

Microscopic Mass Transfer of U and Tc in Porous Media

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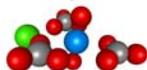
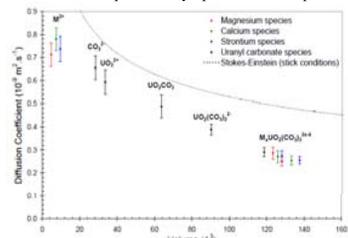
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Introduction

This project focuses on investigating microscopic mass transfer processes of U and Tc, and their influence on and coupling with geochemical and biogeochemical reactions in subsurface sediments. Major goals are: 1) to characterize and model reactive diffusion at the pore and grain scales that exerts a fundamental kinetic control on the microscopic mass transfer and chemical reactivity of U and Tc in subsurface microenvironments; and 2) to derive scaling relationships of mass transfer parameters from the molecular to the pore, and from the pore to the continuum scales in porous media. Research in FY09 has been focused on measuring and developing models to describe U(VI) mass transfer in Hanford 300A sediments at different scales.

Molecular Diffusion of Aqueous U(VI) Species

Molecular dynamics (MD) models are used to simulate the molecular diffusion of uranyl species in groundwater and pore water. The simulation results are then used to calculate the molecular diffusion coefficients of aqueous U(VI) species. In FY09, we have developed a MD model to calculate the molecular diffusion of the aqueous uranyl species that are expected to be dominant in Hanford groundwater.



Species	UO ₂ (CO ₃)	UO ₂ (CO ₃) ₂ ⁻	UO ₂ (CO ₃) ₃ ²⁻
D (10 ¹⁰ m ² ·s ⁻¹)	0.49(5)	0.39(2)	0.29(2)
Species	Mg ²⁺	MgUO ₂ (CO ₃) ₂ ⁻	Mg ₂ UO ₂ (CO ₃) ₂
D (10 ⁹ m ² ·s ⁻¹)	0.71(5)	0.29(3)	0.25(2)
Species	Ca ²⁺	CaUO ₂ (CO ₃) ₂ ⁻	Ca ₂ UO ₂ (CO ₃) ₂
D (10 ⁹ m ² ·s ⁻¹)	0.78(7)	0.27(3)	0.25(2)
Species	Sr ²⁺	SrUO ₂ (CO ₃) ₂ ⁻	Sr ₂ UO ₂ (CO ₃) ₂
D (10 ⁹ m ² ·s ⁻¹)	0.74(5)	0.27(2)	0.26(2)

➤ MD-calculated molecular diffusion coefficient of aqueous uranyl species as a function of molecular size.

➤ The MD-calculated diffusion coefficients of aqueous uranyl species deviate from the Stokes-Einstein theory because of the complex molecular structures and hydration properties of the uranyl species.

➤ The diffusion coefficients of uranyl carbonate complex species, which dominate Hanford groundwater, range from 2.5 - 5 x 10⁻¹⁰ m²/s, which is lower than the apparent measured diffusion coefficient of 1.6-1.7 x 10⁻¹⁰ m²/s in Hanford sediment. Research is ongoing to investigate the charge and surface coupling effects on this difference.

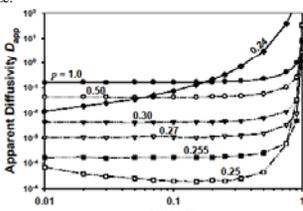
Scaling Molecular Diffusion Coefficient to Pore-Network

Percolation-based theory is used to generate stochastic realization of pore-networks within sediment grains for particle tracking modeling. The simulation results of the particle tracking modeling in the realized pore-networks are used to establish theoretical relationships for scaling molecular diffusion coefficient from pore water to the pore network in the porous media. In FY09, we have derived a scaling relationship of the molecular diffusion coefficient in an idealized system containing spherical particles with variable pore connectivity (i.e., pore coordination number) and grain size.

