Streaming Potential Coupling Coefficient and Transport Properties of Unsaturated Carbonate Rocks

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We measured the streaming potential coupling coefficient of natural saturated and unsaturated carbonate rocks. Saturation was achieved with NaCl brines with salinities ranging from $2 \times 10^{-3}$ to 2.0 mol L$^{-1}$. The magnitude of the coupling coefficient increased with decreasing salinity, similarly to the trend observed for sandstones. The permeability had a low impact on the values of the streaming potential coupling coefficient at high and low salinity. The zeta potential was calculated at full saturation using a modified version of the Helmholtz–Smoluchowski equation that accounts for surface electrical conductivity. Under atmospheric conditions, the magnitude of the zeta potential decreased with the increase in salinity. We also explored the relationships between the streaming potential coupling coefficient and water saturation in three partially saturated limestones using a steady-state flow experiment. We found good agreement between the van Genuchten approach and experimental data, and fitted both the relative permeability and capillary pressure curves with the same value of the van Genuchten exponent $m_v$. We validated the predictive water relative permeability model described by Revil in water-wet rocks when the second fluid phase is non-polar.

Self-potential monitoring is a passive geophysical method based on the measurement of natural electrical fields in the subsurface of the Earth and provides data that are sensitive to water flow (Thony et al., 1997). Among the different processes involved in the variation of these electric fields, electrokinetic processes often tend to dominate in the vadose zone. They have already been studied in unsaturated clayey (Jougnot et al., 2012) or sandy (Mboh et al., 2012) soils and dolomites (Revil and Cerepi, 2004; Revil et al., 2007), but there exist few experiments in unsaturated intact limestones (Cerepi et al., 2017). Streaming potential signals are due to the presence of an electrical double layer at the charged interface of the grains in porous media (Stern, 1924; Overbeek, 1952; Dukhin and Derjaguin, 1974).

The water–calcite interface has been increasingly studied in the last decade due to its use in a large range of applications including CO$_2$ sequestration (Kaszuba et al., 2003; Xu et al., 2003; Lerouge et al., 2010) and oil extraction from carbonate reservoirs (Zullig and Morse, 1988). Complexation models can be used in concert with electrical double layer theory to compute the electrochemical properties of the water–calcite interface (Wolthers et al., 2008, 2012). Recently, Li et al. (2016) focused their work on the surface conductivity effects on the zeta potential of calcite. They showed that the classical Helmholtz–Smoluchowski equation underestimates the zeta potential of calcite at low salinities and that surface conductivity should be included in the expression of the streaming potential coupling coefficient. This coefficient relates the fluid and streaming potential gradients when the total current density is zero (e.g., Sill, 1983). In unsaturated porous media, Revil et al. (1999b) established a relationship between the texture of porous media and this coefficient, later exploited by different researchers (Revil et al., 2007; Jougnot et al., 2012; Cerepi et al., 2017).

Our goal in this study was to provide new experimental evidence for the dependence of the streaming potential coupling coefficient of carbonate rocks with the saturation, comparing our data with the predictive model developed by Revil et al. (2007), including...
the Corey or the van Genuchten exponent, often used to describe multiphase flow in the vadose zone. The water relative permeability has been calculated and successfully compared with the prediction of the model given by Revil et al. (2007). Mboh et al. (2012) showed that the capillary pressure curves, the relative permeability, and the relative streaming potential coefficient could be described in a consistent way for a silica sand.

A new core flooding system based on the study of Cerepi et al. (2017) allowed us to provide the first experiments to date that could measure simultaneously the relative permeability and the streaming potential coupling coefficient for unsaturated carbonates. We show that the relative permeability, the relative streaming potential coupling coefficient, and the capillary pressure can be described in a consistent way for carbonates using the van Genuchten approach.

