FINAL TECHNICAL REPORT

Project Title

Integrated Geophysical Measurements for Bioremediation Monitoring: Combining Spectral Induced Polarization, Nuclear Magnetic Resonance and Magnetic Methods

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1. Executive Summary

Our research aimed to develop borehole measurement techniques capable of monitoring subsurface processes, such as changes in pore geometry and iron/sulfur geochemistry, associated with remediation of heavy metals and radionuclides. Previous work has demonstrated that geophysical method spectral induced polarization (SIP) can be used to assess subsurface contaminant remediation; however, SIP signals can be generated from multiple sources limiting their interpretation value. Integrating multiple geophysical methods, such as nuclear magnetic resonance (NMR) and magnetic susceptibility (MS), with SIP, could reduce the ambiguity of interpretation that might result from a single method. Our research efforts entails combining measurements from these methods, each sensitive to different mineral forms and/or mineral-fluid interfaces, providing better constraints on changes in subsurface biogeochemical processes and pore geometries significantly improving our understanding of processes impacting contaminant remediation.

The Rifle Integrated Field Research Challenge (IFRC) site was used as a test location for our measurements. The Rifle IFRC site is located at a former uranium ore-processing facility in Rifle, Colorado. Leachate from spent mill tailings has resulted in residual uranium contamination of both groundwater and sediments within the local aquifer. Studies at the site include an ongoing acetate amendment strategy, native microbial populations are stimulated by introduction of carbon intended to alter redox conditions and immobilize uranium. To test the geophysical methods in the field, NMR and MS logging measurements were collected before, during, and after acetate amendment. Next, laboratory NMR, MS, and SIP measurements were collected on columns of Rifle sediments during acetate amendment. The laboratory experiments were designed to simulate the field experiments; changes in geophysical signals were expected to correlate with changes in redox conditions and iron speciation.

Field MS logging measurements revealed vertically stratified magnetic mineralization, likely the result of detrital magnetic fraction within the bulk alluvium. Little to no change was observed in the MS data suggesting negligible production of magnetic phases (e.g. magnetite, pyrrhotite) as a result of sulfidogenesis. Borehole NMR measurements contained high levels of noise contamination requiring significant signal processing, and analysis suggests that any changes may be difficult to differentiate from simultaneous changes in water content. Laboratory MS and NMR measurements remained relatively stable throughout the course of the acetate amendment experiment, consistent with field measurements. However, SIP measurements changed during the acetate amendment associated with the formation of iron-sulfide mineral phases; a finding that is consistent with chemical analysis of the solid phase materials in the columns.

2. Technical Summary

2.1 Goals, Objectives, and Accomplishments

The goals of this project were as follows:

(1) Develop a strategy for the interpretation of coupled SIP, NMR and MS measurements during biostimulation.
(2) Assess the feasibility of this approach for field applications.
(3) Improve the fundamental relationships between geochemical subsurface properties and the measured geophysical parameters.

Goal 1 was accomplished through laboratory measurements of SIP, NMR and MS measurements of a series of columns packed with Rifle sediments. The columns were treated with an acetate amendment to stimulate reducing conditions and/or a nitrate amendment to stimulate oxiding conditions. No change was observed in the NMR and MS measurements, which indicated that there was little to no change in the magnetic component of the minerals and no production of iron oxides. Significant changes in the SIP measurement were consistent with the production of iron sulfides. The geophysical results were confirmed with EXAFS measurements (collected at Brookhaven National Laboratory by Dr. Eef Elzing from Rutgers University – Newark) on the solid phase minerals. Goal 2 was accomplished by collecting borehole-logging data at the Rifle IFRC site during a biostimulation project. The results indicate that the site location was too noisy for the NMR measurements and extensive signal processing was necessary to interpret the NMR logs. Since the completion of our initial field experiment, a long-term monitoring project has been completed as part of an SBIR Phase II project (PI: David Walsh, "Low cost in-situ NMR technologies for monitoring biological and geochemical processes in the subsurface" Award# DE-FG02-11ER90025) that demonstrates that the instrument now has increased noise reduction capabilities and can make repeatable measurements. The MS measurements were very repeatable and showed no change in MS associated with the biostimulation. Unfortunately it was not possible to collect the SIP measurements due to lack of available instrumentation. It was hoped that a borehole SIP tool would be available for this project; however, due to an accelerated timetable that was necessary to align our field measurements with ongoing Rifle IFRC experiments, the SIP equipment was not available. Goal 3 remains the subject of ongoing work, but we are hopeful that our current analysis of the chemical data associated with the column experiments will allow us to quantify the changes in the geophysical measurements associated with changes in the geochemistry of the columns.