Scaling function in spherical particles

$$D_{app}(p, R) = \alpha \begin{cases} (p - p_c)^{\mu - \beta} & R > (p - p_c) \\ R^{-(\mu - \beta)/\nu} & R < (p - p_c) \end{cases} \left(\frac{\mu - \beta}{\mu - \beta} \right)^{\nu}$$

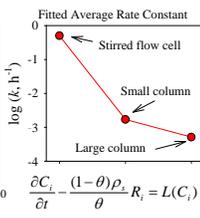
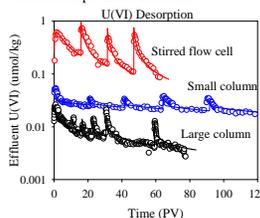
D_{app} is the apparent diffusion coefficient in the pore-network for solute to diffuse out of intragrain regions, p is the pore connectivity, R is the particle radius, and α is a linear function of molecular diffusion coefficient and particle geometry, and other parameters are the percolation parameters that are constants based on percolation theory. The numerical value of the apparent diffusion coefficient was demonstrated in the right plot.



➤ Apparent diffusion coefficient as a function of pore connectivity (p) and residual solute mass in spherical grains. The apparent diffusion coefficient was normalized to molecular diffusion coefficient.

Scale-Dependent U(VI) Desorption Rates

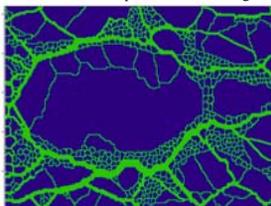
Experimental and modeling studies of U(VI) desorption from a reference 300A sediment were performed to evaluate the scale-dependence of U(VI) desorption rates. The measured effluent U(VI) concentrations and chemical compositions from a stirred-flow reactor and a small column containing the <2 mm size fraction of the sediment, and a large 80 kg column with disturbed field textured sediments (85% > 2mm) were used to estimate the rates of U(VI) desorption using a distributed mass transfer model, which integrates the U(VI) aqueous and surface complexation reactions.



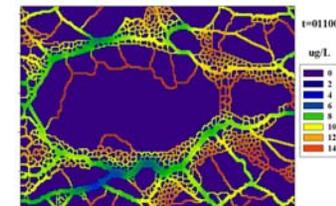
➤ Left plot: The effluent U(VI) concentration after normalizing to the mass of the <2 mm size fraction in the sediment;
➤ Right: averaged rate of U(VI) desorption from the <2 mm size fraction decreased with increasing scale; implying field scale rate will be even slower.
➤ Right bottom: Math equation for describing effluent data in different systems.

Interpretation of Scale-Dependent Rates

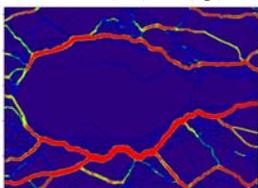
A Lattice Boltzmann model (LBM) was developed to interpret the scale-dependent rates of U(VI) desorption. The LBM model was constructed based on the measured porosity, hydraulic conductivity, and hydraulic dispersivity of the intact sediments from Hanford 300A IFR site. X-ray tomographic measurement of pore and grain structures in the intact sediments provided guidelines for the distributions and orientations of pores and grains. U(VI) exchange between solids and the pore fluid was through the distributed mass transfer model.



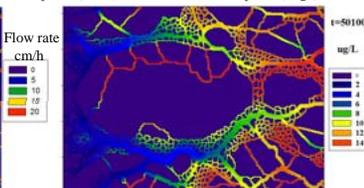
➤ Two-dimensional pore geometry consisting heterogeneous distribution of pores (green) and solid particles (dark blue) with a resolution of 1000 (wide) x 600 (high) nodes.



➤ A snapshot of dissolved U(VI) concentration profiles as a result of: 1) grain-scale mass transfer from solid surfaces to pores and 2) pore phase diffusion from high concentration pores (small) to low concentration pores (large).



➤ A snapshot of heterogeneous distribution of flow field, showing high flow velocity (magnitude) in large pores and low flow velocity in small pores.



➤ A snapshot of dissolved U(VI) concentration profiles as a result of: 1) grain-scale mass transfer, 2) pore-phase diffusion, and 3) pore-scale advection (from left to right).

➤ **Summary:** The LBM model simulations predict that U(VI) desorption rates will decrease with increasing scale as a result of the coupling of the grain-scale mass transfer kinetics and heterogeneous diffusion/advection in the pore phase. The results explained the observed scale-dependent U(VI) desorption rates, and implied that the macroscopic rates of other geochemical and biogeochemical reactions will also be scale-dependent, and incorporating geochemical and biogeochemical reactions in macroscopic reactive transport models will require careful consideration of both the grain-scale and pore-scale mass transfer.

