

Investigating the Impact of Microenvironments on Contaminant Biogeochemical Reactive Transport

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Introduction and Objective

This project is focused on the use of microfluidic pore structures (micromodels) to investigate a range of hypotheses associated with contaminant biogeochemical reactive transport. It is part of the Pore-Scale Reactive Transport and Upscaling theme of the PNNL Science Focus Area (SFA) project which will investigate pore-scale coupled physical, chemical, and biological processes that control contaminant reactive transport in microenvironments and transition zones.

Motivation

► **Microenvironments and transition zones** dominate the subsurface biogeochemical cycling of key contaminants at the Hanford site, including **technetium** and **uranium**, with strong effects resulting from the coupling of **chemical reaction, physical transport** and **microbiological processes**.

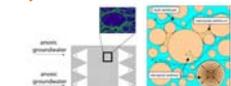
► **Geochemical processes** occurring at microscale are significant drivers of change in natural environments. Microenvironments of porous media where macroscopic advection is slow can chemically react with or hydrophysically retard contaminants through processes dominated by molecular diffusion. Contaminant stability, speciation, and reactivity also varies markedly across transition zones of chemical species such as O₂, H⁺ and organic carbon.

► **Similarly**, pore-scale structure plays an important role in constraining cell colonization and biofilm growth in the subsurface, with subsequent microbial activity in these microenvironments affecting contaminant transport via processes such as biosorption and enzymatic reduction.

► **Understanding** the function of microscale environments and transition zones, and modeling their behavior, is essential for the cleanup of the Hanford site.

Approach

Why use micromodels?



Flexibility in micromodel design allows us to **CONTROL** and **MEASURE** physical, chemical and biological conditions at the pore-scale

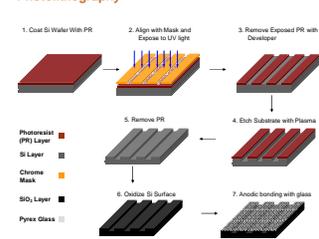
Homogeneous (a) and heterogeneous (b) pore structures in etched silicon substrates

- **PORE STRUCTURE:** a range of pore structures representing different microenvironments using photolithography
- **SURFACE COATING:** metal oxides to simulate mineral coatings via sputtering
- **CHEMICAL GRADIENT:** via multiple inlets/outlets, resulting in the formation of transition zones.
- **AQUEOUS CHEMISTRY:** within micromodel can be measured using IC, ICP-MS and spectrophotometry.
- **CELL COLONIZATION:** can be visualized and quantified using microscopy.
- **MINERAL PHASE:** can be measured at the micron scale using synchrotron-based spectroscopic techniques.

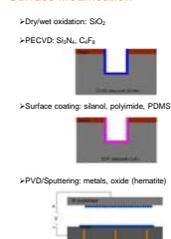
Experimental data will inform pore-scale reactive transport models

Micromodel fabrication

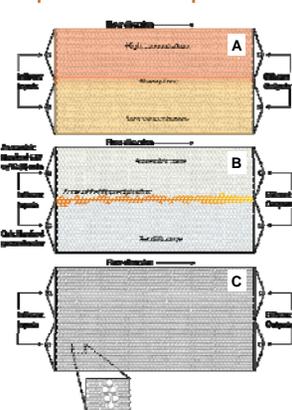
Photolithography



Surface Modification



Experimental concepts



- Geochemical gradients will be generated using multiple inlet ports to the micromodel. Flow rates determine the extent of mixing between layers. Gradients will be created between aerobic and anaerobic zones, and between areas of high electron donor/acceptor and low donor/acceptor (A). By using a fluorescently labeled obligately anaerobic bacterial strain (*Geobacter sulfurreducens*), cell growth under different conditions across the micromodel will be monitored.
- Simulation of Fe-cycling at an aerobic/anaerobic interface (B) by adding an Fe(II)-containing groundwater solution to the micromodel. The effect of the resulting oxidation and precipitation of mixed Fe(II)/Fe(III) oxide phases on microbial growth and contaminant transport will be monitored.
- Other planned studies involve coating the micromodel surface with Fe(III) oxide phases to analyze microbial reductive dissolution and secondary biogenic mineral formation, and investigating how pore size and structure affect microbial colonization and biofilm formation (C).

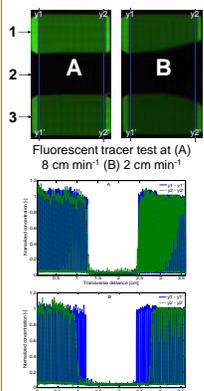
Preliminary data



(A) Computer controlled pumps flow three solutions through three input ports on the micromodel; a low electron donor/acceptor anaerobic solution, a high electron donor/acceptor anaerobic solution and a low electron donor/acceptor aerobic solution. (B) The underside of the micromodel showing pore structure and (C) the top side of the model, showing the input and output ports.

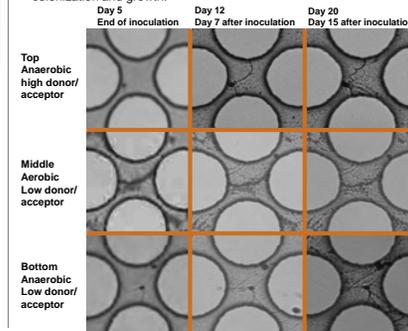
Tracer tests

► Fluorescent tracer was injected into the micromodel through ports 1 and 3 to assess effect of flow rate on mixing within the micromodel



Cell colonization and growth experiment

► An anaerobic Fe(III)-reducing *Geobacter sulfurreducens* strain containing the mcherry protein integrated into the chromosome was used to visualize cells using both fluorescence and light microscopy. The growth media was synthetic groundwater with acetate and AQDS added as the electron donor and acceptor respectively. Early stages of cell colonization show growth in anaerobic zones with both high and low electron donor/acceptor, suggesting that these concentrations are not limiting. There is little evidence of growth in the aerobic zone, suggesting that the geochemical gradients across the micromodel are affecting cell colonization and growth.



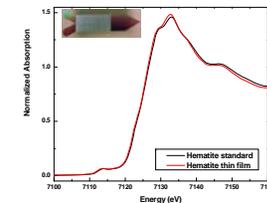
Future Research

Synchrotron experiments

► We propose to carry out **EXAFS/XANES** of Fe/U precipitates using the **X-ray microprobe (XMP)** on ID20 at the Advanced Photon Source. Experiments will involve 'end-point' micromodels subjected to varying physical, chemical and biological conditions, as well as *in-situ* micromodel experiments on the beamline to probe real time events.

Micromodel experiment 1:

Micromodels coated with **hematite** will be used to investigate effect of pore size and structure on microbial reductive dissolution of Fe(III) oxide phases. The micromodel will be colonized by Hanford-relevant organisms (*Geobacter* sp., *Shewanella* sp.) under anaerobic conditions where Fe(III) coatings will act as an electron acceptor for microbial respiration. The oxidation state, structure and distribution of resulting biogenic mineral phases will be mapped on a 5 micron scale using XMP at the Fe K-edge.



Fe K-edge XANES of ~300nm hematite thin film deposited on etched silicon micromodel by PVD (inset showing hematite-coated micromodel with two input ports)

Micromodel experiment 2:

The effect of microbial colonization and mineral precipitation on transport of dilute U(VI) solutions through defined pore structures will be investigated. Oxidation state, structure and distribution of uranium and iron will be determined using XMP at the U L-edge and the Fe K-edge.

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