

# Microscopic Reactive Transport and Its Effect on Scale-Dependency of Geochemical and Biogeochemical Reaction Rates in Subsurface Porous Media

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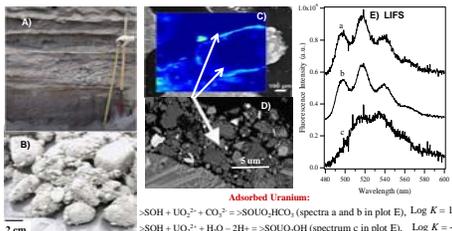


## Introduction and Objective

Geochemical and biogeochemical reaction rates are important variables controlling the reactive transport of contaminants in subsurface environment. The objective of this research is to understand the effect of pore- and subpore-scale reactive mass transfer/transport processes on the rates and their scale-dependency of geochemical and biogeochemical reactions in heterogeneous porous media, and to derive scaling relationships of transport and reaction parameters from the molecular to the pore, and from the pore to the continuum scales. This poster presents: 1) the scale-dependent phenomenon of uranium desorption rates from a contaminated sediment collected from the U.S. Department of Energy's Hanford site; 2) microscopic flow and reactive transport models to interpret the scale-dependent rates at the macroscopic scale; and 3) future microscopic researches in collaboration with other PNNL/SFA projects and activities.

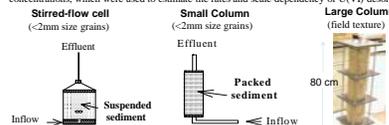
## Sediment and Uranium Properties

The sediment used for U(VI) desorption study was collected from the Hanford 300 Area. The field sediment was a coarse-textured sandy gravel consisting of 86% of river cobbles and gravel, 6% of large sand, and 8% of <2 mm size fraction (Plots A and B). Contaminant U(VI) was associated within the intragrain or intra-coating regions in the <2mm size fraction in the sediment (Plots C and D) and existed as adsorbed (surface-complexed) phases (Plot E).



## Approach

**Experiment:** Stirred flow-cell, small column, and large column systems were used to measure effluent U(VI) concentrations, which were used to estimate the rates and scale-dependency of U(VI) desorption.



**Modeling:** Macroscopic reactive transport model was used to derive the apparent rate constants from the experimental data. Microscopic (pore-scale lattice Boltzmann) model was used to provide insights into the scale-dependent phenomenon of U(VI) desorption rates.

**Flow Equation:** Constant, measured  

$$\rho \frac{\partial \mathbf{v}}{\partial t} + \rho \mathbf{v} \cdot \nabla \mathbf{v} = \rho \mathbf{F} - \nabla p + \mu \nabla^2 \mathbf{v}$$
**Transport Equation:**  

$$\frac{\partial C_i}{\partial t} = \nabla \cdot (D_i \nabla C_i) - \nabla \cdot (\mathbf{v} C_i) + R_i$$

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## Scale-Dependent Rates of U(VI) Desorption

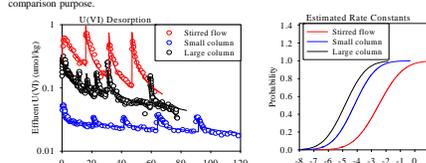
The U(VI) desorption rate was described using a distributed rate model, which couples U(VI) aqueous and surface speciation reactions, and multiple first-order mass exchange expressions. Experimentally measured effluent U(VI) concentrations were used to estimate the apparent rate constants of U(VI) desorption using the macroscopic reactive transport model. The rate constants in the U(VI) desorption rate expression were assumed to follow a lognormal distribution.

**Rate Expression**  

$$R_i = \frac{(1-\theta) \rho_s}{\theta} \sum_{j=1}^n \left( a_j \sum_{l=1}^m \frac{\partial q_{jl}}{\partial t} \right); \frac{\partial q_{jl}}{\partial t} = a_{jl}' (q_{jl}' - q_{jl}')$$
**Rate Constant Distribution**  

$$p(\alpha) = \frac{1}{\sigma \sqrt{2\pi}} \exp\left(-\frac{1}{2\sigma^2} (\ln(\alpha) - \mu)^2\right)$$

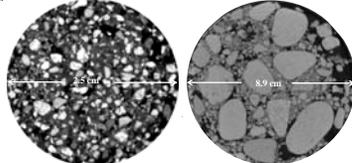
The rate constants ( $a_{jl}'$ ) were normalized to the <2 mm size fraction in all experimental systems for comparison purpose.



- Measured (symbols) and calculated (lines) effluent U(VI) concentrations (left) after normalizing to the mass of the <2 mm size fraction in the sediment with the estimated rate constant distribution (right). The flow residence time is 0.45, 1.22, and 22.7 hours, in stirred flow-cell, small, and large column systems respectively.
- Expected mean (right plot) of the rate constant distribution normalized to the <2 mm size fraction, demonstrating that the apparent rate of U(VI) desorption decreased with increasing scale.

## Porous Media Structure in the Columns

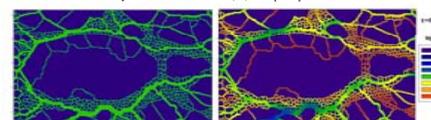
The scale-dependent phenomenon of the U(VI) desorption was attributed to the pore-scale heterogeneity in pore size, surface area, and pore connectivity that was not accounted for by the macroscopic reactive transport model. X-ray CT scanning was performed to provide insights into the pore-scale heterogeneity in the columns.



