

COMPARISON OF LEACHING RESULTS FOR THREE HIGH MERCURY FLY ASH SAMPLES

George Kazonich*

U.S. Department of Energy
National Energy Technology Laboratory
Environmental Science and Technology Division
P.O. Box 10940
Pittsburgh, PA 15236

Ann G. Kim

U.S. Department of Energy
National Energy Technology Laboratory
Environmental Science and Technology Division
P.O. Box 10940
Pittsburgh, PA 15236

Michael D. Dahlberg

U.S. Department of Energy
National Energy Technology Laboratory
Environmental Science and Technology Division
P.O. Box 10940
Pittsburgh, PA 15236

ABSTRACT

Researchers at the National Energy Technology Laboratory (NETL) studied the release of mercury (Hg) from fly ash. FA51 (1.614 ppm Hg) was produced in a commercial utility burning a high Hg coal. FA52 (89.3 ppm Hg) was generated in a full scale test of activated carbon injection (ACI). FA53 (1.091 ppm Hg) was from an ACI test in a NETL combustion pilot plant. One-kg samples of each fly ash were leached in columns with five lixiviants which varied from acidic to alkaline. The concentration of Hg in the leachates of all three samples was less than 80 ng/L. FA52 produced approximately 2 L of leachate. The other two ash samples were leached with 12 to 64 L of lixiviant, and the concentration of Hg in the leachates fell below the detection limit by the end of most tests. In the acetic acid leach of FA51, Hg concentrations remained between 20 and 50 ng/L for nearly a year; and the cumulative leached amount was 0.10% of the Hg in the sample. The total Hg leached from FA52 and FA53 was less than 0.01% of the Hg in the ash. Acetic acid leached 5 to 100 times more Hg than the other solutions.

INTRODUCTION

Approximately one billion tons of coal is consumed each year for generation of electrical power in the United States. Between 6% and 9% of the weight of coal burned by a utility is recovered as fly ash. About 30 million short tons of fly ash were produced in 1970, 50 million in 1980, 60 million in 1996, and 63 million tons in 2000 (ACAA, 2003). Fly ash is commonly used as fill material and in mining applications, where it could be exposed to naturally-occurring acids, possibly releasing metals contained in the fly ash. In order to understand the reactions of coal utilization by-products (CUB) with environmental liquids, the National Energy Technology Laboratory (NETL) has been conducting a long term leaching study on the release of metals in acidic, neutral, and alkaline solutions.

Citing a "plausible link" between emissions of Hg from fossil fuel-fired power plants and methyl mercury in fish, the U.S. Environmental Protection Agency (EPA) announced in December 2000 that it would regulate emissions from coal-and oil-fired power plants (EPA, 2000). EPA is developing a "maximum achievable control technology" standard that may require as much as 90% Hg capture. Generally, the Hg removed from the flue gas will be captured with the CUB. As part of the DOE Innovations for Existing Plants (IEP) program, NETL is conducting a broad spectrum of research projects that are focused on the development of cost-effective Hg control technology for coal-fired power plants (NETL, 2003). This research includes the characterization of Hg and other metals in CUB, and determining their stability in current beneficial uses.

In our earlier studies with fly ash samples from pulverized coal (PC) boilers, the average Hg content of 31 Class F PC fly ash samples was 0.19 ppm Hg. Leachate Hg concentrations were generally below the detection levels of the ICP-AES. In contrast, fly ash samples from experiments on various methods of removing Hg from flue gas were found to range between 1 and 89 ppm Hg. Using cold vapor atomic absorption (CVAA), the Hg concentration in leachates can be determined to less than 1 ng/L.

EXPERIMENTAL

Equipment and Procedures

The fly ash leaching system utilizes columns constructed of 1 m sections of clear PVC pipe. The pipe has a 5 cm inside diameter and a volume of approximately 2 L. PVC pipe caps close each end and have fittings for lixiviant inflow and leachate outflow. Columns are loaded by putting ten g of glass wool into an empty column and pushing it against the bottom cap. The fly ash is then poured into the column and another 10 g of glass wool is inserted on top. The top cap is screwed on and tightened, and the sealed column is hung vertically. The column is then connected to the lixiviant delivery system. A peristaltic pump feeds liquid from a reservoir containing 20 L of lixiviant to 4 or 5 leaching columns containing different fly ash samples. Current flow rates with the peristaltic pumps are 230 mL/day/ column ($\pm 10\%$).

