Methods for Testing Trace Metal Mobility in Coal Fly Ash and FGD Solids

Acknowledgements

- Lynn Brickett, United States Department of Energy
  - National Energy Technology Laboratory

About Us

- Frontier GeoSciences was founded in 1991 in Seattle, Washington.
- Co-author of EPA 1600 series methods (Hg, As, Se, etc.).
- Designed/popularized principles of sorbent trap method for flue gas mercury measurements in 1993 which are now EPA Methods 30B and Appendix K.
- Continued analytical method development for metals in a variety of applications .

Study Overview

- Frontier GeoSciences, in conjunction with the Department of Energy, recently completed an exhaustive 3 year study to better understand trace metals in coal ash
- Our objective was to determine the following:
  - Measure metals accurately on CCP's
  - Assess metals availability and mobility through CCP end use processes
  - Measure the effect of mercury control technologies on CCP's

Industry Overview

- The coal-fired power industry is the largest generator of Coal Combustion Products (CCP's)
- In 2007 this industry generated approximately
  - 71.7 million tons of coal ash
  - 12.3 million tons of FGD solids
- Coal ash can either be a source of **revenue**, or a potential **liability**

Our Goal Today…

- Our goal today is to briefly describe our CCP study, the science behind our examination of metals mobility and trends that we see in the results.
  - Start with total metal content in CCP's.
  - Look at the impact of the leaching of trace metals in coal ash.
  - Better understand how trace metals react at different temperatures in coal ash.
  - Discuss the impact of mercury control technology on coal ash.

Tests to Simulate Various End Uses

Test	Procedure	Purpose
Total Metals	Complete Digestion	Compare to Various Measures
Volatilization	40 C for 30 days	Soil fill / Landfill
Volatilization	190 C for 60 min	Asphalt / Wallboard
Volatilization	1200 C for 5 min	Cement
Microbial Leaching	Batch reactor with *D. propionicus*	Soil fill / Landfill / Impoundment
Chemical Leaching	Tumble @ pH 4.2, 60:40 H_2SO_4:HNO_3	Simulates precipitation/ runoff from any use

CCP's Usage

Use in 1000s of tons	Fly Ash	FGD Gypsum	Bottom Ash	Boiler Slag	Other CUBs	All CUBs
Concrete/concrete products/grout	13705	118	666		27	14516
Blended Cement/faw feed for clinker	3636	657	609	7	81	4990
Structural Fills/embankments	7725		2570	159	144	10598
Road base/sub-base	377		802		1	1180
Soil Modification/Stabilization	857		314		200	1371
Blasting grit/roofing granules			72	1378	0	1450
Mining applications	1306		165		411	1882
Gypsum panel products		8255			0	8255
Waste stabilization/solidification	2680		7		113	2800
Aggregate	135	71	807		0	1013
Other Uses	1205	127	1292	120	420	3164
Total CUBS Used	31626	9228	7304	1664	1397	51219
Total CUBS Produced	71700	12300	18100	2073	22135	126308
Percent used	44.1%	75.0%	40.4%	80.3%	6.3%	40.6%

From ACAA 2007 CCP Production & Use Survey

Basis of the Study

- 25 different sites collected the following types of samples for the study:
  - Fly Ash
  - FGD by-products
- Fly Ash and FGD by-products account for 80% of CCP's that are used in other industries
- Sites collected samples both before mercury control technology use and after

Issues Associated with CCP's

- Trace metals may contaminate end products
- Potential to release trace metals into the environment
- Mercury Control Technologies (MCT) can change properties and impact end use
- MCT can transfer mercury and other volatile metals from emissions to end products

Solution

- Understand your risks
- Quantify trace metals in your CCP's
- Assess trace metals in final product
- Simulate various end uses to predict exposure
- Modify CCP's to minimize metals mobility

Total Metals Results (Fly Ash Only)

Units: mg/kg	Ni	As	Se	Cd	Pb	Hg
Without Hg Control						
Average	49.3	35.1	27.0	0.925	36.3	0.664
Minimum	0.26	2.84	1.33	0.057	0.47	0.0053
Maximum	131	180	309	7.11	82.0	8.35
With Hg Control						
Average	53.3	41.5	86.9	1.04	38.9	3.95
Minimum	5.21	4.70	0.47	0.18	1.97	0.0189
Maximum	128	210	1720	6.56	92.6	80.8
Comercial/Industrial SSL*	23000	2	5700	900	-	340
Residential SSL*	1600	0.4	390	70	400	23
TCLP Limit	-	100	20	20	100	4

