Uranium fate in acidic waste-weathered sediments: Scaling of molecular processes to predict reactive transport

Jon Chorover (chorover@cals.arizona.edu) - University of Arizona (PI), Peggy O'Day; Carl Steefel; Karl Mueller; Wooyong Um; John Zachara; Estela Reinoso-Maset; Nico Perdrial; Angelica Vazquez-Ortega; Masa Kanematsu (Co-PIs).

Objectives: (1) Determine process coupling between mineral transformation and uranium speciation change in acid waste-weathered Hanford sediments; (2) Establish linkages between molecular-scale contaminant speciation and meso-scale contaminant lability, release and reactive transport; (3) Make conjunctive use of molecular- to field-scale data to constrain the development of a reactive transport model that includes contaminant sorption-desorption and mineral transformation reactions.

Hypotheses: (1) Reactive transport modeling of future U releases from the vadose zone of acid-waste weathered sediments can be constrained by combining information on contaminant bonding environment with quantification of contaminant phase partitioning and meso-scale kinetic data on contaminant release from the waste-weathered porous media; (2) Although field contamination and laboratory experiments differ in their diagenetic time scales, sediment and synthesized U minerals dissolution, neophase nucleation, and crystal growth reactions that occur during the initial system disequilibrium leave a strong imprint that persists with memory effects over subsequent longer-term equilibration time scales.

Research Approach: An iterative measure-model approach is applied to elucidate mechanistic underpinnings of reactive contaminant transport in weathering geomedia.

Experimental design: Crib waste simulants were reacted with Hanford sediments in batch and flow-through systems. Coupling of contaminant uptake to mineral weathering was monitored both during waste-sediment interaction, and after, when waste-weathered sediments are subjected to infusion with circumneutral background pore water (BPW).

Results: We completed bench-scale batch weathering to one year and flow-through column experiments where Hanford Sediments were reacted with U-bearing synthetic crib waste (SCW) solutions as a function of pH, U and phosphate concentrations. PO4 exerted strong control over U speciation at all pH with rapid precipitation of meta-ankoleite [K(UO2PO4)•3H2O] leading to near complete immobilization of U. Boltwoodite [K(UO2)(HSiO4)•1.5H2O] increased even in PO4-containing systems. Without PO4, U speciation was controlled by the rate of silicate weathering. In this case, U immobilization was limited to 25-50% as precipitated becquerelite [Ca(UO2)6O4(OH)6•7H2O] or compreignacite [K2(UO2)6O4(OH)6•7 H2O] and boltwoodite. Carbonate dissolution buffered influent solutions to pH ~?, which promoted silicate weathering and boltwoodite precipitation. Dissolution of synthetic compreignacite and Na-compreignacite yielded dissolution rates of 8.89•10-13 and 2.48•10-12 mol m-2 s-1 (normalized to BET surface area), respectively. Desorption experiments of weathered sediments? revealed an incremental desorption of U for phosphate-free systems, indicating dissolution of compreignacite, becquerelite and schoepite, but solutions were saturated with respect to Mg-zippeite. In contrast, slow dissolution of meta-ankoleite and autunite in PO4 systems showed low U release.