Uranium Attenuation and Release Investigated at the Molecular and Column Scales: Responses to Geochemical Gradients in Geologic Media

University-Led Research

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Understanding relationships between physical and chemical processes at different scales is critical to effective prediction of contaminant mobility. This study addresses the molecular-scale response of dissolved uranium to advective chemical gradients, simulating ground water encountering soil and sediment matrices that are representative of subsurface environments at the Oak Ridge Integrated Field Research Challenge (ORIFRC) site.

Column experiments were devised to investigate the role of changing fluid composition on mobility of uranium through a sequence of geologic media. Synthetic ground waters were pumped upwards at 0.05 mL/minute for 21 days through layers of quartz sand alternating with layers of uncontaminated soil, quartz sand mixed with illite, quartz sand coated with iron oxides, and a second soil layer. Increases in pH or concentration of phosphate, bicarbonate, or acetate were imposed on the influent solutions after each 7 pore volumes while uranium (as uranyl) remained constant at 0.1mM. A control column maintained the original synthetic groundwater composition with 0.1mM U. Pore water solutions were extracted to assess U retention and release in relation to the advective ligand or pH gradients. Following the column experiments, subsamples from each layer were characterized using microbeam X-ray absorption spectroscopy (XANES) in conjunction with X-ray fluorescence mapping.

U retention of 55 – 67 mg occurred in phosphate >pH >control >acetate >carbonate columns. The mass of U retained in the first-encountered quartz layer in all columns was highest and increased throughout the experiment. The rate of increase in acetate- and bicarbonate-bearing columns declined after ligand concentrations were raised. U also accumulated in the first soil layer; the pH-varied column retained most, followed by the increasing-bicarbonate column. The mass of U retained in the upper layers was far lower.

A preliminary transport model that incorporates surface complexation, using the code PHREEQC (7, USGS, V.2.18), captures the major features observed in the carbonate and pH gradient experiments but is less successful for the phosphate column. The acetate column was not modeled. In the carbonate column, the model indicates that uranium complexes adsorbed to quartz can account for the observed U uptake and subsequent release. The pH-varied simulation showed increasing pH to lead to U retention, as observed.

Speciation of U, interpreted from microbeam XANES spectra and XRF maps of sediments collected from the columns, varied within and among the materials. Evidence of minor reduction to U(IV) was observed in the first-encountered quartz layer in the phosphate, bicarbonate, and pH columns while only U(VI) was observed in the control and acetate columns. Spectral evidence suggests poorly ordered precipitates in this layer of the phosphate, acetate, and pH columns. In the soil layer, the acetate and bicarbonate columns both indicate minor reduction to U(IV), but U(VI) predominated in all columns. Evidence of precipitates in the soil layer is restricted to the control column. These results will be used to inform and refine the transport models.