ABSTRACT: Multi-faceted lines of inquiry are needed to bridge between molecular- and field-scale information. By focusing them on a common experimental design, we seek to reveal non-linear and emergent behavior in contaminated weathering systems. Silicate weathering reactions in acidic uranium waste streams are expected to result in ripening and aging of waste-containing secondary products.

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) 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; (2) 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; (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 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: Geochemical transformations and transport behaviors that occur in bench-scale studies of waste-sediment interaction will eventually be compared with parallel solid-phase analyses of core sample extractions 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 have accomplished a set of one year bench-scale batch weathering and flow-through column experiments where Hanford Sediment was reacted with U-bearing synthetic crib waste (SCW) solutions as a function of pH, U and phosphate concentrations. PO₄ exerts strong control over U speciation at all pH with the rapid precipitation of meta-ankoleite \([\text{K(UO}_2\text{PO}_4]·3\text{H}_2\text{O}\] leading to near complete immobilization of U. Bolwoodite \([\text{K(UO}_2](\text{HSiO}_4]·3\text{H}_2\text{O}\] increased even in PO₄-containing systems. Without PO₄, U speciation was controlled by the (pH-dependent) rate of silicate weathering. In this case, U immobilization was limited to 25-50% as precipitated becquerelite \([\text{Ca(UO}_2]_2\text{O}_4(\text{OH})_6·3\text{H}_2\text{O}\] or compragneacite \([\text{K}_2(\text{UO}_2]_6\text{O}_4(\text{OH})_6·3\text{H}_2\text{O}\] and bolwoodite. Mineral precipitate composition depends on initial solution pH. Carbonate dissolution buffers influent pH 3 solutions to ca. pH 7-8 and initial pH 2 solutions to ca. pH 3-4, with subsequent silicate weathering that makes Si⁴⁺ available for bolwoodite precipitation. Parallel homogeneous nucleation experiments and thermodynamic calculations
conducted to assess precipitation of reference uranium-bearing phases from supersaturated aqueous solutions confirmed the strong phosphate control over U speciation and multi-speciation of U in its absence. Geochemical modeling was further conducted to assess aqueous speciation and solubility envelopes of U-bearing solids as a function of system composition. These data streams guide follow-on desorption experiments and reactive transport modeling to understand the fate and transport of U in the Hanford subsurface.