

Progress Report: June 15, 2004

EMSP #88615: ER63506-1020409-0009643

Investigating the potential for long-term permeable reactive barrier (PRB) monitoring from the electrical signatures associated with the reduction in reactive iron performance

Lee Slater

Dept. Earth/Env. Sciences, Rutgers University, Newark, NJ 07102

Research Objective

The objective of this project is to quantify the ability of the electrical induced polarization (IP) method to non-invasively monitor the reduction in reactive iron performance that is known to reduce the effectiveness of the permeable reactive barrier (PRB) with time. The primary scientific goals include:

A] fundamental laboratory studies to evaluate the sensitivity of the IP method to:

Fe⁰ total surface area

Fe⁰ surface chemistry

physical/chemical changes to the Fe⁰ surface resulting from oxidation and precipitation

B] monitoring of the electrical tomographic response of the Kansas City PRB over a three-year period and assessment, via correlation with aqueous geochemical data and extracted iron cores, of whether electrical signatures associated with reduced PRB performance are resolvable in field studies

C] optimization of a three-dimensional tomographic imaging algorithm for application to highly conductive, high electrical contrast environments as represented by a PRB

Research progress and implications

This report summarizes laboratory, numerical and field work completed after twenty-one months of this thirty six month project.

Laboratory accomplishments:

PI Slater is responsible for this laboratory research

We have conducted a wide range of fundamental studies aimed at determining the low-frequency electrical properties of Fe⁰-sand systems. Our objectives are two-fold [a] determine the sensitivity of IP to reactive Fe⁰ surface area and its dependence on electrolyte chemistry [b] monitor the changes in electrical properties that result from precipitation of a range of compounds on the reactive Fe⁰ surface. At the time of writing, we have largely completed objective [a] and are monitoring four parallel column experiments (now running for 5 months) to achieve objective [b]. We find that all our measurements show strong polarization relaxation peaks within our measured frequency range (0.1-1000 Hz). We fit these spectra to relaxation models that provide three important parameters (i) the magnitude of the polarization (ii) the magnitude of the conductivity (iii) the characteristic time of the relaxation.

1. IP sensitivity to Fe⁰ surface area

The sensitivity of IP to total Fe⁰ surface area was investigated by synthesizing Fe⁰-sand samples with varying concentrations of Fe⁰ (Fisher 40 mesh, specific surface area 9.3 m²/g) from 0-75% by volume. Silica (Ottawa grade) sand (specific surface area 1.7 m²/g) was used as the background material. An important finding is that polarization magnitude (m_p) shows a strong power law relation to Fe⁰ surface area per unit sample weight (Fig. 1). The time constant (τ_n) of the relaxation is also influenced by the Fe⁰ surface area per unit sample weight (Fig. 1). In contrast, the conductivity magnitude is only weakly sensitive to Fe⁰ surface area (Fig. 1). These results generally support the concept of developing IP as a tool for measuring changes in Fe⁰ surface area in PRB systems.