Theory
Streaming Potential Coupling Coefficient

Revil and Mahardika (2013) defined the generalized cross-coupled \( L(\omega) \) (of electrokinetic nature) Ohm and Darcy constitutive laws for the Darcy velocity \( w (m/s) \), which is the filtration displacement of the fluid with respect to the solid, and the electrical current density \( J (A/m^2) \) under unsaturated conditions:

\[
\begin{bmatrix}
J \\
w \\
L(\omega)
\end{bmatrix} = \begin{bmatrix}
\sigma(w) & L(w) & E \\
k(w) & -\nabla p \\
k(w)QV(w)
\end{bmatrix} \begin{bmatrix}
w \\
\nabla p \\
\nabla p
\end{bmatrix}
\]

where

\[ L(\omega) = \frac{k(w)QV(w)}{\eta(w)} \]

The index \( \omega \) is defined thanks to the classical entry pressure of water in the rock, respectively. Alternatively, the water relative permeability can be explained from the equation of van Genuchten (1980) with the fitting parameter \( m_w \):

\[ k_{rw} = S_e^{N_w} \]

where \( S_{wi} \) and \( S_e \) are the irreducible water saturation and the effective water saturation, respectively, and \( N_w \) and \( N_g \) are the Corey exponents for the water and gas phases, respectively. Alternatively, the water relative permeability can be explained from the equation of van Genuchten (1980) with the fitting parameter \( m_w \):

\[ k_{rw} = S_e^{N_w} \]

The index \( m_w \) can also be derived from the capillary pressure curve (van Genuchten, 1980) as

\[ P_c = P_e(S_e^{-1/m_w} - 1)^{1-m_w} \]

where \( P_e \) and \( P_c \) denote the capillary pressure and the capillary entry pressure of water in the rock, respectively.

Revil et al. (2007) proposed a relationship from modeling (also tested by Cerepi et al. [2017] in an experimental approach) between the relative permeability and the saturation using the streaming potential coupling coefficient, Archie’s exponent, and the water Corey exponent from Brooks and Corey (1964) as

\[ k_r(S_w) = S_w^{n+1}C_1(S_w) \]
with a relative streaming potential coupling coefficient (ratio of the coupling coefficient at saturation $S_w$ to the value of the coupling coefficient at saturation) given by

$$C_r(S_w) = \frac{C(S_w)}{C_{sat}} = \frac{1}{\delta^{w+1}} \left[ \frac{S_w - S_{wi}}{1 - S_{wi}} \right]^N_w$$

Alternatively, using the van Genuchten exponent, we have

$$C_r(S_w) = S_w^{(w+1)} \sqrt{\frac{N_w}{1 - \left(1 - S_c^{1/w_i}\right)^{m_w}}}^2$$

### Zeta Potential

Under steady-state conditions, the zeta potential is calculated from the streaming potential coefficient using the well-known Helmholtz–Smoluchowski equation in the absence of surface conduction in the electrical double layer (e.g., Hunter, 1981):

$$C_{sat} = \frac{\varepsilon_w \zeta}{\eta_w \sigma_w}$$

where $\varepsilon$ $(F \text{ m}^{-1})$ is the dielectric permittivity, $\zeta$ $(V)$ is the zeta potential, and $\sigma_w$ $(S \text{ m}^{-1})$ is the electrical conductivity of the brine saturating the rock. When the surface conductivity is non-negligible (e.g., Revil et al., 1999a; Guichet et al., 2006; Alroudhan et al., 2016; Li et al., 2016), the zeta potential is related to the streaming potential coupling coefficient using the formation factor, $F$, which is the ratio of the conductivity of the electrolyte to the conductivity of the saturated rock sample when surface conductivity is negligible, and the electrical conductivity of the saturated porous material, $\sigma(S_w = 1)$:

$$C_{sat} = \frac{\varepsilon_w \zeta}{\eta_w \sigma(S_w = 1) F}$$

At low salinity, the evolution of the zeta potential was predicted by theoretical models, based on the Nernst–Planck–Poisson–Boltzmann transport equation (Revil et al., 1999a). Pride and Morgan (1991) found a logarithmic relationship in silica materials that relates the zeta potential with brine salinity, and Jaafar et al. (2009) suggested that the zeta potential is constant at high salinity ($>0.4 \text{ mol L}^{-1}$) also in silica-based materials:

$$\zeta = a + b \log_{10} C_f, \quad C_f < 0.4 \text{ mol L}^{-1}$$

$$\zeta = \zeta_c, \quad C_f \geq 0.4 \text{ mol L}^{-1}$$

where $a$, $b$, and $c$ are constant values and $C_f$ is the brine salinity $(\text{mol L}^{-1})$.
a confining pressure of $3 \times 10^6$ Pa. This pressure is regulated by a pump to avoid temperature variations of the room and was constant throughout the experiment. Experiments were controlled with X-ray imaging to verify that there was no brine flowing along the external face of the sample and the rubber sleeve. The stainless steel body of the core holder does not come into contact with the sample or fluids and is electrically connected to the Earth.