Each leaching test includes 4 samples with 5 different lixivants (Table 1) for a total of 20 columns. Each fly ash sample is leached from 60 to 180 days, although one high Hg sample was leached for a year. Leachate samples are collected at 2 to 3 day intervals if flow is sufficient. Samples are analyzed for pH, acidity or alkalinity, aluminum, calcium, iron, magnesium, manganese, potassium, sodium, sulfate and the toxic metals: antimony, arsenic, barium, beryllium, cadmium, chromium, cobalt, copper, lead, mercury, nickel and zinc.

Table 1. Lixivants for column leaching tests.

Lixiviant	ID	pH
Sulfuric Acid ¹	H ₂ SO ₄	1.2
Acetic Acid ¹	HAc	2.9
Synthetic Precipitation ²	SP	4.2
Deionized Water	H ₂ O	6.0
Sodium Carbonate ¹	Na ₂ CO ₃	11.1

¹Concentration = 0.1 N; ² deionized water adjusted to pH 4.2 with a 60/40 mixture of H₂SO₄/HNO₃

Samples and Testing

This paper focuses on three different fly ash samples. Sample FA51 was produced in a commercial PC power plant burning a high Hg coal. Other than the high Hg levels, FA51 was a typical Class F fly ash sample.

Sample FA52 was produced during a full-scale activated carbon injection (ACI) test at a commercial utility. The Hg concentration of this sample was about 100 times higher than the other “high” Hg ashes and about 1000 times more than most PC fly ash. Powdered activated carbon was injected into the flue gas between a hot-side ESP (which removed 99% of the fly ash) and a COHPACTM baghouse. More than 95% of the sample from the baghouse had a particle diameter of less than 0.08 mm; less than 80% of a conventional PC fly ash, on average, falls within this range. The fine particle size produced a high resistance to liquid flow, and the high carbon content of FA52 inhibited wetting of this sample. These factors greatly reduced lixiviant flow through FA52. Generally, the maximum flow rate through a fly ash sample is >1 L/d; the average HAc flowrate through FA52 was less than 14 mL/day.

Sample FA53 was generated in the NETL 500 pound/hr coal combustion pilot plant. This plant was designed to accurately model the operation of a commercial tube wall boiler. FA53 was the product of burning a high Hg coal, ACI, and collection in a baghouse. The LOI of this sample was relatively low, considering that activated carbon had been injected. Sample characteristics are summarized in Table 2.

Table 2. Characteristics of fly ash samples.

Sample# ¹	Combustor	Hg Control	Hg, $\mu\text{g}/\text{kg}$	LOI, %	Hg/C, $\mu\text{g}/\text{g}$
FA51	PC	None	1614	6.46	25
FA52	PC	ACI	89338	28.66	312
FA53	NETL 500#	ACI	1091	2.45	45

¹ Sample# refers to the number assigned in the NETL CUB sample inventory.

When the pumps were shut down at the end of the test, the Hg content of the leachates increased. This was because once the bulk flow of liquid in the column had drained, the remaining liquid surrounding the particles was of much higher Hg concentration. Consequently, the Hg concentration of the leachate increased from the time the pumps were shut down until liquid stopped flowing. Also, there is a possibility that Hg oxidation increased as the columns drained and the fly ash particles were re-exposed to air. Evaporation may also have concentrated the last leachates since the final samples took between one week and one month to collect. To eliminate confusion from these effects, the last few data points from each test were not used in this presentation. The results displayed should be more representative of the results of continuous leaching and consequently be a better prediction of what might occur when fly ash is leached in a specific environment.

RESULTS AND DISCUSSION

In general, very little Hg was released from the 3 fly ash samples during the testing period. Some of the leaching tests were shut down at the end of 3 months because the Hg concentration had fallen below the detection limit of 0.5 ng/L. The rest of the columns were operated for an additional 1 to 2 months. At the end of 5 months, the concentrations of Hg in the acetic acid leachates from FA51 were still between 20 and 50 ng/L. The leaching was continued for an additional 7 months (a total of one year of continuous leaching); when the test was terminated, the Hg concentration of the acetic acid leachate was 29 ng/L.

