



GEOCHEMICAL SPECIATION OF SELENIUM AND OTHER HEAVY METALS IN COAL FLY ASH AFTER PROLONGED SUBMERSION IN THE EMORY RIVER AT THE KINGSTON FOSSIL PLANT SITE

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INTRODUCTION:

On December 22, 2008, over 5 million cubic yards of fly ash were released to the Emory River, TN from the Tennessee Valley Authority (TVA) Kingston Fossil Plant. Remediation and recovery efforts for this event are currently underway. This study was conducted in order to determine concentration and metal species in the fly ash, and to predict potential for significant metals release from fly ash particles during remediation strategies.

METHODS:

Field Collection:

- All field samples collected on June 12, 2009
- Fly ash was collected from the source pile and from the Emory River at five discrete locations approximately 2.2 miles upstream of the confluence of the Emory and Clinch Rivers and composited
- Fly ash and water also collected from the Ash Recovery Ditch (Sluice Channel) on site at the TVA Kingston Fossil Plant
- Reference water for use in preparing elutriates was collected from the Emory River approximately 12 miles upstream of the Kingston Fossil Plant



Figure 1a. Aerial image of the TVA site on 12/23/2008

Figure 1b. Sampling locations



Figure 1b. Sampling locations

Elutriate Studies:

- Elutriates prepared with Emory River (EMR-EL) and Sluice Channel fly ash (SLC-EL) 10 g/L of fly ash added to respective site water, aerated or bubbled with N for 10 days
- This extended elutriate mixing time (10 d versus the normal 1 h) was used to conservatively represent extreme conditions for the release, dissolution, and changes in metal speciation that might occur during dredging
- Both solid and liquid samples were taken at time points throughout the 10 day period and analyzed for total metal and metal speciation (liquid and solid state analyses).

Metal Speciation Techniques:

- Solid state metal speciation was conducted using X-ray absorption near edge structure (XANES) spectroscopy. This work was conducted at the Stanford Synchrotron Radiation Lightsource, National Synchrotron Light Source, and Center for Advanced Molecular Devices.
- Liquid metal speciation was conducted using HPLC-ICP-MS.

RESULTS AND DISCUSSION:

Element	Reference Sediment	Source Pile	Emory River	Sluice Channel
concentration (mg/kg)				
As	1.71	46.9	65.8	76.2
Ba	48	510	655	515
Cr	8.25	33.5	48.7	49.2
Cu	5.58	50	84.1	76.4
Fe	7990	17500	17700	22200
Pb	6.68	20.2	36.4	33.1
Mn	313	88.7	153	187
Ni	11.5	34	52.6	49.9
Se	0.25	5.44	6.97	6.08
V	9.16	86.2	133	124
Zn	35	41.5	77.4	72.1

Table 1. Total elemental composition of the fly ash

- As, Se, Ba, and Cu are above the background levels in the reference sediment

Determining Elemental Distribution Using XRF

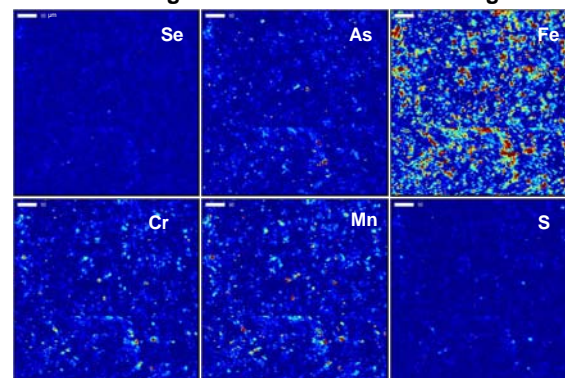


Figure 3. XRF maps depicting elemental distribution of Se, As, Fe, Cr, Mn, and S of fly ash that has been submerged at the bottom of the Emory River

- Elements follow similar trends most likely due to metal sorption to Mn and Fe oxides