The electrical and relative permeability experimental measurements were performed using a steady-state flooding system, allowing us to inject brine and gas simultaneously into the sample (rocks are water wet). One pump was used to inject brine into the core at a constant flow rate, while a gas flow regulator (Bonkorst F-201-CV) regulated the flow of gas (only $N_2$ was used in this study to avoid any chemical reaction with carbonates and gas). The brine used for electrical measurements during the multiphase flow experiments was comprised of only 10 g L$^{-1}$ (0.17 mol L$^{-1}$) NaCl in deionized water and had a conductivity of 1.58 S m$^{-1}$. A separator allows separation of the brine and gas at the outlet of the sample by gravity. The gas goes into the atmosphere while the brine is pumped again by the pump. The brine saturation decreases, whereas the gas saturation increases until the irreducible water saturation. The brine/gas flow rate ratio decreases during the drainage phase. The pressure difference measured for each brine/gas ratio permits measurement of the relative permeabilities using Darcy’s law when steady state is reached and the water saturation is recorded at a sampling frequency of 1 Hz. The streaming potential coupling coefficient are measured. The stabilization process between brine and gas in the sample is extremely fast and controlled by a scanner. This process allows calculation of the irreducible water saturation with an accuracy of ±1% and avoids measurement saturation errors due to the drying of the porous medium after the passage of the gas. At the same time, the capillary curves of the samples are investigated with a porous plate apparatus.

This setup gave us the possibility to measure the streaming potential coupling coefficient under saturated and unsaturated conditions thanks to two non-polarizable Hastelloy (superalloy nickel-based, highly resistant to corrosion) circular electrodes placed on the cross-section of the sample. These electrodes have strictly the same diameter as the samples. The non-polarizable electrodes present a spiral shape and allow injection of the gas at the center of the sample cross-section and the brine at two other positions in order not to create preferential paths. The gas migration and the saturation were controlled with a scanner in real time.

**Core Samples**

Nine carbonate core samples (Table 1) were investigated in this study at full brine saturation and different brine concentrations: two algal rhodolith packstones (ESTA1 and ESTA2) from Provence (southeastern France), three ooid grainstones (BRAU1, BRAU2, and BRAU3) from Meuse (eastern France), two lithoclast packstones (RFF1 and RFF2), one algal rhodolith packstone (STE1) from Saint-Emilion (southwestern France), and one wackestone (LAV1) from Vienne (western France). Only three of them were investigated at partial brine saturation (BRAU2, ESTA2, and RFF2) during multiphase flow experiments at constant brine concentration (10 g L$^{-1}$ NaCl).

All the core samples have a length of 80 mm and a cross-sectional diameter of 39 mm. They were drilled parallel to the stratification and dried in an oven ($60\,^\circ$C) before each experiment. The petrophysical properties of each core sample, including water porosity ($\varphi_w$), scanner porosity ($\varphi_{\text{scan}}$), absolute permeability ($k_0$), Archie’s saturation ($m$) exponent, Corey exponent for water ($N_w$), irreducible water saturation ($S_{wi}$), and entry pressure of water ($P_e$), are recorded at a sampling frequency of 1 Hz. Different flow rates are induced to have a better accuracy in the calculation of permeability values ($0.002$–$0.6 \mu m^2$ or $2$–$600 \mu D$) with the aim to determine the influence of permeability on the electrokinetic properties of carbonate rocks.

