Characterization of Coupled Hydrologic-Biogeochemical Processes Using Geophysical Data

Susan Hubbard (LBNL), Jill Banfield (UCB), Ken Williams (LBNL), Lee Slater (Rutgers), Dimitris Ntarlagiannis (Rutgers), Mary DeFlaun (GeoSyntek), Frank Morrison (LBNL), Guoxiang Zhang (LBNL)

1. Research Objectives:

Biogeochemical and hydrological processes are naturally coupled and variable over a wide range of spatial and temporal scales. Additionally, many remediation approaches also induce *dynamic* transformations in natural systems. Because it is difficult to predict these transformations, our ability to develop effective and sustainable remediation conditions at contaminated sites is often limited. For example, substrate delivery to enhance remediation via biostimulation may initially prove effective, but the conditions necessary for preservation of the sequestered phases may be difficult to sustain. Further complicating the problem is the inability to collect the necessary measurements at a high enough spatial resolution yet over a large enough volume for understanding field-scale transformations. Our research focuses on investigating the capability to characterize and monitor coupled processes at appropriate resolutions and spatial scales using geophysical data. In particular, we are investigating the influence of evolved gasses, precipitates, and biofilms on geophysical signatures. An ability to use geophysical methods to detect system transformations would be very useful for illuminating the conditions of perturbed systems during remediation in a rapid, high-resolution, and in-situ manner. Thus, if successful, such methods might be useful to guide remediation efforts. The resulting measurements will additionally provide the database necessary for investigating coupled processes and for refining numerical modeling approaches.

We are performing experiments to test the geophysical responses and sensitivities to various processes that occur during system transformations. Our work plan includes performing column and field scale experiments, and monitoring the system transformations that occur as geological systems are perturbed using microbial, geochemical, hydrological, and geophysical (seismic, electrical, radar) measurements. All geophysical techniques are based upon the principle of introducing signals through a volume of subsurface material and measuring the changes that occur in these signals as they propagate. Subtle changes in the physical and chemical properties of the material through which the signals pass (such as changes in degree or type of pore fluid, or variations in pore size or grain coatings) can dramatically alter the geophysical signatures.

2. Research Progress and Implications:

The majority of our project focuses on performing column-scale experiments, whereby we can simulate and control remediation conditions while acquiring co-located microbiological, geochemical, hydrological, and geophysical measurements. Our previous work focused on investigating the sensitivities of radar and seismic measurements to gas generation during denitrification in originally water-saturated sandy columns. This study showed that seismic amplitudes decreased dramatically during gas evolution, and that radar velocities could be used to estimate the percentage of bulk pore space that is occupied by the evolved gas (Hubbard and Williams, 2004).

This report summarizes column-scale work performed during the *second year* of our project, which focused on investigating if zinc and iron sequestration via microbe-induced sulfide precipitation creates physical property changes that can be detected using geophysical methods. We focus on this issue because bioremediation of groundwater metals contamination associated with acid-mine drainage (or other industrial sources) has spawned a great deal of recent interest. In this set of experiments, we used seismic, complex electrical (electrical conductivity and induced polarization, or IP), and radar methods to assess changes in geophysical attributes associated with the sulfide precipitation. Lee Slater and Dimitris Ntarlagiannis from Rutgers University assumed the lead role in the complex electrical measurements. Seismic methods are particularly sensitive to changes in the effective bulk moduli of the sediments and saturating fluids, and IP methods can be used to probe the physical and chemical characteristics of the mineral-fluid interface in natural materials.

We examined microbe-induced ZnS and FeS precipitation using *Desulfovibrio vulgaris* subsp. *vulgaris* under advective flow conditions and within experimental columns. *D. vulgaris* is a well characterized motile dissimilatory sulfate-reducing bacterium (SRB) that couples the incomplete oxidation of lactate to acetate with sulfate reduction. The experiment was developed using four inoculated columns and one non-inoculated control column within an anaerobic chamber as shown in Figure 1. Seismic, radar, complex electrical and biogeochemical samples were collected over time and along the length of the four inoculated columns. Measurements of hydraulic conductivity

Figure 1 Anaerobic flow chamber with columns used to conduct biostimulation experiments and collect seismic, radar, electrical, hydrological, and biogeochemical measurements

Figure 2 Microbially-induced metal sulfide precipitation at one point in time in biogeochemical measurement column.

over the length of the column were performed before and after the stimulation experiment. Sulfate reduction was monitored over seven weeks, as indicated by decreasing substrate and metals concentrations, increasing biomass, and visually discernable regions of metal sulfide accumulation. Decreases in lactate and sulfate concentrations followed predicted stoichiometric relationships and metals concentrations were reduced to levels below detection through sequestration as insoluble sulfide phases. The region of sulfide precipitation showed a shift toward the influent portion of the column over time as a result of chemotaxis towards elevated substrate concentrations at the base of the column. Figure 2 shows precipitation front in the biogeochemical measurement column at one point in time.

Regions of sulfide precipitation and accumulation resulted in substantial changes in the seismic and the complex electrical measurements. High-frequency acoustic wave amplitudes were reduced by nearly 84% with only minimal changes in velocity as is illustrated in Figure 2. The largest decreases in amplitude occurred in the regions nearest the base of the column, and hence closest to point of substrate influx. The decreased acoustic wave amplitudes may be explained using a patchy saturation model, wherein wave-induced flow results from the heterogeneous formation of high bulk modulus sulfide precipitates within formerly fluid-filled pores. This conceptual model also helps explain the eventual slight increase in amplitudes as a more homogenous distribution of sulfide-filled pores develops over time.

