The streaming potential of liquid carbon dioxide in Berea sandstone

Jeffrey R. Moore, Steven D. Glaser, and H. Frank Morrison
Department of Civil and Environmental Engineering, University of California, Berkeley, California, USA

G. Michael Hoversten
Earth Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California, USA

Received 17 June 2004; revised 20 July 2004; accepted 10 August 2004; published 15 September 2004.

[1] We report here, for the first time, evolution of the streaming potential coupling coefficient as liquid carbon dioxide infiltrates Berea sandstone. Using 125 Ω-m tap water, the coupling coefficient determined before and after each CO₂ flood of five samples averaged approximately −30 mV/0.1 MPa. After liquid CO₂ passed through the specimens displacing all mobile pore water, trapped water remained and the coupling coefficient was approximately −3 mV/0.1 MPa. A bound water limit of the coupling coefficient for liquid CO₂ flow was found using an air-dried sample to be −0.02 mV/0.1 MPa. For initially water-saturated samples, bulk resistivity varied during CO₂ invasion from 330 Ω-m, to 150 Ω-m during CO₂/water mixing, to a final value of 380 Ω-m. Results suggest that trapped and bound water control electrical conduction and the electrokinetic response. Applications include monitoring CO₂ injectate in subsurface reservoirs using the self potential method. INDEX TERMS: 1694 Global Change: Instruments and techniques; 0925 Exploration Geophysics: Magnetic and electrical methods; 5109 Physical Properties of Rocks: Magnetic and electrical properties; 5104 Physical Properties of Rocks: Fracture and flow; 5139 Physical Properties of Rocks: Transport properties. Citation: Moore, J. R., S. D. Glaser, H. F. Morrison, and G. M. Hoversten (2004), The streaming potential of liquid carbon dioxide in Berea sandstone, Geophys. Res. Lett., 31, L17610, doi:10.1029/2004GL020774.

1. Introduction

[2] In response to global climate change caused by the buildup of greenhouse gasses, several schemes have been proposed to inject liquefied atmospheric CO₂ into the earth for sequestration. For these schemes to be approached rationally, the location of the injectate must be mapped through time. Self potential, in this case streaming potential (SP), is a widely recognized method for identifying flow paths through rock and soil matrices [Corwin and Hoover, 1979; Fagerlund and Heinson, 2002].

[3] Modeling the SP response to CO₂ injection requires knowledge of the coupling parameter between fluid-pressure gradient and electrical current density [Stil, 1983]. Typically this value is determined in the laboratory for specific scenarios including varying pore fluid properties [e.g., Alkafeef et al., 1999]. For this experiment we analyzed the SP response resulting from displacement of in situ pore water by an advancing liquid CO₂ front, mimicking CO₂ injection into subsurface aquifers. We used intact specimens of Berea sandstone as a representative reservoir rock.

[4] Throughout this work we refer to various states of water saturation. We denote trapped water to be water which remains in an initially saturated sample after all mobile water has drained. Specifically, as CO₂ invades the specimen, mobile water drains until eventually no more water leaves the sample. At this point only trapped water remains and may be contained in the microporosity of kaolinite aggregates, which are abundant in Berea sandstone. Distinct from this is bound water, which refers to those layers of water molecularly adsorbed onto mineral grain surfaces that can only be removed by heating and high vacuum.

2. Electrokinetic Phenomena

[5] The laws controlling linear transport in porous media in the presence of electrokinetic coupling are [Pride, 1994]:

\[
q = -L_{11} \nabla p - L_{12} \nabla \phi
\]

\[
j = -L_{21} \nabla p - L_{22} \nabla \phi
\]

where \(q\) is the volumetric fluid flow density, \(j\) is the electric current density, \(p\) is the fluid pressure, and \(\phi\) is the electric potential. When the double layer thickness is much smaller than a typical grain surface curvature the transport coefficients are:

\[
L_{11} = \frac{k}{\eta}
\]

\[
L_{12} = L_{21} = -\frac{\varepsilon \zeta}{\eta F}
\]

\[
L_{22} = \sigma_b
\]

