

The Evolution Of Mercury From Coal Combustion Materials And By-products

Cooperative Agreement DE-FC26-00NT40906



A. M. Schwalb & J. A. Withum

Mercury Control Technology R&D Program Review Meeting

Pittsburgh, PA

August 12-13, 2003

Today's Presentation

- Background
- Program objectives
- Benefits
- Experimental design
- Results to date
- Conclusions



Background

- Typical mercury concentration in coal is 0.05 to 0.20 $\mu\text{g/g}$
- Volatilized during combustion
- Coal mercury fate after combustion
 - Bottom ash
 - Fly ash
 - FGD solids
 - Stack gas
- Previous study by CONSOL
- What is the fate of mercury collected on fly ash and FGD solids?



Program Objectives

- Address concern for mercury evolution into ecosystems
- Gather data on materials from plants with various
 - Coal sources
 - A variety of air pollution control systems with and without scrubbers
 - By-product end uses



Experimental Design

- Sample types
 - Coal, bottom ash, fly ash, FGD sludge and spray dryer solids
 - Portland cement, wallboard, aggregates
- Leaching tests using standard methodology
- Volatility tests of our own design
- Groundwater sampling



Previous CONSOL Study

- Plant burning Ohio bituminous coal
- Mg/lime scrubber sludge (Fixated and Unfixated)
- TCLP leaching tests showed <1.0 ppb in leachate
- Solids analysis confirmed that no mercury leached

	Hg in Solids, ppm	
	Unfixated	Fixated
FGD Solids Before Leaching	0.70 _± 0.11	0.39 _± 0.07
FGD Solids After Leaching - pH 2.8	0.72 _± 0.12	0.38 _± 0.06
FGD Solids After Leaching - pH 4.9	0.73 _± 0.12	0.35 _± 0.06
FGD Solids After Leaching - DI water	0.68 _± 0.11	0.38 _± 0.06
Averages After Leaching	0.71 _± 0.11	0.37 _± 0.06



Source Matrix

Plant Code	Coal Source	Particulate Device	Control Technology	Sampling Completed	Leaching Completed	Analyses Completed	Volatilization Completed	Analyses Completed
1	Pittsburgh Seam	ESP	Mg/ Lime	X	X	X	X	X
2	Pittsburgh Seam	ESP	Forced Oxidation					
3	Ohio 5, 6, or 11	ESP	Mg/ Lime	X	X	X	X	X
4	Illinois 6	ESP	Natural Oxidation	X	X	X	X	X
5	Eastern Low Sulfur Bit.	Baghouse	Lime Spray Dryer					
6	Illinois/ W KY Blend	ESP		X	X	X	X	X
7	PRB	Baghouse		X	X	X		
8	PRB	Baghouse						
9	PRB	ESP		X	X	X	X	X
9a	PRB	ESP	w/ carbon injection	X	X	X	X	X
10	Waste Bituminous Coal	Baghouse	CFB					
11	Southern Appalachian Bit.	Baghouse	CFB	X	X	X	X	X
12	Manufactured Aggregate			X	X	X		
13	Pittsburgh Seam	ESP	Mg/ Lime	X	X	X	X	X
14	Eastern Low Sulfur Bit.	Baghouse	Lime Spray Dryer	X	X	X	X	X
15	Pittsburgh Seam	ESP	Inhibited Oxidation	X	X	X	X	X

