Selenium and Weathering of Wet-Stored Coal Fly Ash

Analyses of Data from Two Coal Fly Ash Spills

by

Bryce F. Payne Jr., PhD
Environmental Engineering and Earth Sciences
Wilkes University
Wilkes-Barre, Pennsylvania

Selenium

Rare, Essential, Toxic

- Rare non-metal element, ≈0.09 mg Kg^{-1} in Earth's crust.
- Most highly enriched element in coal
- Essential trace nutrient
  - Normal levels in freshwater fish tissue = 2.0 to 3.5 mg Kg^{-1} (dry wt.)
  - Toxic (fish reproduction) impacts begin 5.8 to 7.9 mg Kg^{-1} (dry wt.)
  - Fish tissue levels ≥1000X ambient water concentrations
  - Food chain bioaccumulation irreversible on practical time scales
- Strongly bio-accumulated
  - Fish tissue levels ≥1000X ambient water concentrations
  - Food chain bioaccumulation irreversible on practical time scales
- Complex chemistry similar to Sulfur with the same oxidation states (-2, 0, +2, +4, +6) and equivalent oxyanion forms

Selenite (SeO_3^{-2}) and Selenate (SeO_4^{-2})

- Most common inorganic forms in most soils
- Reversible redox reaction Selenite ↔ Selenate at
  pe + 1.69 pH ≈ 22.9
- Both very soluble in water
- Both sorbed by Al, Fe, and Mn oxyhydroxide minerals
- Selenite sorption ≈ 10 X Selenate sorption
- Compete with other oxyanions (PO_4^{-3}, SO_4^{-2}, CO_3^{-2}, others) for sorption sites

Coal Fly Ash

Production and Some Relevant Properties

- Annual U.S. production ≈ 72 million tons
- The major environmental source of Se and other toxic elements.
- Spherical particles of mineral glass comprise >90% of ash
- Major glass constituent elements: Al, Fe, O, Si
- Particle size range (diameter): <1 to ≈100 μm
- Typical pH of field aged fly ash is neutral to alkaline
- Metastable, weathers rapidly forming Fe and Al oxyhydroxide gel coatings on particles
- Weathering releases minor constituent elements, including Se, As and other toxics
- Oxyanions (of S, P, As, Se, others) sorbed by oxyhydroxide gels

Recent Major Coal Fly Ash Spills

- Pennsylvania, August 2005
  - PPL Martins Creek Steam Electric Station (MCSES)
  - Stop log failure in Ash Basin #4
  - Estimated 37,000 m^3, mostly ash laden water onto land
- Tennessee, December 2008
  - TVA Kingston Fossil Plant
  - Dike failure in main fly ash storage pond
  - Estimated 4,100,000 m^3 of ash into Emory River

Pennsylvania Spill

- 24 August 2005
  - Stop log failure in MCSES Basin #4
  - Emergency diversion of plant operational ash slurry flow to Basin #1
- 1 September 2005
  - Intensive ground water monitoring begins (Figure 1.)
  - Elevated selenium found laterally and down gradient of Basin #1 (Figure 2.)
- 7-9 September 2005
  - Possible seep through Basin #1 dike noticed
  - All pumping into Basin #1 terminated
  - Water level in Basin #1 begins dropping immediately
- 9 Sep – 26 October 2005
  - Piezometers installed to monitor subsurface water levels in dikes and ash basin contents
  - Drainage of water from Basin #1 complete by ≈1 October 2005
- Ground water selenium levels decline rapidly toward normal pre-spill levels (Figure 2.)
- 26 Oct – 7 Dec 2005
  - In upper and mid-basin monitoring wells groundwater selenium continues decline to normal historical levels (see MW 1-8 in Figure 2.)
  - In down gradient well outside lower end of Basin #1 (MW 1-6) selenium rises to a maximum of 126 ppb
- Jan 2006
  - Selenium levels in MW 1-6 begin to decline
  - Water from central basin piezometer (PZ 1-17) sampled for first time, Se level = 375 μg L^{-1} selenium
- Feb – Dec 2006
  - Selenium levels in MW 1-6 continue to decline
  - Selenium in PZ 1-17 rises to 1970 μg L^{-1}
  - Investigation of selenium source undertaken (see Figure 3.)

