

Quantifying and Predicting Reactive Transport of Uranium in Waste Plumes (EMSP Project 73775)

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Research Objectives

The Hanford Site is the DOE's largest legacy waste site, with uranium (U) from plutonium processing being a major contaminant in its subsurface. Accident release of highly concentrated high level wastes (e.g. 0.5 lb U(VI)/gal) left large quantities of U in the vadose zone under tank farms (e.g. 7-8 tons U(VI) under tank BX-102 (Jones et al., 2001)). The U contamination has been found in groundwater in both 300 and 200 Areas of Hanford, indicating U(VI) was/is mobile. Because excavation costs are enormous, this U will likely be left in-ground for the foreseeable future. Therefore, understanding the contamination processes and the resulting U spatial and temporary distributions and mobility in the heavily contaminated Hanford site is needed in order to forecast its future transport. The overall objective of this research is to develop an experimentally supported conceptual model of U reactive transport, during and after the tank leakage, at heavily U-contaminated areas of the Hanford vadose zone. The conceptual model will incorporate key geochemical and physical controls on the contamination process, explain the current distribution of U in the vadose zone, and guide predictions of its future mobility under the influence of natural recharge. We do not seek to predict the complex flow geometry of any specific waste plume. Instead, our work is trying to identify the hierarchy of processes relevant along U waste plume paths.

Research Progress and Implications

This report summarizes progress during the first two years (2004-2005) of our project. In pursuit of our research objective, we chose to simulate the tank BX-102 leakage/over-fill event (the largest single event of U release in the country, left 7-8 tons of U in the vadose zone). We synthesized the Metal Waste solution based on the historical recipe. The Metal Waste solution contained 110 mM U(VI), 3.6 M sodium, 0.6 M carbonate, and had a pH of 10.4. The waste solution was injected into a Hanford sand column (0.5 meter long) at 70°C. Flow was stopped prior to emergence of the waste solution in order to collect samples of pore solutions (suspensions) and sediments along the plume length. The profile of extracted pore solutions from a laboratory U plume immediately following sampling (without aging) is shown in Figure 1. Large quantities of U colloids formed at the plume front. The SEM photograph (Figure 2) shows two types of morphologies; sphere-like particles of about 200 nm in diameter, and plate-like particles up to a few μm . The EDS analyses found that U is a major component in both phases. Using synchrotron micro-XRD, the plate-like phase was identified as sodium uranyl carbonate. Shown in Figure 3 are several of the measured properties along plume profiles; normalized electrical conductivity (EC, normalized to that of the influent waste solution), pH, and turbidity. The normalized EC values are close to zero for the displaced soil water, and approach 1 for the plume body pore solution. The inflection point of the EC profile is used to identify the plume front, where the high ionic strength waste solution mixes with the low salinity soil water. The

plume pH decreases to 7 at the plume front, 3 units lower than the pH of initial waste solution (pH 10.4) and one unit lower than the pH of the displaced native sediment water (pH 8.4). Turbidity, a qualitative measure of particle concentration, reaches a peak value as high as 10,000 NTU (independently measured suspended mass content = 5%). The massive U precipitation at the plume front is caused by lower pH in the plume (as pH is lowered from 10 to 7, the solubility of a common U(VI)-oxides decrease by 3 orders of magnitude). Our aged (3 and 12 months) U column samples have recently been analyzed, and show a slightly decreased pH in the body of the plume, no changes at the pH-neutral front and absence of the mobile colloidal fraction (deposition onto sediment grains). More sample analyses are in progress.

Reactive transport modeling of the columns experiments was carried out by first matching the time-dependent liquid saturation and non-reactive tracer fronts in the column. The initially partially saturated column becomes fully saturated with water up to about 0.3 meters as the simulated tank solution is injected from below. Matching of the solution pH was carried out by including various mineral precipitation and dissolution reactions, the most important of which is calcite. Calcite precipitates because of the high bicarbonate in the injection solution and because of the desorption of Ca^{+2} from cation exchange sites on the clays as a result of the elution of the high Na^{+} , which competes for exchange sites with the Ca^{+2} . The precipitation of calcite releases hydrogen ion, thus lowering the pH (Figure 4). The simulations also predict the precipitation of brucite as a result of the high pH of the injection solution and the desorption of Mg^{+2} from exchange sites in the sediment. Other reactions, while less important for modeling of the pH, include the precipitation of various uranium phases, including uranium phosphate and schoepite (Figure 4). The simulations predict the precipitation of minor amounts of sodium uranium carbonate, a phase identified by XRD in the columns, but only upstream of the calcite desorption front, since the precipitation of calcite reduces bicarbonate in solution and de-stabilizes the sodium uranium carbonate.

Although U(VI) geochemistry has been extensively studied in equilibrium and near-equilibrium systems, our new results showing flow and transport induced heterogeneity of U distribution and speciation along the plume path have not been previously recognized. Through this project we expect to develop the experimental, conceptual, and numerical tools to predict field scale U spatial distribution, speciation, mineralogy, and future mobility.

Acknowledgments

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are needed to see this picture.