### Measurements of the Streaming Potential Coupling Coefficient

The streaming potential is created by injections of different brine flow rates in the sample, inducing a pressure and a potential difference between the inlet and the outlet of the sample (Fig. 2). The experiment for each sample at full saturation begins with an electrical potential reference measurement across the sample for a given fluid flow rate. The main parameter is the stability of the voltage between the inlet and the outlet of the sample. Then, another brine flow rate is applied, which induces instantaneous pressure and voltage differences across the sample. Data are recorded at a sampling frequency of 1 Hz. Different flow rates are induced to have a better accuracy in the calculation of the streaming potential coupling coefficient. The same process is

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\varphi_w$</th>
<th>$\varphi_{\text{scan}}$</th>
<th>$k_0$</th>
<th>$m$</th>
<th>$N_w$</th>
<th>$S_{wi}$</th>
<th>$m_w$</th>
<th>$P_e$</th>
</tr>
</thead>
<tbody>
<tr>
<td>BRAU1</td>
<td>30</td>
<td>30</td>
<td>80</td>
<td>24.0</td>
<td>2.0</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>BRAU2</td>
<td>25</td>
<td>–</td>
<td>7</td>
<td>24.5</td>
<td>2.5</td>
<td>9</td>
<td>0.30</td>
<td>0.54</td>
</tr>
<tr>
<td>BRAU3</td>
<td>30</td>
<td>29</td>
<td>80</td>
<td>22.1</td>
<td>2.0</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>ESTA1</td>
<td>25</td>
<td>27</td>
<td>59</td>
<td>17.1</td>
<td>2.5</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>ESTA2</td>
<td>28</td>
<td>–</td>
<td>160</td>
<td>16.4</td>
<td>1.9</td>
<td>8</td>
<td>0.31</td>
<td>0.52</td>
</tr>
<tr>
<td>LAV1</td>
<td>23</td>
<td>24</td>
<td>2</td>
<td>15.0</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>RFF1</td>
<td>33</td>
<td>34</td>
<td>26</td>
<td>13.1</td>
<td>2.3</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>RFF2</td>
<td>34</td>
<td>34</td>
<td>31</td>
<td>10.6</td>
<td>2.3</td>
<td>5</td>
<td>0.35</td>
<td>0.66</td>
</tr>
<tr>
<td>STE1</td>
<td>36</td>
<td>–</td>
<td>600</td>
<td>11.9</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>
performed for each brine concentration. During the multiphase flow experiments, the streaming potential coupling coefficient is also measured at partial brine saturations. As mentioned above, the drainage phase of the sample is achieved by changing the flow rate ratio between brine and gas. The gas flow rate remains unchanged, while that of the water decreases. The streaming potential coupling coefficient is recorded when the brine flow rate is modified. In the experiment, we did not impose backpressure (used to maintain constant pressure downstream) at the outlet of the sample. The outlet pressure remained equal to 100 kPa during all the experiments, under saturated and unsaturated conditions. To validate our protocol, we needed to test streaming potential measurements with different backpressures. The streaming potential coupling coefficient was measured on one sample (BRAU1) at a salinity of 10 g L\(^{-1}\) NaCl with three different backpressures of 100 kPa, 1 MPa, and 1.3 MPa (Fig. 3a). The value of the streaming potential coupling coefficient remained constant and was not affected by the backpressure. The same test was done for two other brine concentrations (30 and 40 g L\(^{-1}\) NaCl) with the same result (Fig. 3b). In conclusion, the streaming potential coupling coefficient is not affected by the backpressure whatever the brine NaCl concentration.

**Measurements of Archie’s Saturation Exponent**

A two-electrode configuration was used to measure the conductivity of the brine-saturated and unsaturated sample. The electrical resistance of the system was measured at the frequency of 1 kHz between the two Hastelloy electrodes. The conductivity of the sample was calculated using

\[
\sigma(S_w) = \frac{L}{\pi r^2}
\]

where \(\sigma\) (Ω) is the sample resistance, \(L\) (m) is the length, and \(r\) (m) is the radius of the cylindrical core sample.

**Calculation of the Zeta Potential**

The zeta potential is calculated from the measured streaming potential coupling coefficient under fully saturated conditions using Eq. [18]. The formation factor \((F)\) was calculated as the ratio of the resistivity of the sample filled with brine \([\sigma(S_w = 1)]\) to the resistivity of the brine \((\sigma_w)\) at high ionic strength (0.17 mol L\(^{-1}\)), when grain surface conductivity can be neglected compared with bulk conductivity.
\[ F = \frac{\sigma_w}{\sigma(S_w = 1)} \]  \[ [22] \]

The brine relative permittivity and the brine viscosity were adjusted as functions of temperature and salinity (e.g., Saunders et al., 2008). Measurements were performed under atmospheric conditions, without gas partial pressure.

