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

DE-FG07-02ER63506: New project

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Background

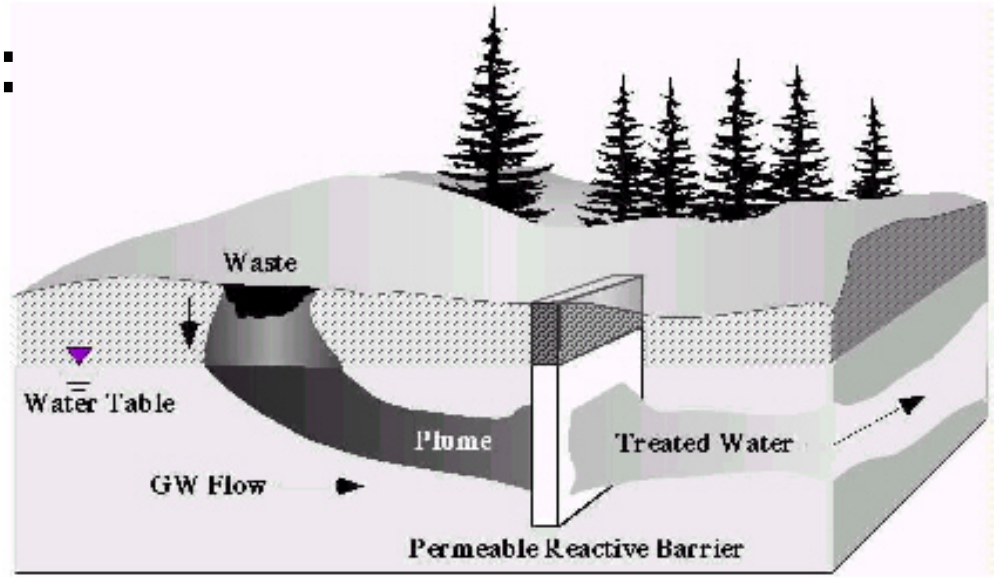
DE-AC04-01-AL66850

Electrical geophysics to assist evaluation of reactive barrier integrity and performance

Permeable reactive barriers

- In-situ hydrocarbon treatment technology
- Granular reactive iron: ***degrades chlorinated organics into non toxic organic & inorganic compounds***

- **Source: Powell & Associates Science Services, http://www.powellassociates.com**



Study site: ***PRB installed at DOE Kansas City plant***

PRB performance & monitoring

Development of non-invasive electrical geophysical methods for:

- **assessing PRB integrity after installation**
  (deficiencies e.g. gaps, collapse structures, variability in iron placement)

proven

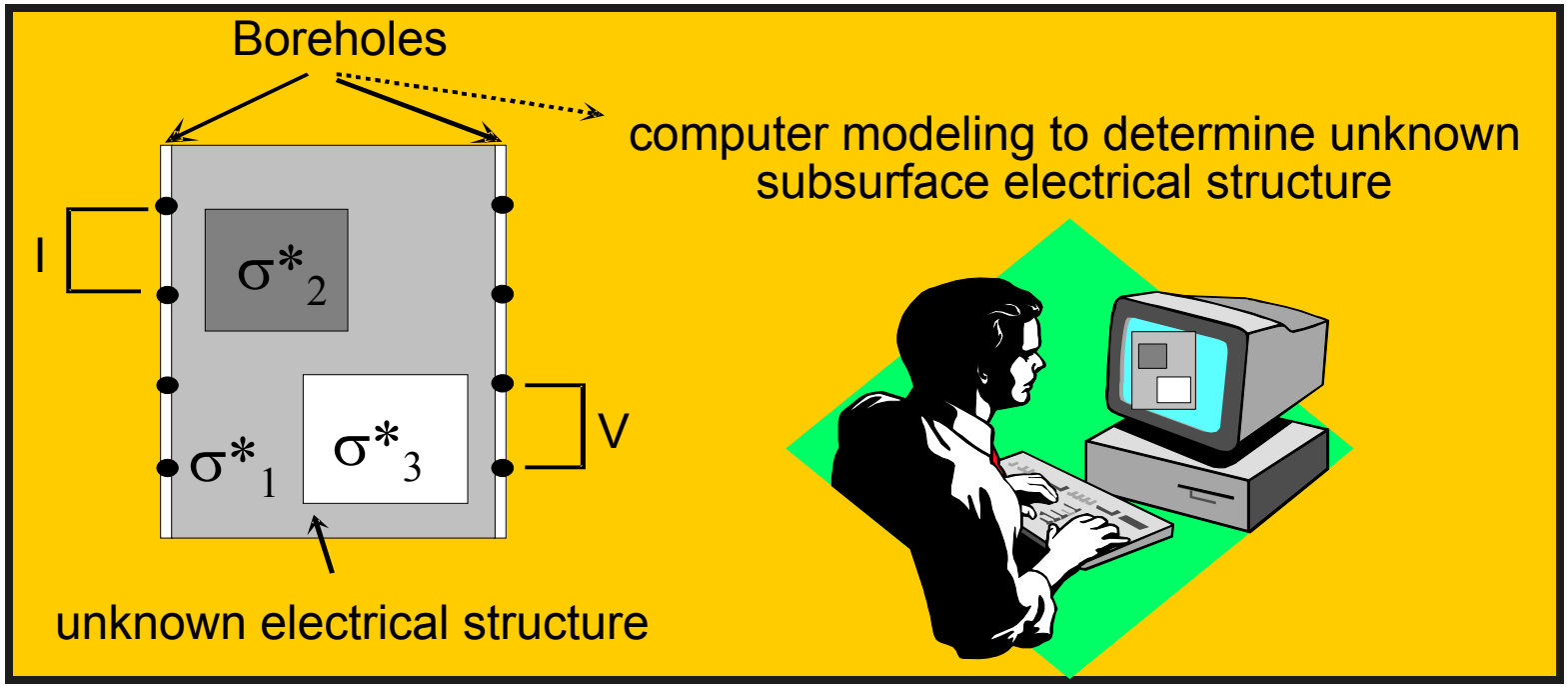
Slater, L. and Binley, A., Evaluation of permeable reactive barrier (PRB) integrity using electrical imaging methods, **Geophysics**, May-June, 2003

