

Kinetic Controls on the Desorption/Dissolution of Sorbed U(VI) and Their Influence on Reactive Transport

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BACKGROUND

A number of published studies have sought to understand geochemical kinetic process of uranium (U) that are relevant to nuclear waste sites and repositories by studying the weathering of U ore bodies and downgradient transport of weathering products. Such studies have provided important insights on processes operating over many thousands to millions of years. This project also seeks knowledge on the geochemical kinetics of U, but for shorter in-ground time periods (e.g., 20-50 years) relevant to DOE legacy waste sites. Several representative field sites were selected for intense study at Hanford as part of ENSP research to provide: (i) fundamental insights on intermediate duration geochemical events of U controlling fate and transport, and (ii) key scientific information needed for remedial action assessment and informed decision making.

The site discussed in this poster is the 300 A uranium plume. This plume is located at the south end of Hanford and discharges directly to the Columbia River (see right). The plume resulted from the discharge of fuels fabrication wastes (nitric acid solutions containing U and Pu) and cladding dissolution wastes (basic sodium aluminate) to the North and South Process Ponds between 1943 and 1975 near the Columbia River (see right). A KI-based remedial action assessment three years ago predicted that the plume would dissipate to concentrations below the DWQS within 10 y. As a result of this assessment, an interim, MNA remedial decision was agreed to by DOE and state/federal regulators. It has been 15 y since the above assessment, and groundwater concentrations have not decreased (attenuated) as projected. Stakeholders are now demanding remedial intervention, and DOE seeks science-based conceptual and numeric models for more accurate future projections.

OBJECTIVES

- Identify the chemical speciation (e.g., adsorption complexes or precipitates), mineral residence, and physical location of contaminant U in a depth sequence of sediments from the disposal source to groundwater.
- Measure desorption/dissolution rates of sorbed U(VI), quantify controlling factors, and develop descriptive kinetic models to provide a scientific basis for forecast U(VI) fluxes to groundwater, future plume dynamics, and long-term contaminant attenuation.
- Establish reaction networks and determine geochemically/physically realistic reaction parameters to drive state-of-the-art reactive transport modeling of U in vadose zone pore fluids and groundwater.

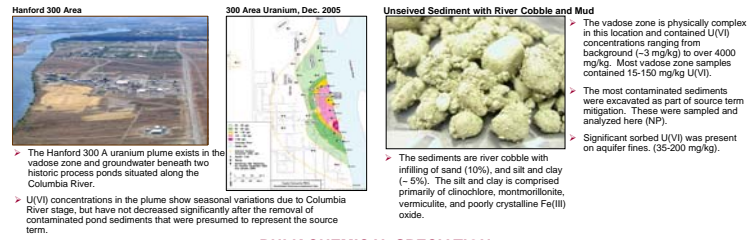
METHODS

- Sediments collected from excavations in the historic process ponds (see right).
- Bulk x-ray absorption spectroscopy (EXAFS) and cryogenic laser-induced fluorescence spectroscopy (CLIFS) to determine U(VI) mineral environment.
- X-ray and electron microscope, and transmission and scanning electron microscopy for spatial distribution, element association, and physical location mapping.
- Batch experiments at different solid-to-solution ratios to evaluate rates and equilibrium states of adsorption and solubility reactions.
- Column experiments of different sizes to assess in-situ rates of desorption/dissolution, mass transfer effects, and reaction parameter scaling.

PUBLICATIONS

- Arai, Y., M. A. Marcus, N. Tamura, J. A. Davis, and J. M. Zachara. 2007. Spectroscopic evidence for uranium bearing precipitates in vadose zone sediments at the Hanford 300-A site. *Environmental Science & Technology* (Accepted).
- Bond, D. L., J. A. Davis, and J. M. Zachara. 2007. Uranium(VI) dissolution and desorption from contaminated vadose zone sediments. *Geochimica et Cosmochimica Acta* (Accepted).
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- Fox, P. A., J. A. Davis, and J. M. Zachara. 2006. The effect of calcium on aqueous uranium(VI) speciation and adsorption to ferrihydrite and quartz. *Geochim. Cosmochim. Acta* 70(6):1379-1387.

