LBNL Sustainable Systems SFA: Evolution of Pore Structures and Flowpath Challenge

Dynamic Synchrotron Imaging of Pore Structure Evolution

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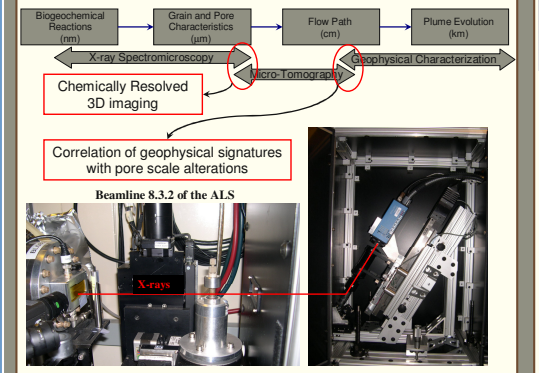
ABSTRACT

As part of the *Evolution of Pore Structures and Flowpaths* challenge area within the LBNL Sustainable Systems SFA, we have begun developing the capabilities necessary to image alterations in pore structure resulting from subsurface manipulations. In situ remediation strategies are frequently considered for cleanup of DOE sites. However, the impact of feedbacks between multi-scale heterogeneity and induced biogeochemical transformations on remediation efficacy is not well understood. Critical to the design, execution, and interpretation of in situ remediation approaches is an understanding of how reaction processes modify the properties of the porous medium, or the "*Evolution of Pore Structure to Flowpaths*".

The *Evolution of Pore Structures and Flowpaths* challenge is driven by four specific hypotheses:

- Remediation treatments can induce significant enough biogeochemical perturbations to alter pore structures.
- The cumulative impact of remediation-induced biogeochemical transformations will be significant enough to impact flowpaths at the field scale.
- The dynamic nature of field-scale flowpaths will impact the efficacy and sustainability of remediation treatments.
- Geophysical and isotopic methods can be used to track biogeochemical changes at the field scale.

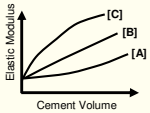
The *Dynamic Synchrotron Imaging of Pore Structure Evolution* task is designed to address the first of these four hypotheses and has two important subtasks: time-lapse imaging to image the evolution of pore structures in response to external perturbations and chemically resolved micro-tomography to help identify the minerals whose precipitation or dissolution are causing the changes in pore structure.

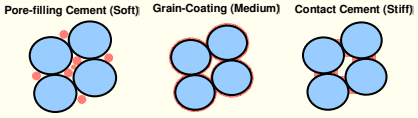


Time Lapse Imaging

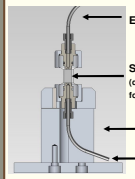
Correlating Geophysical Properties with Specific Pore Scale Changes

Different pore alteration motifs (three examples below) should produce distinct changes in geophysical response (right). By conducting time lapse micro-tomography imaging in concert with geophysical analysis, we intend to link these specific solid phase chances with their respective geophysical response.





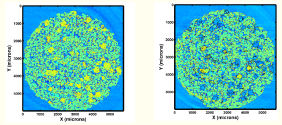
Micro-tomography Flow Cell



Imaging changes in pore structure resulting from treatment activity or other perturbations of the subsurface requires a reaction vessel which faithful reproduces field conditions while maintaining a high degree of spatial stability. At left we show the design of our new micro-tomography flow cell which meets these requirement.

Time Lapse Imaging Verification

The performance of the flow call was verified by imaging a test mixture before and after NaCl crystals were dissolved with water. Pair of images shows good spatial reproducibility and obvious holes left by dissolving NaCl crystals.

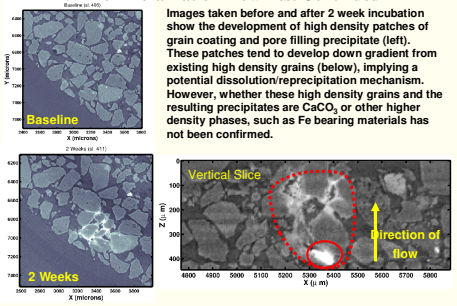


INL Biomineralization Flow Test

The flow cell was wet packed with INL sediment and equilibrated for one week with site ground water flowing at a rate of ~2 mL/day. After which point influent was amended with molasses (5 mg/L) and urea (10mM) to promote biological activity and $CaCO_3$ precipitation and pumping continued for 2 weeks. Sample was scanned after equilibration time and after treatment time to look for biomineralization activity.

