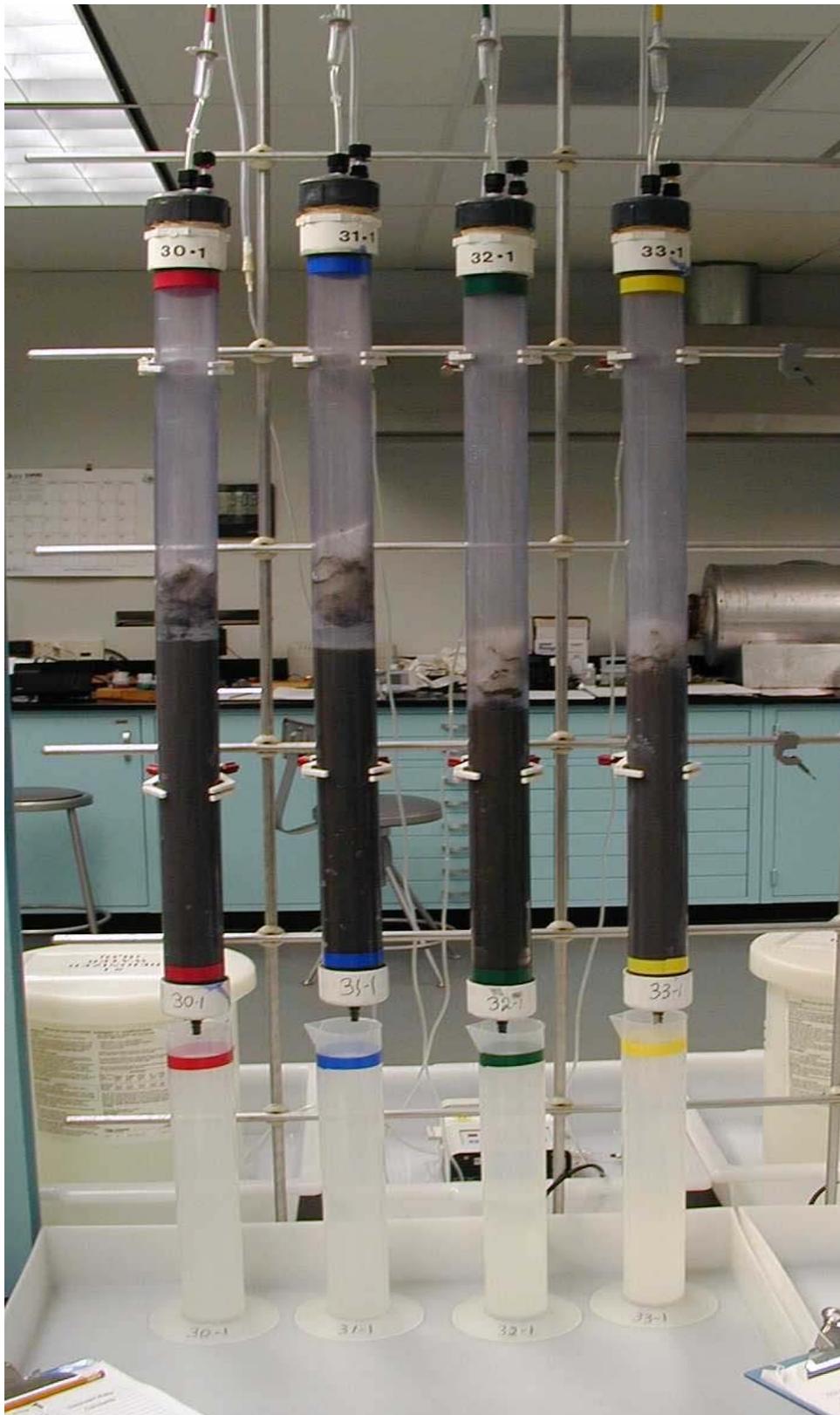


Figure 1. Column leaching system

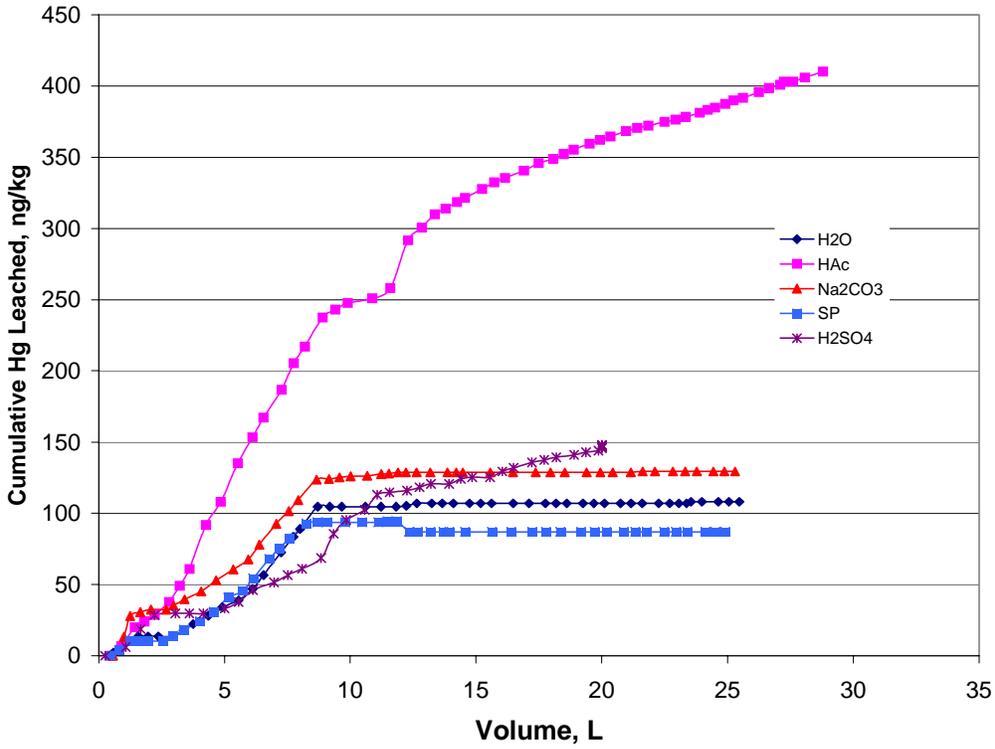


Figure 2. Cumulative release of Hg from FA50. Hg concentration falls below detection limit for all leachants except HAc.

