Electrical properties of sand-Fe^0 columns: implications for long-term monitoring of PRB chemistry

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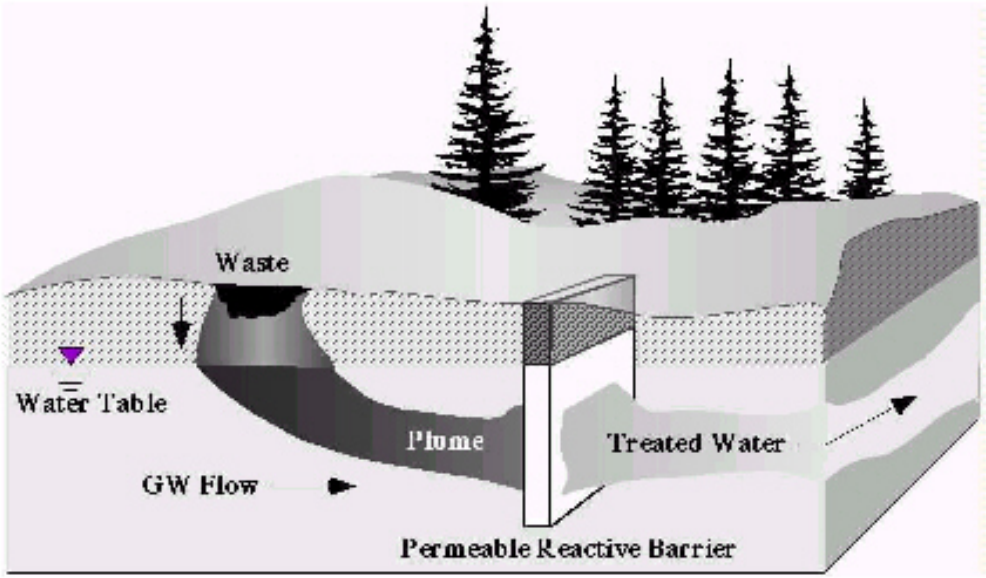
Permeable reactive barriers

- 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***

Motivation

- Evaluating PRB integrity in-situ (post installation) – *are design requirements met?*
- Remote monitoring of long-term reduction in PRB performance due to precipitation and clogging

