Self-potential and induced polarization: Geophysical tools to map flowpaths and monitor contaminant plumes

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Rocks have a complex texture and chemistry, Geophysics is sensitive to both

New science: Mechanistic understanding of the geophysical signals
Medical Science
(electro-encephalography)

Self-potential

Network of non-polarizing electrodes connected to a voltmeter

Geophysics (self-potential)
"M"-form of the transport equations

Generalized constitutive equations

Take-home message: any kind of non-equilibrium disturbance generate an EM signal

<table>
<thead>
<tr>
<th>&quot;M&quot;-form</th>
<th>Chemical potential</th>
<th>Electric potential</th>
<th>Fluid pressure</th>
<th>Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Salt flux $J_a$</td>
<td>Fick's law</td>
<td>Electrophoresis</td>
<td>Convective diffusion</td>
<td>Soret effect</td>
</tr>
<tr>
<td>Current density $J$</td>
<td>Diffusion current</td>
<td>Ohm's law</td>
<td>Electrofiltration</td>
<td>Thermo-electricity</td>
</tr>
<tr>
<td>Darcy velocity $u$</td>
<td>Osmosis</td>
<td>Electro-osmosis</td>
<td>Darcy's law</td>
<td>Thermo-osmosis</td>
</tr>
<tr>
<td>Heat flux $H$</td>
<td>Dufour effect</td>
<td>Peltier effect</td>
<td>Convective flux</td>
<td>Fourier's law</td>
</tr>
</tbody>
</table>
Self-potential associated with a salt plume

Multichannel system (256 ch., 7 kHz)
Ag/AgCl smart electrodes
Time-lapse self-potential signals

Snap shots of the electrical potential distribution over time
Modeling Buoyancy driven saline plume

Darcy equation

Generalized Fick law

Continuity equation for the mass of the fluid

Continuity equation for the mass of the solute

State equations

\[ \rho_f = \rho_f^0 + \gamma C_m \]  \hspace{1cm} \text{Mass density} \\

\[ \eta_f = \eta_f^0 (1 + \tau_1 C_m + \tau_2 C_m^2 + \tau_3 C_m^3) \]  \hspace{1cm} \text{Viscosity} \\

Hydrodynamic dispersion tensor (Fickian model)

\[ D = \left[ D_m + \alpha_T \nu \right] I + \frac{\alpha_L - \alpha_T}{\nu} \nu \otimes \nu \]

\text{Fickian model (change with scale?)}
Finite element simulation of the forward problem (comsol multiphysics)

Self-potential field

Salinity

Constitutive equation \( \mathbf{j} = \sigma \mathbf{E} + \mathbf{j}_s \)

Continuity equation \( \nabla \cdot \mathbf{j} = 0 \)

Source term \( \mathbf{j}_s = \overline{Q}_v \mathbf{u} - \frac{k_b T}{F_e} (2t_{(+) - 1}) \nabla \sigma_f \)
Self-potential time lapse tomography (deterministic)

\[
G(t) = (d(t) - Km(t))^T W_d (d(t) - Km(t)) + \lambda (m(t) - m(t-1))^T W_m (m(t) - m(t-1))
\]

Data misfit

Regularization over time

Martinez-Pagan, Revil et al., in press in Geophysics
Stochastic inversion (AMA) of the permeability and dispersivities

(15,000 realizations)

(the vertical bar represents the measured horizontal permeability)
Spectral induced polarization (complex conductivity)

Can be used as a geophysical tomographic technique (see Williams et al. Work at Rifle)
Excess Surface (in Siemens)

$$\Sigma_S = \int_{0}^{\infty} \left( \sigma(x) - \sigma_f \right) dx = \Sigma^S + \Sigma^d$$

Similar values for clays and silica
The spectral polarization of a granular material

\[ \sigma^* = \frac{1}{\rho^*} = i\omega\varepsilon^* \]

Complex conductivity

\[ \sigma^* = |\sigma| \exp(i\varphi) = \sigma' + i\sigma'' \]

Magnitude

\[ |\sigma| = \sqrt{\sigma'^2 + \sigma''^2} \]

Phase

\[ \tan \varphi = \frac{\sigma''}{\sigma'} \]
Polarization of a single grain

\[
\sigma_S = \frac{4}{d_0} \left( \Sigma^d + \Sigma^s \right) - \frac{4}{d_0} \frac{\Sigma^s}{1 + i\omega\tau_0}
\]

\[
\tau_0 = \frac{d_0^2}{8D_i}
\]
Polarization of a single grain

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\[
\tau_0 = \frac{d_0^2}{8D_i}
\]

Upscaling using DEM theory for instance
Determination of permeability from spectral induced polarization in granular media

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Accepted 2010 February 21. Received 2010 February 15; in original form 2009 September 11

SUMMARY
The surface conductivity of porous rocks has two contributions: the first is associated with the diffuse layer coating the grains and is frequency-independent as long as the diffuse layer is above a percolation threshold. The second contribution is associated with the Stern layer of weakly sorbed counterions on the mineral surface and is frequency-dependent if the Stern layer is discontinuous at the scale of the representative elementary volume. In the frequency range 1 mHz–100 Hz, this second contribution is also associated with the main polarization mechanism observed by the spectral induced polarization method in granular media (neglecting the contribution of other polarization processes like those associated with redox processes and membrane polarization). At the macroscale, we connect the Stern layer contribution to the complex conductivity and to the expectation of the probability distribution of the inverse of the grain size. This is done by performing a convolution between the probability distribution of the inverse of the grain size and the surface conductivity response obtained when all the grains have the same size. Surface conductivity at the macroscopic scale is also connected to an effective pore size used to characterize permeability. From these relationships, a new equation is derived connecting this effective pore size, the electrical formation factor, and the expected value of the probability distribution for the inverse of the grain size, which is in turn related to the distribution of the relaxation times. These new relationships are consistent with various formula derived in the literature in the limit where the grain size distribution is given by the delta function or a log normal distribution and agree fairly well with various experimental data showing also some limitations of the induced polarization method to infer permeability.

