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Modeling the evolution of spectral induced polarization during calcite precipitation on glass beads

Leroy Philippe
BRGM
Orléans, France
p.leroy@brgm.fr

Li Shuai
Imperial College
London, England
lshuai8002@yahoo.com

Jougnot Damien
CNRS, UMR 7619 METIS
Paris, France
damien.jougnot@upmc.fr

Revil André
CNRS, UMR 5275
Le Bourget du Lac, France
andre.revil@univ-smb.fr

Wu Yuxin
LBNL
Berkeley, USA.
ywu3@lbl.gov

SUMMARY

When pH and alkalinity increase, calcite frequently precipitates and hence modifies the petrophysical properties of porous media. The complex conductivity method can be used to directly monitor calcite precipitation in porous media because it is very sensitive to the evolution of the pore structure and its connectivity. We have developed a mechanistic grain polarization model considering the electrochemical polarization of the Stern layer surrounding calcite particles. This model depends on the surface charge density and mobility of the counter-ions in the Stern layer. Our induced polarization model predicts the evolution of the size of calcite particles, of the pore structure and connectivity during spectral induced polarization experiments of calcite precipitation on glass beads pack. Model predictions are in very good agreement with the complex conductivity measurements. During the first phase of calcite precipitation experiment, calcite crystals growth, and the inverted particle size distribution moves towards larger calcite particles. When calcite continues to precipitate and during pore clogging, inverted particle size distribution moves towards smaller particles because large particles do not polarize sufficiently. The pore clogging is also responsible for the decrease of the connectivity of the pores, which is observed through the increasing electrical formation factor of the porous medium.

Key words: calcite precipitation, complex conductivity, Stern layer, particle size, pore clogging.

INTRODUCTION

Calcite is one of the most abundant minerals in the earth crust and frequently precipitates when alkalinity and pH increase (Vancappellen *et al.*, 1993). Calcite precipitation modifies the rock porosity, and can have positive or harmful effects for the mechanical and transport properties of porous media. Calcite precipitation in porous media has broad applications in geotechnical engineering for soil strengthening (DeJong *et al.*, 2006) and in environmental studies for the sequestration of heavy metals (Sturchio *et al.*, 1997), radionuclides (Fujita *et al.*, 2004) and CO2 in geological formations (Pruess *et al.*, 2003). However, calcite precipitation can also have undesirable effects such as the decrease of the efficiency and permeability of reactive barriers for the remediation of aquifers (Wilkin *et al.*, 2003).

Wu *et al.* (2010) performed complex conductivity measurements and modeling of calcite precipitation on glass beads packed column. From their imaginary part of complex conductivity data, the evolution of calcite precipitation in porous media was clearly observed. The empirical Cole-Cole model (Cole and Cole, 1941) was used by Wu et *al.* (2010) to interpret the complex conductivity signature of calcite precipitation in glass beads. However, the lack of physical processes in the Cole-Cole model to interpret the complex conductivity data restricts the understanding of the effects of calcite precipitation on the evolution of the pore structure and connectivity in glass beads column. The induced polarization of calcite precipitates needs to be further clarified using a mechanistic complex conductivity model accounting for the EDL properties and the particle size distribution. In this study, a mechanistic model for the induced polarization of calcite is proposed, which depends on the surface charge density and ions mobility of the counter-ions in the Stern layer and on the particle size distribution. The predictions of the model are compared to the imaginary conductivity data of Wu et *al.* (2010), and the evolution of the pore structure during calcite precipitation in glass beads is estimated accordingly.

THEORETICAL BACKGROUND AND COMPARISON WITH EXPERIMENTAL DATA

We consider a porous medium containing particles, glass beads grains (of millimetric size) and calcite crystals (of micrometric size), and water (subscript "w"). The complex conductivity model is presented at Figure 1.