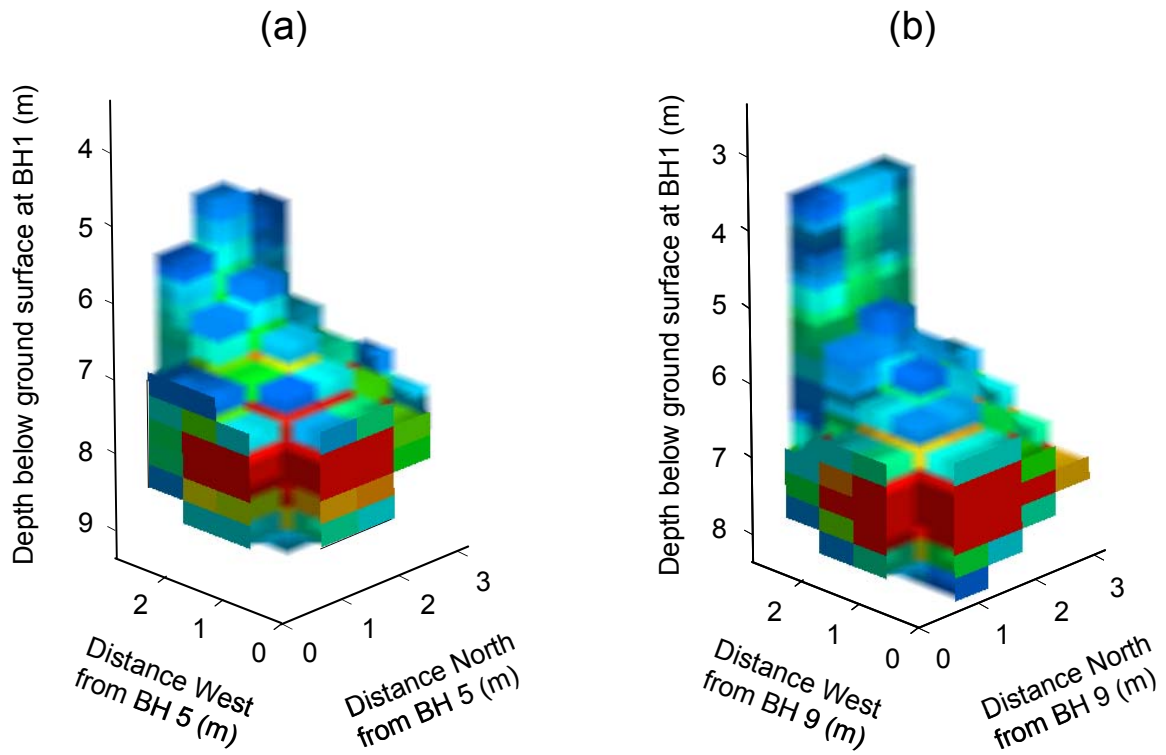
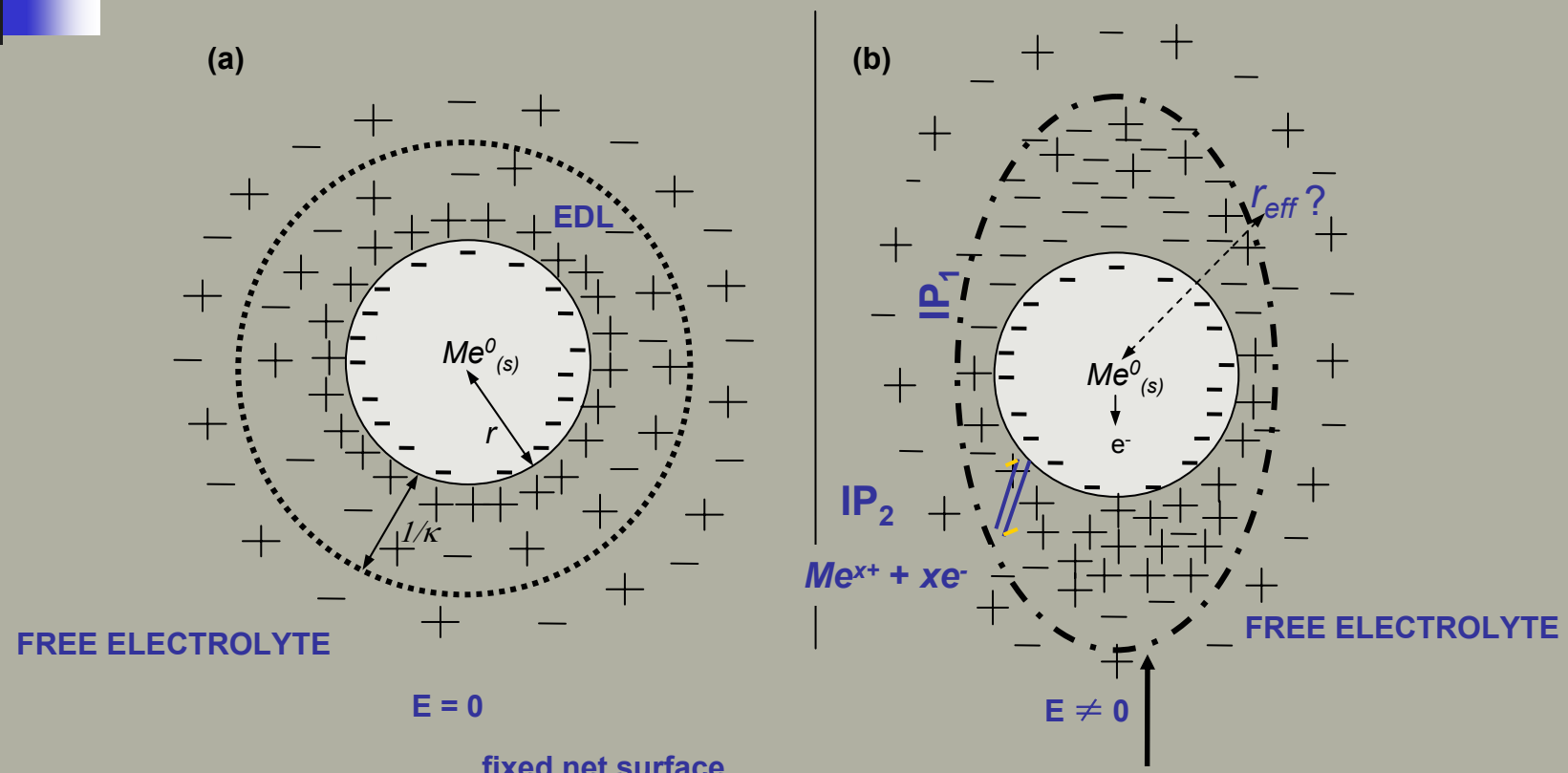


Fig. 1: Results of electrical imaging at two locations on the PRB installation at Kansas City

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

Polarization at a metallic interface



- fixed net surface charge
- negative ion
- positive ion
- Me^{x+} redox active ion
- e^- electron

IP mechanisms

IP_1: inactive ion related

IP_2: redox active ion related

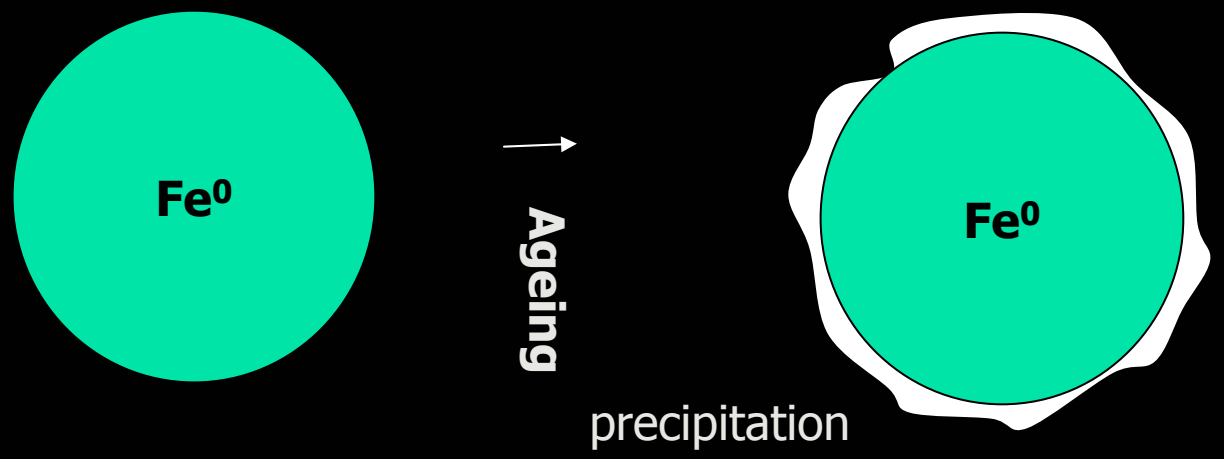
Electrical parameters as proxy indicators of PRB longevity

Known

- IP magnitude correlated with surface area (e.g. Wong, 1979)
- IP relaxation time correlated with grain size (e.g. Pelton et al., 1978; Wong, 1979)

Effect of precipitation?