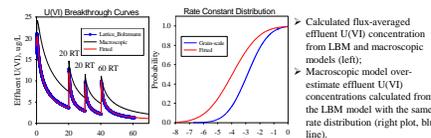
- Heterogeneous porous medium in the small column containing the <2 mm size fraction of the sediment (left) and field-textured sediment (right).

## Interpretation of Scale-Dependent Rates

A 2-D (D2Q9) LBM was assembled to interpret the scale-dependent phenomenon of the U(VI) desorption rates. The pore scale model was constructed based on the measured porosity, grain-size distribution, hydraulic conductivity and dispersivity in the columns. X-ray CT information provided guidelines for assembling the distribution and orientations of pores and grains. The U(VI) desorption was treated as a boundary reaction, which supplied U(VI) to the pore phase. Rate constants estimated from the stirred flow-cell system were used for the U(VI) desorption process.



- Model pore geometry (green: pore domain; dark blue: solid domain).
- A snapshot of dissolved U(VI) concentrations as a result of U(VI) desorption and diffusion from solid surfaces. No advection.
- Steady state flow field, showing high flow velocity (magnitudes) in large pores and low flow velocity in small pores. Average pore flow velocity = 10 cm/hour when L=4 mm.
- A snapshot of dissolved U(VI) concentration as a result of: 1) desorption from solid surfaces, 2) pore-phase diffusion, and 3) pore-scale advection (from left to right).



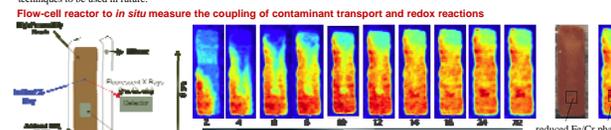
- Calculated flux-averaged effluent U(VI) concentration from LBM and macroscopic models (left).
- Macroscopic model over-estimate effluent U(VI) concentrations calculated from the LBM model with the same rate distribution (right plot, blue line).

## Summary and Conclusions

- The rate constants of U(VI) desorption estimated from the effluent concentrations decreased with increasing scale.
- The scale-dependency of U(VI) desorption rates was attributed to the pore-scale reactive mass transport, which was lumped into the desorption rate term in the macroscopic model. The LBM simulations confirmed the role of the pore-scale mass transport in decreasing the apparent rate of U(VI) desorption.
- Further researches at different scales are needed to understand the effect of coupled pore-scale mass transport and reactions on the scale-dependent rates for other geochemical and biogeochemical reactions, and to develop approaches to scale reaction rates.

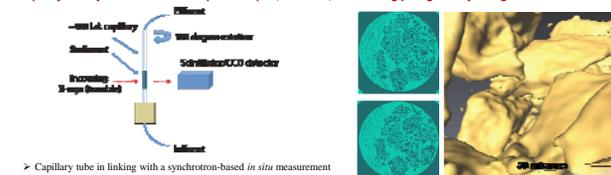
## Future Research

**Experimental Investigation:** Microscopic experiments using micromodel, capillary tube, and flow-cell systems with *in situ* measurement techniques will be developed or modified to evaluate pore- and subpore-scale mass transfer/transport processes, and coupling of transport and reactions at the pore-scale in collaboration with other SFA projects and activities. The following demonstrates some of the new techniques to be used in future.



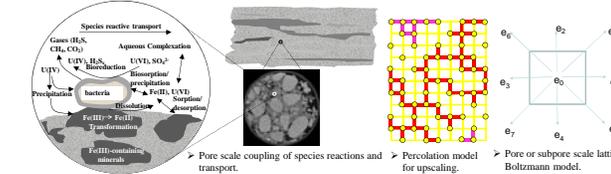
- (Left) The milled-polyester flow-cell reactor with an internal geometry of 2x6 cm and influent/effluent ports. The face of the reactor is made of a highly X-ray transparent thin polyester film for *in situ* 2-D X-ray fluorescence mapping of elements, oxidation states, and coordination environment.
- (Right) An example of *in situ* mapping the contaminant (Cr) reduction in the flow-cell.
- The flow-cell reactor will be used to examine the diffusion and redox reactions in Ringold sediments.

## Capillary tube system to measure coupled transport, reactions, and evolving pore geometry changes



- Capillary tube in linking with a synchrotron-based *in situ* measurement system to map 3-D physical structure of porous media at the pore scale and pore structure evolution during coupled transport and reactions.
- Tunable X-rays to map the distribution of heavy elements within an evolving pore-network (e.g. uranium-bearing solids).
- Synchrotron-based X-ray tomography of the grain and pore distribution in the capillary tube (left).
- Reconstruction of a 3-D solid/pore network (right).

**Model Development and Validation:** Microscopic reactive transport models using percolation, lattice Boltzmann, and continuum approaches will be developed or modified to understand the pore and subpore scale coupling of transport and reactions for experimental data interpretation, scientific concept validation, and upscaling of geochemical and biogeochemical reaction rates.



Pore scale coupling of species reactions and transport. Percolation model for upscaling. Pore or subpore scale lattice Boltzmann model.

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