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
Department of Earth and
Environmental Science
Rutgers, The State University of New Jersey
195 University Avenue
Room 411

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 IP theory and empirical data resulting from the original development of the method for mineral exploration suggests that the method is highly relevant in the study of reactive iron barriers. Laboratory and field IP studies on mineral deposits illustrate the sensitivity of IP parameters to metal concentration, particle size and metal surface chemistry. IP theory, based on electrical (Warburg) impedance associated with diffusive ion transfer to/from the electrolyte to electron exchange sites on the metal surface, provides a framework for interpreting IP signatures of PRBs as a function of redox chemistry. Research progress and implications This report summarizes laboratory, numerical and field work completed after seventeen months of this thirty six month project. Laboratory accomplishments: Postdoctoral research scientist Jaeyoung Choi and PI Slater are 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 initiated four parallel column experiments (currently running for 6 weeks) 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 is highly sensitive to Fe0 concentration. The time constant (t) of the polarization relaxation is also strongly surface area dependent. In contrast, the conductivity magnitude shows much weaker sensitivity to Fe0 surface area. These results provide strong support for the concept of developing IP as a tool for measuring changes in Fe0 surface area in PB systems. 2. IP dependence on fluid chemistry The IP response of Fe0 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 NaNO3). Polarization magnitude shows a power law relationship to electrolyte activity for all solutions and measurable dependence on electrolyte composition (Fig. 2a). The time constant shows a weak dependence on electrolyte activity for 1 valent solutions tested, but a strong dependence on electrolyte activity for 2 valent solutions. The polarization magnitude is pH independent, whereas the time constant shows an order of magnitude increase above the point of zero charge for Fe0. These results illustrate that IP is sensitive to the

metal surface chemistry. Development of the IP method for monitoring reductions in Fe0 performance will require accurate knowledge of the electrolyte composition. We are currently expanding the range of electrolytic conditions studied. 3. IP dependence on Fe0 oxidation and induced precipitation The effect of Fe0 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-phenanthronline 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 Fe0 surface. Four parallel enhanced precipitation experiments are currently in progress using the following electrolyte chemistries: carbonate oxides (CO3); sulfate (SO4), Phosphate (PO4); O2 (Ultra pure water for control). These columns have been running for six weeks and we anticipate monitoring for another two months. 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 by blocking off sections of the image associated with the PRB. Binley is testing this idea on theoretical and field data. 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. 3a) 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. Repeat measurements were made at the site in July and November 2003 (travel funds permit monitoring on a 3-4 month basis over the three years of the project). 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 ZVI, potentially indicating that water is not flowing through all of the PRB. Related activities to be conducted in the next few weeks include: additional review and comparison to historical data, geochemical calculations and comparisons to field geophysical data and laboratory column studies. 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): Fe0 oxidation and precipitation in background solutions LE3: (early 04) active TCE degradation LE4: (early 04) active PCE degradation LE5: (early 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) 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)