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

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The vadose zone is physically comple

in this location and contained U(VI)



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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 repositiories by tudying the weathering of U ore bodies and downgradient transport of weathering products. Such studies have provided important insights on processes operative over many thousand to millions of years. This project also seeks knowledge on the eochemical kinetics of U. but for shorter in-ground time periods (e.g., 20-50 years) elevant to DOE legacy waste sites. Several representative field sites were selected for intense study at Hanford as part of EMSP research to provide; i) fundamental nsights 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 olutions 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 Kd-based remedial action assessment fifteen years ago predicted that the plume would dissipate to concentrations below the DWS within 0 v. As a result of this assessment, an interim, MNA remedial decision was agreed o by DOE and state/federal regulators. It has been 15 v since the above assessment, and groundwater concentrations have not decreased (attenuated) as projected. Stakeholders are now demanding remedial intervention, and DOE seeks cience-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 to 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 microprobe 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

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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

Two Fit Models were Applied to the EXAFS Data

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Results of Linear Combination Fitting

| Fit 1 | NP 4-1 | NP 4-2 | NP 1-4.5 | NP 1-6 | NPP 2-0.5 | NPP 2-4 | NPP 2- |
|---|-----------------------|---|---|---|--|--|-------------------------------|
| Liebigite | 0.49(2)" | 0.52(4) | 0.45(4) | 0.34(4) | 0.00(5) | 0.00(4) | 0.02(6) |
| U(VI)-sorbed montmorillonite | 0.42(4) | 0.42(6) | 0.37(6) | 0.54(6) | 0.84(8) | 0.54(6) | 0.87(9) |
| Metatoebernite | 0.03(2) | 0.00(4) | 0.00(4) | 0.11(4) | 0.05(5) | 0.41(4) | 0.00(6) |
| Component Sum" | 0.92 | 0.94 | 0.83 | 0.98 | 0.89 | 0.95 | 0.89 |
| 27 | de start | 10 A 10 | | | de desta | the second | de sete |
| 2 | 0.05 | 0.16 | 0.17 | 0.18 | 0.28 | 0.18 | 0.42 |
| 2 Fit 2 | NP 4-1 | 0.16 NP 4-2 | NP 1-43 | NP 1-6 | 0.28 NPP 2-0.5 | NPP 2-4 | 0.42 NPP 2- |
| Z Fit 2 NP 4-1 | NP 4-1 | 0.16 NP 4-2 1.00(5) | NP 1-4.5 0.98(4) | 0.18 NP 1-6 0.75(4) | 0.28 NPP 2-0.5 0.16(4) | 0.18 NPP 2-4 0.02(4) | 0.42 NPP 2- 0 |
| Z FR 2 NP 4-1 NP 2-GW | NP 4-1 1 0 | NP 4-2 1.00(5) 0.03(6) | NP 1-4.5 0.98(4) 0.00(5) | 0.18 NP 1-6 0.75(4) 0.17(5) | 0.28 NPP 2-0.5 0.16(4) 0.63(5) | 0.18 NPP 2-4 0.02(4) 0.43(5) | 0.42 NPP 2- 0 1 |
| Z Fit 2 NP 4-1 NP 2-CW Metatoebernite | NP 4-1 1 0 0 | 0.16 NP 4-2 1.00(5) 0.03(6) 0.00(3) | NP 1-4.5 0.98(4) 0.00(5) 0.00(2) | 0.18 NP 1-6 0.75(4) 0.17(5) 0.15(2) | 0.28 NPP 2-0.5 0.16(4) 0.63(5) 0.22(2) | 0.18 NPP 2-4 0.02(4) 0.43(5) 0.55(2) | 0.42 NPP 2- 0 1 0 |
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em of fractional fit components. hi-squared, a goodness-of-fit parameter



HANFORD 300 A URANIUM PLUME

eived Sediment with River Cobble and Muc



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 LI(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 clinochlore, montmorillonite vermiculite, and poorly crystalline Fe/III oxide

BULK CHEMICAL SPECIATION

EXAFS was performed on samples with U(VI)_{TOT} > 75 mg/kg.

- Two linear combination fit approaches were tried to estimate species distribution
- Fit 1 Based on model compound spectra: Liebigite {Ca₂[(UO₂)(CO₃)₃]•H₂O₁₃} metatorbernite (Cu(UO,PO,),+8H,O), and smectite
- Fit 2 Based on the assumption of NP4-1 [U(VI) substituted calcite] and NPP2-GW [chlorite surface complexes] as "natural" reference spectra, and metatorhernite as the only autunite-type phase

Higher sensitivity CLIFS analyses performed in EMSL have provided a spectral fingernrint for adsorbed LI(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 spectra.

NPP2-0.5 for example is projected to contain 16% U(VI)-calcite 22% metatorbernite, and 66% adsorption complexes

Both U(VI) calcite and metatorbernite are believed to represent residual phases that formed during disposal operations

BATCH KINETIC BEHAVIOR



PRECIPITATED U(VI) IN SEDIMENT NPP2-4





[Cu(UO₂)₂(PO₄)₂8H₂O] by microfocused, reflectance XRD (bottom left).

indicated that approximate 8 µm metatorbernite crystallites existed within aluminosilicater grain coatings (above right)



SEM and EDS measurements of thin sections

Time (hr)

Batch Dissolution Behavio



with limited porosity

PORE VOLUME V/V, U(VI) effluent cond Column dissolution shows strong pH-variable not easily describe solubility effects. Less than 10% of the total U(VI) measured molecul was dissolved during the column experiment

GW 3. pH = 1



- 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 nore domains
- Leaching of the columns was periodically stopped to quantify concentration rebound by diffusion and chemical kinetic processes. The concentration rehound 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 then 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.

Column Dissolution Rehavio

80W 2 nH = 8

175 h SF

ERO 750 000 1050 1000 1050 1500 1651



- > 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 3H O breakthrough data

MULTI-CONTINUUM REACTIVE TRANSPORT MODEL

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 sho 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 contact. These associations are as follows ranging from shallow on the left to deep on the right: red indicates regions of U localization.

Calcium carbonate coatings with coprecipitated U(VI) exist on lithic fragments in the source term area [U(V]) > 500 mg/kg]

5-10 um metatorbernite laths [Cu(LO_PO_)_8H_O] exist as discrete crystallites within anthropogénic aluminosilicate grain coatings



and Fe(III) oxide) on river gravels, and



O Data 335 h Si --- Fitter 0 2 6 8 Pore volume $\theta \frac{\partial C_i^n}{\partial c_i} + (1 - \theta) \rho_i \frac{\partial q_i^n}{\partial a} + \theta_{in} \frac{\partial C_i^{in}}{\partial a} + (1 - \theta_{in}) \rho_i$ $\frac{\partial q_i^m}{\partial q_i} = \theta AD(C_i^m)$ i=1, 2, ..., N



- ∂q_i^{h} $\sum_{i=1}^{ME} \frac{\partial q_i^{im,k}}{\partial q_i} =$ $-a_{i}^{in,k}$) $S_{i}^{in} = f(C_{i}^{in}C_{2}^{in},...)$ ∂t *d* ∂t
- Reactions log K $>SOH + UO_3^{2+} + H_3O = >SOUO_3OH + 2H_3OH +$ -4.72 >SOH + UO32+ + CO32 = >SOUO3HCO3 1679