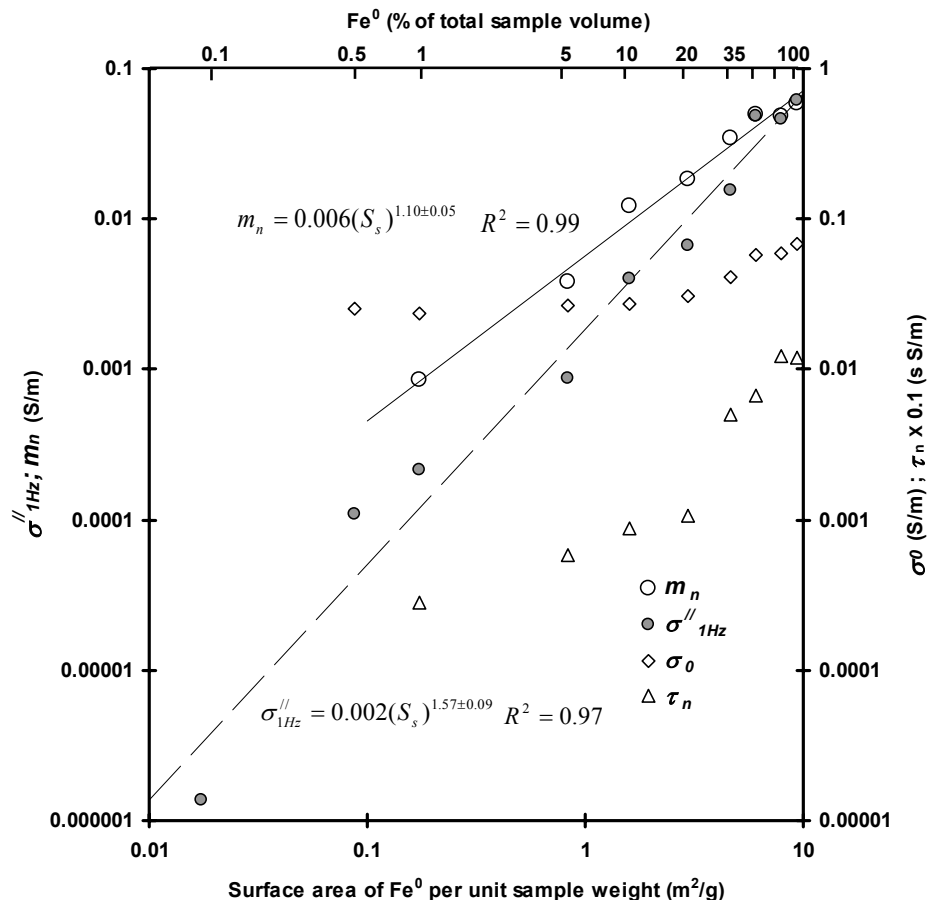


Figure 1: Low frequency electrical parameters as a function of Fe^0 reactive surface area. Plotted parameters are (1) global polarization magnitude (m_n) determined from relaxation model (2) local (1 Hz) measured polarization magnitude ($\sigma_{1\text{Hz}}$) (3) conductivity magnitude (σ_0) determined from relaxation model (4) time constant determined from relaxation model (τ_n)
Sample saturated with 0.01 M NaNO_3

2. IP dependence on fluid chemistry

The IP response of Fe^0 containing sand samples was evaluated as a function of electrolyte activity (0.001-10 mol/L), valence (+1, +2, +3) and pH (1.5-10.5 using 0.01 M NaNO_3). Polarization magnitude shows a power law relationship to electrolyte activity for all solutions and measurable dependence on electrolyte composition (Fig. 2a). The time constant (τ_n) shows a weak dependence on electrolyte activity for 1 valent solutions tested, but a strong dependence on electrolyte activity for 2 valent solutions (Fig 2b). We tentatively explain the variation in τ_n in terms of variation in the thickness of the EDL at low electrolyte concentration and reduced ionic mobility in the EDL at high electrolyte concentration (Fig. 2b). The polarization magnitude is pH independent (Fig. 3), whereas the time constant shows an order of magnitude increase above pH of 7 that may relate to the point of zero charge of Fe^0 (Fig. 3). These results illustrate that IP is sensitive to the metal surface chemistry. Development of the IP method for monitoring reductions in Fe^0 performance will require accurate knowledge of the electrolyte composition. We are currently expanding the range of electrolytic conditions studied.

3. IP dependence on Fe^0 oxidation and induced precipitation

The effect of Fe^0 oxidation and precipitation on IP as a function of time is currently being assessed in accelerated column experiments. Samples for aqueous chemistry determination (pH, Eh, electrical conductivity) are periodically collected during the study. Ferrous and ferric iron concentrations in outflow are measured by 0-phenanthroline method with UV-spectrophotometer. The solid-phase mineralogy is analyzed by XRD and SEM before and after column experiments. Results of the first experiment (oxidation only) indicate that the IP method is not sensitive to the level of oxidation of the Fe^0 surface. Four parallel enhanced precipitation experiments are

currently in progress using the following electrolyte chemistries: carbonate oxides (CO_3); sulfate (SO_4), phosphate (PO_4); O_2 (Ultra pure water for control). These columns have now been running for five months.

