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

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Research Objective

The ultimate 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 physical/chemical changes to the iron surface resulting from oxidation, precipitation and clogging
B] monitoring of the electrical tomographic response of an installed 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 nine months of this thirty six month project.

Laboratory accomplishments:

Postdoctoral research scientist Jaeyoung Choi and PI Slater are responsible for this laboratory research

1. IP dependence on reactive iron concentration (surface area)
   The sensitivity of IP to zero-valent iron (Fe⁰) concentration (i.e. Fe surface area) was investigated by synthesizing Fe-sand samples with varying Fe⁰ concentration from 0-10%. Silica (Ottawa grade) sand was used as the background material. IP parameters are highly sensitive to Fe⁰ concentration (Fig. 1a). In contrast, conductivity measured with the resistivity method was insensitive to Fe⁰ concentration over the investigated range (Fig. 1b).

2. IP dependence on fluid chemistry
   The IP response of Fe⁰ containing sand samples was evaluated as a function of ionic strength and electrolyte activity. Electrolyte activity was varied between 0.001-1.0 for NaNO₃, NaCl and CaCl₂ solutions. The electrical impedance associated with the iron-electrolyte interface shows a power law relationship to electrolyte activity for all solutions (Fig. 2a). The impedance of the iron-electrolyte interface depends on ionic composition of the electrolyte, being greater for NaNO₃ than for NaCl (Fig. 2a). Power-law exponents are slightly higher than that predicted for the active ion species based on Warburg impedance theory (Fig. 2a). The real part of the impedance is insensitive to the metal-electrolyte interface and is dominated by the electrolytic conduction through the pore space (Fig. 2b).
Figure 1: Low frequency electrical parameters as a function of % Fe\(^0\) concentration (a) imaginary conductivity [IP] (b) real conductivity (c) phase. Open circles indicates samples saturated with 0.01 M NaNO\(_3\), closed circles indicates sample saturated with distilled water.

Figure 2: Impedance at 1 Hz as a function of electrolyte activity for Ottawa sand with 5% zero valent iron (a) imaginary impedance (b) real impedance. In (a) \(z''\) (NaNO\(_3\))\(^{-1.14}\), \(z''\) (NaCl)\(^{-1.11}\)

3. IP dependence on Fe\(^0\) oxidation
This experiment is currently in progress. The effects of Fe\(^0\) oxidation on IP as a function of time are being measured in column experiments. The electrical response of synthesized Fe-sand samples with varying Fe\(^0\) concentration from 0-10% with Ottawa sand will be tested for 3 months. The samples for aqueous chemistry determination (pH, Eh, electrical conductivity) will be periodically collected during the study. Ferrous and ferric iron concentrations in outflow are being measured by 0-phenanthroline method with UV-spectrophotometer. The solid-phase samples for mineralogy are analyzed by XRD and SEM before and after column experiments.

Modeling accomplishments:
*PI Slater and collaborator Binley have primary responsibility*

Synthetic electrical datasets were generated for different electrode configurations in an attempt to improve resolution of the PRB structure at the Kansas City site. The two-dimensional measurement sequence adopted during a previously funded study caused artifacts in the image structure misrepresentative of the true PRB.
structure. An empirical study was conducted to refine the measurement sequence used in this study. Tests were conducted with measurement sequences using a variety of borehole-borehole, within borehole and borehole-surface electrode arrangements. Inversion of synthetic and new field data (next section) indicates significant improvement in definition of PRB geometry without artifacts.

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. Figure 3b shows inverted PRB images obtained with the new sequence across wells 4-1-5 and wells 8-10-9 in January 2003. These panels will form the primary image planes for long-term field monitoring.

![Figure 3: [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](image)

**Specific implications of results to base of scientific knowledge and/or DOE/EM activities:**

The laboratory studies reaffirm the high sensitivity of the IP method to metal concentration as discovered during the development of the method in mineral exploration. Figure 1 shows a two order of magnitude increase in the IP response between 0% and 0.1% Fe⁰ concentration. Measurements obtained with the resistivity method are insensitive to Fe⁰ concentration over the studied range (Fig. 1b). Reliable geophysical quantification of metal concentration in soils could assist in DOE/EM activities related to heavy metal contaminants and corrosion 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: pH, eH, Fe$^{2+}$ concentration, additional background solution chemistries (particularly carbonates)
LE 2 (initiated): Fe$^{0}$ oxidation and precipitation in background solutions
LE3: active TCE degradation
LE4: active PCE degradation
LE5: 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)
FE2: Aqueous geochemical sampling to support electrical monitoring and assess PRB performance (ongoing)
FE3: PRB coring and direct analysis of surface chemistry

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

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AGU: "American Geophysical Union, Fall Meeting"
SAGEEP: "Symposium on Application of Geophysics to Engineering & Environmental Problems"

Information Access
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