Time Lapse Imaging Continued

INL Biomineralization Flow Test Continued

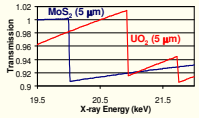


Images taken before and after 2 week incubation show the development of high density patches of grain coating and pore filling precipitate (left). These patches tend to develop down gradient from existing high density grains (below), implying a potential dissolution/reprecipitation mechanism. However, whether these high density grains and the resulting precipitates are $CaCO_3$ or other higher density phases, such as Fe bearing materials has not been confirmed.

Chemically Resolved Imaging

As illustrated by the inability to identify the composition of the precipitates seen above, one of micro-tomography's limitations is its lack of elemental sensitive. However, this short coming can be addressed by acquiring two spatially identical data sets spanning the absorption edge of a particular element of interest, i.e. one below and one above the absorption edge. In this case, grains containing sufficient quantities of the element of interest should show increased absorption at higher energy, while the bulk of the materials show a decrease in absorption.

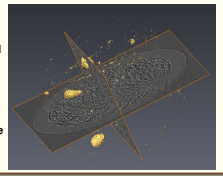
Model Compound Tests



The dissolution and precipitation of U bearing solid phases is of great interest at many DOE and other contaminated sites. To test the potential sensitivity of micro-tomography to U bearing phases, we used Mo containing compounds as models. Both U and Mo have an absorption edge of similar sensitivity in the ~20-21keV range.

$CaCO_3$ and $MoSi_2$

In order to identify $MoSi_2$ in a mixture of $CaCO_3$ two data sets were collected, one at 19500 eV and one at 20500 eV. The image at right shows the 3D distribution of $MoSi_2$ (yellow) obtained by subtraction of the 19500 eV data (below the Mo edge) from the 20500 eV data (above the Mo edge). Without the enhanced absorption of the $MoSi_2$ seen in the 20500 eV data set, it would have been impossible to unequivocally distinguish the $MoSi_2$ from the $CaCO_3$.



Chemically Resolved Imaging Continued

SiO_2 Sand Coated with MoS_2

Images below are from a mixture of SiO_2 sand and MoS_2. By taking data at multiple energies and comparing, small coatings of MoS_2 are identifiable and distinguishable from other high density coatings.

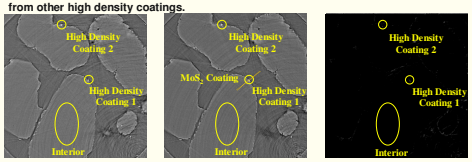
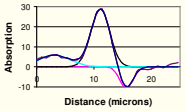


Image at 19500 eV | Image at 20500 eV | Difference

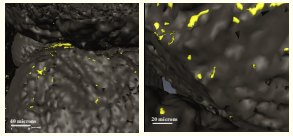
Absorption Values	19500 eV	20500 eV	Change
Grain Interior	2.6	2.5	-0.1
High Density Coating 1	12.2	21	8.7
High Density Coating 2	9.5	7.6	-1.9

Absorption value changes in the regions identified above as a function of energy.



Profile taken along orange line in 20500 eV image above.

The positive change in absorption value of region 1 confirms it as a Mo containing material and distinguishes it form the other region which shows a decrease in absorption with energy. Fitting of the profile across region one yields a main peak shows FWHM value of ~4 microns



MoS_2 (yellow) coatings on SiO_2 grains (gray).

SUMMARY

Time lapse micro-tomography imaging of a biostimulation experiment allowed direct imaging of pore scale biomineralization process, both grain coating and pore filling. The process appears to be directed by local geochemical conditions created down-gradient of particular existing mineral grains.

Building on the success of the INL biostimulation experiment, we will conduct an additional column biostimulation experiment using materials from Rifle, Co. This next experiment will focus not only on pore changes due to mineral dissolution anf precipitation but also on those due to biomass growth.

Multi energy imaging was successfully employed to identify precipitates with specific elemental composition in an energy range appropriate for use with U bearing materials. Currently the size of resolvable features is in the 3-4 micron range. This resolution should improve with future planned upgrades to the 8.3.2 beamline.

Next steps of the chemical imaging work will be to apply this approach to materials collected from Fry Canyon Co. permeable reactive barriers designed to immobilize and precipitate U. (see poster of Bargar, et al. SLAC-SFA)

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