**Results**

**Relative Permeability**

In Fig. 4a to 4c, we fit the relative permeability data calculated with a steady-state apparatus as a function of the saturation using the Brooks and Corey and the van Genuchten approaches for three samples: BRAU2, RFF2, and ESTA2. Corey exponents are equal to 9, 5, and 8, respectively, whereas van Genuchten exponents are 0.54, 0.66, and 0.52, respectively. The Corey exponents are in the same range as in previous studies that investigated relative permeabilities in a brine–gas system (Krevor et al., 2012). The van Genuchten exponents are also consistent because they are smaller than unity (Brooks and Corey, 1964).

**Streaming Potential Coupling Coefficient**

**Effective Volumetric Charge Density Dependence**

According to Jardani et al. (2007), recently discussed by Jougnot et al. (2015) and validated by a theoretical model (Guarracino and Jougnott, 2018), the volumetric charge density \( \dot{Q}_v^0 \) can be directly estimated from the quasi-static permeability in silica materials (at full saturation) by

\[
\log_{10}(\dot{Q}_v^0) = -9.23 - 0.82 \log_{10}(k_0) \tag{23}
\]

The samples studied have an absolute permeability in the range 0.002 to 0.6 \( \mu \)m\(^2\) (Table 1) and streaming potential coupling coefficient values as reported in Table 2. Our values of volumetric charge densities for carbonates are slightly below the predictions of Eq. [23] (Fig. 5) and give an empirical law in the 0.002- to 0.6- \( \mu \)m\(^2\) permeability range:

\[
\log_{10}(\dot{Q}_v^0) = -11.37 - 0.94 \log_{10}(k_0) \tag{24}
\]

In Fig. 6, data for five samples are represented depending on the salinity of the electrolyte, and compared with the theoretical value calculated from the model of Guarracino and Jougnott (2018). The excess charge density was calculated using the empirical zeta potential law that we define in this study (see Eq. [26] below) and the tortuosity formula from Winsauer et al. (1952). This model has never been applied to carbonates, but our data are consistent with other values calculated on limestone samples (Pengra et al., 1999; Revil et al., 2007).

**Permeability Dependence**

The streaming potential coupling coefficient was measured on different carbonate rock samples for three different NaCl concentrations (0.4, 1.0, and 10.0 g L\(^{-1}\)). The goal was to determine which parameter between absolute permeability and brine concentration mainly controls the magnitude of the streaming potential coupling coefficient in carbonate rocks (Fig. 7). The streaming potential coupling coefficient seems independent of the permeability at saturation whatever the brine concentration (with a factor of 3 between low and high permeabilities). That said, its magnitude depends significantly on the brine concentration (factor of ~3000 between the measurements at 0.4 and 10 g L\(^{-1}\) NaCl). The brine concentration has therefore a much stronger influence on the magnitude of the streaming potential coupling coefficient than the permeability at saturation (Fig. 7).

**Salinity Dependence**

We establish now a relationship between the salinity of the NaCl electrolyte and the streaming potential coupling coefficient in the carbonate rocks. The streaming potential coupling coefficients were measured for the salinity range 0.002 to 2 mol L\(^{-1}\). Nine samples were investigated for different brine concentrations (Fig. 8). The magnitude of the measured coupling coefficient decreased with increasing salinity. The trend between the magnitude of the streaming potential coupling coefficient and the salinity \( C_f \) (mol L\(^{-1}\)) is a power law (\( R^2 = 0.96 \)):

\[
C = -1.41 \times 10^{-9} C_f^{-0.862} \tag{25}
\]

Vinogradov et al. (2010) also established an empirical relationship between the streaming potential coupling coefficient and brine salinity in sandstones and found a trend close to Eq. [24] (dashed line in Fig. 8).