Here, \(k\) is the fluid-flow permeability, \(\eta\) is the fluid viscosity, \(\varepsilon\) is the dielectric constant of the fluid, \(\sigma_b\) is the bulk sample conductivity, \(F\) is the electrical formation factor (a pore topology term), and \(\zeta\) is the zeta potential, which is a measure of how much charge resides in the diffuse part of the double layer. The first term on the right-hand side of equation (1) is Darcy’s Law, the second term of equation (2) is Ohm’s Law, and the remaining terms represent the coupled electrokinetic effect with \(L_{12} = L_{21}\) [Onsager, 1931].

[6] Electrokinetic phenomena arise from movement of ions in the electric double layer under a pore pressure gradient. Fluid flow causes mobile ions to be convected relative to the bound charge on the mineral grain surfaces, charge motion known as the convection current. As this
Following each CO₂ flood, the samples were again saturated. CO₂ pressure was maintained at 6.5 MPa. CO₂ was flowed through the sample intermittently throughout a testing period. Table 1 lists Cc values for liquid CO₂ flow through initially water-saturated samples was approximately –3 mV/0.1 MPa. Variance shown in Table 1 arises from multiple tests performed on each specimen.

### 4. Results

[11] Testing for the Cc before and after each CO₂ flood was accomplished using a static head at low pressure drops. Results indicated linear correlation between applied pressure drop and observed electric potential. Table 1 summarizes these results, revealing that for specimens Berea-1 and Berea-5 the Cc decreased following the CO₂ flood, while for specimens Berea-2, Berea-3 and Berea-4 the Cc increased. For all five Berea specimens, the gross average Cc for 125 Ω·m water flow was approximately –30 mV/0.1 MPa. Variance shown in Table 1 arises from multiple tests performed on each specimen.

[12] During liquid CO₂ invasion, the Cc evolved in response to the mixing and displacement of pore water. Figure 1 shows the Cc evolution for samples Berea-1, Berea-2 and Berea-3 during the initial 20 minutes of CO₂ infiltration, with time as a proxy for the volume of CO₂ flowed through the sample. Table 1 lists Cc values for liquid CO₂ flow after the Cc became steady and mixing was assumed to be complete (t > 700 sec). The steady-state Cc for liquid CO₂ flow through initially water-saturated samples was approximately –3 mV/0.1 MPa.

[13] The relationship between coupling coefficient and pressure drop is illustrated in Figure 2. We noted a decrease in the Cc with pressure drop and observed that the Cc tended toward a constant value as pressure drop increases.

[14] We next measured the Cc for liquid CO₂ flow through a dry specimen. This sample was not oven-dried, but rather air-dried for 30 days, and can therefore be assumed to contain only bound water remaining on mineral grain surfaces. We determined the Cc to be –0.02 mV/0.1 MPa for liquid CO₂ flow.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pre-Flood Cc (Water)</th>
<th>Steady-State Cc (CO₂)</th>
<th>Post-Flood Cc (Water)</th>
<th>Post-Flood Cc (CO₂)</th>
<th>Cc Post-Flood (%)</th>
<th>Porosity %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Berea-1</td>
<td>–47 ± 2</td>
<td>–2.5 ± 0.5</td>
<td>–16 ± 1</td>
<td>18.70</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Berea-2</td>
<td>–19 ± 0.5</td>
<td>–3.5 ± 0.5</td>
<td>–30 ± 2</td>
<td>18.75</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Berea-3</td>
<td>–35 ± 0.5</td>
<td>–2.0 ± 0.5</td>
<td>–41 ± 0.5</td>
<td>18.76</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Berea-4</td>
<td>–15 ± 0.5</td>
<td>–18 ± 0.5</td>
<td>–21 ± 1</td>
<td>18.64</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Berea-5</td>
<td>–29 ± 0.5</td>
<td>–2.5 ± 0.5</td>
<td>–16 ± 1</td>
<td>18.70</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Cc units are mV/0.1 MPa. The average porosity for fresh specimens was 18.75%.**

