

CHARACTERIZATION OF COAL COMBUSTION BY-PRODUCTS FOR THE RE-EVOLUTION OF MERCURY INTO ECOSYSTEMS

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ABSTRACT

There is concern that Hg in solid by-products of coal combustion could be emitted into local ecosystems during disposal and utilization. The two primary mechanisms for re-emission are leaching and revolatilization. To address this concern, CONSOL is conducting TCLP leaching tests and volatilization studies using a wide range of coal combustion materials, including fly ash, wet and dry FGD scrubber solids, and by-products made from FGD solids and fly ash. The TCLP leaching results for samples collected at 14 power plants are described in this paper. This work was supported by the U.S. Department of Energy (National Energy Technology Laboratory) and CONSOL Energy Inc.

INTRODUCTION

In December 2000, the U.S. Environmental Protection Agency, under the authority of the Clean Air Act Amendments of 1990, made a regulatory determination that mercury emissions from electricity generating plants must be reduced, using Maximum Achievable Control Technology (MACT), to protect public health. The definition of MACT for coal-fired power plants is still under evaluation, and various alternative legislative initiatives related to mercury control are under consideration. However, it is likely that wet or dry scrubbers installed for SO₂ control, and injection of carbon absorbents will be important technologies for mercury control at coal-fired power plants. The mercury that is collected in this manner will be retained in the solid by-products and may be disposed of in a landfill or, possibly, recycled into another product such as cement. This raises the concern that mercury retained on the solid products might be leached or volatilized, and thus reintroduced into the environment as a water or air emission. Previous work by CONSOL¹ had indicated that mercury in by-products from wet lime and limestone FGD units was stable with respect to leaching and volatilization, but that work was limited in the number and type of materials studied.

In response to this concern, the Department of Energy and CONSOL Energy are conducting a project to evaluate the potential for mercury leaching and volatilization from coal combustion by-products using the Toxicity Characteristics Leaching Procedure (TCLP) and a volatility test procedure designed specifically for this project. The project is designed to gather data for combustion byproducts representing every major coal-producing region, to evaluate the by-products from different types of FGD scrubbers, and to evaluate the impact of different end-uses of the by-products on the potential for mercury emission. Solid materials from sixteen different sources will be studied. In addition, ground water samples from two sites will be analyzed to evaluating mercury leaching. This paper will present results of the TCLP tests conducted to date.

EXPERIMENTAL

The materials studied in this project (Table 1) include coal, bottom ash, fly ash, FGD by-products, and products from activated carbon injection tests. They also include products made with coal combustion by-products such as Portland cement, gypsum wallboard, and manufactured aggregates. The solid samples are collected by participating utility personnel following a procedure written by CONSOL to ensure sample integrity and provenance.

Table 1. Sample Matrix.

Plant Code	Sample Type	FGD Type	Coal Source	Sampling Completed	Leaching Completed	Analyses Completed
1	C, BA, FA, FGDS	Mg/Lime	Pittsburgh Seam	X		
2	C, BA, FA, FGDS	Forced Oxidation	Pittsburgh Seam			
3	C, BA, FA, FGDS	Mg/Lime	Ohio 5, 6, or 11	X	X	X
4	C, BA, FA, FGDS	Natural Oxidation	Illinois 6	X	X	X
5	C, BA, FA, SDS	Lime Spray Dryer	Eastern Low Sulfur Bituminous			
6	C, BA, FA		Illinois/W KY Blend	X	X	X
7	C, BA, FA		Powder River Basin			
8	C, BA, FA		Powder River Basin			
9	C, BA, FA		Powder River Basin	X	X	X
9a	C, BA, FA	"Carbon Injection"	Powder River Basin	X	X	X
10	C, BA, FA	CFB Boiler	Waste Bit. Coal			
11	FA	CFB	Eastern Low Sulfur Bit.	X	X	X
13	C, BA, FA, FGDS	Mg/Lime	Pittsburgh Seam	X	X	
14	FGDS, SDS, Aggregate	Lime Spray Dryer	Eastern Low Sulfur Bit.	X	X	X
15	FGDS, SDS, Aggregate	Inhibited Oxidation	Pittsburgh Seam	X	X	X
16	C, BA, FA, FGDS	Mg/Lime	High Sulfur Ohio	X	X	X

To evaluate the leaching potential of these materials, the program employs the TCLP described in EPA Method 1311 and ASTM Method 3987 with the leaching solutions buffered to three pHs (2.8, 4.9, and distilled water). A TCLP sample handling flow chart is presented in Figure 1. The samples are analyzed after they are leached, by Cold Vapor Atomic Absorption according to ASTM D6414 "Total Mercury in Coal and Coal Combustion Residues by Acid Extraction or Wet Oxidation/Cold Vapor Atomic Absorption". The mercury is extracted from the coal/coal combustion residue by digesting the sample in a mixture of nitric and hydrochloric acids. Stannous chloride is mixed with an aliquot of the digestate to reduce the mercury to its elemental state. The mixture is aerated thus releasing the mercury as a vapor. The mercury is determined by cold vapor atomic absorption spectroscopy.