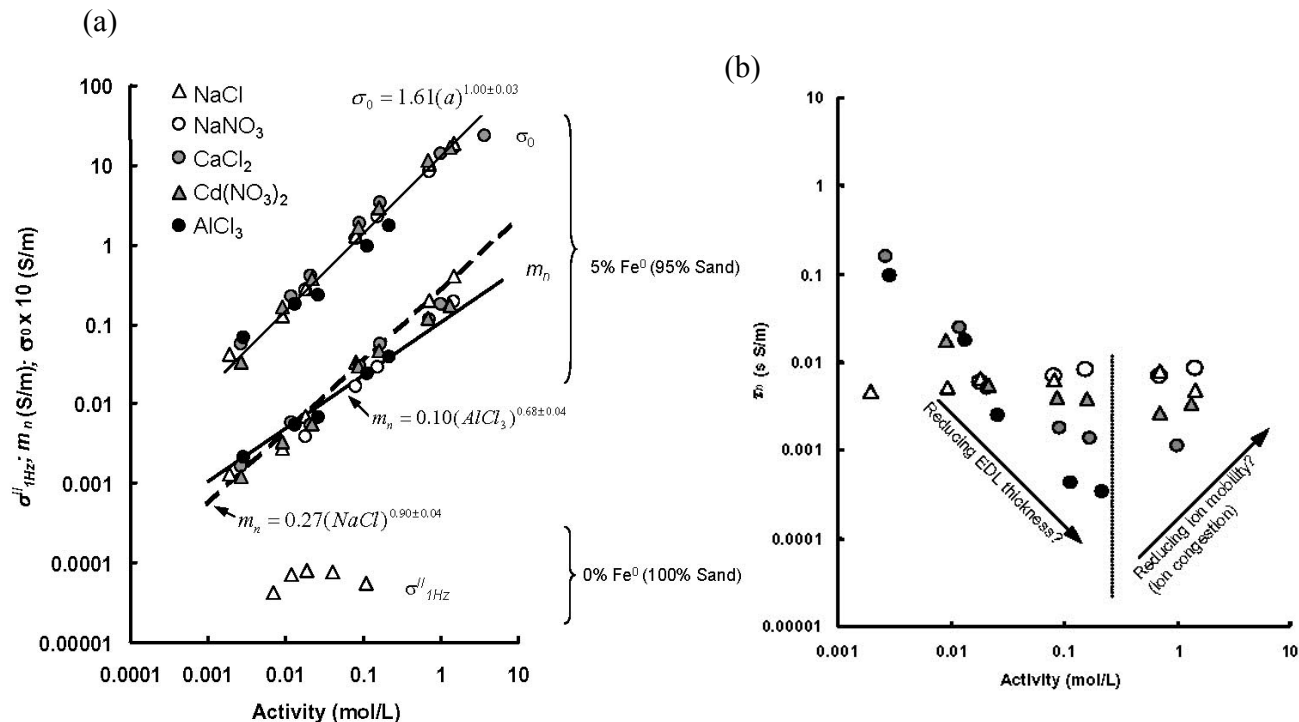


Figure 2: IP parameters as a function of electrolyte chemistry (a) polarization magnitude as a function of electrolyte activity and valence (b) relaxation time as a function of electrolyte activity