**Saturation Dependence**

Measurements of the streaming potential coupling coefficient during the drainage phase of the samples by \( N_2 \) were made on three limestone cores: BRAU2, RFF2, and ESTA2. The relative streaming potential coupling coefficient is determined from the ratio between its value under unsaturated and saturated conditions (Fig. 4d–4i). The three samples exhibit a non-monotonic decrease of the relative streaming potential coupling coefficient with the decrease in the saturation. At the reference state (\( C_f = 1 \)), the streaming potential coupling coefficient is equal to ~5.79, ~3.97, and ~4.47 nV Pa\(^{-1}\) for the RFF2, BRAU2, and ESTA2 samples, respectively. In each case, measurements were compared with the laws established by Revil et al. (2007), based on the Brooks and Corey and the van Genuchten approaches, which predict a decrease in the streaming potential when the saturation decreases also (Eq. [15–16]). Models were fitted with the same Corey and van Genuchten exponents used above and predicted that the streaming potential coupling coefficient falls to zero at the irreducible water saturation. The same behavior was already observed by different researchers (e.g., Revil and Cerepi, 2004; Revil et al., 2007; Vinogradov and Jackson, 2011).
Fig. 4. Modeling of water drainage relative permeability on three carbonated rocks: (a–c) experimental data of water relative permeability for three limestone cores: BRAU2, RFF2, and ESTA2—data have been fitted with the Brooks and Corey model and the van Genuchten model; (d–f) relative streaming potential coupling coefficient for the three samples—at the reference state ($C_r = 1$), the streaming potential coupling coefficient is $−3.97$, $−5.79$, and $−4.47$ nV Pa$^{-1}$ for BRAU2 (gray squares), RFF2 (black triangles), and ESTA2 (black diamonds) samples, respectively, and the NaCl concentration of the electrolyte is $10$ g L$^{-1}$—these data are fitted (plain lines) with a model from Revil et al. (2007) (Eq. [15]) with the initial Corey exponent, while dashed lines represent Eq. [15] with variable $N_w$; (g–i) relative streaming potential coupling coefficient fitted (plain lines) with a model from Revil et al. (2007) (Eq. [16]) with the initial van Genuchten exponent; and (j–l) water relative permeability of the three samples (same markers as above), calculated with the Revil et al. (2007) model (Eq. [14]). Data are compared with the Brooks and Corey model (plain lines) and van Genuchten models (dashed lines) with a quite good correlation.
Capillary Pressure

Capillary pressure curves were fitted with the van Genuchten exponent, $m_v$, (Fig. 9). We observe a good correlation between the model and capillary pressure data recorded from porous plate experiments. The entry pressure of water, $P_e$, which is a characteristic constant of the medium, has a value of 12, 33, and 16 kPa for the ESTA2, RFF2, and BRAU2 samples, respectively. In spite of the different experiments (steady-state flooding and porous plate), the van Genuchten exponent used to fit the capillary pressure model and the relative permeability model (above) described by van Genuchten (1980) is the same. This shows the consistency of the measurements in steady-state and porous-plate experiments.

Zeta Potential

Figure 10 shows the zeta potential (calculated from the Eq. [18]) as a function of brine salinity for the samples investigated in this study. The magnitude of the zeta potential decreases with increasing salinity under atmospheric conditions, as observed in other studies that focused only on silica materials (e.g., Vinogradov et al., 2010). Vinogradov et al. (2010) found that the zeta potential reaches a constant value at salinity approximately above 0.4 mol L$^{-1}$. We don’t have enough data to verify this point. According to the studies of Jaafar et al. (2009) and Vinogradov et al. (2010) (Eq. [19]), the trend of the zeta potential in the carbonate samples investigated in this study is given by

$$\log_{10}(Q_{s}) = -11.37 - 0.94 \log_{10}(k_p)$$

**Table 2.** Calculated streaming potential coupling coefficient ($C_{sat}$) at a given NaCl concentration ($C_f$).

<table>
<thead>
<tr>
<th>Sample</th>
<th>$C_f$</th>
<th>$C_{sat}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>BRAU1</td>
<td>0.24</td>
<td>-5.00</td>
</tr>
<tr>
<td>BRAU2</td>
<td>0.17</td>
<td>-3.97</td>
</tr>
<tr>
<td>ESTA1</td>
<td>0.17</td>
<td>-7.20</td>
</tr>
<tr>
<td>ESTA2</td>
<td>0.17</td>
<td>-4.47</td>
</tr>
<tr>
<td>LAV1</td>
<td>0.17</td>
<td>-4.95</td>
</tr>
<tr>
<td>RFF1</td>
<td>0.17</td>
<td>-7.31</td>
</tr>
<tr>
<td>RFF2</td>
<td>0.17</td>
<td>-5.79</td>
</tr>
<tr>
<td>STE1</td>
<td>0.017</td>
<td>-51.7</td>
</tr>
</tbody>
</table>