Figure 3 Changes in seismic waveforms near base of column as a function of time after

Figure 4 Change in imaginary and real conductivity near base of column as a function of time after inoculation.

Significant increases in complex electrical conductivity were observed with only minimal changes in the fluid conductivity (Figure 4). Over the frequency range recorded during the induced polarization measurements (0.1-1000Hz), significant changes in both the phase shift and calculated imaginary conductivity were observed. As the imaginary component of measured conductivity represents the flow of current along surfaces (in contrast to electrolytic flow), the observed changes are presumed to be a direct result of sulfide precipitation. Either the surface charge density or the intrinsic dipole moment of the sulfide precipitates may be responsible for the polarization phenomena. No significant polarization effects were observed in the downgradient regions lacking visible precipitates. The slight increase in fluid conductivity over time (i.e. the real conductivity) may be the result of quartz grain dissolution associated with prolonged microbial attachment and the production of weak inorganic and organic acids.

Figure 5 Sulfide-encrusted microbe (top) and pore through occlusion (bottom).

Scanning and transmission electron microscopy were performed at the Environmental Molecular Science Laboratory (EMSL) at PNNL with the assistance of A. Dohnalkova (PNNL). SEM revealed dense accumulations of metal sulfide-encrusted microbes covering grain surfaces with the sulfides being nanoparticulate and extra-cellular and periplasmic in nature (Figure 5). Energy dispersive x-ray analysis confirmed the precipitates to be a mixture of zinc and iron sulfide with the majority being associated with either cell surfaces or with the extracellular organic material encompassing the cells. In

some instances, the accumulation of microbes, sulfides, and biofilm material visibly spanned grain surfaces and occluded pore throat openings (Figure 5). Such occlusions likely resulted in the column flow restriction over time; hydraulic head measurements indicated that hydraulic conductivity values decreases during the course of this experiment by nearly 98%.

This experiment suggested that geophysical techniques are capable of detecting the onset and evolution of microbe-induced sulfide precipitation, and that the precipitation and related processes are capable of dramatically altering the hydraulic properties of a system.

3. Planned Activities

Geophysical Method	Geophysical Attribute	Gas Evolution	Precipitation Formation	Biofilm Formation
Radar	Velocity	<i>Large Increase</i>	<i>Not Significant</i>	<i>In progress</i>
	Amplitude	<i>Increase</i>	<i>Not Significant</i>	
Seismic	Velocity	<i>Small Decrease</i>	<i>Small Increase</i>	
	Amplitude	<i>Large Decrease</i>	<i>Large Decrease</i>	
Electrical	Conductivity		<i>Small Response</i>	
	Phase		<i>Large Response</i>	

The table summarizes our results to date, which include those responses to gas generation and precipitation formation. We are currently initiating a new suite of column experiments, which will investigate the sensitivities of geophysical attributes to biofilm formation. For these experiments, we are using the same microbe used in the sulfate reduction studies, but we will not introduce metals into the system. After we have completed the column experiments, we will test the ability of using time-lapse geophysical methods, such as crosshole radar, seismic, and electrical, to detect

system transformations during remediation at the field scale, to test the applicability of using geophysical approaches for the time-course monitoring of contaminant remediation during engineered bioremediation. In order

to keep field costs reasonable, the field portion of the project will focus on monitoring of a remediation effort that is funded by BER independently from this project.

4. Information Access:

Several manuscripts associated with the most recent column experiments are in submission, including one to *Science*. This project has additionally been the focus of several presentations at professional conferences. The references for these communications are given below, many of which are available for download at:

<http://esd.lbl.gov/people/shubbard/vita/webpage/monitoring.html>

4.1 Submitted Manuscripts:

1. Williams, K.H., D. Ntarlagiannis, L. Slater, A. Dohnalkova, S.S. Hubbard and J.F. Banfield, Remote sensing of subsurface microbial biomineralization, in submission to *Science*, 2004.
2. Ntarlagiannis, D., K. H. Williams, L. Slater and S. Hubbard, IP response of microbial induced sulfide precipitation, in submission to *Journal of Geophysical Research*, 2004.
3. Chen, J, S. Hubbard, E. Rodin, C. Murray and E. Majer, Estimation of geochemical parameters using geophysical data, submitted to *Water Resources Research*, 2004.

4.2 Extended Abstracts:

Hubbard, S.S. and K. Williams, Geophysical Monitoring of Gas Stimulation during Remediation, WM04 Symposium Proceedings, Tuscon, AZ, March 2004.

4.3 Recent Presentations:

1. Hubbard, S.S., K. H. Williams, B. Mailloux, E. Majer, Monitoring of microbially-induced physical property changes using geophysical data, Invited Presentation, AGU 83(19), Spring Meet. Suppl., Abstract # H21A-02, 2002.
2. Williams, K.H., S. Hubbard, D. Ntarlagiannis, L.D. Slater, and J.F. Banfield, Monitoring microbe-induced sulfide precipitation under dynamic flow conditions using multiple geophysical techniques, Eos. Trans. AGU Spring Meet. Suppl., 2004.
3. Ntarlagiannis, D., K. Williams, L. Slater and S. Hubbard, IP response of bacterially-induced sulfide mineral precipitation, Eos. Trans. AGU Suppl., 2004.