

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 related 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 operative 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 EMS² 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 and nitric acid solutions containing U and Cu) 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 K-1 based remedial action assessment (three years ago) predicted that the plume would dissipate to concentrations below the DWG 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) molecular 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 area. *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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- Catalano, J. G., J. P. McKinley, J. M. Zachara, S. C. Smith, and G. E. Brown, Jr. 2006. Changes in uranium speciation through a depth sequence of contaminated Hanford sediments. *Environ. Sci. Technol.*, 40(9):2517-2524.
- Chang, H.-S., G. V. Korshin, Z. Wang, and J. M. Zachara. 2006. Adsorption of uranyl on gibbsite: A time-resolved laser-induced fluorescence spectroscopy (TRIFS) study. *Environ. Sci. Technol.*, 40(4):1244-1249.
- 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

Hanford 300 Area



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

U(VI) concentrations in the plume show seasonal variations due to Columbia River stage, but have not decreased significantly after the removal of contaminated pond sediments that were presumed to represent the source term.

300 Area Uranium, Dec. 2005



Unsewed Sediment with River Cobble and Mud



The vadose zone is physically complex in this location and contains U(VI) concentrations ranging from background (~3 mg/kg) to over 4000 mg/kg. Most vadose zone samples contained 15-150 mg/kg U(VI).

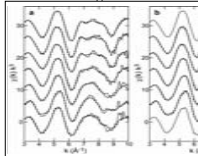
The most contaminated sediments were excavated as part of source term mitigation. These were sampled and analyzed here (NP).

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

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

BULK CHEMICAL SPECIATION

Two Fit Models were Applied to the EXAFS Data



Results of Linear Combination Fitting

Fit	NP-1.4	NP-2.4	NP-1.4.3	NP-1.4	NP-2.4.5	NP-2.4	NP-2.4.6W
U(VI) sorbed monometallic	0.4977	0.2121	0.4741	0.3444	0.0075	0.0041	0.0210
U(VI) dissolved monometallic	0.5124	0.2100	0.2700	0.5144	0.0416	0.0416	0.0416
U(VI) sorbed bimetallic	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
U(VI) dissolved bimetallic	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Chi-squared	0.022	0.024	0.024	0.014	0.019	0.019	0.019
Standard Error	0.01	0.01	0.01	0.01	0.01	0.01	0.01

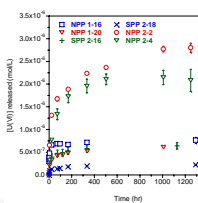
*Estimated standard deviation of the final fit; all errors are shown in parentheses.

Chi-squared, a goodness-of-fit parameter.

- EXAFS was performed on samples with U(VI)_{total} > 75 mg/kg.
- Two linear combination fit approaches were tried to estimate species distribution
 - Fit 1 – Based on model compounds: Liebigite (Ca₂[UO₂(CO₃)₂·3H₂O]·nH₂O), metaborite (Cu(UO₂)₂·8H₂O), and smectite
 - Fit 2 – Based on the assumption of NP-1 (U(VI) substituted calcite) and NPP2-GW (chlorite surface complexes) as 'natural' reference species, and metaborite as the only autunite-type phase.
- Higher sensitivity CLIFS analyses performed in EMSL have provided a spectral fingerprint for adsorbed U(VI) that is widely observed in lower concentration (7-20 mg/kg) contaminated samples.

- Although the goodness of fit parameters χ^2 were equivalent, Fit 2 was considered more realistic because CLIFS measurements showed that U(VI)-calcite, and not liebigite was present.
- The fitting procedure described each sample spectra as linear, fractional contributions of reference species.
- NPP2-0.5, for example is projected to contain 16% U(VI)-calcite, 22% metaborite, and 66% adsorption complexes.
- Both U(VI) calcite and metaborite are believed to represent residual phases that formed during disposal operations.

BATCH KINETIC BEHAVIOR

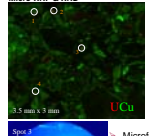


- U(VI) desorbs from the contaminated sediments slowly requiring in excess of 1000 hr to reach steady state.
- The concentration of U(VI) released (mol/L) increases with sorbed U concentration and aqueous bicarbonate concentration, and decreases with increasing fines content and extractable Fe(II) in the sediments.
- Sediments 1-16, 1-20, 2-16 and 2-18 contained surface complexed U(VI) while sample 2-2 and 2-4 contained precipitated U(VI).

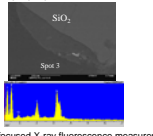
- One of the <2.0 mm sediments to which fit (1-20) was size-fractionated by coarse sieving, and the U(VI) desorption behavior of the individual fractions were studied.
- The desorption behavior of the whole sediment was adequately simulated as the sum of the desorption behavior of the individual fractions.
- The intermediate (0.5-1.0 mm) and large (1-2 mm) fractions dominated the slow desorption behavior.

