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Electroosmotic permeability in kaolinite and CaCO₃ poultice mixtures

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Electrokinetic treatment of masonry for desalination or electroosmotic dewatering depends on a poultice, in which the electrodes are placed, which fulfills several purposes. Poultice composed of kaolinite and CaCO₃ have been shown to have good workability and high pH buffering capacity. In this work, the electroosmotic (EO) permeability is studied in different kaolinite - CaCO₃ mixtures. In addition, the effect on EO of using NaCl as a mixing solution is investigated. A special cell is used to test the EO in the specimens. A phenomenological approach, based on the potential gradient and the flux of solution, was used to calculate the EO flow rate and EO permeability coefficient. Results showed that by increasing the concentration of CaCO₃ in the poultice mixture, the EO flow rate decreased and the poultice with 80 % CaCO₃ and more did not have any EO flow. Furthermore, the ionic strength in the mixing solution decreases the EO flow rate.

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1. Introduction and research aim

Electrokinetics (EK) is recognized as a powerful tool for transporting matter in fine-porous materials. Intensive research is conducted worldwide on electrokinetic phenomena for numerous applications within civil, geotechnical, and environmental engineering [1]. Often there is no other technical solution to these challenges, as sufficient mass transport cannot be obtained in dense, porous materials by means of other gradients than an electrical potential gradient. There are many application examples e.g., remediation of polluted soil [2], chloride extraction from reinforced concrete [3], and consolidation and strengthening of soils [4]. The methods are based on the EK transport processes: electroosmosis (EO) and electrophoresis (EP) and electromigration (EM). EO is the movement of a solution in a porous media under the application of an electric field. EP is the movement of electrically charged particles in a fluid under the influence of an electric field. EM is the transport of ionic species in the applied electric field, i.e., the current carriers in the system.

The application of EK methods for preserving heritage monuments and buildings made of stone and masonry is under development. These methods aim at desalination [5,6] or consolidation [7], where the main mechanism is EM, or dewatering of moist masonry [8], which is based on EO. Crucial to these systems is to hinder acidification of the stone or masonry from the anode reaction in order to avoid irreversible damage to the material. When placing the anode in a clay poultice, including certain amount of calcium on the surface of the stone material, the poultice has been shown to be efficient as a buffer medium [9]. If the poultice is likely to experience significant EO transport, it will dry out during the electrokinetic treatment. As a result, the needed contact between the anode and the poultice will be gradually lost. Consequently, electrical resistivity in the system will increase, and eventually, the passage of current will be no longer possible. Thus, developing a poultice mix where EO transport is insignificant is important for the efficiency of the treatment.

Theoretic descriptions of EO use two approaches: the mechanism-based approach and the phenomenological approach. The mechanism-based approach models flow on the nanoscale and are based on the governing equations of mass and momentum continuity, which are a clear physical meaning. This approach is used, e.g., for describing the EO flow in single micro-channels (e.g., [10]). The phenomenological approach is based on averaged (macroscopic) parameters without describing the flow field in
detail, i.e., it correlates macroscopic parameters such as flow rate to the overall properties of the material. This approach is based on irreversible thermodynamics and is used in membrane science (e.g., [11]).

The engineering methods based on applied electrokinetics are developed to work in heterogeneous matrices and often in meter scale. Still, most models developed are taking offset in the mechanism-based approach. Traditionally, the Helmholtz–Smoluchowski equation has been used to estimate the EO permeability [12]. However, this equation has several drawbacks that make it difficult to apply to large-scale heterogeneous material volumes, as it was deduced for large capillaries (unusual in clays) and it depends on the zeta potential, which is difficult to measure and is related to a wide variety of factors [13]. An example of a mechanism-based model is in [14], where a fractal theory in porous media is applied to obtain an analytical model to describe EO flow in porous media using a capillary tube model. Models for combined electrokinetic transport and chemical reactions in porous media are developed from the mechanism-based approach [15,16]. The models are often verified through model systems such as glass beads [14].