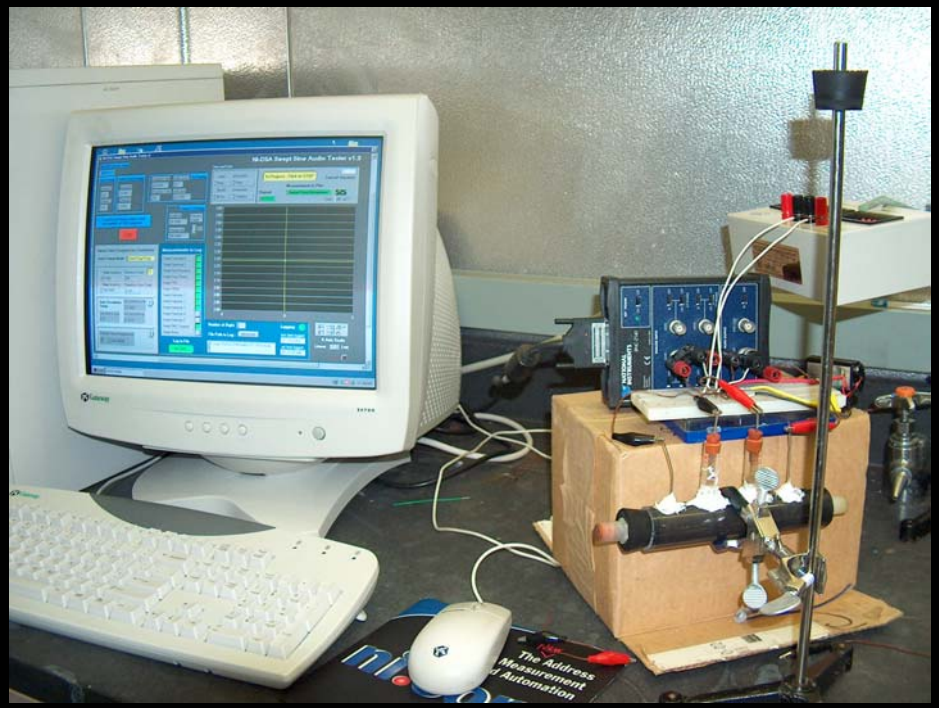
- reduction in IP magnitude due to reduction in surface area of exposed Fe^0?
- Increase in relaxation time as result of increase in effective grain size



Laboratory measurements on Fe^0-Ottawa sand columns

- **Low-frequency (0.1-1000 Hz) electrical measurements as a function of:**
  (a) Fe0 surface area per unit pore volume
  (b) electrolyte activity; 0.001-10 mol/L
  (c) valence: +1, +2, +3
  (d) pH: 1.5-10.5 using 0.01 M NaNO3
  (e) precipitation of iron hydroxides and iron carbonates

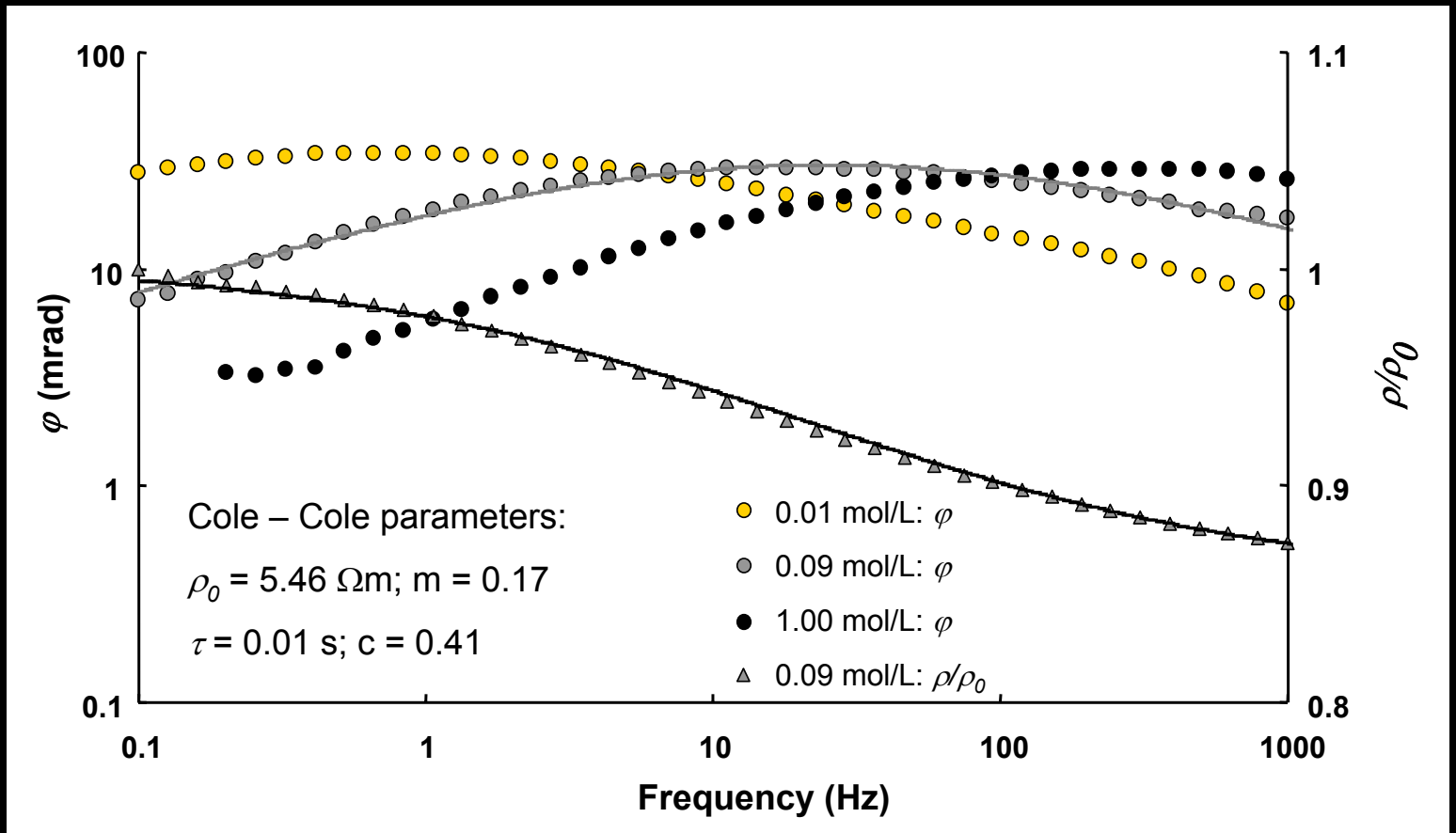
Slater, L, Choi, J. and Wu, Y., Electrical properties of iron-sand columns: implications for induced polarization investigation and performance monitoring of iron-wall barriers, **Geophysics**, In Press