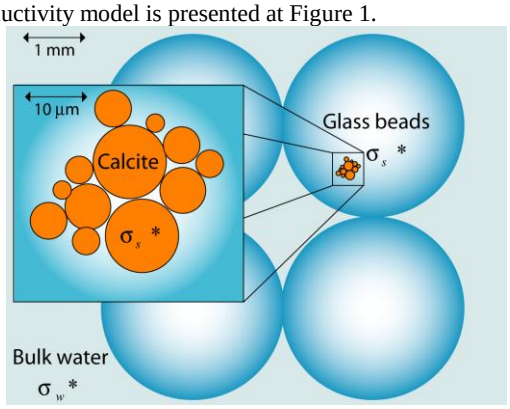

Figure 1. Sketch of thecomplex conductivity model of the porous medium.

Maxwell-Wagner polarization occurs at the boundary between the different phases (solid, water) possessing different electrical properties. The differential effective medium (DEM) theory (Sen et *al.*, 1981) is used to compute the electrical conductivity of the porous medium according to the conductivity of the particles and liquid. The complex surface conductivity of the particles of different sizes is calculated considering the superposition principle and using the particle

size distribution (PSD) (Leroy *et al.*, 2008). The complex surface conductivity of the particle is computed using the spectral induced polarization model of Leroy *et al.* (2008) generalized to the electrochemical polarization of different counter-ions at the mineral/water interface. The specific surface conductivity of the particle is calculated considering the superposition of the AC (Stern layer) and DC current densities (diffuse layer) (Figure 2). The distribution of ions in the Stern and diffuse layer of the calcite/water interface is computed using an electrostatic surface complexation model (Li *et al.*, 2016) (Figure 3).

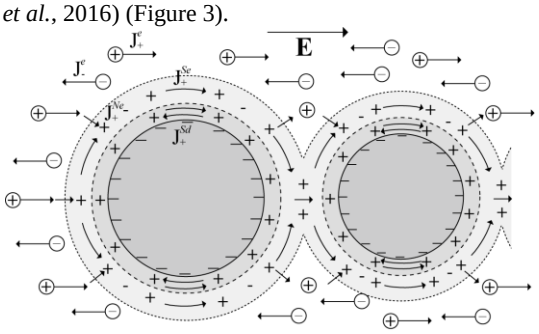

Figure 2. Sketch of the complex conductivity model of Leroy et *al.* (2008) for particles of different sizes surrounded by discontinuous Stern layers and overlapping diffuse layers in a saline aqueous solution.

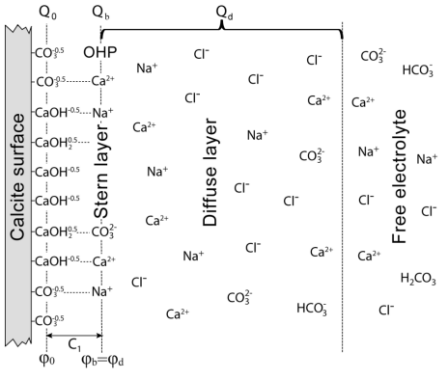

Figure 3. The basic Stern model used by Li *et al.* (2016) to describe the calcite/water interface (calcite (1 0 4) surface) when calcite is in contact with a NaCl and $CaCl_2$ aqueous solution at equilibrium with a pCO_2.