Mercury extraction, as shown in the graph of Hg concentration versus cumulative volume for water leaching of the three fly ash samples (Figure 1), was not typical of leaching reactions. The first part of the leaching curve for FA51 is a normal leaching curve in which the concentration in the leachate is highest in the initial sample then declines to below the detection limit as leaching continues. At 5 liters (L), however, the Hg concentration in two leachate samples increased abruptly. Subsequent samples were all below the detection level. The concentration of Hg from FA53 ranged from below the detection level (< 1 ng/L) to 3 ng/L during the H₂O leach. This may be due to analytical calibration changes on concentrations near the detection limit. The high resistance to liquid flow limited the total leachate for FA52 to slightly more than 2 L over a 5-month period. The concentrations of Hg in the leachates of FA52 are of the same magnitude as those of FA53 even though FA52 had 90 times more Hg in the ash sample being leached. Some of the variations in Hg concentration in the leachates of FA52 may also have been caused by leachate evaporation because 1 month was needed to collect each of the last 2 samples.

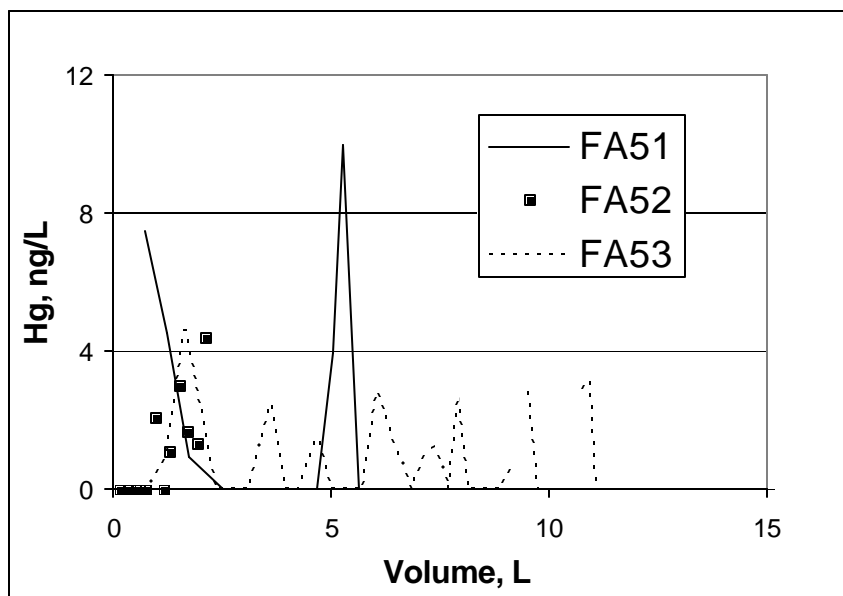


Fig. 1. The concentration of Hg in leachates when fly ashes with relatively high Hg concentrations were leached with deionized water.

Similar variations in Hg concentration are seen in the graph of synthetic precipitation (SP) leachates (Figure 2), but the Hg concentrations are slightly higher.

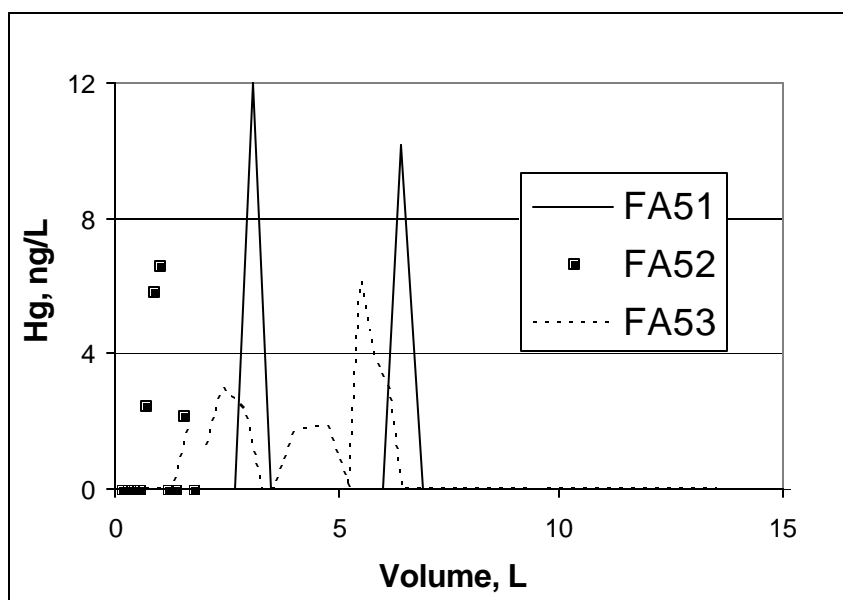


Fig. 2. The concentration of Hg in leachates when fly ashes with relatively high Hg concentrations were leached with synthetic precipitation.