Fisher 40-mesh Fe^0 particles
$NaNO_3$, NaCl and CaCl electrolytes.
Specfific surface area: Fe^0=2.8 m^2/g;
Ottawa sand = 0.05 m^2/g)

Example datasets

- Low-frequency (0.1-1000 Hz) measurements as a function of $NaNO_3$ electrolyte concentration: 5% Fe^0



Dispersion models

Cole-Cole type:

$$\rho^* = \rho_0\left[1 - m\left(1 - \frac{1}{1+(\omega\tau)^c}\right)\right] \quad [1]$$

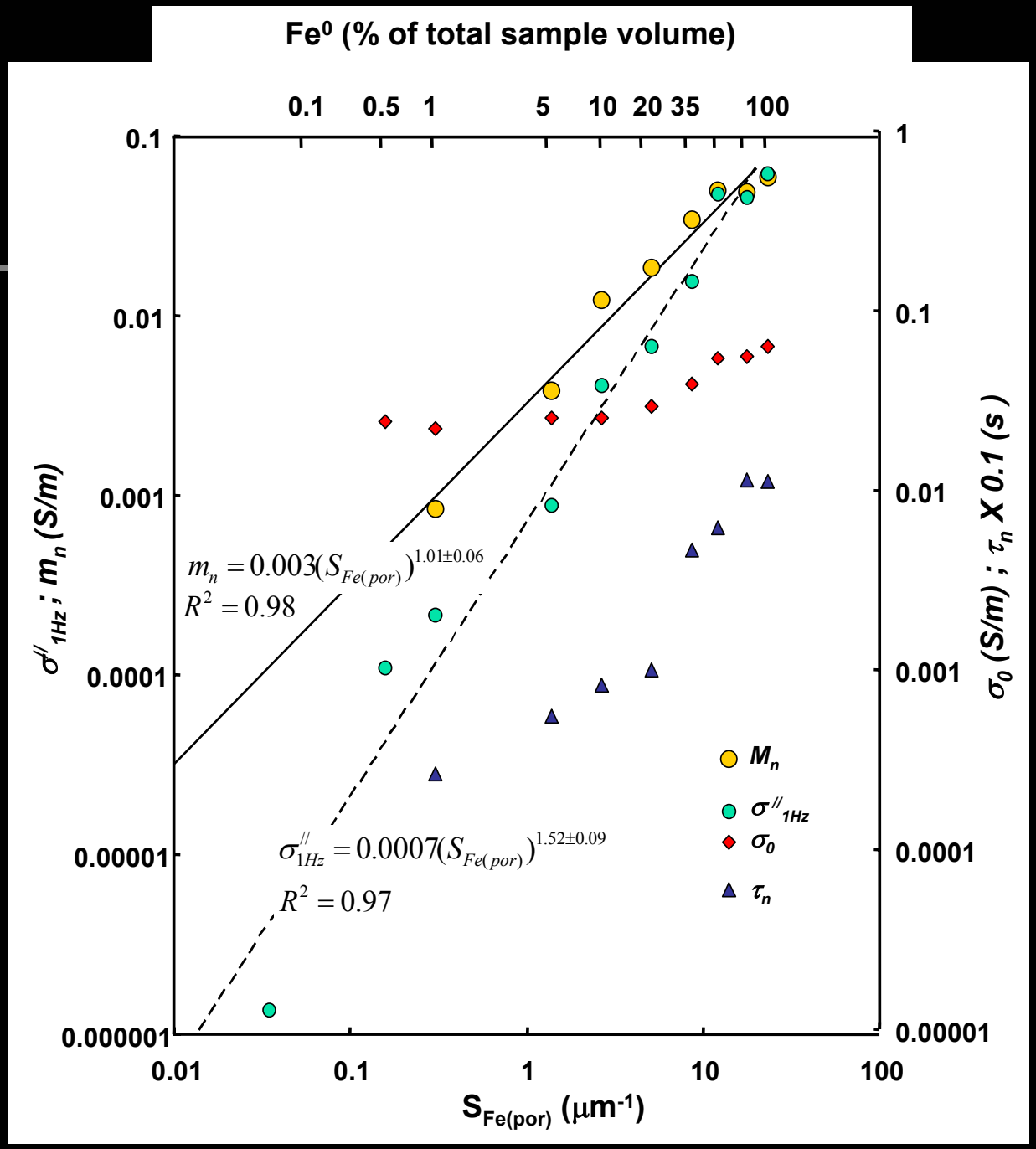
[ρ^* = complex resistivity; ρ_o = dc resistivity; m = chargeability; ω = frequency; τ = time constant; c = shape parameter]