Ash/Soil Sample Descriptions

- Sampling depths to 10 meters
- Depth sampling increments distinguished on rooting density, texture, moisture content, anomalous inclusions, other
- Fly ash strata saturated when resting above contact with coarser materials (bottom ash or local sand/gravel soil on basin floor)
- Low redox colors, odors not apparent in ash samples (but readily apparent in reduced soil samples)

Selenium in Basin #1 Ash Samples (Jan 2006)

- Oxidation-Reduction Potential and pH measurements taken on processed & stored samples (no field or fresh sample data)
- Se extraction methods (run on selected samples)
  - SPLP (solid waste regulatory compliance method, suspected of "missing" the Se impacting Basin #1 groundwater)
  - 0.1 *N* HCl extraction (readily executed soil procedure that should access some oxyhydroxide sorbed Se)
  - Interstitial water (most direct estimator of in-situ Se concentrations potentially affecting groundwater)

Figure 1. Basin #1 Groundwater Monitoring Well (MW) and Piezometer (PZ) Locations

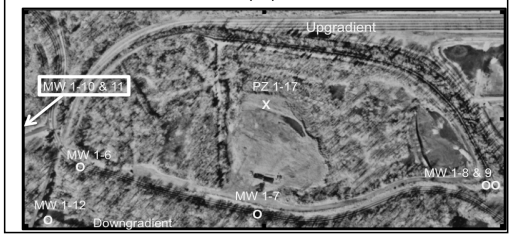


Figure 2. Selenium in Basin #1 Groundwater 2001-2009

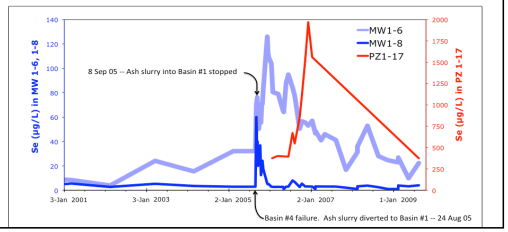


Figure 3. Basin #1 Ash/Soil Sampling Points
January 2007 & January 2008

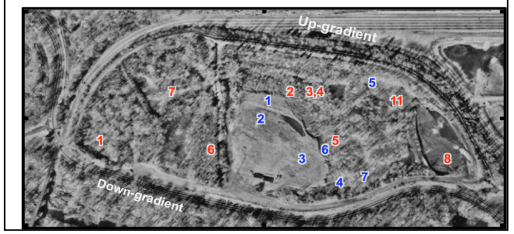
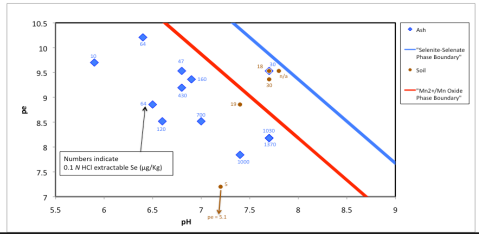


Table 1. Selected Basin #1 Ash and Soil Samples
pH, Eh, and Extractable Se

Sampling Location	Depth (cm) (below surface)	pH	Eh (mV)	0.1 N HCl Se (μg/Kg)	SPLP Se (μg/Kg)
Ash					
1	420-530	7.4	460	1000	n.a.
4	380-470	7.7	480	1030	n.a.
4	470-590	7.7	480	1370	26
4	260-380	7	500	700	n.a.
7	240-450	6.6	500	120	3
5	470-610	6.5	520	64	n.a.
4	160-260	6.8	540	430	n.a.
4	120-160	6.9	550	160	n.a.
4	0-51	7.7	560	30	23
7	450-670	6.8	560	47	2
7	10-240	5.9	570	10	3
5	0-120	6.4	600	64	6
Soils					
1	40-63	7.2	300	5	8
3	0-35	7.4	520	19	6
1	0-13	7.7	550	30	11
2	0-13	7.7	560	18	8

Figure 4. Basin #1 Ash and Soils
Redox Status and 0.1 *N* HCl Extractable Se



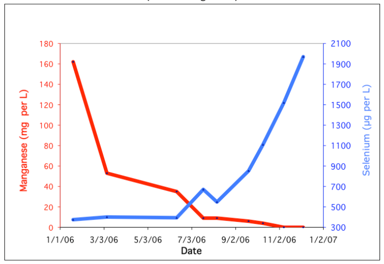
pH, Eh, Selenium Results

- SPLP Se (see Table 1.) did not identify "hot spots" or correlate with redox or pH.
- 0.1 *N* HCl extractable Se (see Table 1. and Figure 4.) identified "hot spots", correlated with pe-pH for ash, and distinguished ash (all but one ≥ 30 μg Kg^{-1}) from soils (all ≤ 30 μg Kg^{-1}).
- Se levels in interstitial water recovered from 3 deep ash samples were 49, 62, and 90 μg L^{-1} (MCL is 50 μg L^{-1}).