- **monitoring long term PRB degradation and performance**
  (PRB life span is currently very uncertain)

current EMSP research

Electrical imaging

- **Electrical conductivity:** Granular iron of PRB is highly conductive relative to background geology
- **Induced polarization (IP):** Metal-fluid interface exhibits high electrical impedance and is polarizable (electrode polarization)



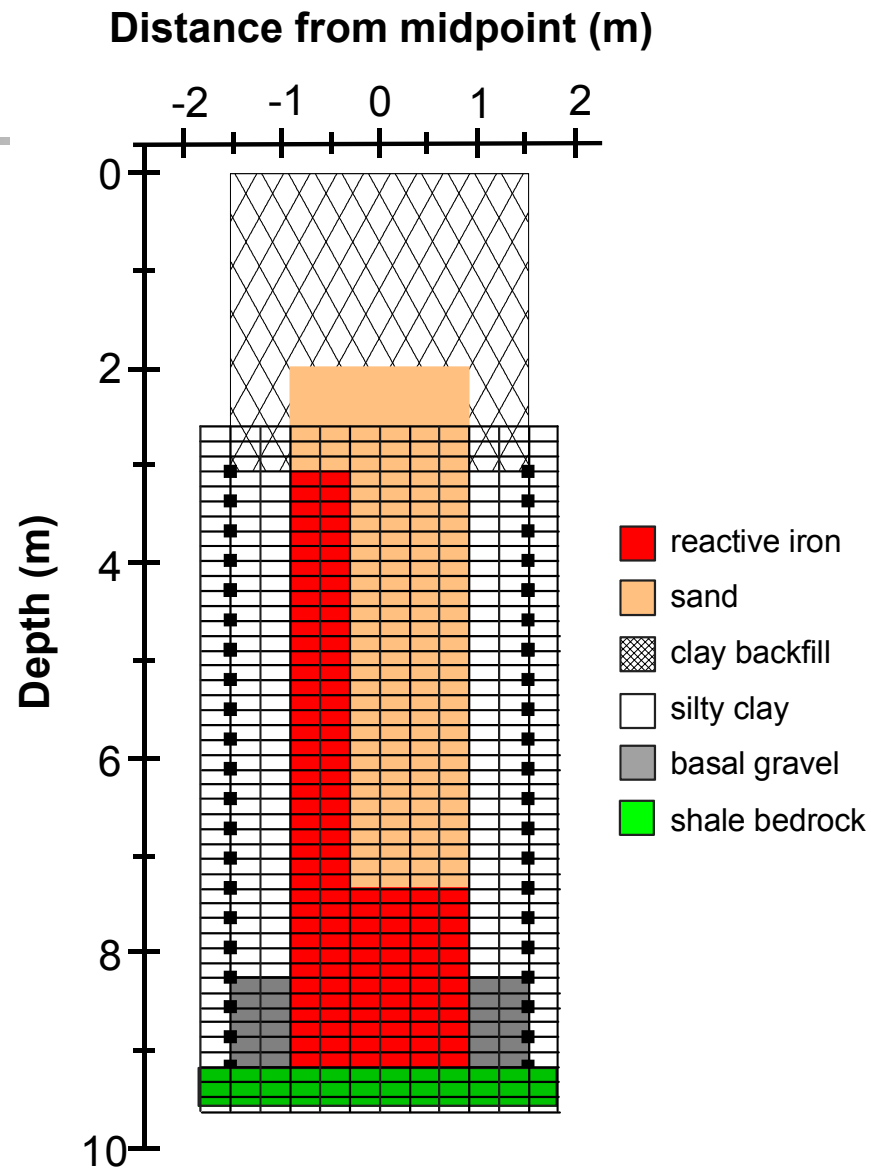
Array installations

- 16 holes
- 10-12 ft spacing across barrier

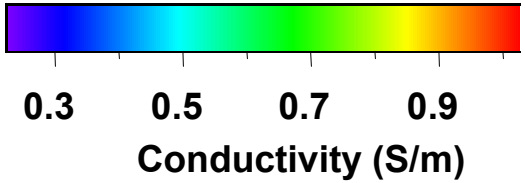
- Electrodes at 1 ft intervals

PRB acquisition parameters

- Imaging mesh superimposed on idealized in-situ barrier structure
- 2D panels consisted of 770 independent measurements
- 3D datasets consist of 4620 measurements

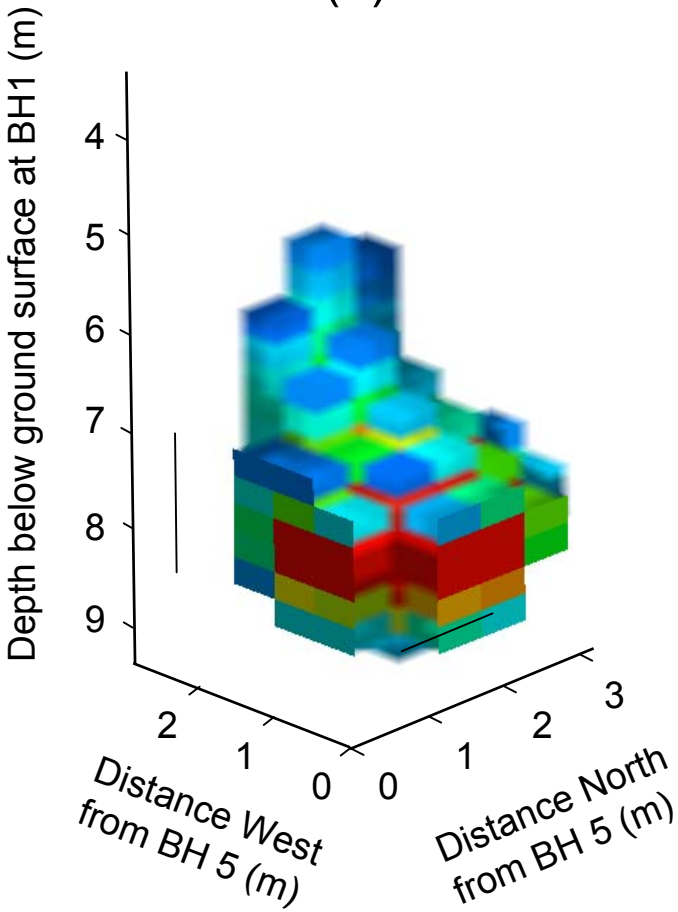


Conductivity images:



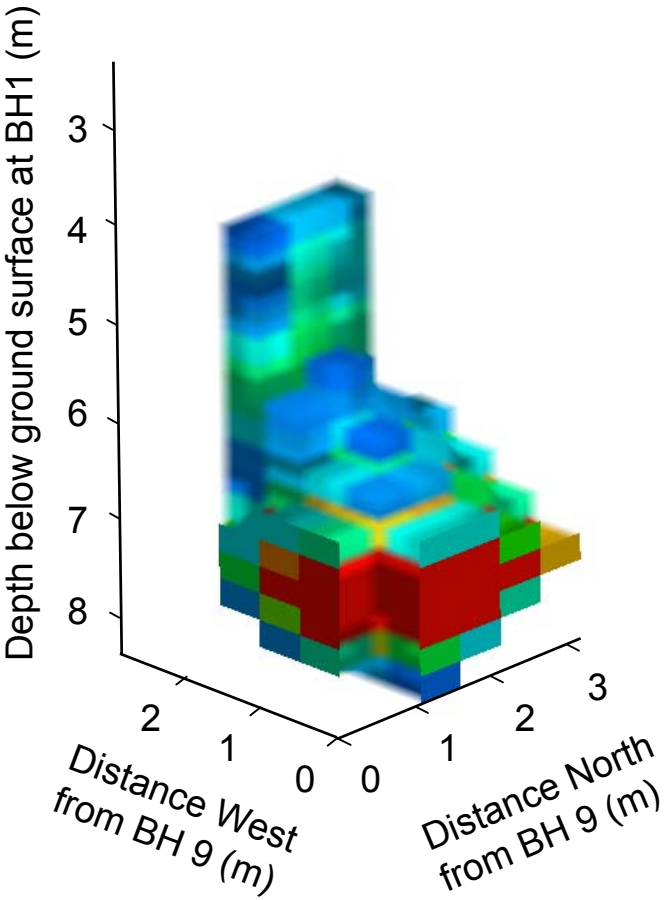
BH 5-8

(a)

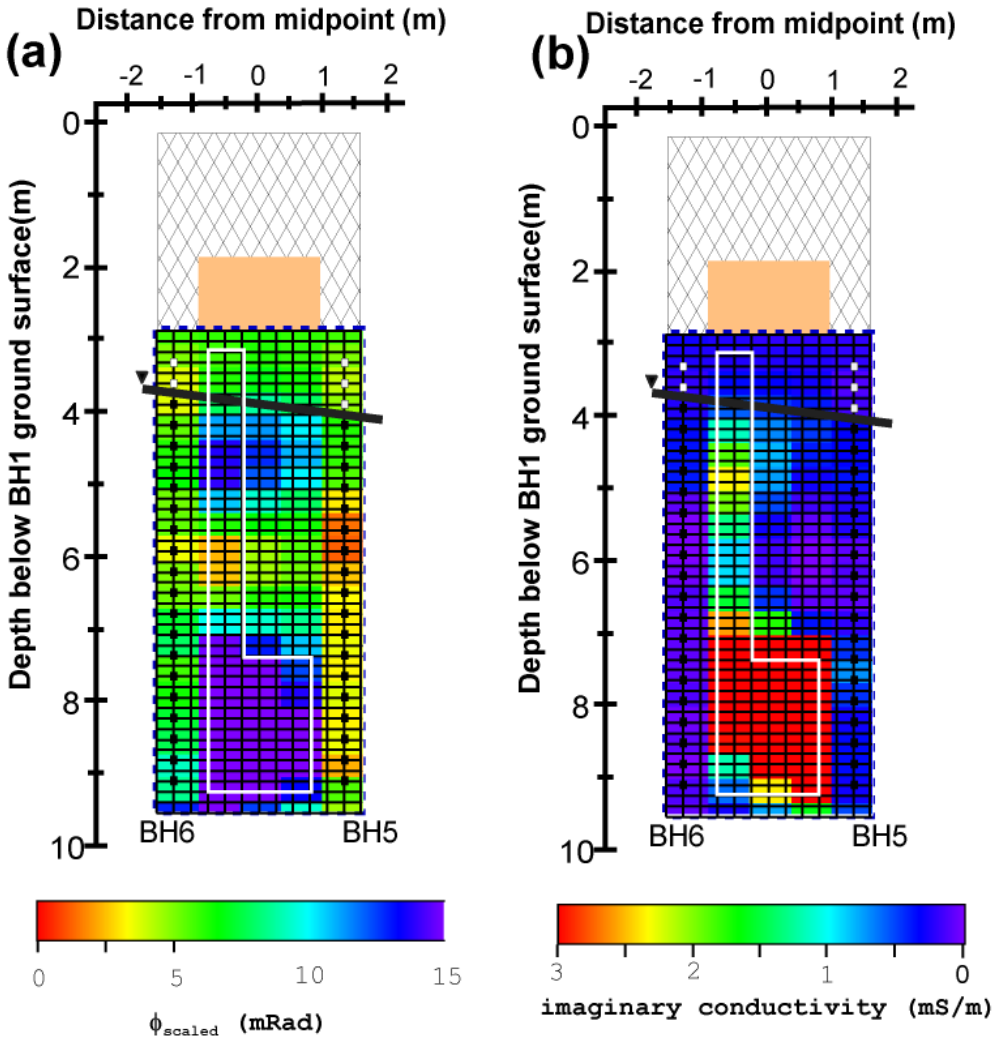


(b)