- $\sigma_0 = 1/\rho_0$: conduction magnitude term
- $\mathbf{m_n = m/\rho_0}$: polarization magnitude term
- $\tau_n = \tau/\rho_0$: characteristic time of polarization mechanism

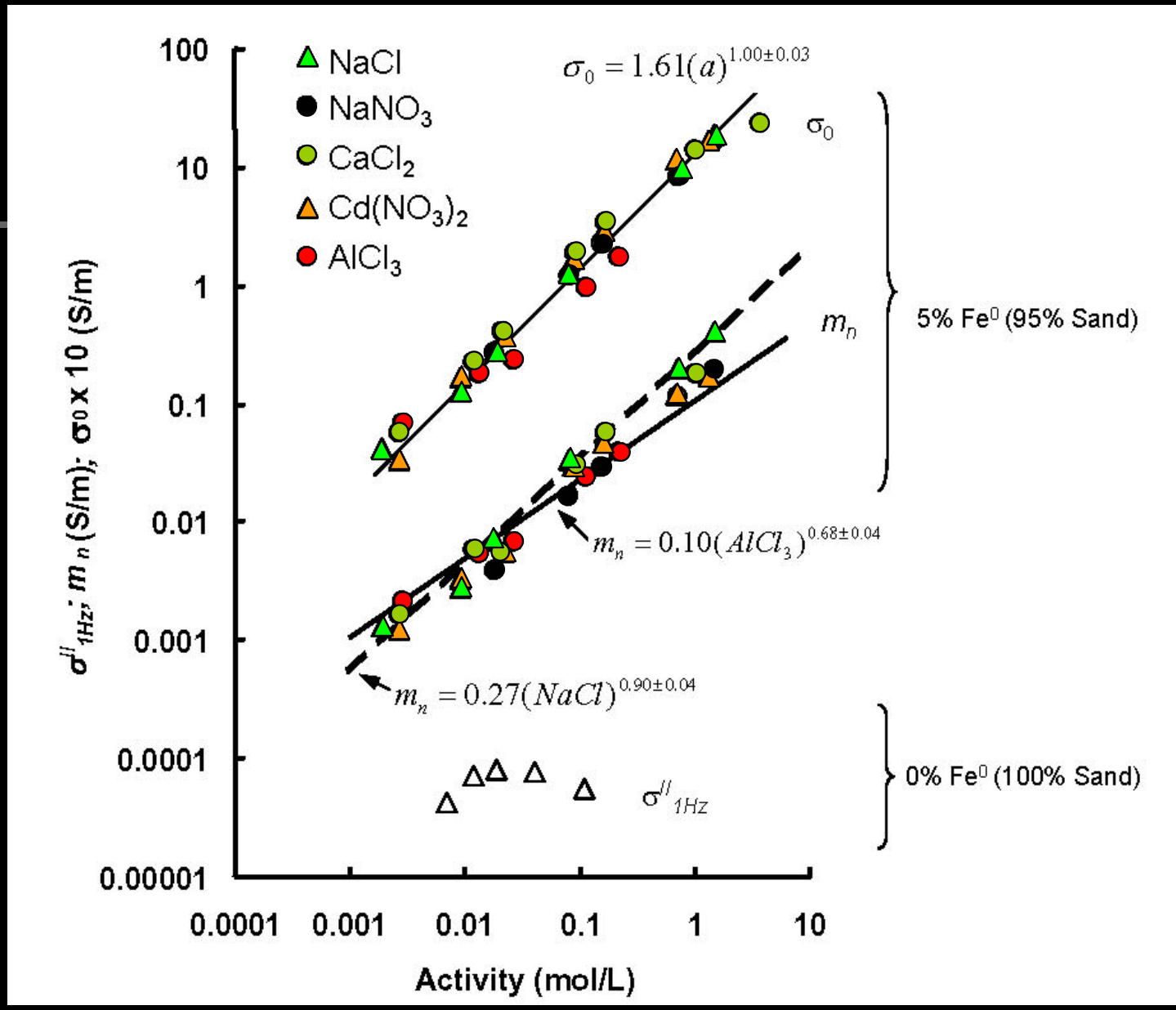
→ **volumetric electrical properties**