*Table 1. Summary of Coupling Coefficient and Porosity Results*

![Figure 1](image-url)  
**Figure 1.** Coupling coefficient vs. time for samples Berea-1, Berea-2 and Berea-3. Only the initial portion of the tests are shown. The Cc was constant for times greater than 700 seconds. The size of the individual symbols approximates experimental variance. See color version of this figure in the HTML.
Figure 2. Relationship of Cc to pressure drop for sample Berea-2 from that time after water/CO2 mixing was assumed to be complete, or t > 700 sec (Figure 1). Error bars reflect experimental variation due to pressure and voltage signal noise. See color version of this figure in the HTML.

[15] Specimen porosity was measured following each CO2 flood. For comparison we also measured the porosity of 2 fresh cores taken from the same block to be 18.75%. Table 1 lists the porosity of each sample after CO2 infiltration. Results indicate no change in porosity.

[16] Bulk resistivity variation during liquid CO2 infiltration was investigated for specimens Berea-4 and Berea-5. Results for specimen Berea-5 are presented in Figure 3, where time is again used as a proxy to represent the volume of CO2 flowed through the specimen. We observed an initial resistivity of 330 Ω-m, followed by a rapid decrease to 150 Ω-m while the CO2 and water were mixing. For longer times, when many pore volumes of CO2 had flowed through the sample, resistivity reached 380 Ω-m.

5. Discussion

[17] The average coupling coefficient for 125 Ω-m tap water flow was −27 mV/0.1 MPa (Table 2), a result within the range of reported values for similar pore fluids [Pengra et al., 1999; Revil, 2002b]. Transport coefficients (L12, L22) for equations (1) and (2) are reported in Table 2. The electrical conductivity of the water-saturated sample was 3.0 × 10⁻³ S/m (Figure 3). The zeta potential for our rock/water system was thus determined from equation (6) to be −28 mV, a result within the range of observed values for pore fluids with bivalent cations [Alkafœf et al., 1999]. Ca²⁺ ion concentrations up to 8 mg/l in our tap water have the effect of decreasing the zeta potential by a factor of two compared to monovalent cation solutions [Lorne et al., 1999].

[19] The observation of any streaming potential in the presence of non-conducting liquid CO2 indicates lasting effects of trapped and bound water. As the pore water was initially displaced by invading CO2, the Cc decreased (Figure 1). At longer times all mobile pore water was displaced, but trapped water remained, and the Cc became steady at about −3 mV/0.1 MPa. Flowing CO2 may be shearing the trapped water resulting in counter charge displacement from water layers. Trapped water then acts as a pathway for return electrical conduction. The combined effect explains the apparent steady-state trapped water limit of the streaming potential.

[20] To test the hypothesis that trapped water is controlling the electrokinetic response, we measured the Cc for liquid CO2 flow through an air-dried specimen that was assumed to have only bound water remaining on the mineral surfaces. The results reveal a bound water limit of the Cc to be −0.02 mV/0.1 MPa, which is 2 orders of magnitude lower than the Cc for an initially water-saturated sample. This indicates that significant water remained in the initially saturated specimens even after a steady Cc was attained.

[21] The relatively minor change in bulk resistivity as liquid CO2 infiltrated the specimens supports the hypothesis that trapped water is controlling electrical conduction. For longer times, and therefore greater pore volumes of CO2, all mobile pore water had been displaced, yet the sample resistivity was only slightly higher (380 Ω-m) than when it was originally water saturated (330 Ω-m). These results are in spite of the fact that liquid CO2 may be up to one million times more resistive than water.