BH 9-12



IP imaging


(a)
Distance from midpoint (m)
-2 -1 0 1 2
Depth below BH1 ground surface(m)
0 2 4 6 8 10
BH6
BH5
0 5 10 15
ϕ_{scaled} (mRad)
(b)
Distance from midpoint (m)
-2 -1 0 1 2
Depth below BH1 ground surface(m)
0 2 4 6 8 10
BH6
BH5
3 2 1 0
imaginary conductivity (mS/m)

Theory

Induced polarization (IP)

- Electrical impedance resulting from electrochemical energy barrier between electronic conduction in metal and ionic conduction in fluid
- At low frequencies (0.1-100 Hz) diffusion of ions from electrolyte to/from electrode surface with associated electron transfer or diffusion of absorbed ions to electron exchange sites controls impedance
- Electrical impedance thus controlled by redox chemistry
- IP theory developed for mineral exploration – adapt to environmental issues e.g. PRBs

What we measure

- Magnitude/phase or real/imaginary component of a complex impedance, resistivity or conductivity
- Magnitude/real component: defines ohmic conduction magnitude (*basically a resistivity measurement*)
- Imaginary component: defines polarization magnitude
- Phase: defines ratio of polarization to ohmic conduction

Warburg impedance (Z_W) sensed with IP

For single active electrolyte species assuming diffusion of ions from solution:

$$Z_w = \frac{v^2 RT}{n^2 [A] \sqrt{j\omega D}}$$

v = stochiometric #
$[A]$ = activity (moles/liter)
R = gas constant
T = absolute temperature
n = number of electrons in redox reaction
ω = angular frequency
f = frequency (Hz)
D = diffusivity
$j = \sqrt{-1}$

For D = 2×10^{-5} cm^2/s:

$$Z_w = \frac{v^2 0.0233}{n^2 [A] \sqrt{f}} e^{-j\frac{\pi}{4}}$$

Z_w in Ohm/cm^2

Angoran, Y. and Madden, T. R., 1977, Induced polarisation: a preliminary study of its chemical basis. Geophysics, 42, 788-803.

Equivalent Warburg impedance can be defined for diffusion of surface absorbed ions e.g. Morgan, 1981

Hypotheses

Induced polarization sensitive to:

- surface area of iron in contact with groundwater:
  - PRB integrity
  - precipitation/clogging [performance reduction]

- redox chemistry of iron-electrolyte interface:
  - *natural oxidation [performance reduction]*
  - enhanced oxidation due to contaminant (hydrocarbon or heavy metal) conversion [performance reduction]

Laboratory studies

Experiments

Electrical properties of sand/iron mixtures as a function of:

- *varying Fe content*
- *Electrolyte chemistry*
- *Natural oxidation/precipitation*
- *TCE/PCE degradation*
- *Chromium degradation*

Effects of iron concentration

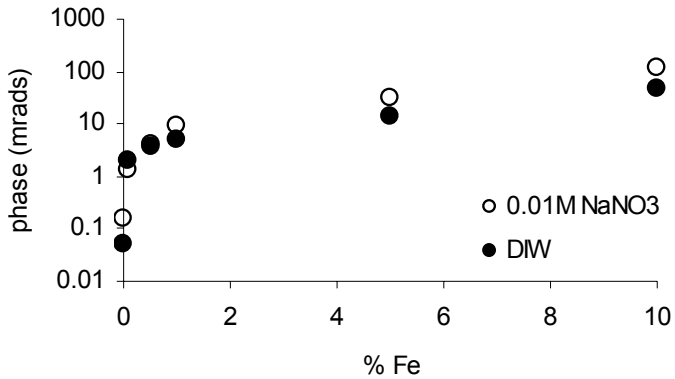


Fig. 1. Plot of Phase versus % Fe in Ottawa sand at 1 Hz

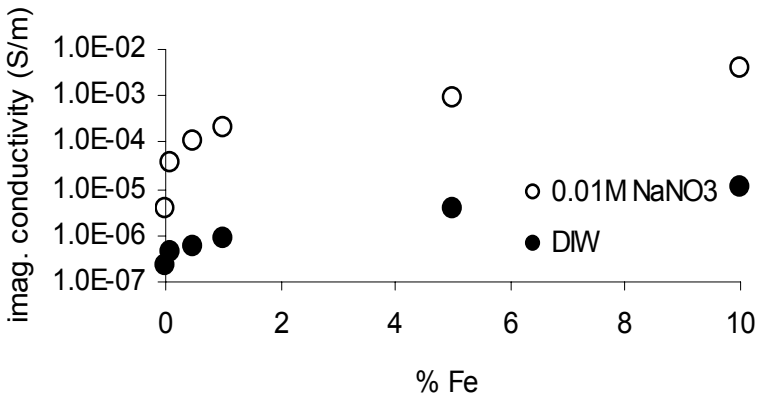


Fig. 2. Plot of imaginary conductivity versus % Fe in Ottawa sand at 1 Hz

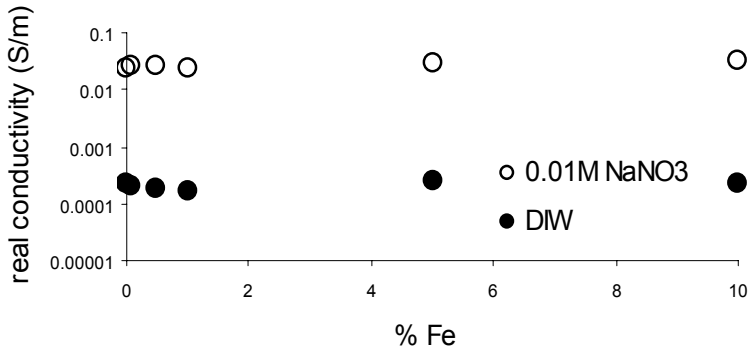


Fig. 3. Plot of real conductivity versus % Fe in Ottawa sand at 1 Hz

Effect of activity of $NaNO_3$ vs. NaCl for 5% Fe

$$Z''_{f(NaNO_3)} = \frac{1}{(Activity)_{NaNO_3}^{1.14}} \qquad Z''_{f(NaCl)} = \frac{1}{(Activity)_{NaCl}^{1.11}}$$

