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

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The need for better prediction of contaminant transport motivates multi-faceted lines of inquiry to build a strong bridge between molecular- and field-scale information. By focusing multiple lines and scales of observation on a common experimental design, our collaborative team seeks to reveal non-linear and emergent behavior in contaminated weathering systems. In prior work, we have successfully coupled weathering, adsorption and transport in geochemical models of sediments impacted by *hyperalkaline* waste streams. A goal of the current project is to expand our modeling capabilities to include *acidic* weathering reactions that, as described above, are expected to result in profoundly different products that will nonetheless undergo analogous silicate and non-silicate transformation, ripening and aging processes. We predict that these weathering reactions will vary with waste stimulant chemistry in ways that can be directly incorporated into the model structure.

Objectives of the project: (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) Uranium speciation in legacy sediments from the U-8 and U-12 Crib sites can be reproduced in bench-scale weathering experiments conducted on unimpacted Hanford sediments from the same formations; (2) Reactive transport modeling of future U releases from the vadose zone of acid-waste weathered sediments can be constrained by combining molecular-scale information on contaminant bonding environment with grain-scale information on contaminant phase partitioning, and meso-scale kinetic data on contaminant release from the waste-weathered porous media; (3) Although field contamination and laboratory experiments differ in their diagenetic time scales (decades for field vs. months to years for lab), sediment dissolution, neophase nucleation, and crystal growth reactions that occur during the initial disequilibrium induced by waste-sediment interaction leave a strong imprint that persists with memory effects over subsequent longer-term equilibration time scales.

Research Approach: We are developing an iterative measure-model approach that is applicable to elucidate mechanistic underpinnings of reactive contaminant transport in weathering geomedia.

Experimental design: Hypotheses are being tested by comparing the geochemical transformations and transport behaviors that occur in bench-scale studies of waste-sediment interaction with parallel solid-phase analyses of core sample extractions (scheduled for 2012-2013) from the acid uranium waste impacted U-8 and U-12 Cribs at Hanford. Crib waste aqueous simulants are being reacted with Hanford sediments in batch and column systems. Coupling of contaminant uptake to mineral weathering is being monitored using a suite of methods both during waste-sediment interaction, and after, when waste-weathered sediments are subjected to infusion with circumneutral background pore water solutions.

Results: We are currently in year 1 of the project, and have initiated a set of bench-scale batch weathering experiments where we are reacting Hanford Sediment with acidic, uranium bearing synthetic crib waste (SCW) solutions comprising a range in pH, uranium and phosphate concentrations. Parallel homogeneous nucleation experiments are being conducted to assess precipitation of reference uranium-bearing phases from supersaturated aqueous solution. Geochemical modeling is being conducted to assess aqueous speciation and the solubility envelopes of uranium-bearing solids as a function of system composition. These initial data streams guide follow-on experimental design and reactive transport modeling. These initial data streams guide follow-on experimental design and reactive transport modeling to understand the fate and transport of U in the Hanford subsurface.