Mineral surface/electrical double-layer chemistry/redox chemistry

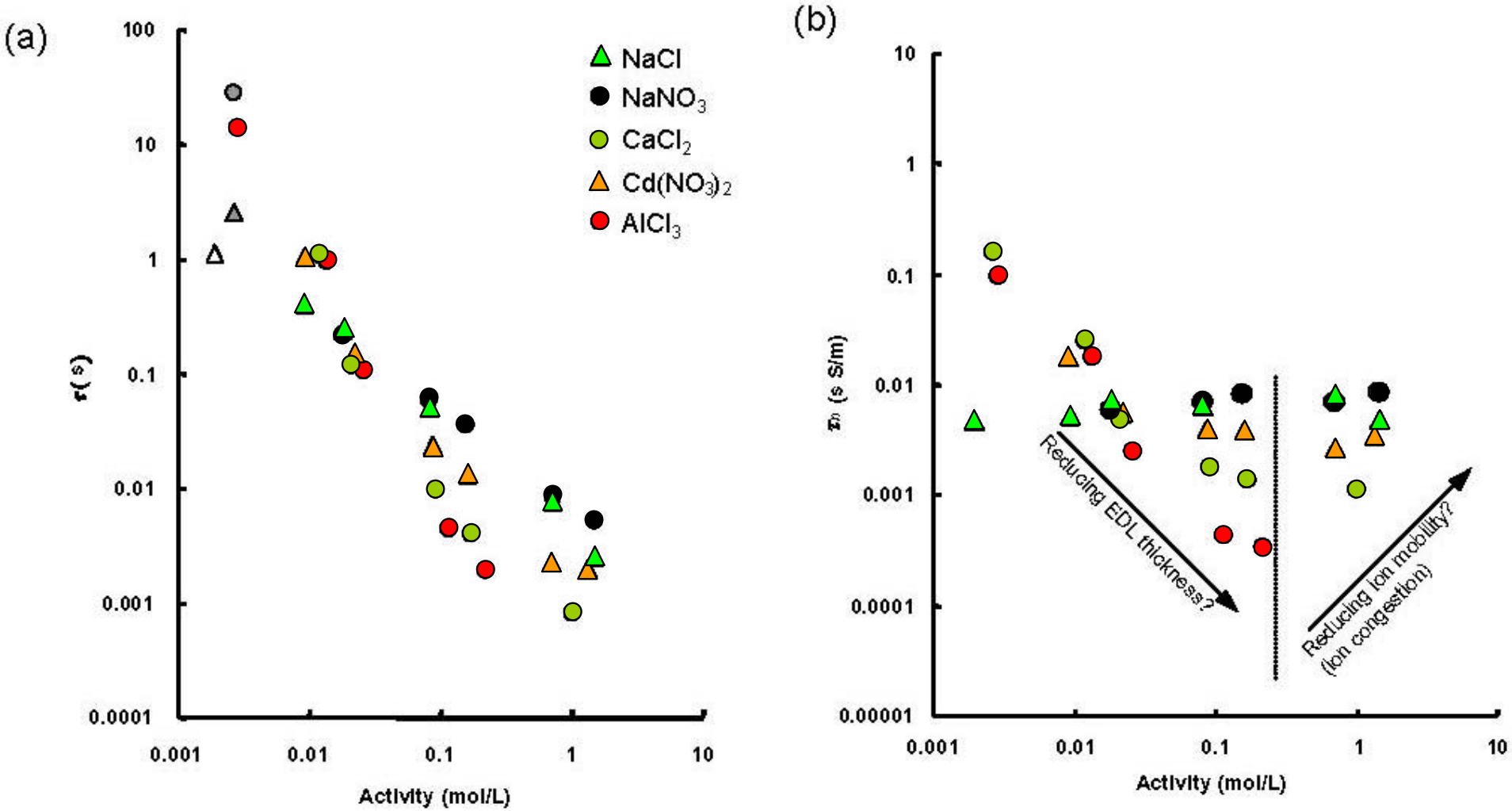
- Sand-Fe^0 mixtures as a function of surface area of Fe^0 per unit pore volume



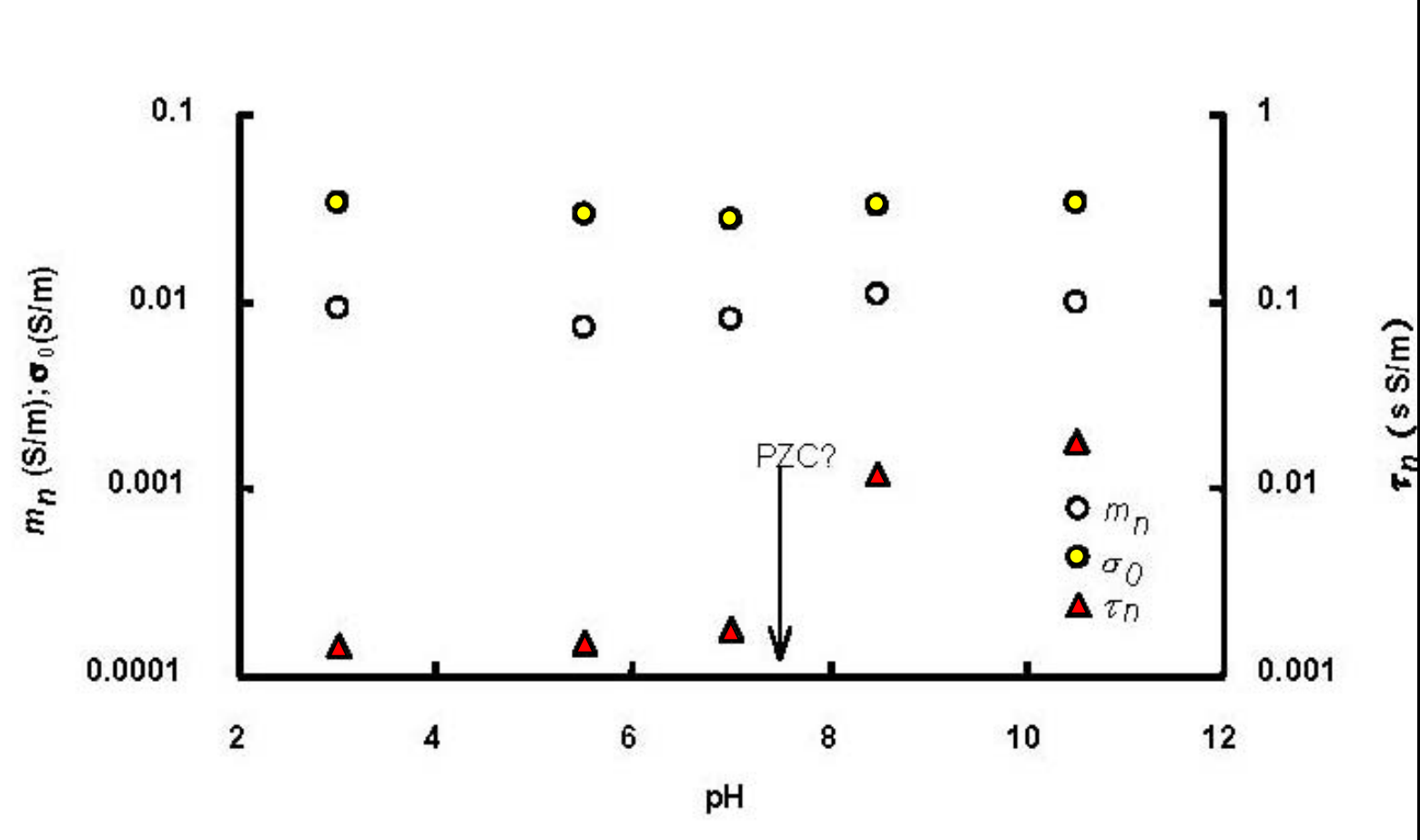
- **5% Fe^0 (95% sand) as a function of electrolyte activity and valence**