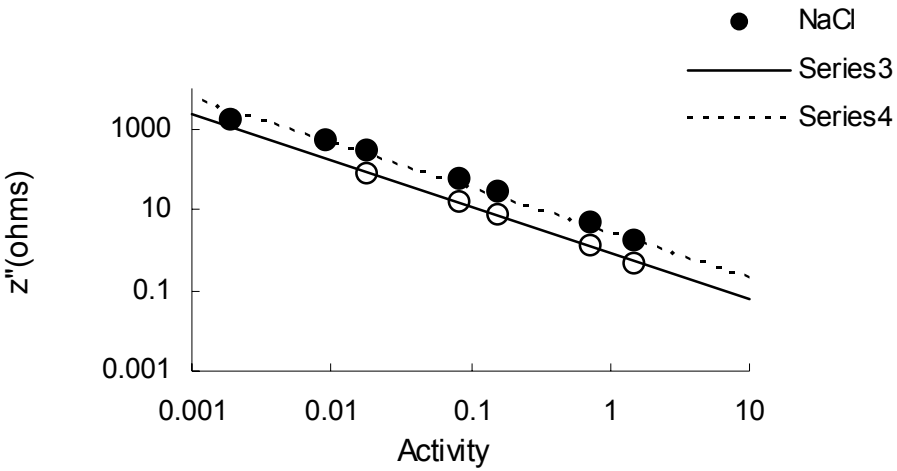


Fig. 1. Dependence of imaginary impedence on activity of $NaNO_3$ and NaCl in Ottawa sand contained with 5% Fe (1Hz).

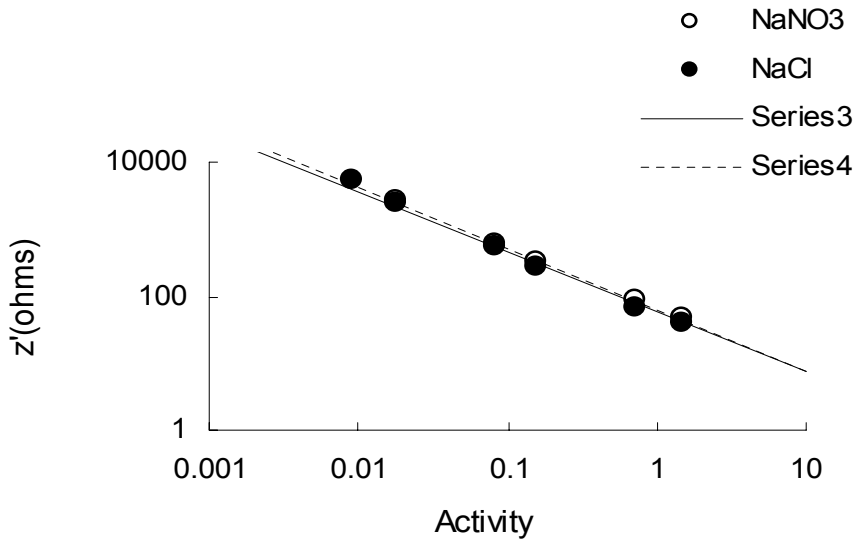


Fig. 2. Dependence of real impedance on activity of $NaNO_3$ and NaCl in Ottawa sand contained with 5 % Fe (1Hz).

Effect of activity($NaNO_3$) - 5% Fe vs. 10 % Fe

$$Z''_{f(10\%Fe)} = \frac{1}{(Activity)_{NaNO_3}^{1.01}} \qquad Z''_{f(5\%Fe_3)} = \frac{1}{(Activity)_{NaNO_3}^{1.15}}$$

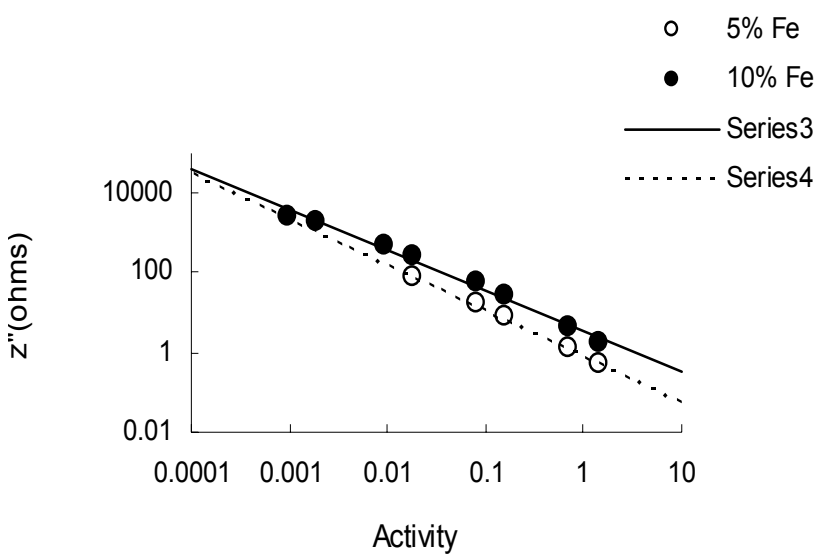


Fig. 1. Dependence of imaginary impedence on activity of $NaNO_3$ for 2 samples (OS) contained with 5 and 10% Fe (1Hz).