**Fig. 5.** Charge density at electrical conductivity $S_w = 1$ vs. the absolute water permeability for eight carbonate core samples studied: BRAU1, BRAU2, ESTA1, ESTA2, LAV1, RFF1, RFF2, and STE1. The relationship in carbonate rocks is also represented (solid line) as well as data from the literature: clayrocks (Revil et al., 2005), glass beads (Boleve et al., 2007; Pengra et al., 1999), and limestones (Revil et al., 2007; Pengra et al., 1999). The relationship in silica materials from Jardani et al. (2007) is also shown (dashed line).

**Fig. 6.** Charge density at electrical conductivity $S_w = 1$ vs. the absolute water permeability for five carbonate core samples. Data were calculated for different brine salinities ($C_f$) and compared with the model of Guaracino and Jougnot (2018). We used the zeta potential trend of this study (Eq. [26]) and the tortuosity formula from Winsauer et al. (1952) in this model.

**Fig. 7.** Absolute value of the streaming potential coupling coefficient dependence on permeability. Measurements were performed with three different NaCl salinity rates: 0.4, 1.0, and 10.0 g L$^{-1}$. 

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where $C_f$ is the brine salinity (mol L$^{-1}$). The logarithmic equation has a theoretical argument in sandstones (Revil et al., 1999a) and seems applicable to limestone under atmospheric conditions without CO$_2$ partial pressure.

**Discussion**

**Streaming Potential Coupling Coefficient**

Influence of Saturation

The relative streaming potential coefficient obtained from the data does not decrease monotonically with decreasing water saturation, as expected considering Eq. [5]. This effect is commonly accepted and has been shown in other studies (Revil and Cerepi, 2004; Revil et al., 2007; Jackson, 2010; Jougnot et al., 2012; Cerepi et al., 2017) when water is the wetting phase and the second phase (gas) is non-polar, and may be due to counterbalancing effects at partial water saturation between the conductivity, the permeability, and the excess charge density. Moreover, the excess charge density at partial saturation (Fig. 11a) was calculated from Eq. [5] using relative streaming potential coupling coefficient data and compared with Eq. [7] with a quite good correlation. This can confirm the non-monotonic trend between the relative streaming potential coefficient and the saturation.

Due to the complexity of measuring the streaming potential coupling coefficient during a drainage experiment, only a few data are available for the three samples investigated. Models imply a direct relationship between the relative streaming potential coupling coefficient and the saturation. This also includes petrophysical parameters, as the Corey exponent ($n_w$) (Brooks and Corey approach, Eq. [15]), the van Genuchten exponent ($m_v$) (van Genuchten approach, Eq. [16]), or the second Archie exponent ($n$) and therefore takes into account wettability effects. As shown in Fig. 4d to 4i, the Corey and van Genuchten exponents have a huge influence on the models and imply the need to realize drainage experiments under rigorous conditions. The solid lines (Fig. 4d–4i) were fitted using Corey and van Genuchten exponents calculated from experimental relative permeability data and were used in the relative permeability model (see below). Although the Corey and van Genuchten exponents vary in magnitude at $N_w \pm 2$ and $m_v \pm 0.2$, respectively, the predicted and measured relative streaming potential coupling coefficients seem to follow the same trend ($R^2 = 0.83$ and $R^2 = 0.79$, respectively). Nevertheless, these models have some limits. When another nonaqueous or nonpolar phase (oil) is the wetting phase, the relative streaming potential coupling coefficient increases with decreasing water saturation (Jackson, 2010) and Eq. [15–16] cannot be applied.