*Ingestion route

Chemical Leaching Metals Results

Units: µg/L	Ni	As	Se	Cd	Pb	Hg
Without Hg Control						
Average	13.7	7.87	94.4	1.20	0.75	1.13
Median	1.06	1.63	24.8	0.17	<0.10	<0.010
Minimum	<0.5	<0.75	<0.75	<0.10	<0.10	<0.010
Maximum	319	157	579	66.8	6.69	43.4
With Hg Control						
Average	16.0	8.62	533	0.708	0.76	0.051
Median	1.02	1.57	<0.75	0.17	<0.10	<0.010
Minimum	<0.5	<0.75	0.47	<0.10	<0.10	<0.010
Maximum	516	179	13592	29.06	8.43	1.65
National Drinking Water Standard	-	10	50	5	15	2
National Recommended Surface Water Criteria*	52	0.018	5	0.25	8.1	0.77
TCLP Limit	-	5000	1000	1000	5000	200

*Assumes Hardness of 100 mg/L

Volatilization Of Metals From CCP's

- Mercury and other metals are:
  - Naturally present in coal and coal ash
  - Volatilized during coal combustion and to some extent deposited back onto coal ash
- Regulatory community concern that:
  - Mercury/metals to some extent are removed from emissions via fly ash capture
  - Metals are therefore not emitted in emissions at the coal combustor
  - Potentially re-emitted during thermal end use process of CCP's.
  - EPA does not want re-emission of metals from CCP's (CAIR/CAMR)
- Study focus on examining potential release of mercury during CCP thermal processes:
  - Soil fill / Landfill ~ 40 C
  - Asphalt / Wallboard Mfg ~ 190 C
  - Cement Mfg ~ 1200 C

Soil Fill Volatility Metals Results

Units: mg/kg	Ni	As	Se	Cd	Pb	Hg
Without Hg Control						
Average	1.25	<1.0	4.5	<0.050	2.02	<0.010
Minimum	<0.2	<1.0	<1.0	<0.050	<0.40	<0.010
Maximum	23.7	14.0	193	0.318	10.1	0.067
With Hg Control						
Average	1.09	1.05	<1.0	<0.050	1.42	<0.010
Minimum	<0.20	<1.0	<1.0	<0.050	<0.40	<0.010
Maximum	23.9	90.2	28.8	0.861	31.8	0.193

Wallboard Volatility Metals Results

Units: mg/kg	Ni	As	Se	Cd	Pb	Hg
Without Hg Control						
Average	2.62	<1.0	3.9	0.052	2.42	0.058
Minimum	<0.20	<1.0	<1.0	<0.050	<0.40	<0.010
Maximum	25.7	12.4	221	0.506	15.6	0.597
With Hg Control						
Average	1.43	1.04	8.2	<0.050	1.05	0.022
Minimum	<0.20	<1.0	<1.0	<0.050	<0.40	<0.010
Maximum	17.4	32.7	452	0.241	15.5	0.337

Cement Volatility Metals Results

Units: mg/kg	Ni	As	Se	Cd	Pb	Hg
Without Hg Control						
Average	<0.20	<1.0	12.0	< 0.050	0.88	0.183
Minimum	<0.20	<1.0	<1.0	< 0.050	<0.40	<0.010
Maximum	18.0	13.2	305	0.276	15.0	2.10
With Hg Control						
Average	<0.20	1.28	69.2	< 0.050	<0.40	2.89
Minimum	<0.20	<1.0	<1.0	< 0.050	<0.40	0.012
Maximum	7.23	54.2	1671	0.282	17.3	59.7

Summary

- All CCP's used as soil fill where there is direct human contact are greater than national soil standards for arsenic
- All CCP's disposed in landfills will most likely pass RCRA TCLP metals requirements
- Chemical leaching of CCP’s is very dependant on the type of coal, processing of the coal, and mercury control technology. Some are below drinking water and surface water criteria, some are not. Testing of the individual materials is suggested to determine chemical leaching.

Summary II

- Volatility of metals in landfill and soil fill applications are minimal.
- Volatility in wallboard and cement application is very dependant on the type of coal, processing of the coal, and mercury control technology. In some cases almost 100% of Hg and Se is re-released but others have 0%. Testing to determine the amount of metals released in various processes is suggested to determine the fate of volatile metals.
- Mercury control technologies increase the total concentrations of metals such as selenium and mercury but do not necessarily increase the leaching and volatility of these metals

Questions

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