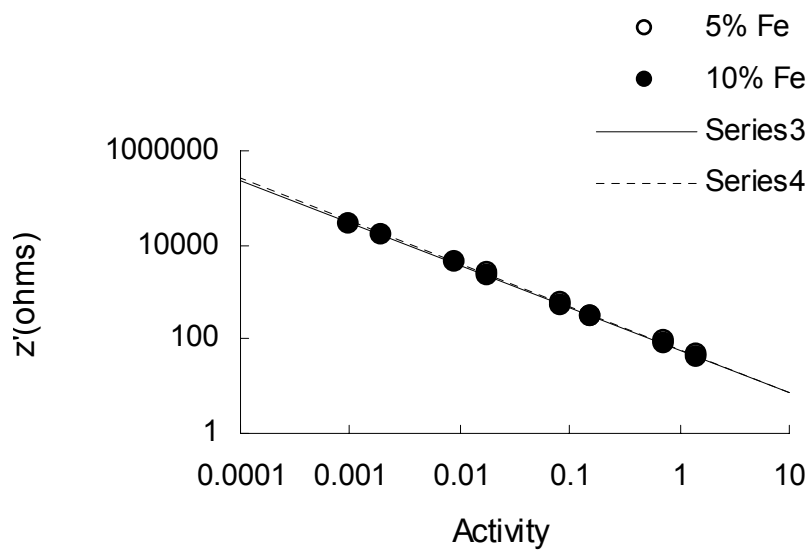


Fig. 2. Dependence of real impedance on $NaNO_3$ conductivity for 2 samples (OS) contained with 5 and 10% Fe (1Hz).

Effect of current density

- Identify range of current density over which IP measurements are constant

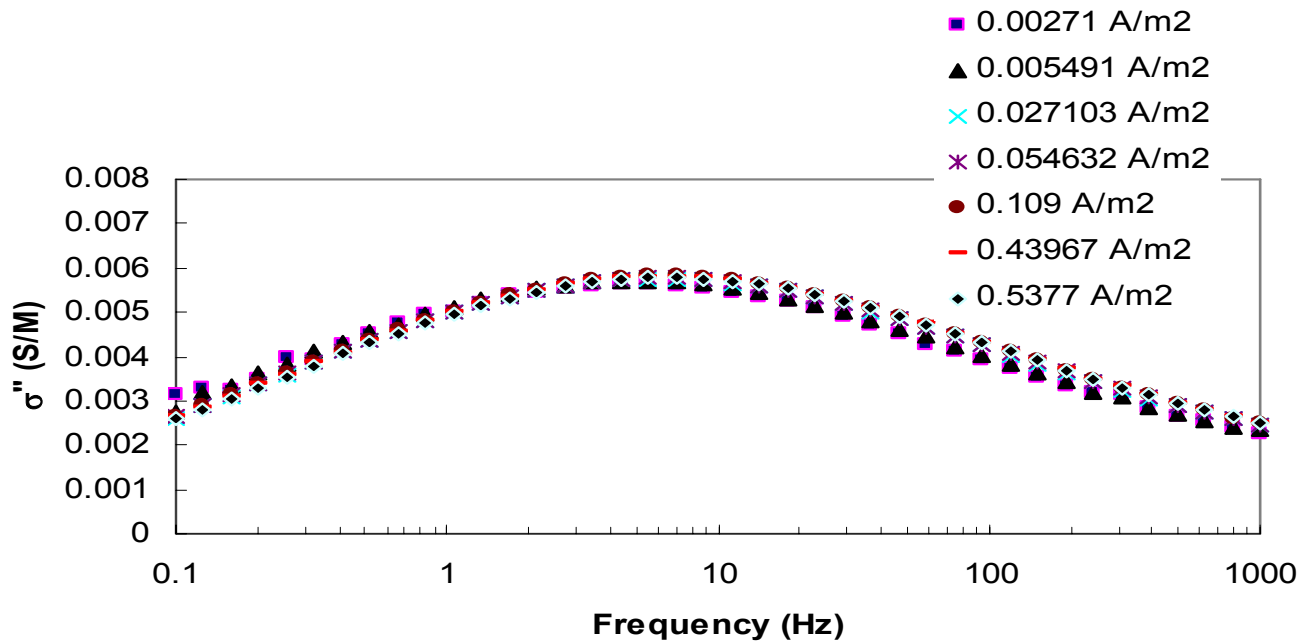


Fig. 2. Imaginary conductivity of Ottawa sand including 10% Fe saturated with 0.01 M $NaNO_3$ solution as a function of current density.

Spectral (shape) characteristics

Fluid concentration

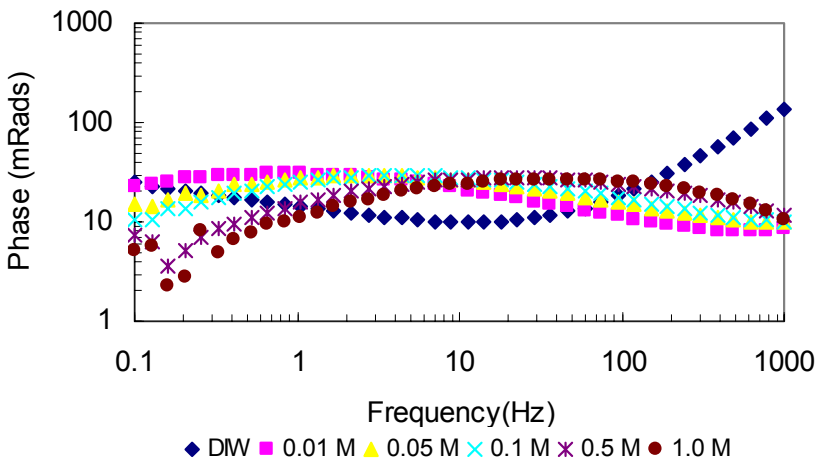


Fig. 1. Phase of Ottawa sand contained with 5% Fe as a function of $NaNO_3$ concentration.