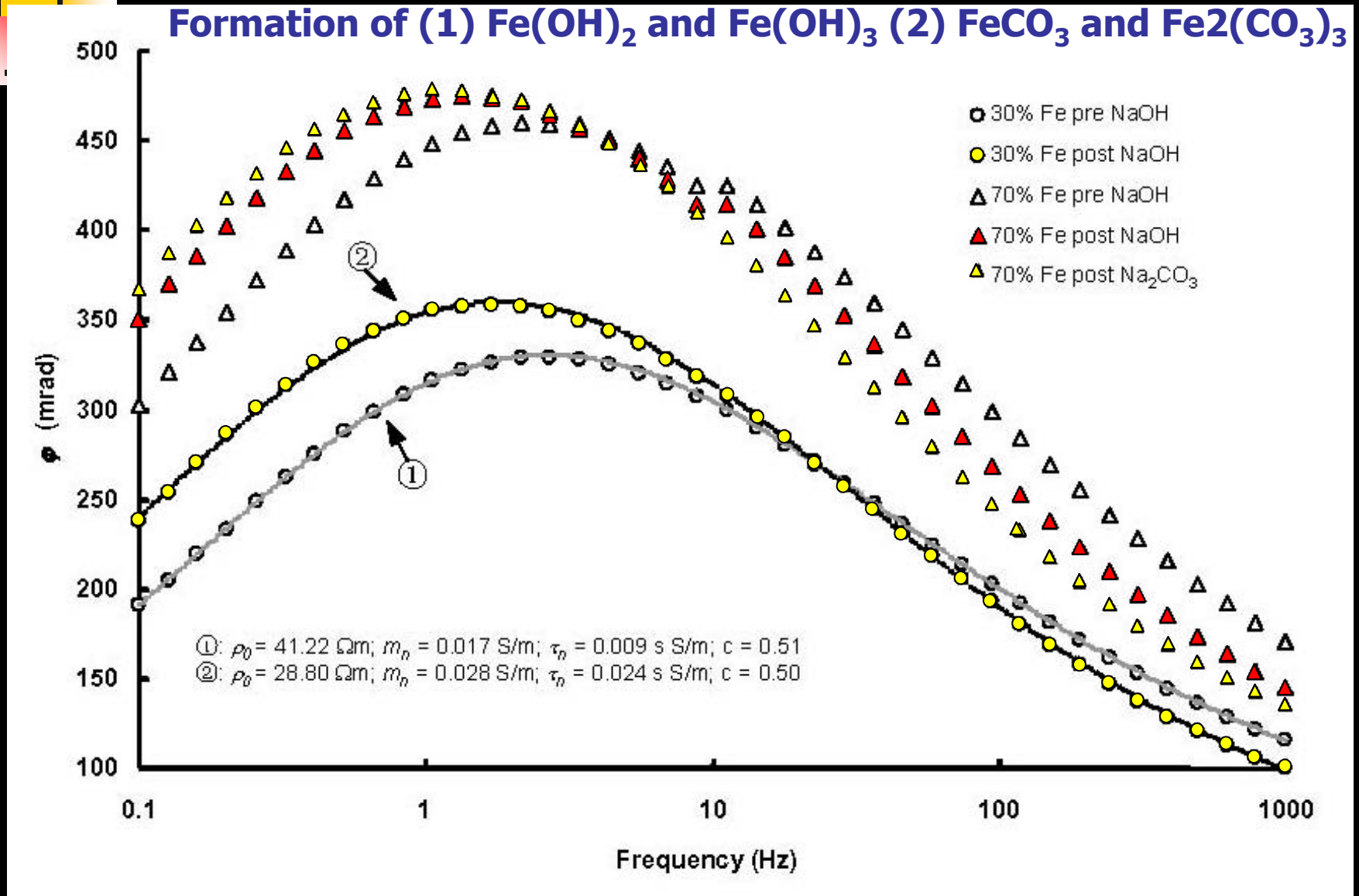
Time constant (τ) as a function of activity and valence