Metal Determinations Using HPLC-ICP-MS

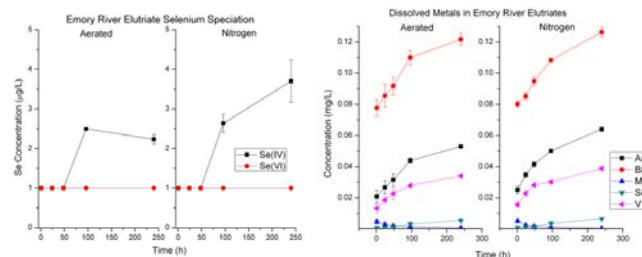
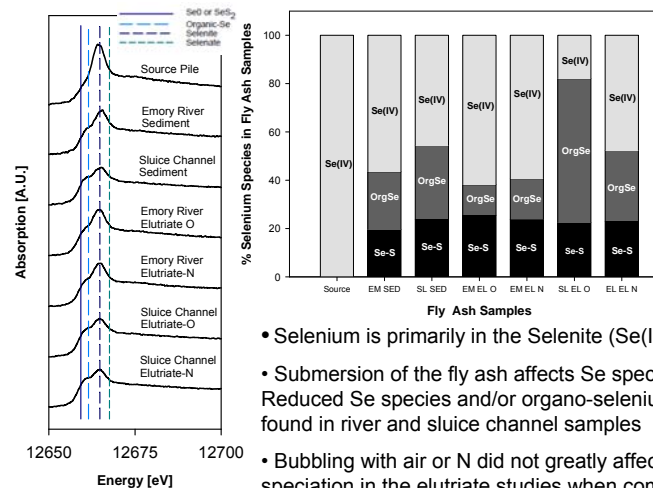


Figure 2a. Selenium speciation of Emory River elutriates.

Figure 2b. Total dissolved metal content of Emory River elutriate studies.

- Figure 2a shows that bubbling with N or air does not affect Se speciation. Selenite is the dominant Se species in both systems. No selenate (Se(VI)) was detected in solution.
- Figure 2b shows that total dissolved metals in solution increase with increasing time, with the exception of Mn.

Selenium Speciation Using XANES Spectroscopy



- Selenium is primarily in the Selenite (Se(IV)) form

- Submersion of the fly ash affects Se speciation. Reduced Se species and/or organo-selenium are found in river and sluice channel samples

- Bubbling with air or N did not greatly affect Se speciation in the elutriate studies when compared to the Emory River or Sluice Channel sediments

Iron and Manganese Speciation Using XANES Spectroscopy

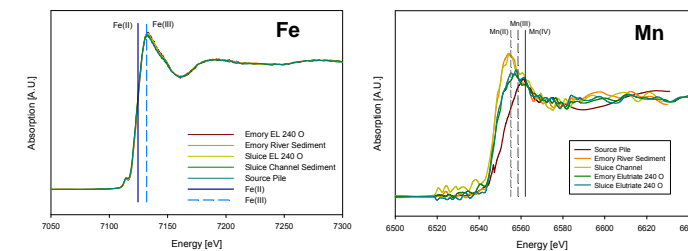


Figure 4. Solid state speciation of Fe and Mn in fly ash and elutriate samples

- Iron speciation in the fly ash was not affected by submersion at the bottom of the Emory River or by aerating the elutriate solution.
- Manganese was reduced to Mn(II) after ash submersion. Bubbling the elutriate solution with air caused Mn(II) oxidation.

- Both liquid and solid state speciation data indicates that As(V) is the dominant form of arsenic in all fly ash sediments and elutriates

- Chromium speciation data indicates that the dominant form of Cr in the fly ash is Cr(III)

CONCLUSION

- The results show that the fly ash exhibits geochemical stability, but it is undergoing kinetically slow transformations while submerged in the Emory River
- Since these experiments overestimate natural field conditions, it is not likely that dredging submerged sediments will cause Se oxidation to Se(VI)
- The major elements of concern are found in the less toxic forms:
 - Se(IV), As(V), and Cr(III)

ACKNOWLEDGMENT

Permission was granted by the Chief of Engineers to publish this material. The authors thank Jonathan Burr (TDEC) for assistance in field sampling.