Fe concentration

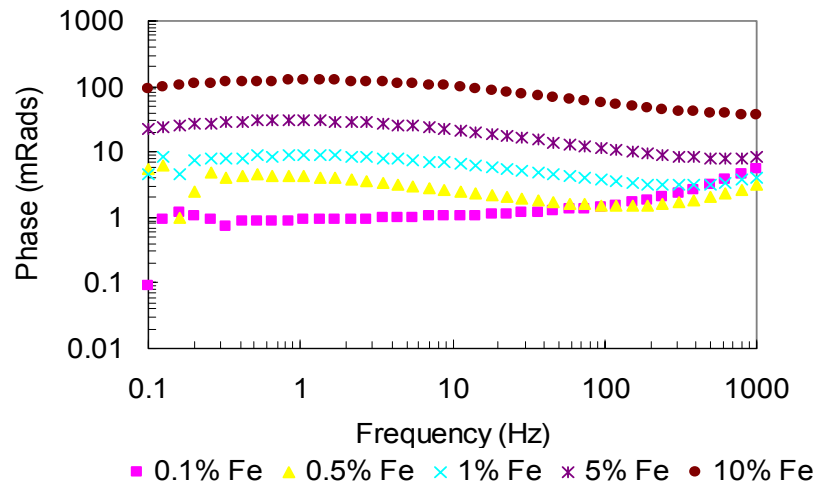


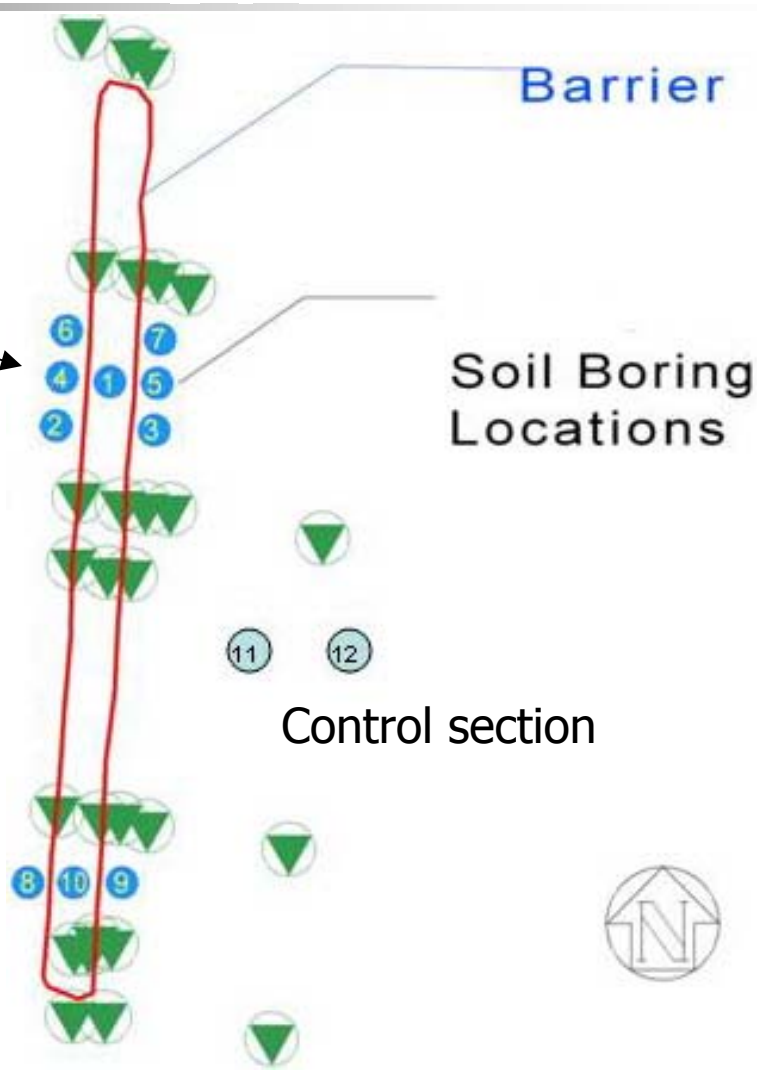
Fig. 2. Phase of Ottawa sand with 0.01 M $NaNO_3$ as a fuctio of % Fe.

Field studies

Experiments

- Three year electrical imaging study of Kansas City PRB
- Groundwater chemistry sampling to evaluate oxidation/precipitation/clogging and associated reduction in performance – control on geophysical signatures
- Iron core retrieval and analysis of iron surface at end of experiment