One of these limitations is the difficulty to detect the relaxation, in the phase, associated with the smaller grains, as this polarization may be hidden by the Maxwell–Wagner polarization at relatively high frequencies (>100 Hz). Also, cemented aggregates of grains can behave as coarser grains.

Key words: Probability distributions; Electrical properties; Hydrogeophysics; Permeability and porosity.
Application to the data of Tong et al. (2006)

Model
\[ k = \frac{D_{Na^+} \tau_0}{4m^2(F-1)^2 F} \]
\[ F = \phi^{-m}, \ m = 2 \]
Presence of a second fluid phase (immiscible, non wetting)
Comparison with the prediction from the model

Experimental data

- non-wetting oil $sw=1.26$
- sample v110 $sw=1.27$
- sample 1883 $sw=1.20$

Model prediction
Influence of a change in the composition of the aqueous phase
Change in the composition of the aqueous phase over time
No change in resistivity

Change in the phase

Modeling with PHREEQC
Complexation model (with electrostatics)

<table>
<thead>
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<th>Reactions</th>
<th>Equilibrium constants</th>
</tr>
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<tbody>
<tr>
<td>$\text{SiOH} + H^+ \leftrightarrow \text{SiOH}_2^+$</td>
<td>$K_{\text{SiOH}_2^+} = 10^{-2}$</td>
</tr>
<tr>
<td>$\text{SiOH} \leftrightarrow \text{SiO}^- + H^+$</td>
<td>$K_{\text{SiO}^-} = 10^{-7.2}$</td>
</tr>
<tr>
<td>$\text{SiOH} + Na^+ \leftrightarrow \text{SiO}^-Na^+$</td>
<td>$K_{\text{SiO}^-Na^+} = 10^{-3.25}$</td>
</tr>
<tr>
<td>$\text{SiOH} + Cu^{2+} \leftrightarrow \text{SiOCu}^{+} + H^+$</td>
<td>$K_{\text{SiOCu}^+} = 10^{-5.52}$</td>
</tr>
<tr>
<td>$2\text{SiOH} + Cu^{2+} \leftrightarrow 2(\text{SiO})Cu^{2+} + 2H^+$</td>
<td>$K_{2\text{SiO}^-Cu^{2+}} = 10^{-11.19}$</td>
</tr>
</tbody>
</table>

Induced polarization is truly a geophysical spectroscopic tool sensitive to chemistry
The effects of biofilms

Pili = 100 S/m (electron transfer possibly by tunneling effect between the hemes packed in the pili)
Electronic contribution to EC through biofilms

At the interface between sharp redox gradient
Self-potential anomaly associated with an oil spill

(a) Graph showing the self-potential anomaly with distance.

(b) Geophysical cross-section illustrating the contaminated area and electrical resistivity.
Understanding biogebatteries: Where geophysics meets microbiology

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Received 2 June 2009; revised 2 September 2009; accepted 22 September 2009; published 17 February 2010.

[1] Although recent research suggests that contaminant plumes behave as geobatteries that produce an electrical current in the ground, no associated model exists that honors both geophysical and biogeochemical constraints. Here, we develop such a model to explain the two main electrochemical contributions to self-potential signals in contaminated areas. Both contributions are associated with the gradient of the activity of two types of charge carriers, ions and electrons. In the case of electrons, bacteria act as catalysts for reducing the activation energy needed to exchange the electrons between electron donors and electron acceptors. Possible mechanisms that facilitate electron migration include iron oxides, clays, and conductive biological materials, such as bacterial conductive pili or other conductive extracellular polymeric substances. Because we explicitly consider the role of biotic processes in the geobattery model, we coined the term “biogebattery.” After theoretical development of the biogebattery model, we compare model predictions with self-potential responses associated with laboratory and field scale investigations conducted in contaminated environments. We demonstrate that the amplitude and polarity of large (>100 mV) self-potential signatures requires the presence of an electronic conductor to serve as a bridge between electron donors and acceptors. Small self-potential anomalies imply that electron donors and electron acceptors are not directly interconnected, but instead result simply from the gradient of the activity of the ionic species that are present in the system.

From Atekwana et al. (2004)

Responsible for a conductivity increase at the water table
In few weeks: Application to Oak Ridge

**Cooperation with David Watson**

- Imaging the preferential flow-paths
- Model the transport of contaminants (effect of recharge…)

**Manipulations and remobilization studies**

- Shale/saprolite - low pH
- Plot 1 - pH adjustments
- Plot 2 - ethanol, formate, $\text{SO}_4$, organic P, length of treatment zone
- Carbonate gravel - high pH
- Plot 3 - ethanol, Ca-oleate, organic P

**Natural attenuation studies**

- Drainage ditch recharge
- Geophysics transects
- Well transects

![Diagram of groundwater flow and contaminant plume](Image)
Conclusions

- Get a catalog of the effect of contaminants/bacteria upon induced polarization
- Develop the inverse problem (speciation using SIP)
- Developing joint inversion tools for map permeability change / chemistry amendments
- Use of chemical tracers to follow them using geophysical techniques
- Use of electromigration / electroosmosis to bring specific chemical components (redox active) to specific targets non-intrusively
- Can we act non-intrusivey on bacteria with electrical field?
- Doing all the couplings in TOUGHREACT (Nic Spycher & Magnus Skold)

We thank the DOE for Financial support

Scientific papers can be downloaded at http://www.andre-revil.com