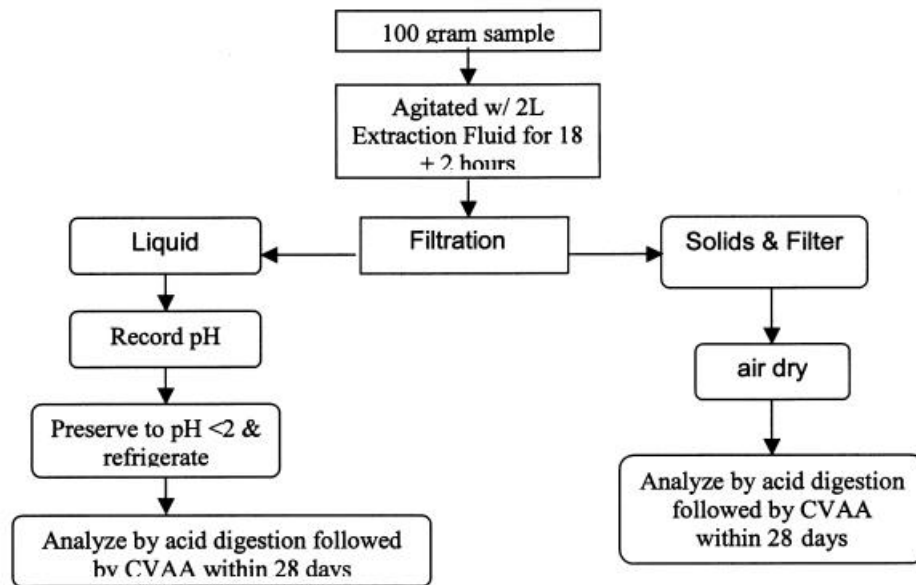


Figure 1. Flow chart showing sample leaching procedure.

A method developed in-house is used for mercury determination in liquid samples. It is essentially a liquid version of the D 6414 method, except there is no digestion step since the sample is already in liquid form. The sample is acidified with hydrochloric acid. Stannous chloride is mixed with an aliquot of the acidified sample to reduce the mercury to its elemental state. The mixture is aerated thus releasing the mercury as a vapor. The mercury is determined by cold vapor atomic absorption spectroscopy.

The volatility of the mercury in the solid samples is evaluated using a procedure designed by the authors. In the volatilization tests, two portions of the sample are heated in two ovens, one at 100 °F and the other at 140 °F. The samples are held at these temperatures for six months and the coal combustion by-product is sampled at three and six month intervals and its mercury content is determined. The revolatilization work is still in progress. These samples are analyzed by ASTM Method D 6722, "Total Mercury in Coal and Coal Combustion Residues by Direct Combustion Analysis". The mercury is extracted from the coal/coal combustion residue by decomposing the sample in a combustion tube at

approximately 750 °C. Carrier gas transports the mercury across a catalyst, which removes all interferences. The mercury is then removed from the gas stream by collection onto a gold coated ceramic substrate called the amalgamator. The amalgamator is heated to approximately 900 °C, releasing the mercury as a vapor. The mercury vapor is detected by an atomic absorption spectrometer.

The ground water in and around two combustion by-product disposal sites are being monitored for a one-year period. Samples are being collected quarterly from existing monitoring wells at each site, and from any seeps within the disposal area. Three aliquots of each sample are obtained. One is preserved with nitric acid; one is not preserved, and the third is treated to maintain the sulfite ion concentration for determination.

The status of the work is shown in Table 1.

RESULTS AND DISCUSSION

In Table 2, the results from the TCLP procedure are presented. About half of the samples have been leached thus far. As part of our statistical quality control, one-third of the collected samples are leached in duplicate. The table includes sample type, control equipment at the facility, coal type, and the mercury concentration of the various TCLP leachates. The mercury concentrations for all of the leachates are less than 1 part per billion. For comparison, the drinking water standard is 2 parts per billion.

Table 2. Mercury concentrations of TCLP filtrates.

Plant ID	Sample Type	Control Equipment	Coal Source	Hg Conc., ppb*		
				pH 4.9	pH 2.8	DI H ₂ O
9	ESP Ash	Carbon Injection - ESP	Powder River Basin	<1.0	<1.0	<1.0
4	Fly ash	ESP	Illinois 6	<1.0	<1.0	<1.0
15	Aggregate	Inhibited Oxidation	Pittsburgh Seam	<1.0	<1.0	<1.0
11	Fly ash	Circulating Fluidized Bed	Eastern Low Sulfur Bit.	<1.0	<1.0	<1.0
3	Coal	Mg/Lime	High Sulfur Ohio	<1.0	<1.0	<1.0
6	Fly ash	ESP	Illinois/W KY Blend	<1.0	<1.0	<1.0
14	SDA	Baghouse	Eastern Low Sulfur Bit.	<1.0	<1.0	<1.0
3	Bottom Ash	Mg/Lime	High Sulfur Ohio	<1.0	<1.0	<1.0

*For reference, the Primary Drinking Water Standard concentration for mercury is 2.0 ppb.