HANFORD 300 A URANIUM PLUME



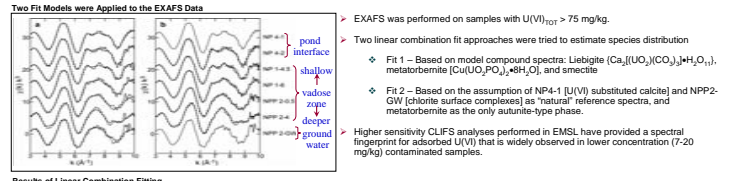
The Hanford 300 A uranium plume exists in the vadose zone and groundwater beneath two historic process ponds situated along the Columbia River.

The sediments are river cobble with infilling of sand (10%, and silt and clay (~5%). The silt and clay is comprised primarily of clinchroite, montmorillonite, vermiculite, and poorly crystalline Fe(II) oxide.

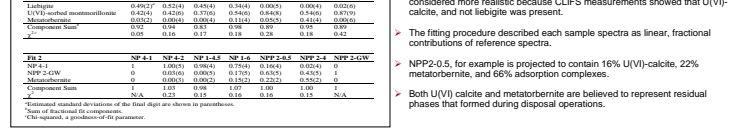
The most contaminated sediments were excavated as part of source term mitigation. These were sampled and analyzed here (NP).

Significant sorbed U(VI) was present on aquifer fines. (35-200 mg/kg).

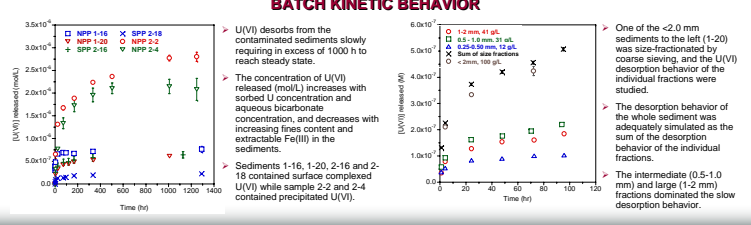
BULK CHEMICAL SPECIATION



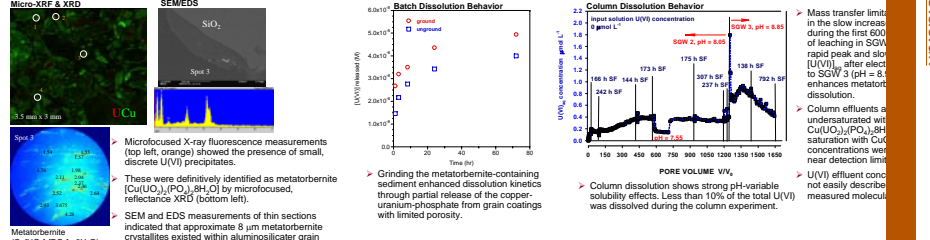
BATCH DISSOLUTION BEHAVIOR



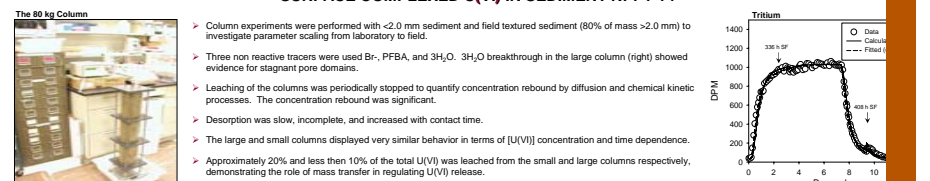
BATCH KINETIC BEHAVIOR



PRECIPITATED U(VI) IN SEDIMENT NPP2-4



SURFACE COMPLEXED U(VI) IN SEDIMENT NPP1-14



TRANSPORT EQUATION

$$\theta \frac{\partial C^*}{\partial t} + (1 - \theta) \rho_p \frac{\partial q}{\partial t} + \theta_m \frac{\partial C^*}{\partial t} + (1 - \theta_m) \rho_p \frac{\partial q_m}{\partial t} = \theta \partial D (C^*)^2$$

$$\frac{\partial q}{\partial t} = \frac{\partial q_{eq}}{\partial t} - \frac{\partial q_{eq}}{\partial t} = \sum_{i=1}^n \alpha_i (S_i^{n_i} - q_i^{n_i}) \quad S_i^* = f(C^*, C^*, \dots, C^*)$$

$$\frac{\partial q_m}{\partial t} = \frac{\partial q_m}{\partial t} = \sum_{i=1}^n \alpha_i (S_i^{n_i} - q_i^{n_i}) \quad S_i^* = f(C^*, C^*, \dots, C^*)$$

MULTI-CONTINUUM REACTIVE TRANSPORT MODEL