PRECIPITATED U(VI) IN SEDIMENT NPP2-4

Micro-XRF & XRD



SEM/EDS

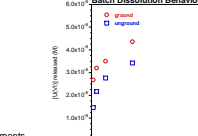


Microfocused X-ray fluorescence measurements (top left, orange) showed the presence of small, discrete U(VI) precipitates.

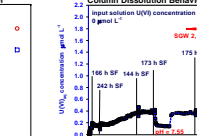
These were definitively identified as metaborite (Cu(UO₂)₂(PO₄)₂·8H₂O) by microfocused, reflectance XRD (bottom left).

SEM and EDS measurements of thin sections indicated that approximately 8 μm metaborite crystallites existed within aluminosilicate grain coatings (above right).

Batch Dissolution Behavior



Column Dissolution Behavior



- Grinding the metaborite-containing sediment enhanced dissolution kinetics through partial release of the copper-uranium-phosphate from grain coatings with limited porosity.
- Column dissolution shows strong pH-variable solubility effects. Less than 10% of the total U(VI) was dissolved during the column experiment.

Mass transfer limitations evident in the slow increase in [U(VI)]_{eff} during the first 600 pore volumes of leaching in SGV 2, and the rapid peak and slow decrease in [U(VI)]_{eff} after electrolyte change to SGV 3 (pH = 8.5) which enhances metaborite dissolution.

Column effluents are under-saturated with Cu(UO₂)₂(PO₄)₂·8H₂O but near saturation with Cu₂(PO₄)₂. U(VI) effluent concentrations are not easily described using measured molecular speciation.

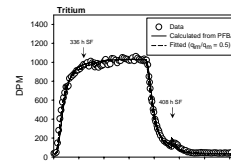
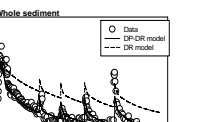
SURFACE COMPLEXED U(VI) IN SEDIMENT NPP1-14

The 80 kg Column



- Column experiments were performed with <2.0 mm sediment and field textured sediment (80% of mass >2.0 mm) to investigate parameter scaling from laboratory to field.
- Three non reactive tracers were used: Br-, PFBA, and 3H₂O. 3H₂O breakthrough in the large column (right) showed evidence for stagnant pore domains.
- Leaching of the columns was periodically stopped to quantify concentration rebound by diffusion and chemical kinetic processes. The concentration rebound was significant.
- Desorption was slow, incomplete, and increased with contact time.
- The large and small columns displayed very similar behavior in terms of [U(VI)] concentration and time dependence.
- Approximately 20% and less than 10% of the total U(VI) was leached from the small and large columns respectively, demonstrating the role of mass transfer in regulating U(VI) release.

Whole sediment



Transport Equation:

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

Mobile Domain Multi-Rate Equation:

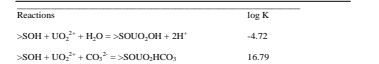
$$\frac{\partial C^*}{\partial t} = \sum_{i=1}^n \frac{\partial C_i^*}{\partial t} = \sum_{i=1}^n (S_i^* q_i^* - q_i^{*n}) \quad S_i^* = f(C_i^*, C^*, C^*)$$

Mass Exchange Between Mobile and Immobile Domains:

$$\theta_m \frac{\partial C^*}{\partial t} + (1-\theta_m) \rho_s \frac{\partial q_m}{\partial t} = \theta_m \alpha_m (C^* - C^*)$$

Immobile Domain Multi-Rate Equation:

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



MULTI-CONTINUUM REACTIVE TRANSPORT MODEL

- The column experiments were modeled with a surface complexation model to describe the adsorption process, and a distributed first order rate model to describe the apparently slow mass transfer of competitive sorbates (see right).
- The same model parameters (site density in moles/m²; SCM reaction constants, and first order rate distribution function) could be used to describe both columns only when a stagnant or immobile water domain was added to the large column model. This immobile domain was characterized from the 3H₂O breakthrough data.
- A combination of bulk and spatially resolved molecular speciation measurements (XAS, CLIFS), high resolution electron microscopy (SEM, TEM), and batch and column desorption/dissolution studies have shown that U(VI) is associated with microporous, diffusion-limited domains (grain coatings and interparticle fractures) in contaminated 300 A sediment that impart strong time dependency to chemical reactions instigated by water contact. These associations are as follows ranging from shallow on the left; red indicates regions of U localization.
- Calcium carbonate coatings with coprecipitated U(VI) exist on lithic fragments in the source term area [U(VI) > 500 mg/kg].
- 5-10 μm metaborite laths (Cu(UO₂)₂(PO₄)₂·8H₂O) exist as discrete crystallites within anthropogenic aluminosilicate grain coatings.
- Surface complexed U exists within natural physicochemical aggregates (containing chlorite, mica/vermiculite, and Fe(II) oxide) on river gravels, and within intra-particle fractures of lithic fragments.
- Highly distributed, adsorbed U(VI) exists within mud domains (aggregated physicochemicals) in fine-textured facies of Hanford formation aquifer sediments.