[22] Employing a linear model for electrical conductivity [Lorne et al., 1999; Revil, 2002a]:

\[
\sigma_b \approx \sigma_f + \sigma_s,
\]

where \(\sigma_f\) is the conductivity of the pore fluid (8.0 × 10⁻³ S/m), we calculate the surface conductivity to be \(\sigma_s = 2.7 \times 10^{-3} \text{ S/m}\). When insulating liquid CO₂ has replaced all mobile water as the pore fluid, the bulk sample conductivity is equal to only the surface conductivity (\(\sigma_b \approx \sigma_s\)), or the resistivity (\(\rho_b = 1/\sigma_b\)) is 375 Ω-m, consistent with the limiting value shown in Figure 3.

[23] The pH of the pore fluid strongly effects the zeta potential and consequently the Cc [Ishido and Mizutani, 1999]. The pH of our sample was 7.5, using the relationship of Cc to pH reported by [Ishido and Mizutani, 1999].
were unable to detect any change in porosity. A liquid CO2 sample of Berea sandstone. Liquid CO2 then invaded and CO2 at single-phase liquid conditions at 20 °C. Therefore, the fluid may have entered the two-phase liquid/gas regime. Recent works that have quantified the Cc in 2-phase conditions have noted that the Cc may be quite high. For areas farther away from the injection point, the Cc will be greater as indicated in part by the data shown in Figure 2.

Changes in the Cc determined before and after each CO2 flood were initially thought to be caused by changes in sample porosity. Carbonic acid formed by mixing CO2 and water may have dissolved the mineral ankerite which is present in minor fractions (~0.5%) in Berea sandstone. The resulting change in the pore fabric could result in higher functional porosity and explain the increase in Cc observed following the CO2 flood [Revil et al., 1999]. However, we were unable to detect any change in porosity.

Another possible explanation for the observed change in the Cc following each CO2 flood is permeability changes caused by release and capture of matrix particles, especially kaolinite clays. The concept of particle release and capture by both chemical and mechanical means is discussed by Ochi and Vernoux [1998]. In our testing, variable flow conditions between specimens may have resulted in permeability changes following each CO2 flood that would cause corresponding changes in the Cc. Correlation between the Cc and permeability has been demonstrated for samples undergoing deformation, but the intrinsic dependence is as yet unclear [Jouniaux and Pozzi, 1995; Lorne et al., 1999].

Pressure of about 5.7 MPa is required to maintain CO2 at single-phase liquid conditions at 20°C. In our tests, the inlet pressure was held constant at 6.5 MPa, but the maximum tested pressure drop across the samples was 1.6 MPa. Therefore, the fluid may have entered the two-phase liquid/gas regime. Recent works that have quantified the Cc in 2-phase conditions have noted that the Cc decreases with increasing gas content, despite the increase in resistivity [Guichet et al., 2003; Revil and Cerepi, 2004]. We observed a nearly constant Cc following CO2/water mixing, and although we may have inadvertently had some CO2 gas present for some of the larger pressure drops, we feel the effect was minimal.

6. Conclusion

This testing revealed an average Cc of about ~30 mV/0.1MPa for water flow through a water-saturated sample of Berea sandstone. Liquid CO2 then invaded and displaced mobile pore water until only trapped water remained, and the Cc was found to be ~3 mV/0.1MPa. For liquid CO2 flow in an air-dried sample where only bound water initially existed, the Cc was ~0.02 mV/0.1 MPa. Bulk resistivity variation during CO2 infiltration was marked by a decline during mixing where the formation of acid aided electrical conduction. Results suggest that trapped and bound water in the sample control the electrokinetic response.

Acknowledgments. This work was supported in part by the U.S. Dept. of Energy contract DE-AC07-99ID13727 to the Idaho Natl. Eng. and Env. Laboratory. The authors thank André Revil and Steven Pride for insightful reviews and input. This work benefited greatly from their generous contributions. We also thank the UC Center for Information Technology Research in the Interest of Society, and the NSF CMS division for additional facilities and funding.

References


S. D. Glaser, J. R. Moore, and H. F. Morrison, Department of Civil and Environmental Engineering, University of California, 440 Davis Hall, Berkeley, CA 94720, USA. (moore@decf.berkeley.edu)

G. M. Hovenstien, Earth Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA, USA.