Modeling the electrochemical properties and the complex conductivity of calcite

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Complex conductivity in frequency or spectral induced polarization (SIP)

> Sinusoidal electrical current injected. Electrical potential difference measured.

> Phase shift between imposed current and measured voltage.

> Method sensitive to conduction and polarization currents at the solid/water interface and inside conductive metals.

Thesis A. Ghorbani (2007)  
Pierre and Marie Curie University
Complex conductivity (CC) or complex resistivity

> Method developed initially for the mining exploration because of its sensitivity to conduction and polarization currents in conductive metals.

> High increase of the accuracy of CC measurements, inversion and interpretation during the last decades.

Application of the CC method in hydrogeophysics to estimate for instance the transport properties of porous media for environmental and hydrogeological investigations.

> Example: monitoring remediation of groundwaters contaminated by organic pollutants using zero valent iron microparticles.

Orozco et al. (2015) EST
Grain polarization model

> However, frequency behavior of SIP spectra still not exactly known.

> Necessity to develop mechanistic SIP models describing key transport phenomena at the pore scale responsible for the measured SIP response.

> Grain polarization model applied to calcite precipitation in porous media.
Grain polarization model of calcite - experimental data (1)

> Spectral induced polarization (SIP) experiment of calcite precipitation

Wu et al. (2010),
On the complex conductivity signatures of calcite precipitation,
Grain polarization model of calcite - experimental data (2)

> Measured sample complex conductivities

\[
\sigma^*(\omega) = \frac{I(\omega)}{U(\omega) \times k}
\]

\[
\sigma^*(\omega) = \sigma' + i\sigma'' = |\sigma| e^{i\phi}
\]

\[
|\sigma| = (\sigma'^2 + \sigma''^2)^{0.5}
\]

\[
\phi = \tan^{-1}(\frac{\sigma''}{\sigma'}) \cong \frac{\sigma''}{\sigma'}
\]

\[
\sigma' \text{ sensitive to conduction currents} \quad \sigma'' \text{ sensitive to polarization currents}
\]

> Imaginary conductivity response of calcite precipitation

![Graph showing imaginary conductivity response of calcite precipitation before and during clogging.](image)
Zeta potential of the calcite/water interface

> Surface complexation and dissolution/precipitation phenomena controlled by the electrical double layer (EDL) surrounding calcite in water.

> No reliable surface charge density measurements of calcite in water.

> Zeta potential: key parameter to constrain surface complexation models of the calcite/water interface.

> Helmholtz-Smoluchowski (HS) equation used to infer zeta potentials from streaming potential measurements.

> Is the HS equation reliable to describe the zeta potential of calcite particle?
Streaming potential measurements of calcite

> Imposed water pressure difference $\Delta p$ across coarse crystal powder:
  - water flow $U$, streaming current $J_{\text{str}}$
  - shear plane at the calcite/water interface, zeta potential $\zeta$
  - displacement of the excess of charge in the diffuse layer
  - macroscopic electric field, streaming potential $\Delta \psi$
  - conduction current in the sample $J_C$

But, is it possible to neglect conduction currents at the surface of calcite to infer zeta potential from streaming potential?
Theory of the streaming potential in steady-state conditions

> Conduction and streaming current densities for viscous laminar flows:
\[ \mathbf{J} = \mathbf{J}_c + \mathbf{J}_{str} = -\sigma \nabla \psi + \frac{\varepsilon_w \zeta}{\eta_w F} \nabla p \]


> Streaming potential coupling coefficient \( C \) + sample electrical conductivity \( \sigma \) :
\[ C = \frac{\Delta \psi}{\Delta p} \bigg|_{J=0} = \frac{\varepsilon_w}{\eta_w F \sigma} \zeta \]

\[ \Rightarrow \text{Zeta potential} \quad \zeta = C \frac{\eta_w F \sigma}{\varepsilon_w} \]

> Helmholtz-Smoluchowski equation:
\[ \mathbf{J} = \mathbf{J}_c + \mathbf{J}_{str} = -\frac{\sigma_w}{F} \nabla \psi + \frac{\varepsilon_w \zeta}{\eta_w F} \nabla p \]
\[ C = \frac{\Delta \psi}{\Delta p} \bigg|_{J=0} = \frac{\varepsilon_w}{\eta_w \sigma_w} \zeta_a \]

\[ \Rightarrow \text{Apparent zeta potential} \quad \zeta_a = C \frac{\eta_w \sigma_w}{\varepsilon_w} \]

> Sample conductivity:
\[ \sigma = \frac{\sigma_w}{F} + \sigma_s \]

Can \( \sigma_s \) be neglected to infer \( \zeta \) from \( C \)?
Apparent zeta potential vs corrected zeta potential of calcite powder

High surface conductivity effects

HS equation

Corrected zeta potentials
Electrical double layer around calcite ((104) plane)

> Surface charge of the calcite particle in water due to the:
  - calcium surface sites $>\text{Ca-OH}^{-0.5}$
  - carbonate surface sites $>\text{CO}_3^{-0.5}$

> Surface charge compensated by:
  - adsorbed counter-ions at the Stern,
  - adsorbed counter-ions and co-ions in the diffuse layer.