The cumulative amount of Hg leached was generally more revealing. A decrease in the slope of a cumulative curve indicates that leaching is slowing, while a horizontal line shows that leaching has essentially stopped. Less than 15 ng of Hg was extracted from each of the 3 fly ash samples by deionized H₂O (pH 6) (Figure 3).

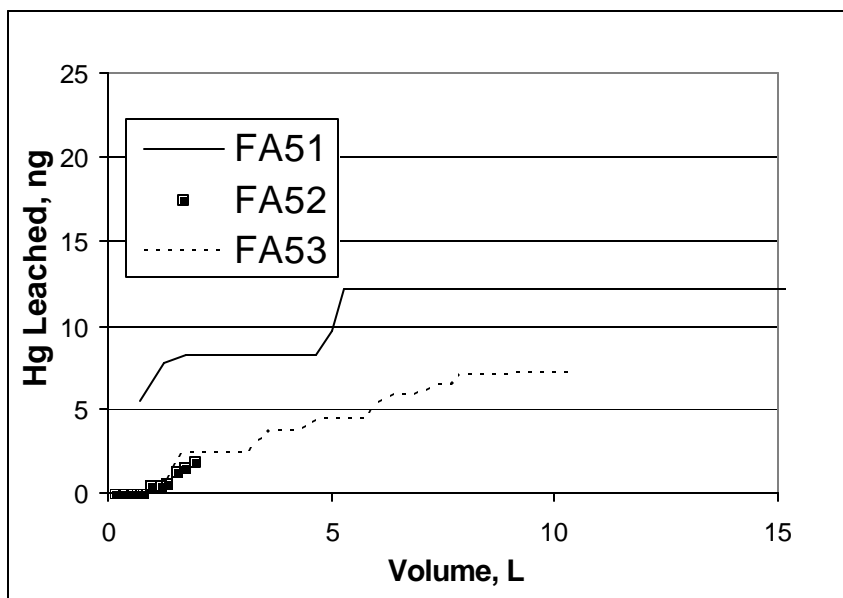


Fig. 3. The cumulative amount of Hg leached from a kg of each fly ash by deionized water.

With SP, it appears that less Hg was extracted from FA51, but more Hg was extracted from FA53 (Figure 4). Given the low total release and the analytical uncertainties, all of the totals for FA51 and FA53 shown on Figures 3 and 4 are essentially equal.

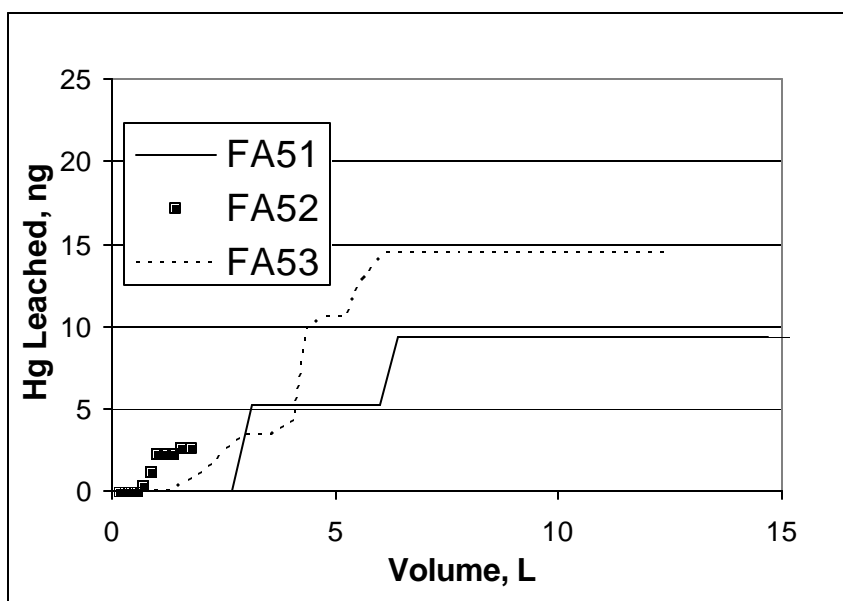


Fig. 4. The cumulative amount of Hg leached from a kg of each fly ash by synthetic precipitation (SP).

