

## Solubilization of trace elements from coal fly ash in relation to chemical speciation

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### Abstract

In December 2008, approximately 4.2 million cubic meters of coal fly ash were discharged into the Emory and Clinch Rivers from a holding pond in Kingston, TN. A fundamental understanding of the chemistry of the ash is required to develop long-term management strategies for the site. The objective of this study was to relate the pH-dependent kinetics of trace-element dissolution to chemical speciation in the ash. A fly ash sample from TVA's Kingston power plant contained 60% aluminosilicate glass in addition to mullite, quartz, and other minerals. Synchrotron x-ray absorption spectroscopy (XAS) indicated that trace elements (As, Cr, Cu, Se, Sr, and Zn) were associated with both the glass and mineral phases.

Initial experiments on dissolution kinetics were conducted on suspensions of ash in 0.05 M KCl (10 g kg<sup>-1</sup>) in a continuously stirred batch reactor at 25 °C under oxic conditions, both at pH 5 and at ambient pH (buffered at pH 10) over a period of 10 days. Similar trends in increasing dissolved Sr and Ca concentrations with time at both pH levels were observed, and both elements were found predominantly in the glassy phase. General trends of increasing dissolution with time of As, Cr, Se, and S at pH 10, and of Zn, Mn, and Fe at pH 5 were observed. Speciation analyses of unweathered ash samples indicated the presence of mainly As(V), Se(IV) and Cr(III), along with ferrihydrite-like Fe and discrete Zn phases. A decline in dissolved concentrations of some elements with time was attributable to precipitation of secondary solids. Results from a stirred-flow reactor system will also be presented.

### Conclusions

Over time, alkaline fly ash residues in circumneutral or acidic river sediments are expected to become acidified. Elemental speciation in fly ash provides insights on solubilization of potentially toxic trace elements under varying pH conditions. However, transformations of initial solid-phase species into other, possibly more insoluble species, must also be considered. Continuing experiments across a range of geochemical conditions to which fly ash residues might be exposed will assess potential, long-term environmental impacts of ash-contaminated sediments.

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## Modeling the impact of soil aggregate size on selenium immobilization

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Soil mineral and organic particles are commonly bound together into mm to cm sized microporous structures (aggregates) separated by macropores. While fast advective transport prevails in macropores, the transport inside aggregates is mostly diffusive (slow) which leads to the formation of aggregate-scale concentration gradients impacting biogeochemical reactions. Selenium (Se) is an essential micronutrient that has recently emerged as an environmental contaminant. The bioavailable oxyanions selenate, Se(VI), and selenite, Se(IV), can be microbially reduced to solid, elemental Se, Se(0), and anoxic microzones within aggregates are thought to promote this process in soils. A mechanistic understanding of Se reduction and retention in soil aggregates can lead to better predictions of Se transport and attenuation in seleniferous soils which may help improve the management of such ecosystems.

Using a dynamic 3D reactive transport model of a single idealized aggregate, we model the coupling between physical transport and biogeochemical reactions controlling Se reduction at the aggregate scale. The model was developed and validated based on a series of flow-through reactor experiments involving artificial soil aggregates. Each experiment/model scenario consisted of a spherical aggregate (experimental diameter: 2.5 cm) surrounded by a constant flow providing Se(VI) (0.4 or 0.8 mM) and pyruvate (0.3 or 1.2 mM) for 8 days under oxic or anoxic conditions. Aggregates contained a Se-reducing bacterial strain (*Enterobacter cloacae* SLD1a-1) that oxidizes pyruvate while reducing Se(VI) to Se(IV) and Se(IV) to Se(0). These two reactions were implemented in the model as double-Monod rate equations with literature based kinetic parameters. Reactions were coupled to transport of pyruvate, O<sub>2</sub>, and Se species modelled *via* advection-diffusion equations with static flow fields calculated using Navier-Stokes/Brinkman equations (macropore/aggregate). Concentrations of Se(VI) and reduced Se (Se(IV)+Se(0)) were measured in the outflow solution (temporally resolved) and in concentric solid phase sections of aggregates (spatially resolved). This data was used to validate the dynamics of the reactive transport model and all subsequent simulations were performed within experimentally validated dimensions (≤2.5 cm, 8 days).

Simulations predict that larger aggregate size leads to increased Se retention. For example aggregates, surrounded by oxic conditions and a flow of 0.3 mM pyruvate/0.4 mM Se(VI) solution, are predicted to retain 0.4 and 0.1 nmol/g/day of Se(IV) and Se(0) respectively if they are 2.5 cm in diameter, but this decreases continuously over the simulated size spectrum to 0.07 and 0.01 nmol/g/day for 1 cm diameter aggregates. While the absolute amount of reduction depends on aeration, as well as Se(VI) and carbon concentrations, this trend persists across all chemical conditions investigated. Promoting soil aggregation on seleniferous agricultural soils, through addition of organic matter and decreased use of tillage may thus be an effective management practice to decrease impacts of Se contaminated drainage water on downstream ecosystems.