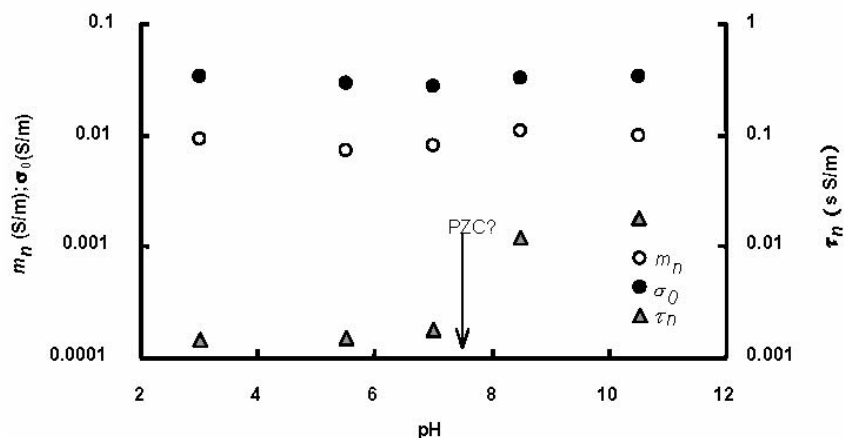


Figure 3: Cole-Cole model parameters as a function of pH for a 5% Fe^0 by volume Fe^0 -sand sample saturated with 0.01 M NaNO_3 solution and doped with 1 M HNO_3 or 1 M NaOH . PZC denotes possible point of zero charge

We have also conducted preliminary assessments of the sensitivity of IP measurements to precipitation on the Fe^0 surface. Sand- Fe^0 columns were prepared at high Fe^0 concentrations (30% and 70%) to increase the likelihood of detecting the effects of precipitation. Columns were initially saturated with 0.01M NaNO_3 electrolyte and electrical measurements obtained under this background condition. Precipitation was first induced by slowly invading each column with 1 L of 1 M NaOH electrolyte; geochemical modeling with MINTEQA2 predicted the formation of $\text{Fe}(\text{OH})_2$ and $\text{Fe}(\text{OH})_3$ precipitates on the Fe^0 surface under these experimental conditions. Columns were then reinvaded with 1 L 0.01M NaNO_3 to return the electrolyte chemistry to the background condition and electrical measurements obtained. The 70% Fe^0 column was then invaded with 1 L of 0.5M

Na_2CO_3 electrolyte to encourage further precipitation; geochemical modeling with MINTEQA2 predicted the formation of FeCO_3 and $\text{Fe}_2(\text{CO}_3)_3$ under these conditions. Electrical measurements were again obtained after reinvasion with 1 L 0.01M NaNO_3 to return the electrolyte chemistry to the background condition. Measurements before and after this experiment suggest that IP measurements are sufficiently sensitive to detect precipitation on the surface of Fe^0 (Figure 4).