The amounts of Hg released from FA51 and FA52 in Na_2CO_3 (Figure 5) are slightly lower than the amounts for other non-acetic leachants. However, the Na_2CO_3 leach of FA52 extracted more Hg than the other leachants.

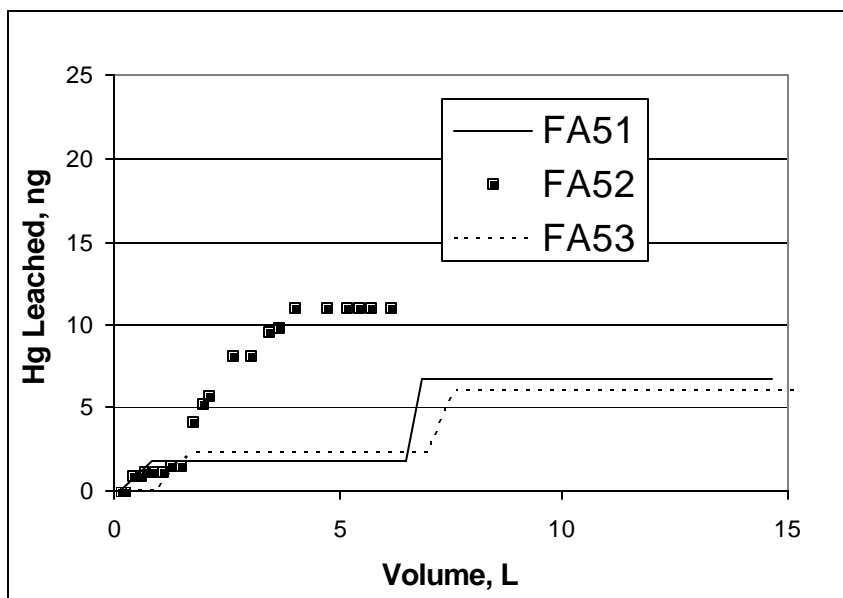


Fig. 5. The cumulative amount of Hg leached from a kg of each fly ash by Na_2CO_3 .

The amount of Hg released from FA52 in H_2SO_4 was comparable to that released in SP and H_2O although the total extractions (2-3 ng) were so low that differences may not have been detectable. The total Hg extracted in H_2SO_4 leaches of FA51 and FA53 is twice the average for SP and H_2O ; plots of H_2SO_4 extraction for FA51, FA52, and FA53 are shown in Figure 6.

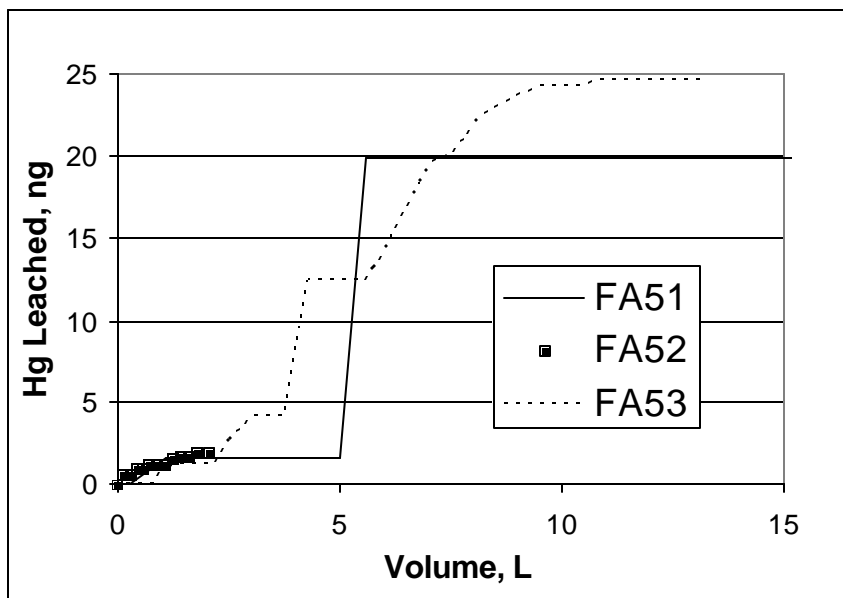


Fig. 6. The cumulative amount of Hg leached from a kg of each fly ash by H_2SO_4 .