Proposed Research at FY10

FY10 will continuously investigate physical and chemical factors controlling the microscopic mass transfer rates of U(VI) and its scale dependent behavior in porous media. The following specific research tasks are proposed:

- 1) The molecular model established in FY09 to simulate the diffusion of aqueous uranyl species that dominate in the Hanford groundwater will be modified and extended to simulate the molecular diffusion of uranyl species in pore water in the microporous domains with variable pore size and mineral surface charge properties. The results will be used to calculate the apparent diffusion coefficients of uranyl species in pore water affected by the coupling of charge and surface in microporous domains and to explain the apparent deviations (observed in FY09 research) between the molecular diffusion coefficients in free groundwater and restricted porewater in porous media.
- 2) Species-based diffusion model will be established at the continuous scale which directly integrates the MD-calculated molecular diffusion coefficients to evaluate the coupling effect of uranyl speciation and charges, and aqueous and surface complexation reactions on the apparent rates of U(VI) adsorption and desorption in microenvironments. The model will be evaluated against experimental data in low permeability materials.
- 3) The Lattice Boltzmann model (LBM) developed in FY09 is for a single reactive species only. In FY10, a multi-component, multi-species U(VI) diffusion theory will be developed in a format of LBM to describe U(VI) reactive diffusion at the pore and sub-pore scale. The model will be cross-validated against other numerical models and analytical solutions in collaboration with Dr. Scheibe's project.
- 4) The multi-component, multi-species LBM model will be used to simulate the grain-scale U(VI) mass transfer in select microporous media (e.g., 200A feldspar grains) to provide fundamental insights on the apparent mass transfer kinetics of U(VI) between solid and aqueous phases. The results will be used to evaluate the advantages and limitation of the distributed rate model that is currently designed to describe U(VI) mass transfer in the Hanford sediments at different scales.
- 5) The applicability and upscaling of the alternative grain-scale mass transfer models will be evaluated against the "intact column" and field-scale results in collaboration with Dr. Zachara's SFA project and IFR project.

Collaboration

Besides the collaborations with PNNL internal investigators as described in the proposed researches (items 4 and 5) for FY10. This project also collaborates with two external investigators:

- 1) This project collaborates with Dr. Robert (Toby) Ewing at Iowa State University (ISU) to investigate the effect of pore connectivity, pore size distribution, and grain size on the apparent diffusion rates of uranyl species in the Hanford 300A sediment. The ISU's research is to apply the percolation theory in generating stochastic realizations of the pore-network in the intragrain regions and use particle tracking models to investigate the grain-scale manifestation of the molecular diffusion processes. The goal of this work is to derive theoretical scaling relationships to link the molecular diffusion coefficients to the measurable macroscopic, grain-scale effective diffusion coefficients and apparent tortuosity. PNNL will perform experiments for model validation. FY09 research and proposed FY10 research are:
 - The FY09 research at ISU has been focused on deriving the theoretical expressions of apparent solute diffusion coefficient as a function of molecular diffusion coefficient, intragrain pore connectivity, and grain diameter under well defined conditions (e.g., spherical grains).
 - FY10 research will focus on real sediment grains with complex particle geometry, measured pore size and pore connectivity in the Hanford 300A sediments. N₂ condensation/evaporation and tritium diffusion data in the 300A sediments will be obtained at PNNL to provide insights on the pore coordination number and to verify the applicability of the derived fundamental scaling functions.
- 2) This project also collaborates with Dr. Scott Fendorf at Stanford University to investigate the pore scale coupling of biogeochemical reactions and diffusive mass transfer in microenvironments. Stanford U. will derive microscopic data and PNNL will develop models for simulations. The goal of this collaboration is to provide fundamental insights on the development and evolution of microenvironments that have distinctive physical, chemical, and/or biological properties from groundwater flow domains. This is a new collaboration starting in FY10.
 - FY10 will investigate the coupled redox reactions and diffusion in Hanford fine-grained materials collected from the Ringold/Hanford formation interfaces. Stanford U. will use synchrotron-based reactive diffusion systems to collect the microscopic data of coupled O-Fe redox reactions and O₂ diffusion in the sediments, and PNNL will perform pore-scale (LBM) numerical analysis. This research will collaborate with Dr. Zachara's SFA project in investigating redox reaction in batch and stirred flow reactors. The research is to provide microscopic insights into the mass transfer limitation on the O₂ consumption and its effect on the development of redox microenvironments in subsurface sediments.



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