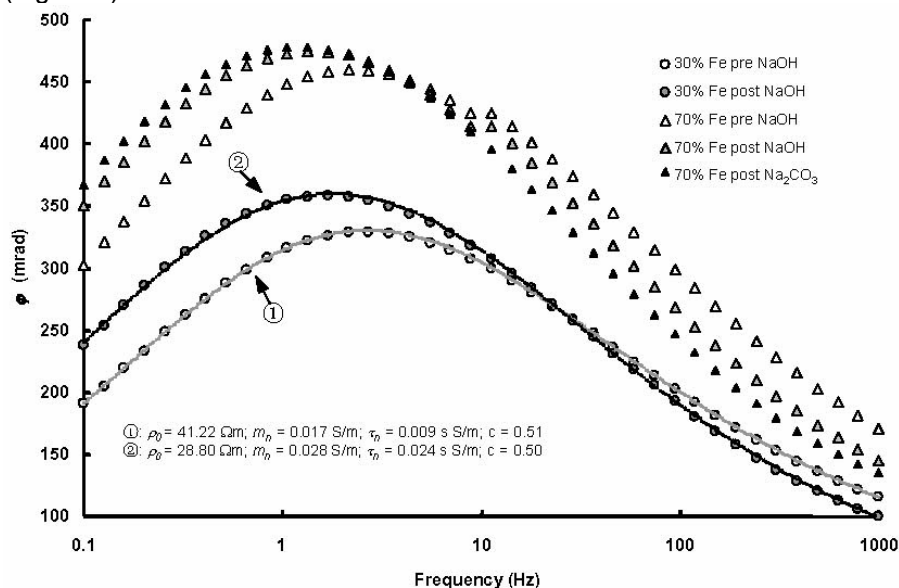


Figure 4: Phase versus frequency for 30% Fe^0 by volume and 70% Fe^0 by volume sand- Fe^0 samples prior to and after inducing precipitation on the Fe^0 surface by invasion with NaOH and Na_2CO_3 . Cole-Cole model parameters for the 30% Fe^0 sample prior to and after invasion with NaOH are also shown. Note that measurements both prior to and after precipitation were made with the sample flushed with 1 L (± 38 pore volumes) of 0.01 M NaNO_3 solution.

Modeling accomplishments:

PI Slater and collaborator Binley have primary responsibility

Slater and Binley met for one week at Lancaster University in June 2003 and formulated an approach to improve resolution of electrical changes in PRBs. The basic concept is to perform smoothness-constrained electrical imaging to resolve the PRB structure and then condition the imaging of changes in the electrical properties of PRBs on this structure with time by blocking off sections of the image associated with the PRB. Binley is testing this idea on theoretical and field data. Binley visited Slater for 10 days in February 2004 and worked further on the modeling of field data collected from the Kansas City PRB. This work focused on analysis of measurement errors, particularly in the cross-borehole IP data, and image appraisal.

Field accomplishments:

PI Slater, co-PI Baker and co-PI Korte have primary responsibility

Twelve electrode arrays were installed at the PRB located on the Kansas City site (Fig. 5a) during January 2003. Wells 1-7 were located at a region on the barrier to permit 2D/3D imaging where existing geochemical data suggest that plume flow-through is concentrated. Wells 8-10 were located towards the southern end of the barrier to permit 2D imaging where the PRB is relatively unaffected by the contaminant plume. Wells 11-12 were drilled to permit collection of 2D control imaging data off the barrier. Each well was installed with an array containing 20 electrodes at 0.3 m intervals across the region of the PRB installation. Electrical measurements were made using the best measurement sequence obtained from numerical studies. Figure 5b shows inverted PRB images obtained with the new sequence across wells 4-1-5 and wells 8-10-9 in January 2003 (background dataset). These panels form the primary image planes for long-term field monitoring. Repeat measurements were made at the site in July 2003, November 2003 and March 2004. The next trip is scheduled for July 2004 and measurements will continue at a 3-4 month intervals until the end of the current funding period. Water from twenty-three monitoring wells positioned up and down gradient and within the PRB was sampled in September 03 and analyzed to determine geochemical effects of the barrier. Review of these data is in progress.

but several preliminary observations are possible. Wells within the barrier demonstrate order of magnitude decreases in silica, calcium, magnesium and alkalinity. Considering the pH of the water and absence of detectable iron, both calcite and siderite are precipitating within the barrier. The loss of silica is probably not relevant from the standpoint of clogging but may be passivating the iron surface. Sulfate, present in upgradient wells at approximately 100mg/L is not detectable within the PRB providing definite evidence of sulfur-reducing bacteria and the likely precipitation of ferrous sulfide. The latter results correlate with field measurements of pE, which independently indicate sulfate reduction may be occurring. Three of the wells sampled are just downgradient of the barrier. The two wells on the south side show no evidence of contact with the Fe^0 , potentially indicating that water is not flowing through all of the PRB. Related activities to be conducted include: additional review and comparison to historical data, geochemical calculations and comparisons to field geophysical data and laboratory column studies.