The increased extraction of Hg as the pH of the leachate decreases indicates a positive relationship to H^+ concentration. However, pH is apparently not the dominant factor. As shown in Figure 7, the cumulative amounts of Hg released in acetic acid (HAc) were much greater than in the other acid leachants. HAc is more effective than its pH would predict,

presumably due to the high solubility of Hg acetate. Also, the releases of Hg continued at approximately constant rates throughout the tests (Table 3). FA51 did not contain activated carbon, which may partially account for the much higher release rate.

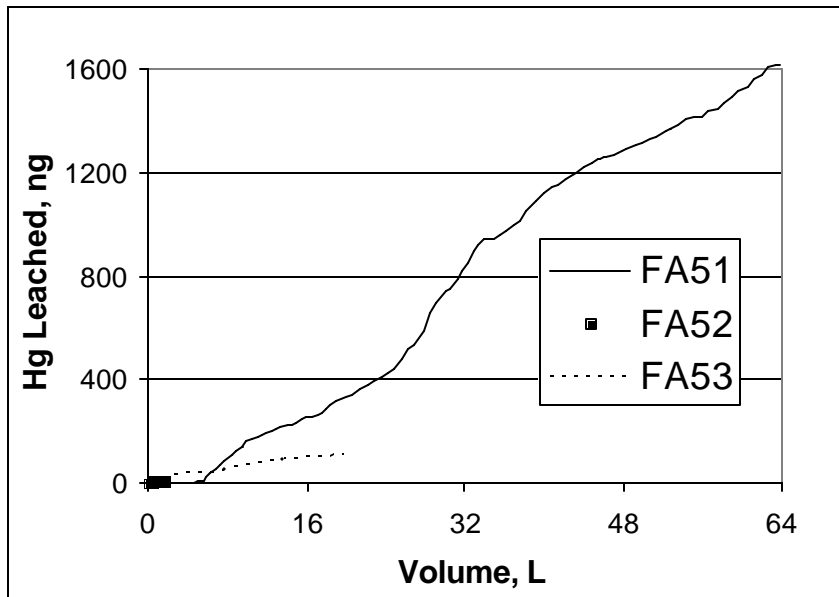


Fig. 7. The cumulative amount of Hg leached from a kg of each fly ash by acetic acid (HAc).

Table 3. Average rates of Hg release.

	FA51		FA52		FA53	
	ng/L	ng/d	ng/L	ng/d	ng/L	Ng/d
H ₂ SO ₄	1.016	.249	.943	.025	1.863	.093
HAc	25.318	4.654	5.176	.039	5.439	.113
SP	.601	.114	1.507	.006	1.171	.226
H ₂ O	.732	.150	.951	.026	.709	.141
Na ₂ CO ₃	.457	.083	1.781	.000	.383	.000

The results of all leaching tests are summarized in Table 4.

Table 4. Total mercury extracted, relative extraction, time and volume for all tests.

Leachant	FA 51				FA 52				FA53			
	Hg,ng	%	t, d	V, L	Hg,ng	%	t, d	V, L	Hg,ng	%	t, d	V, L
H ₂ SO ₄	20	.0013	81	19.9	2	<.0000	133	2.1	25	.0023	79	13.2
HAc	1615	.1000	347	63.8	9	<.0000	127	1.8	107	.0098	133	19.7
SP	9	.0006	81	15.4	3	<.0000	133	1.8	15	.0013	79	12.4
H ₂ O	12	.0008	81	16.6	2	<.0000	133	1.9	7	.0007	79	10.0
Na ₂ CO ₃	7	.0004	81	14.7	11	<.0000	137	6.2	6	.0005	79	15.7

With the exception of the two acetic acid leaches, all of the leaching tests extracted less than 25 ng of Hg from the 1 kg fly ash samples (Figure 8). That amount of Hg was about 0.001 % of the Hg in FA51 and 0.002 % of the Hg in FA53 (Figure 9). Because FA52 contained so much Hg, none of the extractions exceeded 0.00001% of the Hg in that sample.