New installations for electrical imaging



Focus area: active TCE/PCE degradation

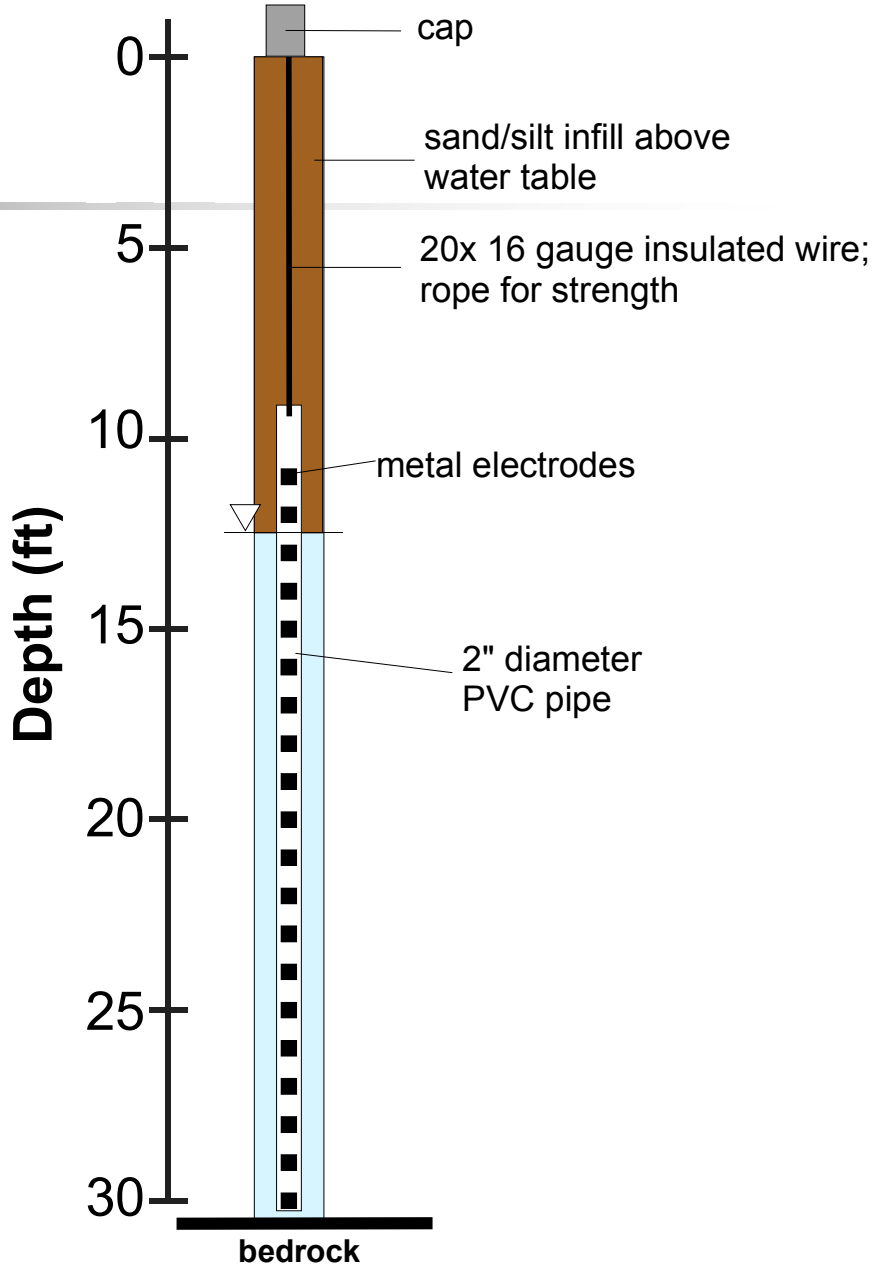
Minimal TCE/PCE degradation

Control section

January 2003

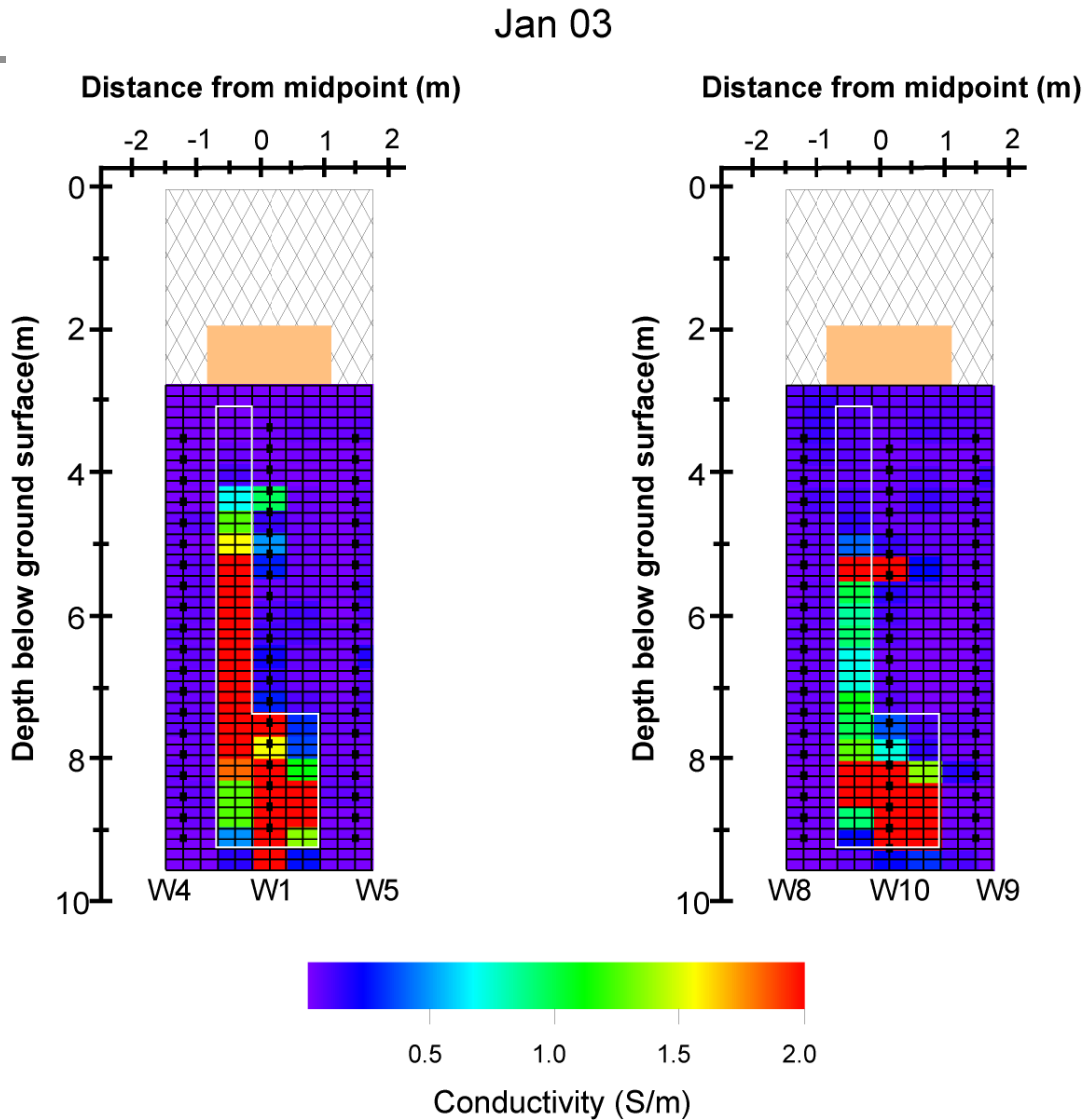
Electrode arrays

- Installation in both saturated and unsaturated zone



Primary control panels

- January 2003



Major issues

- Can laboratory electrical signatures of PRBs be predicted with current theory?
- Are electrical signatures due to reduced PRB performance resolvable with current field instrumentation/inverse algorithms?
- Are electrical signatures interpretable in terms of electrochemical properties associated with reduced iron performance?

Thank you…..