2.2 Products Developed

We are currently preparing a manuscript for submission to Environmental Science and Technology (estimated submission date, March 30, 2015) entitled "Geophysical monitoring of microbial and geochemical transformation during stimulated subsurface bioremediation: combining NMR, magnetic susceptibility and complex resistivity". This manuscript contains results from the laboratory column experiments that were performed as a part of this research.

The results from our research were presented at three conferences (1) Goldschmidt 2014, (2) the annual AGU fall meeting 2013, and (3) the 2012 Symposium on Applied Geophysical Engineering and Environmental Problems. In addition the PI attended and presented at the annual SBR PI's meeting in 2012 and the annual joint SBR/TES PI's meeting in 2013 and 2014.

3. Budget Summary

Total spending was $2275.18 below the total budget of $150,000. The primary differences between the budgeted amounts and the actual spending were in category A Senior Personnel, where we underspent by $6912.34, and category G-1 Materials and Supplies where we overspent by $5354.77.

Section Category	Budgeted	Spent	Difference
A Senior Personnel	$30 437	$23 524.66	+$6912.34
B Other Personnel	$12 000	$11 200.00	+$800
C Fringe Benefits	$3168	$4219.87	–$1051.87
D Permanent Equipment	$13 785	$13 926.09	–$141.09
E Travel	$13 550	$15 613.46	–$2063.46
G-1 Materials and Supplies	$5083	$10437.77	–$5354.77
G-2 Publication Costs	$1500	$0	+$1500
G-6 Other	$27 240	$25 087	+$2153
Indirect Costs (55%)	$43 237	$43 715.97	–$478.97
Total Costs	$150 000	$147 724.82	+$2275.18

4. Products Developed

This section lists the Scientific and Technical Information (STI) under award DE-SC0007049. Each of the products developed as a part of this grant will be made available through the DOE Energy Link (E-Link).

4.1 Current Report

DOE-RUN-0007049-1
Keating, K. (2015) Integrated Geophysical Measurements for Bioremediation Monitoring: Combining Spectral Induced Polarization, Nuclear Magnetic Resonance and Magnetic Methods. Final Technical Report, Subsurface Biogeochemical Research Program, U.S. Department of Energy, Office of Science Washington, DC.

4.2 Refereed Publications

(IN PREPARATION – to be uploaded to E-Link following publication)
Rosier, C., K. Keating, K. Williams, D. Ntarlagiannis, and E. Elzinga (2015) Geophysical monitoring of microbial and geochemical transformation during stimulated

subsurface bioremediation: combining NMR, magnetic susceptibility and complex resistivity. *Manuscript in prep for Environmental Science and Technology.*

4.3 Conference Presentations

DOE-RUN-0007049-2
Rosier, C., K. Keating, K. Williams, D. Ntarlagiannis, E. Grunewald, and D. Walsh (2014) Assessing the potential of geophysical methods to detect subsurface changes in iron-mineral chemistry. Goldschmidt, Sacramento, CA.

DOE-RUN-0007049-3
Rosier, C., K. Keating, K. Williams, and D. Ntarlagiannis (2014) Integrated Geophysical Measurements for Bioremediation Monitoring: Combining Spectral Induced Polarization, Nuclear Magnetic Resonance and Magnetic Methods. DOE Office of Science TES/SBR Joint PI meeting, Potomac, MD.

DOE-RUN-0007049-4
Rosier, C., K. Keating, K. Williams, D. Ntarlagiannis, E. Grunewald, and D. Walsh (2013) Using NMR, SIP, and MS measurements for monitoring subsurface biogeochemical reactions at the Rifle IFRC site. 2013 Fall Meeting, AGU, San Francisco, CA.

DOE-RUN-0007049-5
Keating, K., K. Williams, and D. Ntarlagiannis (2013) Integrated Geophysical Measurements for Bioremediation Monitoring: Combining Spectral Induced Polarization, Nuclear Magnetic Resonance and Magnetic Methods. DOE Office of Science TES/SBR Joint PI meeting, Potomac, MD.

DOE-RUN-0007049-6
Keating. K., K. Williams, D. Ntarlagiannis, L. Slater (2012) Monitoring in situ bioremediation at the Rifle, Colorado IFRC site with nuclear magnetic resonance and magnetic susceptibility measurements. SAGEEP, Tucson, AZ.

DOE-RUN-0007049-7
Keating, K., K. Williams, and D. Ntarlagiannis (2012) Integrated Geophysical Measurements for Bioremediation Monitoring: Combining Spectral Induced Polarization, Nuclear Magnetic Resonance and Magnetic Methods. DOE Office of Science SBR Annual PI meeting, Washington, DC.