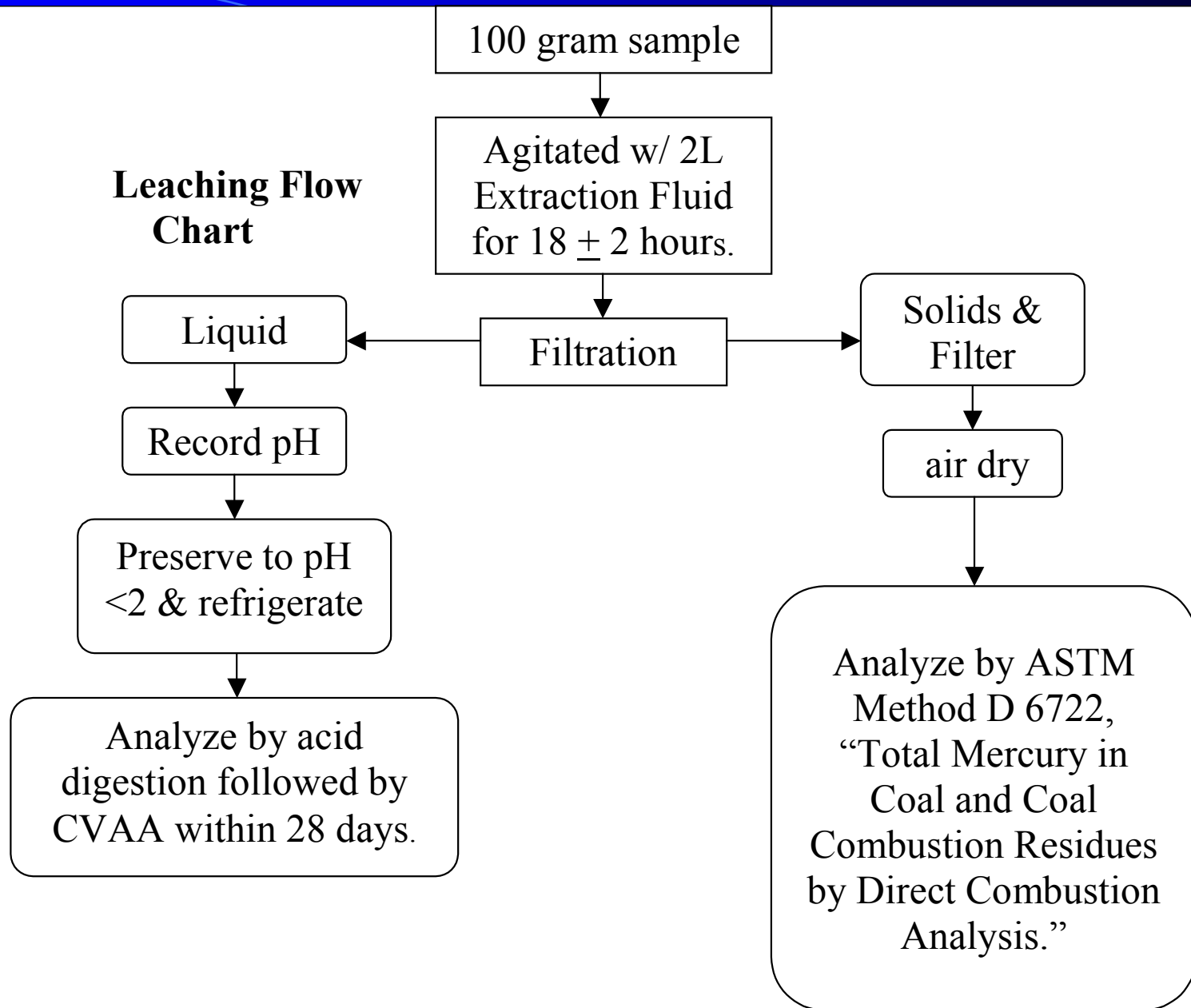


Leaching Tests

- EPA Method 1311 & ASTM Method D3987
- Leaching is conducted at three pH values.
 - Acetic acid buffered to a pH of 4.9
 - Acetic acid buffered to a pH of 2.8
 - Deionized water



Leaching Flow Chart



Leaching Results

Plant ID #	Sample Type	Control Equipment	Coal Source	Hg Conc., ppb		
				pH 2.8	pH 4.9	DI H2O
3	Bottom Ash	Mg/Lime FGD	High Sulfur Ohio	<1.0	<1.0	<1.0
9	ESP Ash	Carbon Injection - ESP	Powder River Basin	<1.0	<1.0	<1.0
15	FGD Sludge	Inhibited Oxidation FGD	Pittsburgh Seam	<1.0	<1.0	<1.0
4	FGD Sludge	Mg/Lime FGD	High Sulfur Ohio	<1.0	<1.0	<1.0
11	Fly ash	Circulating Fluidized Bed	Eastern Low Sulfur Bit.	<1.0	<1.0	<1.0
4	Fly ash	ESP	Illinois 6	<1.0	<1.0	<1.0
6	Fly ash	ESP	Illinois/W KY Blend	<1.0	<1.0	<1.0
14	SDA	Spray Dryer - Baghouse	Eastern Low Sulfur Bit.	<1.0	<1.0	<1.0

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



CV-AFS Results for Leaching Filtrates

Coal Source	As-Received Hg conc. ppm	Extraction Fluid pH	Total Hg ppt*
PRB Fly Ash	0.12±0.02	4.98	11
PRB Fly Ash		2.90	38
PRB Fly Ash		DI	7.5**
Illinois 6 Fly Ash	0.07±0.02	4.98	38
Illinois 6 Fly Ash		2.90	50
Illinois 6 Fly Ash		DI	84

* Blank and dilution corrected

**This sample was run in duplicate with a Relative Percent Difference of ± 4.0%.



Volatilization Tests

- Samples of ash, FGD solids, spray dryer solids, aggregate, cement, and wallboard are being analyzed.
- Two temperatures: 100 °F and 140 °F
- Continuous Hg-free N₂ purge
- Samples held for six months
- Sampled and analyzed at three and six months by ASTM method D 6722.