> Assumed shear plane at the beginning of the diffuse layer.

Heberling et al. (2014) Applied geochemistry
Basic Stern model (BSM) of calcite (1)

> Stoichiometric matrix of aqueous and surface reactions

<table>
<thead>
<tr>
<th>Product species</th>
<th>H^+</th>
<th>Cl^-</th>
<th>Na^+</th>
<th>Ca^{2+}</th>
<th>HCO_3^-</th>
<th>&gt;CaOH^-0.5</th>
<th>&gt;CO_3^{2-}</th>
<th>-c_0 \cdot e^{-k_0 t}</th>
<th>-c_0 \cdot e^{-k_0 t}</th>
<th>log_{10} K</th>
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<tr>
<td>CO_3^{2-}</td>
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<td>0</td>
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<td>0</td>
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<td>0</td>
<td>1</td>
<td>0</td>
<td>1</td>
<td>0.56</td>
</tr>
<tr>
<td>&gt;CO_3^- ⋯ Ca^{2+}</td>
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<td>0</td>
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<td>0</td>
<td>1</td>
<td>0</td>
<td>2</td>
<td>1.68</td>
</tr>
</tbody>
</table>

Li, Leroy et al. (2016), Influence of surface conductivity on the apparent zeta potential of calcite, *Journal of Colloid and Interface Science*
Basic Stern model of calcite (2)

> Parameters
- total surface site density,
- equilibrium constants of adsorption,
- capacitance $C_1$.

> Measured data
- electrophoresis,
- streaming potential.

> Output data
- electrical potentials, zeta potential,
- surface site densities of adsorbed ions,
- surface charge densities of the Stern and diffuse layer.

Computed excess of charge controlling the complex conductivity response.

Assumption: $\phi_d = \zeta$
Grain polarization model of Leroy et al. (2008)

- Assumptions
  - continuous diffuse layer and discontinuous Stern layer.

- Application of a sinusoidal electrical field
  - ions electromigration in the diffuse layer
    - conduction of the diffuse layer.

  - ions electromigration and diffusion in the Stern layer
    - polarization of the Stern layer.

Leroy, Revil et al. (2008), Complex conductivity of water-saturated packs of glass beads, JCIS
Improvement of the grain polarization model of Leroy et al. (2008)

- Multivalent and monovalent ions adsorbed in the Stern layer
- Effects of the diffuse layer on Stern layer polarization

$\tau = \frac{a^2}{2D_SM}$

$\mathbf{E}$

$\omega = 2\pi f$

$\mathbf{E}$

Decrease of the relaxation time $\tau$ of the polarization of the Stern layer

Increase of the associated characteristic frequency $f$

$D_S$: diffusion coefficient of the counter-ions in the Stern layer

$M$: effects of the diffuse layer on Stern layer polarization ($M \geq 1$)

$\omega$: angular frequency

Lyklema et al. (1983) JEC
Grain polarization model – theory (1)

1. BSM ➔ electrical potential at the onset of the diffuse layer $\varphi_d$
   surface charge density of the Stern layer $Q_b$
   ions surface site densities in the diffuse layer $\Gamma_i^d$

2. Specific surface conductivities of the Stern and diffuse layer
   \[ \Sigma_s^b = \pm \beta_b Q_b \quad \Sigma_s^d = \sum_{i=1}^{N} e z_i B_i^d \Gamma_i^d \]

   $\beta_b$ : ions surface mobility in the Stern layer
   $B_i^d$ : ions effective mobility in the diffuse layer (electromigration+electroosmosis)

3. Complex surface conductivity of the particle
   \[ \sigma_s^*(a, \omega) = \sigma_s(a, \omega) + i \omega \varepsilon_s \]
   \[ \varepsilon_s : \text{dielectric permittivity of the particle (constant)} \]
   \[ \sigma_s^*(a, \omega) = \frac{2}{a} \left\{ \sum_s^b \left[ \frac{i \omega \tau_b(a)}{1 + i \omega \tau_b(a)} \right] + \sum_s^d \right\} + i \omega \alpha \rho_s \varepsilon_0 \]

   \[ \tau_b = \frac{1}{f_b} = \frac{a^2}{2 D_b M} = \frac{a^2 |q|}{2 k_B T \beta_b M} \quad M = 1 + \frac{q Q_b}{k_B T C_d} \]

   $C_d$ : differential capacitance of the diffuse layer
Grain polarization model – theory (2)

4. Superposition principle: complex conductivity of particles of different sizes

\[
\sigma_s^* = \sum_{i=1}^{Q} f(d_i) \sigma_s^* (d_i, \omega)
\]

\(f(d_i)\): particle size distribution

5. Differential effective medium theory: porous medium complex conductivity

\[
\sigma^* = \frac{\sigma_w^*}{F} \left( \frac{1 - \sigma_s^* / \sigma_w^*}{1 - \sigma_s^*/\sigma^*} \right)^m
\]

\[
\sigma_w^* = \sigma_w + i\omega \varepsilon_w
\]