Wu *et al.* (2010) monitored calcite precipitation in glass beads pack using spectral induced polarization measurements in the frequency range [0.1 10000 Hz] under controlled laboratory conditions. Their porous medium consisted in smooth glass beads of mean diameter of 3 mm packed in a transparent plexiglass column 8.4 cm long and 2.54 cm wide. The measured porosity was equal to 30%. Wu et *al.* (2010) mixed two aqueous electrolytes, one containing $CaCl_2$ at a concentration of 26.2 milli mol L^{-1} (mM) (water electrical conductivity 0.635 S m^{-1}), and the other containing Na_2CO_3 at a concentration of 29 mM (water electrical conductivity 0.567 S m^{-1}) at a fixed pH value of 9 to favor calcite precipitation in glass beads column. The saline $CaCl_2$ solution was injected through the bottom of the column to establish an equilibrated baseline state. Following this, a second stream of Na_2CO_3 solution was introduced into the column from the injection port at the middle section to initiate calcite precipitation. The ionic concentrations were diluted once inside the column due to the equal volume mixing of these two solutions (initial ionic concentrations divided by two). The flow rate of both solutions was kept at 36 µL min^{-1} for the duration of the experiment, which continued for 12 days past injection of Na_2CO_3. In the complex conductivity experiment of Wu et *al.* (2010), sodium ion is the dominating cation in solution.

The evolution of the modeled imaginary conductivity as a function of frequency and time (in days) is in good agreement with the measurements of Wu et *al.* (2010) (Figure 4). The model parameters are presented at Table 1.

Table 1. Parameters of our complex conductivity model.

Parameters	Values
Ions mobility in the Stern layer (m^2 s^{-1} V^{-1})	5.7×10^{-8}
Surface charge density in the Stern layer (C m^{-2})	0.1
Initial cementation exponent of the particles	1.5
Initial glass beads porosity	0.30
Bulk pore water conductivity (S m^{-1})	0.356

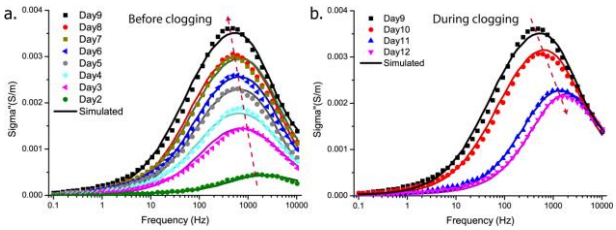

Figure 4. Imaginary conductivity spectra of calcite precipitation on glass beads pack as a function of time in days before the pore clogging by the calcite precipitates (a.) and during the pore clogging by the calcite precipitates (b.). The predictions of the complex conductivity model are represented by the lines and the symbols represent the imaginary conductivity measurements of Wu et *al.* (2010).

The evolution of the modeled particle size distribution during the precipitation experiment is presented at Figure 5.

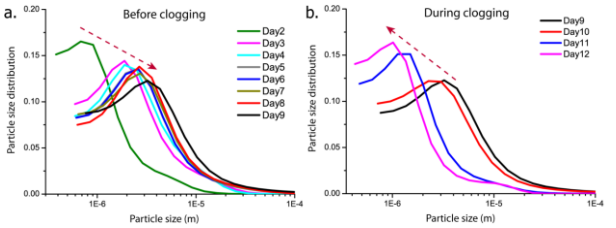

Figure 5. Evolution of the computed calcite particle size distribution during calcite precipitation experiments.

The quadrature conductivity measurements of Wu et *al.* (2010) were inverted using the Matlab code developed by Florsch *et al.* (2014) to obtain the discretized relaxation time and particle size distribution. Florsch *et al.* (2014) used generalized relaxation basis functions (such as the generalized Cole–Cole function) and the L-curve approach to optimize the damping parameter required to get smooth and realistic inverse solutions (read Florsch et *al.*, 2014 for further information relative to the inversion procedure). The relaxation time distribution was converted to the particle size distribution using the surface mobility value of the counter-ions in the Stern layer.

The smallest particles size information is missing due to lack of the complex conductivity measurements at high frequency (> 10 kHz). Before clogging (referred to phase 1 in Wu et *al.*, 2010, at day 9), the modeled particles size increases as experiment continues (also shown in Figure 5). It is consistent

with the visual observations from SEM (scanning electron microscopy) images in the experiment (Wu *et al.*, 2010). The calcite particles increase approximately from less than 1 to 20 µm, as reported by Wu *et al.* (2010). During the first stage of calcite precipitation, the modeled volume of the pore water decreases due to calcite precipitation (Figure 6).