Fly Ash Volatilization Results

Plant ID	As	3 Month		6 Month	
	Received	100 F	140 F	100 F	140 F
	Hg conc. ppm	Hg conc. ppm	Hg conc. ppm	Hg conc. ppm	Hg conc. ppm
3	0.09 <u>±</u> 0.02	0.09	0.10	0.12	0.17
6	0.29 <u>±</u> 0.05	0.34	0.32	0.38	0.34
6	0.19 <u>±</u> 0.04	0.22	0.25	0.28	0.24
6	0.69 <u>±</u> 0.11	0.72	0.69	0.69	0.69
4	0.08 <u>±</u> 0.02	0.11	0.12	0.13	0.12
4	0.08 <u>±</u> 0.02	0.09	0.10	0.11	0.13



Groundwater Study

- To determine the potential for mercury release from an active FGD sludge disposal site and an active fly ash slurry impoundment.
- Sampling sites
- Samples collected quarterly
- Sample analysis



FGD Active Disposal Area Ground Water Results

1st Quarter											
Well ID #	pH	Acidity as CaCO ₃ ppm	Alkalinity as CaCO ₃ ppm	Total Susp. Solids ppm	Total Dis. Solids ppm	Specific Cond. ppm	Chloride ppm	Nitrate as N ppm	Nitrite as N ppm	Sulfide ppm	Hg ppb
1 - Seep	7.80	-16	31	8	3280	4090	400/450/425	0.14	3.15	<1.0	<1.0
2 - DG	6.55	-189	199	3	1100	1500	100/105/103	<0.02	<0.02	1.1	<1.0
3 - UG	8.51	-489	495	29	620	1050	2	2.13	<0.02	<1.0	<1.0
4 - DG	7.52	-249	249	6	2230	2720	90	<0.02	<0.02	21	<1.0
5 - DG	8.02	-382	390	9	710	1220	85	0.22	<0.02	1.3	<1.0
6 - UG	8.16	-410	418	10	558	960	2	0.57	<0.02	1.5	<1.0
7 - Seep	7.03	-23	45	12	3780	5070	850/860/855	0.10	<0.02	6.7	<1.0
8 - UG	6.71	-211	221	116	456	713	2.00/5.00/3.50	<0.02	<0.02	1.6	<1.0
2nd Quarter											
Well ID #	pH	Acidity as CaCO ₃ ppm	Alkalinity as CaCO ₃ ppm	Total Susp. Solids ppm	Total Dis. Solids ppm	Specific Cond. ppm	Chloride ppm	Nitrate as N ppm	Nitrite as N ppm	Sulfide ppm	Hg ppb
1 - Seep	7.11	-33	43	5	3330	3770	540	1.07	<0.05	<1.0	<1.0
2 - DG	6.52	-192	197	3	1050	1270	105	0.08	<0.05	<1.0	<1.0
3 - UG	7.90	-424	426	3	540	810	2	2.10	<0.05	<1.0	<1.0
4 - DG	6.93	-244	288	1	1900	2150	275	<0.05	<0.05	12	<1.0
5 - DG	7.73	-381	385	2	700	1050	100	<0.05	<0.05	<1.0	<1.0
6 - UG	8.09	-416	417	3	572	825	<1.0	0.26	<0.05	<1.0	<1.0
9 - DG	7.30	-200	204	2	646	898	76	0.40	<0.05	<1.0	<1.0
7 - Seep	8.15	-43	64	6	3350	4110	625	0.60	<0.05	7.1	<1.0
8 - UG	6.66	-210	216	11	448	593	<1.0	<0.05	<0.05	<1.0	<1.0

Seep= seep site, DG= downgradient, UG= upgradient



Fly Ash Active Slurry Impoundment Ground Water Results

1st Quarter

Presentation ID #	pH	Acidity as CaCO ₃	Alkalinity as CaCO ₃	Total Susp. Solids	Total Dis. Solids	Specific Cond.	Chloride	Nitrate as N	Nitrite as N	Sulfide	Hg
		ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppb
1 - DG	6.48	-46	54	1	110	106	1	0.3	<0.1	<1.0	<1.0
2 - CG	5.06	-1	14	6	1340	1840	455	<0.1	<0.1	<1.0	<1.0
3 - DG	6.35	-38	47	6	198	251	10	4.2	<0.1	1.5	<1.0
4 - LS	7.80	-211	218	7	462	646	2	0.5	<0.1	<1.0	<1.0
5 - DG	5.15	0	8	5	290	367	21	<0.1	<0.1	<1.0	<1.0
6 - CG	6.43	-27	36	3	92	88	1	0.1	<0.1	1.0	<1.0
7 - CG	6.77	-29	35	30	88	76	1	0.1	<0.1	1.9	<1.0
8 - DG	6.38	-45	52	20	394	526	21	0.1	<0.1	<1.0	<1.0
9 - DG	5.90	-34	44	7	234	414	16	<0.1	<0.1	<1.0	<1.0
10 - DG	6.89	-93	99	5	164	212	1	0.4	<0.1	<1.0	<1.0
11 - UG	5.53	-4	10	2	88	83	8	3.5	<0.1	<1.0	<1.0
12 - DG	6.23	-58	67	6	314	421	15	0.2	<0.1	<1.0	<1.0

DG= downgradient, CG= crossgradient, LS= leachate site, UG= upgradient



Conclusions To Date

- The Hg concentrations in the groundwater samples are less than the CVAA detection limit of 1 ppb.
- The data show a less than the detection limit of <1.0 ppb of mercury in the filtrates of all fly ash, FGD sludge, and bottom ash samples.



Acknowledgments

- Department of Energy
 - National Energy Technology Laboratory
 - Cooperative Agreement DE-FC26-00NT40906
 - Lynn Brickett, contract manager
- CONSOL Energy
- Participating power plants