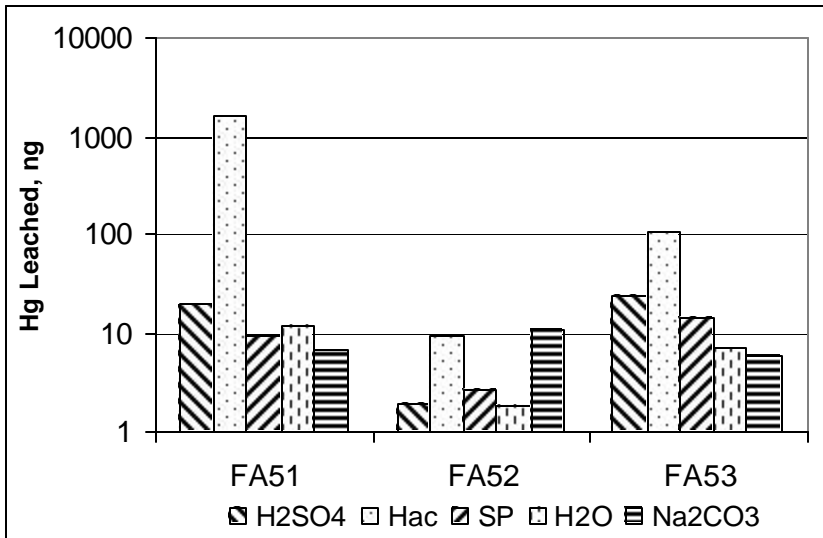


Fig. 8. Total amount of Hg leached from a kg of each fly ash by the various lixiviants.

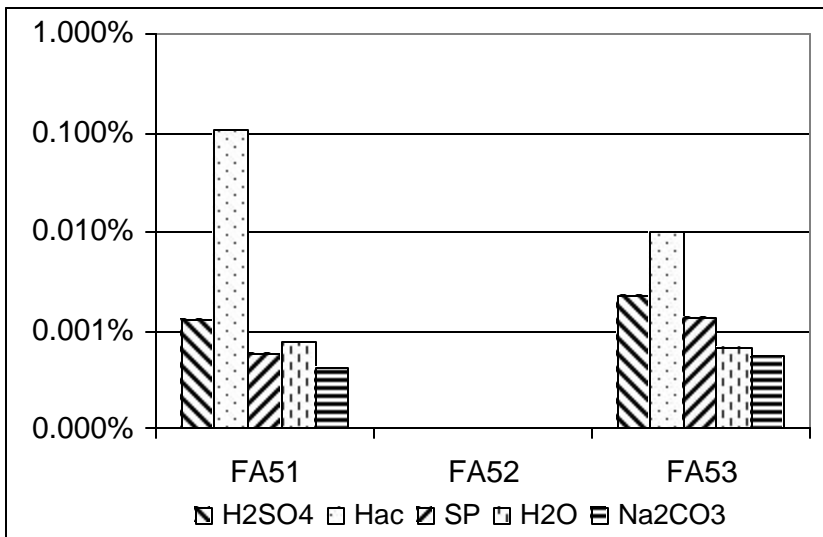


Fig. 9. The total amount of Hg leached from each fly ash by the various lixiviants as a percentage of the total amount of Hg present in the ash.

CONCLUSIONS

The concentration of hydrogen ions (H^+) in the leachant had a weak relationship to Hg extraction as evidenced by the increasing average extraction for all three fly ash samples by Na_2CO_3 , H_2O , SP, and H_2SO_4 (0.0003%, 0.0005%, 0.0006%, and 0.0012% respectively). HAC was much more effective than its pH would justify with an average extraction of 0.0366%. HAC continued to extract Hg from the solids (for 1 year in the FA51 test) rather than stopping like the other leachants. The HAC also leached Hg faster than the other leachants (Table 3). The HAC leaching rate for FA51 was 25 to 55 times faster than the other leachants on a volume basis.

However, even for the acetic acid leaches, the 107.1 ng of Hg extracted from FA53 was only 0.01% of the Hg in the ash, and the 1614.8 ng extracted from FA51 was only 0.10% of the Hg in that sample. Thus, it appears that very little of the Hg in the fly ashes was susceptible to mobilization by leaching. Moreover, if one assumes that most of the Hg in the fly ash is associated with carbon, it appears that the powdered activated carbon (PAC) in FA53 resisted Hg dissolution 10 times better than the unburned carbon (UBC) in FA51. And because FA51 had nearly 3 times as much carbon as FA53, PAC could be 30 times more effective at holding Hg than UBC. The true factor could be even higher because some of the 2.45% LOI in FA53 was probably UBC. None of the other leachants demonstrated a large difference in the effectiveness of PAC versus UBC but the extraction of Hg by the other leachants was so low (10 of the 13 extracted less than 0.001%) that the difference may have been undetectable. FA52 had an LOI of 28.66%, predominantly due to PAC. It released an average of only 0.000006% of the Hg that it contained.

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