Electrical parameters as a function of pH



Spectral changes due to chemically induced precipitation



Gouy-Chapman theory

- Variation of τ_n is in part consistent with Gouy-Chapman electrical double layer model

$$\kappa = \left(\frac{8\pi N Z^2 e^2 C}{\varepsilon k T}\right)^{1/2}$$

- $1/\kappa$ = double layer thickness
- C = electrolyte concentration
- Z = valence
- T = temperature
- N = Avogadro's number
- ε = dielectric constant
- k = Boltzman's constant
- e = electronic charge

Summary

- **Integrity evaluation** based on sensitivity of IP magnitude to Fe^0 surface area

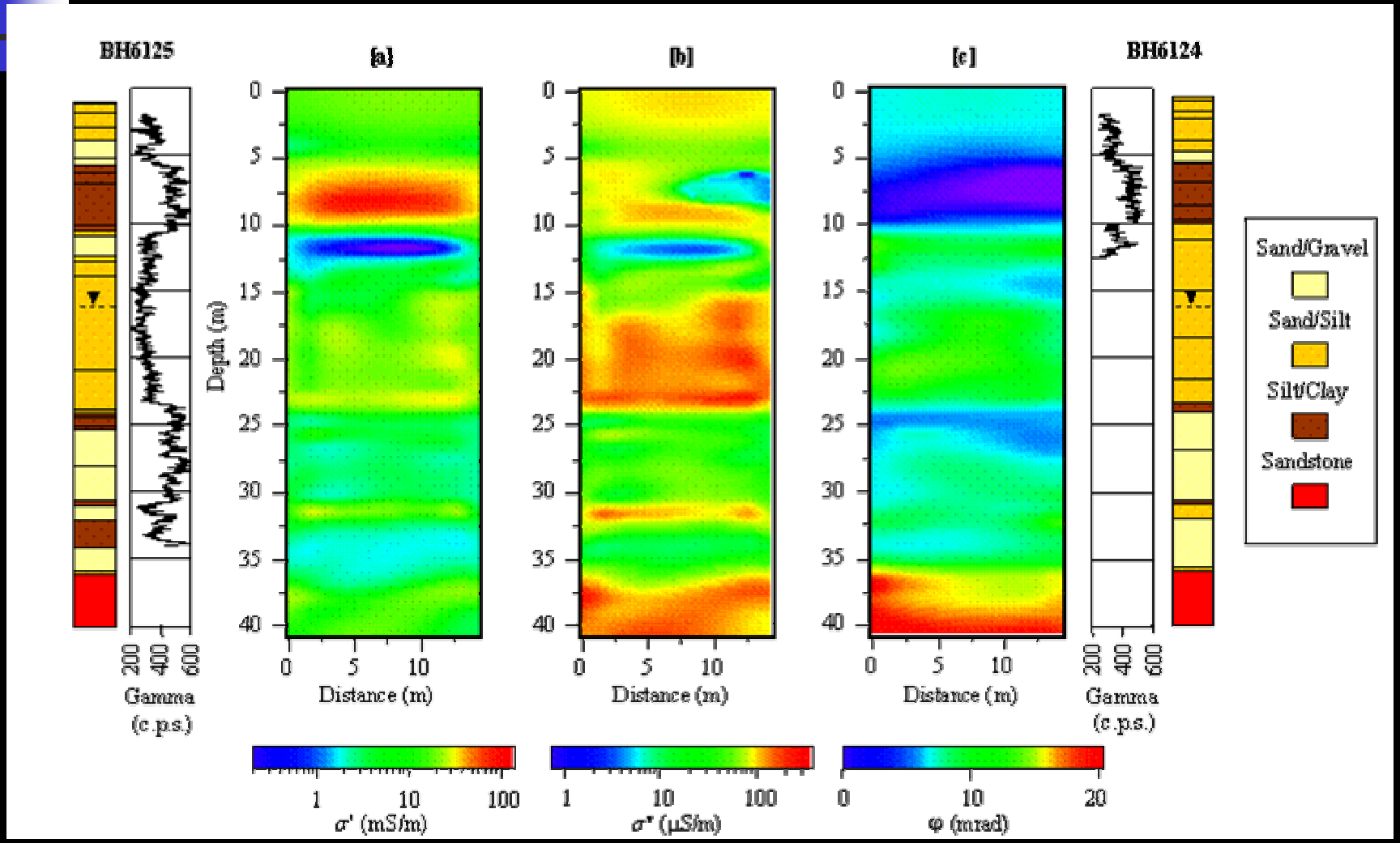
Future experiments:

- Focus is now on precipitation in column experiments
- Self potentials
- Measurements during active TCE degradation

- **Long-term monitoring** based on sensitivity of IP magnitude and relaxation time to precipitation?
- Will require accurate knowledge of solution chemistry

- Imaging?
- Borehole probes?

Lithologic characterization



Source: Kemna, A., A. Binley, and L. Slater. 2004. Cross-borehole IP Imaging for engineering and environmental applications. Geophysics 69:97-107.

Closing thought

- Induced polarization is the <u>only</u> geophysical method directly sensitive to interfacial chemistry
- Potential application in monitoring of precipitation processes in a wide range of environmental systems****