**Relative Permeability Model**

The relative permeability model proposed by Revil et al. (2007) (Eq. [14]) was tested for the first time (to our knowledge) in this study with experimental data. It relies on the streaming potential measurements to predict water relative permeability, also using Archie’s saturation exponent. Figure 4 shows the water relative permeability calculated from Eq. [14] (Fig. 4i–4l) and the water relative permeability curves fitted with experimental data, using both the Brooks and Corey (Eq. [9]) and the van Genuchten (Eq. [12]) models (Fig. 4a–4c). Measurements predicted from Eq. [14] and the experimental data are close (Fig. 11b, $R^2 = 0.95$), which confirms that this model gives a quite good approximation of the relative permeability when water is the wetting phase and the second phase is nonpolar.

**Zeta Potential Dependence with Salinity**

Jaafar et al. (2009) estimated that the diffuse layer collapses to zero when the salinity is >0.4 mol L$^{-1}$ in silica materials. Therefore, we only took into account zeta potential values <1 mol L$^{-1}$ of
magnitude because the rock mineralogy does not seem to influence the streaming potential coupling coefficient values. A logarithmic relationship can connect the zeta potential and the salinity (Eq. [26]) (up to approximately 1 mol L\(^{-1}\)) (see Jaafar et al., 2009; Vinogradov et al., 2010), validating the model proposed by Revil et al. (1999a). The logarithmic trend seems applicable to limestone samples (Chen et al., 2014) under atmospheric conditions without CO\(_2\) partial pressure. We expect that this result would be different under reservoir conditions, with CO\(_2\) partial pressure, due to chemical reactions and catalysts as pressure and temperature. The magnitude of the zeta potential at salinity <1 mol L\(^{-1}\) increases with decreasing salinity (Fig. 10), as observed in previous studies, but is lower than that observed in silica materials.

### Excess Charge Density Dependence with Salinity

Guarracino and Jougnot (2018) argued that a higher salinity leads to a lower excess charge density in silica materials. They related \(Q_0^e\) from hydraulic (porosity, absolute permeability, tortuosity) and pore water (electrolyte concentration, Debye length, zeta potential) parameters. The only parameter affected by the rock mineralogy is the zeta potential, hence the interest in defining a specific law for the zeta potential in carbonates (Eq. [26]). Their model seems more robust than that of Jardani et al. (2007) because it takes into account the pore water chemistry. We can see the huge influence of the salinity on the saturated excess charge (Fig. 6), with a saturated excess charge approximately five times higher at a concentration of 1 mol m\(^{-3}\) than 1000 mol m\(^{-3}\). The data are quite well correlated with the model of Guarracino and Jougnot (2018), which allows us at first sight to validate this model for carbonates with a monovalent electrolyte.

### Conclusion

A core-scale experimental investigation was undertaken to investigate the relationships among the capillary pressure, the relative permeability, and the streaming potential coupling coefficient in carbonate rocks. We used pure NaCl brines and N\(_2\) to perform...
The magnitude of the streaming potential coupling coefficient decreases with increasing salinity as predicted by current models. The zeta potential in carbonate rocks can be related to salinity with a logarithmic law in the same way as for silica materials for salinity <1 mol L⁻¹ under atmospheric conditions.

2. The volumetric charge density can be directly estimated from measurements, using the steady-state flow method. The following conclusions were reached:

1. The magnitude of the streaming potential coupling coefficient decreases with increasing salinity as predicted by current models. The zeta potential in carbonate rocks can be related to salinity with a logarithmic law in the same way as for silica materials for salinity <1 mol L⁻¹ under atmospheric conditions.

2. The volumetric charge density can be directly estimated from the quasi-static permeability at full saturation. Our values of volumetric charge density are in the same range as the empirical conclusions were reached:

3. We were able to fit experimental data of the relative permeability model proposed by Revil et al. (2007), based on the relative streaming potential coupling coefficient, was tested under water-wet conditions and presented a quite good correlation with experimental measurements performed on three limestones ($R^2 = 0.95$).

4. The relative streaming potential coupling coefficient is strongly dependent on the saturation and decreases non-monotonically with it. The Brooks and Corey approach ($R^2 = 0.83$) provides a slightly better fit with experimental data than the van Genuchten approach ($R^2 = 0.79$).

5. The relative permeability model proposed by Revil et al. (2007), based on the relative streaming potential coupling coefficient, was tested under water-wet conditions and presented a quite good correlation with experimental measurements performed on three limestones ($R^2 = 0.95$).

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