Exceptional Characteristics of PZ 1-17

- Only water sampling point inside Basin #1
- Constructed in October 2005, first sampled January 2006
- Constructed as piezometer
  - Not cased as a well, engaged water from range of depths, probably including within or just beneath the deep ash in Basin #1
  - Turbidity data indicated surrounding ash/soil unstable
  - Temperatures, sulfate, ORP, conductivity, other data indicate principle water source was surface waters percolating through previously isolated deep ash
- PZ 1-17 water only sample point receiving water through artificially altered drainage of and/or mechanically disturbed deep fly ash
- Selenium levels inversely related to Manganese (see Figure 5.)

Figure 5. Manganese and Selenium in PZ 1-17 Water
(see also Figure 1.)



Conclusions from Basin #1 Investigation

- SPLP data does not speak to causes, likelihood, rate or amount of potential Se releases from wet-aged coal fly ash (ash aged in stagnant, saturated, or drained, moderately reduced conditions).
- 0.1 N HCl extraction provides convenient, relevant data on mechanisms and crude (probably low) estimates of potential Se releases from wet-aged coal fly ash.
- Limited interstitial water samples suggested SPLP may underestimate actual soluble Se in raw wet-aged coal fly ash samples.
- Eh-pH status all ash samples below Mn^{2+}/MnO_2 phase boundary (see Figure 4.) → Selenite oxidation inhibited until Mn^{2+} oxidation approaches completion (see Figure 5.)
- 0.1 *N* HCl extractable Se in ash (see Figure 4.) increases generally with pH and decreasing Eh → ash stored under lower redox conditions retains more adsorbed selenite and potential for Se release if ash is exposed to higher redox conditions

Conclusions from PA

- Early Se spikes in Basin #1 ground water due to infiltration of ash slurry water, implying ash settling pond effluents likely exceed MCL, and displacement of interstitial water in previously saturated deep fly ash.
- Subsequent spikes due to Se releases from ash in Basin #1 caused by exposure to higher ORP of percolating slurry water inducing oxidation of adsorbed selenite to selenate and desorption and release of selenate to ground water.
- 0.1 N HCl extraction provided useful data relating to mechanisms and intensities of selenium releases following ash spill emergency response uses of ash basin while SPLP did not.

Figure 6. Tennessee Ash Spill Site
Aerial Photography Images

Before | 1 Day After

Tennessee Spill

Largest volume industrial spill in U.S. history
(see Figure 6.)

- 22 December 2008
  - 1:00 A.M. main ash storage pond dike failure
  - 4.1 million m^3 of stored ash liquefy and flow over 300 acres of adjacent land and waters
  - Substantial property damage, but no loss of human life
- 22 December 2008 – March 2009
  - Emergency response and spilled ash management actions
  - Clean up plan developed
- March 2009 – Present
  - Hydraulic dredging of ash from Emory River
  - Dredged ash sent to landfill in Alabama

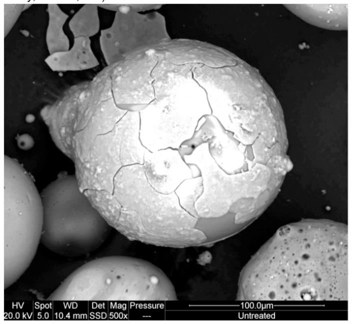
Selenium Monitoring Problems

- Water quality, fish tissue and ash composition data currently contradictory and in dispute
- Planning and implementation of sampling and analytical methods in contention
- Some data indicate Se contamination of local fish
  - pre-dated ash spill
  - spill-related contamination may have begun by June 2009
- SEM imaging established spilled ash particles have oxyhydroxide coatings with disproportionate concentrations of As (Se concentrations presumed but levels below method detection limits) (see Figure 7.)

Preliminary Conclusions from TN

- Difficulties with Se assessment and analytical methods as in PA (but worse)
- Recent data indicate Mn/Se relationship is effective as in PA
- SEM work confirmed aged ash particles have As-loaded oxyhydroxide coatings on ash particles, that can be reasonably presumed to bear elevated Se levels as well
- Substantial portions of selenium is associated with fine particulates
- Elevated Se in ash slurry effluent water is likely source of suspected selenium contamination in fish (as suggested by PA ground water data)

Figure 7. Oxyhydroxide coatings (primarily Fe) on ash particles from TN spill.
(SEM image courtesy of Dr. Sarah Carmichael, Department of Geology, Appalachian State University, Boone, NC)



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