Figure 1. A photograph of a profile of extracted pore solutions from a simulated U plume at the time of initial plume formation (without aging). The flow direction is towards the right. Note the large quantity of U colloids formed at the plume front (unpublished).

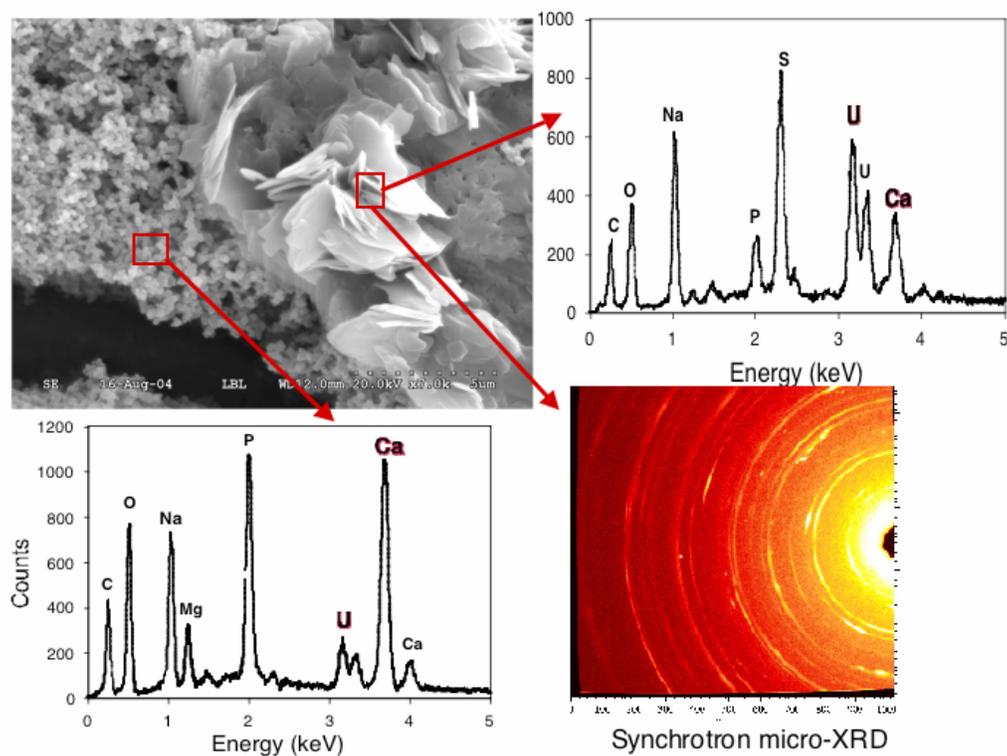


Figure 2. Characterization of the plume front colloids: morphology, chemical composition, and structure (unpublished).

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Figure 3. Measured profiles of normalized EC, pH and turbidity, along the plume length (unpublished).

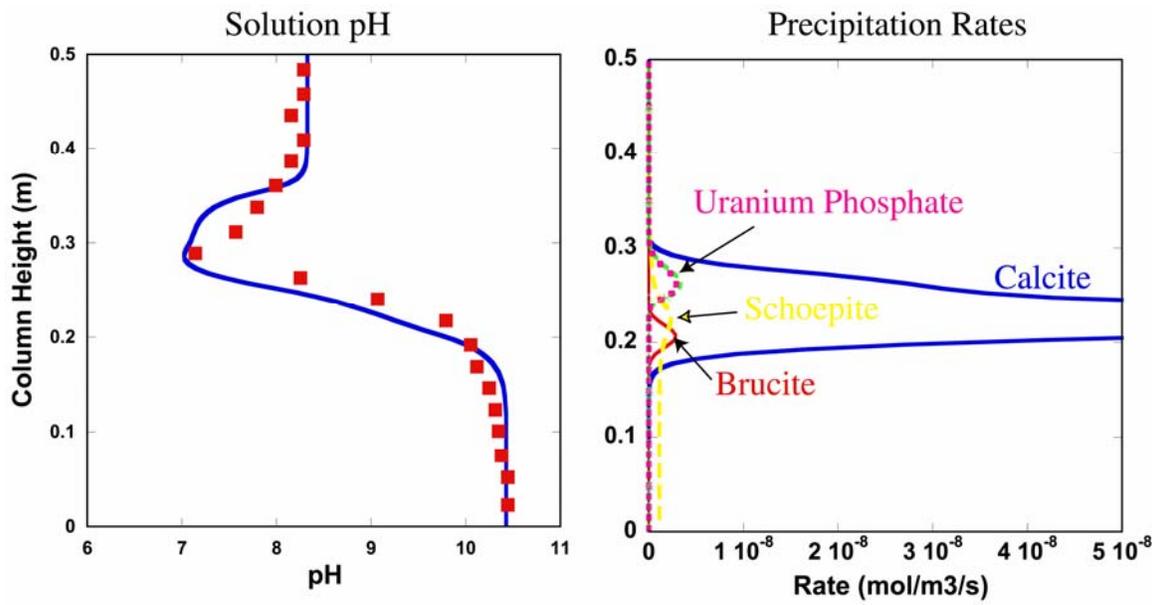


Figure 4. Example of reactive transport modeling of the columns experiments (unpublished).