\(F\): formation factor

\(\varepsilon_w\): water dielectric permittivity

\(\phi\): porosity

\(m\): cementation exponent

Self-similar model of rock
(from Sen et al. (1981), A self-similar model for sedimentary rocks with application to the dielectric constant of fused glass beads, Geophysics)
Grain polarization model - comparison with experimental data (1)

> Real and Imaginary conductivity response of calcite precipitation

![Graph showing real and imaginary conductivity response of calcite precipitation.](image-url)
Grain polarization model - comparison with experimental data (2)

> Inverted particle size distribution

Leroy et al., Modeling the evolution of spectral induced polarization during calcite precipitation on glass beads, under review in Geophysical Journal International
Grain polarization model - comparison with experimental data (3)

Adjusted cementation exponent for the shape of the calcite particles

\[ F = \phi^{-m} \]

\[ \phi = 0.3 \]

\( \sigma' \sim 0.06 \text{ S m}^{-1} \) (day 2 - day 12)
Grain polarization model - comparison with experimental data (4)

> Modeled electrochemical properties of the calcite/water interface

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na$^+$ concentration in bulk water (mM)</td>
<td>29.00</td>
</tr>
<tr>
<td>Ca$^{2+}$ concentration in bulk water (mM)</td>
<td>1.20</td>
</tr>
<tr>
<td>Cl$^-$ concentration in bulk water (mM)</td>
<td>29.00</td>
</tr>
<tr>
<td>CO$_3^{2-}$ concentration in bulk water (mM)</td>
<td>0.09</td>
</tr>
<tr>
<td>HCO$_3^-$ concentration in bulk water (mM)</td>
<td>1.20</td>
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<tr>
<td>pH</td>
<td>9.00</td>
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<tr>
<td>Surface charge density of the Stern layer $\tilde{Q}_s$ (C m$^{-2}$)</td>
<td>0.56</td>
</tr>
<tr>
<td>Surface site density of adsorbed Na$^+$ in the Stern layer (10$^{17}$ sites m$^{-2}$)</td>
<td>17.30</td>
</tr>
<tr>
<td>Surface site density of adsorbed Ca$^{2+}$ in the Stern layer (10$^{17}$ sites m$^{-2}$)</td>
<td>8.91</td>
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<tr>
<td>Surface charge density of the diffuse layer $\tilde{Q}_d$ (C m$^{-2}$)</td>
<td>0.012</td>
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<td>Surface site density of adsorbed Na$^+$ in the diffuse layer (10$^{17}$ sites m$^{-2}$)</td>
<td>0.383</td>
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<td>Surface site density of adsorbed Ca$^{2+}$ in the diffuse layer (10$^{17}$ sites m$^{-2}$)</td>
<td>0.032</td>
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<td>Surface site density of adsorbed Cl$^-$ in the diffuse layer (10$^{17}$ sites m$^{-2}$)</td>
<td>0.189</td>
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<td>Surface site density of adsorbed CO$_3^{2-}$ in the diffuse layer (10$^{17}$ sites m$^{-2}$)</td>
<td>0.0005</td>
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<td>Surface site density of adsorbed HCO$_3^-$ in the diffuse layer (10$^{17}$ sites m$^{-2}$)</td>
<td>0.033</td>
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<tr>
<td>Electrical potential at the beginning of the diffuse layer $\phi_d$ (mV)</td>
<td>-29.00</td>
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<tr>
<td>Differential capacitance of the diffuse layer $C_d$ (C m$^{-2} V^{-1}$)</td>
<td>0.69</td>
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<tr>
<td>Diffuse layer polarization effects on Stern layer polarization $M$</td>
<td>30.70</td>
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</tbody>
</table>

> Complex conductivity model parameters

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ions mobility in the Stern layer $\beta_h$ (m$^2$ s$^{-1}$ V$^{-1}$)</td>
<td>$5.7 \times 10^{-9}$</td>
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<tr>
<td>Initial cementation exponent of the particles $m$</td>
<td>1.35</td>
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<tr>
<td>Initial glass beads porosity $\phi$</td>
<td>0.30</td>
</tr>
<tr>
<td>Bulk pore water conductivity $\sigma_w$ (S m$^{-1}$)</td>
<td>0.356</td>
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</table>
Conclusions and perspectives

> Complex conductivity model of the electrochemical polarization of the Stern layer surrounding calcite particles

> Monovalent and multivalent counter-ions in the Stern layer

> Effects of the diffuse layer on Stern layer polarization

> Grain complex conductivity model combined with a basic Stern model of the electrochemical properties of the calcite/water interface

> Zeta potentials of calcite corrected of surface conductivity effects

> Measured complex conductivity spectra of calcite precipitation on glass beads successfully reproduced by our models

> Particle size distribution and particle shape deduced from our models

> Application of our approach to non-intrusively estimate transport properties of porous media where calcite precipitation occurs
Thank you for your attention!