As the calcite precipitation experiment continued over 9 days, the clogging occurred in the sample holder. At the second stage, the formation factor of glass beads increases significantly as shown in Figure 6, from 6.08 to 7 (day 10), 11 (day 11) and 12 (day 12). The changes of the formation factor is due to the loss of connectivity of glass beads pores affected by the clogging even though the porosity of the sample (glass beads, porous medium) has a tiny change. The modeled particle size distribution obtained from the inverted imaginary conductivity spectra (quadrature conductivity) moves towards smaller particles as experiment continues (Figure 4b and Figure 5b). This could be explained by that the large calcite particles created during the clogging process do not play an important role in the complex conductivity spectra (they do not polarize sufficiently) and only smaller particles are the effective ones contributed to the complex surface conductivity. Calcite precipitation induces a smaller pore volume fraction, therefore, a slight increase of the formation factor F. The occurrence of pore clogging may explain the increase of the cement exponent from 1.5 to 2 for glass beads materials, which leads the formation factor F increasing from 6.08 to 12 under the same porosity.

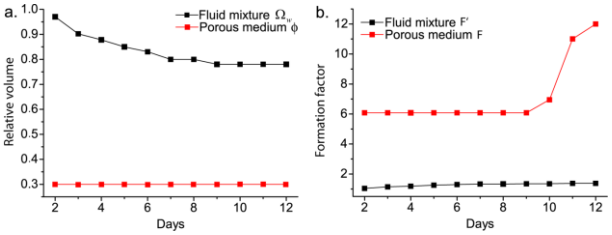

Figure 6. Computed relative volume of the fluid to the volume of the porous medium and relative volume of the bulk water to the volume of the fluid mixture and formation factors F and F' changes during the calcite precipitation experiment of Wu et *al.* (2010). The pore clogging happens at day 9, the formation factor of the porous medium (glass beads) changes dramatically.

CONCLUSIONS

A mechanistic complex conductivity model was used to interpret spectral induced polarization experiments of calcite precipitation on millimetric glass beads containing $CaCl_2$ and Na_2CO_3 aqueous electrolytes in equal concentration. The conductivity model considers the electrochemical polarization of the Stern layer surrounding calcite particles and depends on the surface site density and surface mobility of counter-ions in the Stern layer, which were kept constant during the simulation of the precipitation experiment. The particle size distribution, porosity and electrical formation factor evolution during the precipitation process were inverted from imaginary conductivity data.

Model predictions are in very good agreement with the measured imaginary conductivity spectra and the microscopy observations of the evolution of the pore structure and connectivity during calcite precipitation. The tangential mobility of the counter-ions in the Stern layer is found to be similar to their mobility in bulk water. The kinetic of calcite precipitation in glass beads column is described by considering two different stages, one before the pores clogging where modeled particle size distribution moves to larger particles due to the growth of calcite crystals, and another during the pores clogging where only the smaller particles influence the polarization response. During the first stage of calcite precipitation, the electrical formation factor of glass beads remains constant and the modeled pore water volume decreases due to calcite precipitation. During the second stage of calcite precipitation, the electrical formation factor of glass beads increases considerably because of the loss of pores connectivity due to the clogging process and the modeled pore water volume remains constant. These observations can be explained by the aggregation of the calcite precipitates merging at the surface of glass beads, which can significantly alter the connectivity and current paths of the pore space of glass beads even though the total porosity remains nearly unchanged.

This study shows that spectral induced polarization can be an efficient and cost effective geophysical method to monitor non-invasively and continuously calcite precipitation in porous media because of its sensitivity to polarization processes occurring at the mineral/water interface. A mechanistic induced polarization model is also necessary to interpret induced polarization experiments in terms of evolution of particle size distribution, pores structure and connectivity during calcite precipitation.

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