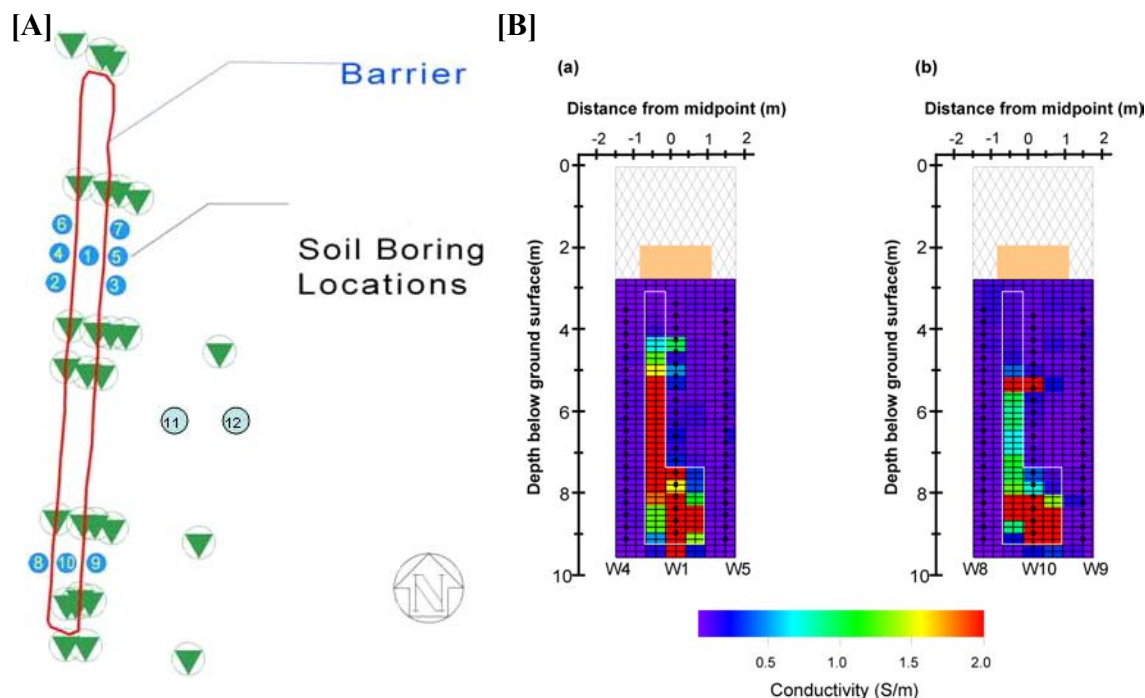


Figure 5: [A] Electrical imaging arrays installed at the PRB at the DOE Kansas City site [B] 2D conductivity images obtained on the two primary electrical monitoring panels at the DOE Kansas City site (a) Panel 4-1-5 (b) Panel 8-10-9

Planned Activities

Laboratory Experiment (LE): [Choi/Slater]

In the following experiments induced polarization measurements will be correlated with key geochemical parameters defining the chemistry of the reactive iron surface:

LE1 (*ongoing*): controls on electrolyte chemistry: additional background solution chemistries (particularly carbonates)

LE 2 (*in progress*): Fe^0 oxidation and precipitation in background solutions - running for 5 months

LE3: (*mid 04*) active TCE degradation - under preparation

LE4: (*mid 04*) active PCE degradation - under preparation

LE5: (*late 04*) active Chromium degradation

Numerical Experiment (NE): [Binley/Slater]

NE1: Synthetic trials to improve algorithm performance in PRB imaging (*ongoing*)

NE2: Inversion of 2D and 3D field electrical data (*ongoing*)

Field Experiment (FE): [Slater/Baker/Korte]