Because all of the concentrations shown in Table 1 are less than the detection limit of the analytical method used, selected samples were sent to Frontier Geoscience for analysis using mercury cold vapor atomic fluorescence, which has a detection limit of 0.2 parts per trillion. These results are shown in Table 3. All of the mercury concentrations are between 7 and 83 parts per trillion or 0.007 and 0.083 parts per billion.

Table 3. Cold vapor atomic fluorescence analyses of selected TCLP filtrates.

Plant Code	Sample Type	Scrubber Type	Coal Source	Frontier	Extraction Fluid	CONSOL
				Total Hg	pH	Total Hg
				ppt*		ppb
9	ESP Ash	ESP	Powder River Basin	11.0	4.98	<1.0
9	ESP Ash	ESP	Powder River Basin	38.0	2.90	<1.0
9	ESP Ash	ESP	Powder River Basin	7.5**	DI	<1.0
4	Fly Ash	ESP	Illinois 6	38.0	4.98	<1.0
4	Fly Ash	ESP	Illinois 6	50.0	2.90	<1.0
4	Fly Ash	ESP	Illinois 6	84.0	DI	<1.0

* Blank and dilution corrected

**This sample was run in duplicate with a relative percent difference of $\pm 4.0\%$.

The mercury concentrations in the coal combustion by-products were determined prior to the TCLP leaching procedure. After the TCLP leaching procedure was completed, the solid samples were dried and analyzed. The results from these pre- and post-leaching mercury determinations are presented in Table 4. The mercury concentrations after leaching are comparable to those of the as-received samples for most of the samples. In many cases, the post-leach concentration is higher than the pre-leach concentration. This could be due to non-mercury components being solubilized during the leaching procedure. Additional analyses will be performed to confirm this. The average of the ratios of the mercury concentrations before and after leaching is 1.00 ± 0.25 . This good agreement between the mercury contents of the solids before and after leaching supports the conclusion from the leachate analyses that little mercury is leaching from the coal combustion by-products tested, regardless of the leachate pH, within the range tested.

Table 4. Mercury concentrations of solids after TCLP extraction.

Plant ID	Sample Type	Mercury Concentrations, ppm				Average Post-Leach Pre-Leach
		Before Leaching	pH 4.9	pH 2.8	DI H ₂ O	
14	SDA	0.52 \pm 0.09	0.57	0.56	0.54	1.07
14	Aggregate	0.39 \pm 0.07	0.41	0.43	0.40	1.06
15	Sludge Filter Cake	0.41 \pm 0.07	0.53	0.57	0.54	1.33
15	Aggregate	0.39 \pm 0.07	0.31	0.29	0.33	0.79
11	Fly Ash	0.33 \pm 0.06	0.36	0.53	0.47	1.37
3	Coal	0.28 \pm 0.05	0.30	0.28	0.28	1.02
3	Fly Ash	0.07 \pm 0.02	0.07	0.08	0.08	1.10
3	Fly Ash	0.08 \pm 0.02	0.08	0.08	0.07	0.96
3	Bottom Ash	0.04 \pm 0.01	0.02	0.01	0.03	0.50
9	Ash	0.08 \pm 0.02	0.06	0.07	0.07	0.83

A sample of spray dryer ash that was converted into a manufactured aggregate (Plant 15 in Table 2) was subjected to the TCLP procedure. The manufactured aggregate process was developed by CONSOL Energy and is described elsewhere.² The TCLP results indicate that the mercury concentration in the leachate was below the detection limit of 1 ppb.

The volatilization testing is under way. The first three-month interval samples were analyzed. These results are still being evaluated.

CONCLUSIONS

1. A minimal amount of mercury is leached from coal combustion by-products, regardless of leachate pH in the range of 3 to 7. For the materials studied to date, less than 1 ppb of mercury has been detected in all of the leachate samples. One ppb is one-half of the drinking water standard.
2. Mercury determinations were made on several leachate samples using cold vapor atomic fluorescence analysis. The mercury concentrations ranged from 7 and 83 ppt, consistent with the <1 ppb concentrations determined by cold vapor atomic absorption.
3. The mercury concentrations of the solid samples after leaching are equivalent to those of the original samples. This is consistent with the results of the leachate analyses, that no significant quantity of mercury is leaching from the coal ash samples, the activated carbon injection sample, or the manufactured aggregate sample.

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