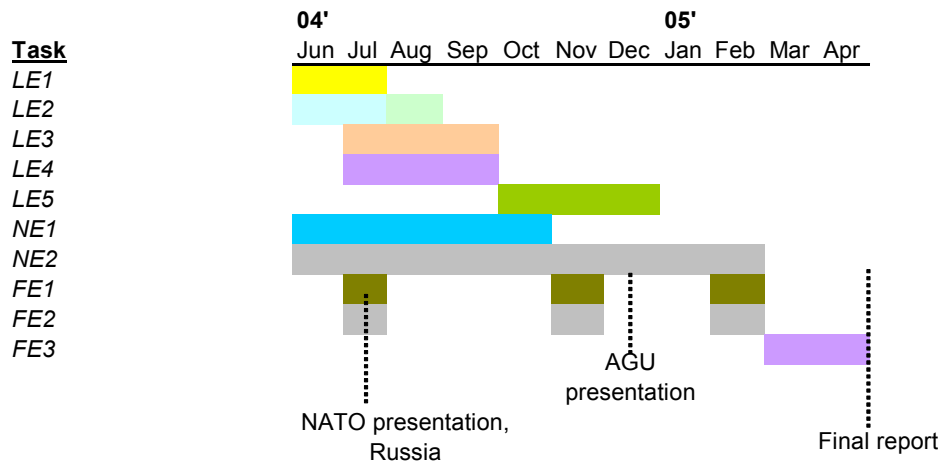
FE1: Repeated electrical imaging at the Kansas City PRB (*ongoing for entire 3 yr period @ 3-4 month intervals*)

FE2: Aqueous geochemical sampling to support electrical monitoring and assess PRB performance (*ongoing for entire 3 yr period*)

FE3: PRB coring and direct analysis of surface chemistry (*final quarter of project*)

Table 1 is a Gantt Chart showing the approximate timeframe for activities on this project.

Table 1: Gantt chart showing anticipated timeframe for planned and in progress activities



Information Access

Papers, presentations, etc.

The following journal article describes results of electrical imaging at the Kansas City PRB. It was in part supported by this EMSP award:

Slater, L. and Binley, A., 2003, Evaluation of permeable reactive barrier (PRB) integrity using electrical imaging methods, **Geophysics**, 68, 3, 911-921

The following journal article currently in review describes the laboratory experiments conducted during the first year of this project:

Slater, L., Choi, J. and Wu, Y., Electrical properties of iron-sand columns: implications for induced polarization investigation and performance monitoring of iron-wall barriers, **Geophysics**, Submitted 04/15/04

The following presentations of this EMSP supported work were made in 2003:

Choi, J., Slater, L. and Wu, Y., 2003, Low-Frequency Electrical Properties of Zero Valent Iron Sand Columns: Implications for Monitoring the Performance of Reactive Iron Wall Barriers in DNAPL Degradation, **Partners in Environmental Technology Technical Symposium & Workshop**, sponsored by SERDP and ESTCP, Dec. 2-4, 2003, Washington D.C., Poster #155

Choi, J., Slater, L. and Wu, Y., 2003, Low-Frequency Electrical Properties of Zero Valent Iron-Sand Columns: Implications for Monitoring the Performance of Reactive Iron Wall Barriers, **American Geophysical Union Fall Meeting**, Dec 6-10, 2003, San Francisco, CA, Abstract # H12H-06

Work conducted under this project will be presented in two invited papers at a NATO Programme Security Through Science Advanced Research Workshop:

"Interfacial electrical properties of soils measurable with induced polarization: implications for hydraulic characterization, contaminant assessment and monitoring of chemical and biological processes", **NATO Advanced Research Workshop "Soils and Groundwater Contamination: Improved Risk Assessment"**, July 26-30, 2004, St. Petersburg, Russia (presented by Lee Slater)

"Imaging permeable reactive barriers using resistivity and IP methods", **NATO Advanced Research Workshop "Soils and Groundwater Contamination: Improved Risk Assessment"**, July 26-30, 2004, St. Petersburg, Russia

(presented by Andrew Binley).

Collaborations resulting from this work

PI Slater was invited to collaborate on the following EMSP project: DE-AC03-76SF00098 to S. Hubbard, Lawrence Berkeley Laboratory (LBL). Slater is assisting with electrical measurements on column experiments during microbial-mediated metal sulfide precipitation. A Rutgers university Ph.D. student is conducting this research in conjunction with LBL staff.