The phenomenological approach was applied in [17] and the fluxes are given as a linear function of the driving forces. In consistency with this, the EO volume flux ($J_V$ (m/s)) and the charge flux (the current density) ($J_q$ (A/m²)) can be expressed as:

$$J_V = L_{11} \nabla (-p) + L_{12} \nabla (-\psi)$$

$$J_q = L_{21} \nabla (-p) + L_{22} \nabla (-\psi)$$

where $p$ (Pa) is the fluid pressure, and $\psi$ (V) is the electric potential. The coefficients $L_{11}$ and $L_{22}$ are direct coefficients, where the flux is directly linked to the force [17]. The coefficient $L_{11}$ is the factor of proportionality between solution flow and pressure gradient in the case of no electric field (Darcy’s law). Similarly, $L_{22}$ relates the electric current and applied potential gradient (Ohm’s law). The cross coefficient $L_{21}$ describes the proportionality between an applied pressure and the resulting current (the streaming current). Finally, the coefficient $L_{12}$ is the coefficient of proportionality between volume flow and applied electric field. Therefore, $L_{12}$ (m²/V s⁻¹) represents the electro-osmotic permeability coefficient. According to Onsager reciprocity, $L_{12} = L_{21}$. In a system with no pressure gradients:

$$L_{12} = J_V/\nabla (-\psi)$$

$$L_{22} = J_q/\nabla (-\psi)$$

i.e., the electro-osmotic permeability coefficient, $L_{12}$ [m²/(V·s)], can be calculated from the volume flow and the applied potential gradient.

Numerous laboratory investigations on, e.g., electrokinetic properties of soils have been reported on model matrices or soils sampled in the field. However, despite such data, it is difficult to single out the influence of different experimental conditions and soil characteristics on the EO coefficient. The availability of complete experimental data for a wide variety of soils under different conditions of pore water salinity and electrical gradients is still limited, and this information would be required to validate the models further [12]. Thus, the theoretical formulations are not available for the optimization of the poultice composition to obtain a minimum EO flow.

This work aims to directly measure the EO coefficient in different poultice mixes of kaolinite and calcium carbonate with different salts concentrations for optimization of the poultice composition to be used during EK treatment for heritage preservation. Besides this, the experimental setup and methodology can be used to measure EO coefficients in other matrices.

2. Materials and methods

2.1. The electroosmotic cell

An EO cell developed in [17] was used for this study (Fig. 1). The cell is unique in the sense that it enables simultaneous measurement of the EO flow and the potential gradient over the matrix without any interference from, e.g., pH changes from the electrode processes or the build-up of concentration gradients in the clay poultice. The electroosmotic cell was designed so that the only driving force of flow over the sample plug is a potential gradient.

The electroosmotic cell has four chambers and it is symmetrical around the central vertical axis. The poultice is placed in a sample holder (glass tube) between the two upper chambers. The sample holder has a diameter of 0.8 cm and a length of 8.5 cm. Ground glass seals the connections to the upper chambers. Ag/AgCl reference electrodes are placed horizontally in the center of the upper chamber opposite the sample holder (see Fig. 1). They are fastened in rubber stoppers. The reference electrodes are insulated with shrink tubing over most of the length, and only the 10 mm closest to the poultice plug is free Ag/AgCl. The tip is about 10 mm from the surface of the poultice sample during the experiments. The reference electrodes are connected to a voltmeter. The upper compartments are filled with the same solution used for the poultice mix.
The working electrodes, connected to a power supply (Agilent E3612A), which was set to supply a constant current, are placed in the lower chambers. They are Cu rods (diameter 1 mm and length 35 mm) (Fig. 2). The lower chambers were filled with 1 M CuSO₄, and the electrode reactions were:

Anode reaction \[ \text{Cu}^{0} \rightarrow \text{Cu}^{2+} + 2e^- \] (5)

Cathode reaction \[ \text{Cu}^{2+} + 2e^- \rightarrow \text{Cu}^{0} \] (6)

The upper and lower chambers were separated by a 2.5 cm high plug of glass beads. The plug had a diameter of 35 mm and hindered the mixing of the solutions in the two chambers. Each of the four chambers was equipped with two valves, which are used when filling them. In this study, a constant current (2.0 mA) was applied to the poultices. This allows us to minimize the variable parameters to study the effect of ion content, conductivity of the solution, zeta potential, and intended parameters on electroosmotic flow in different poultices.

Capillary tubes with an internal diameter of 0.35 mm and a length of 15 cm were mounted on the top of each upper chamber. These capillary tubes are the only openings of both chambers at each side of the sample. Therefore, water flow through the sample from one chamber to the other one results in one of the capillary tubes getting empty, and the other one getting filled up.

The cell is designed in such a way that water flow is not possible through other mechanisms different than EO. Therefore, the velocity of the water through the capillary tubes, with a known inner diameter, is used for measuring the EO flow.

2.2. Preparation for an EO experiment

The Ag/AgCl electrodes were prepared after the procedure of oxidation of Ag in a Cl⁻ rich solution. This was done by placing the Ag wire into sodium hypochlorite (NaOCl) for 30 min and then putting it in KCl solution as suggested in [18].

During the preparation for an EO experiment, the poultice was first filled into the sample holder, which was then inserted between the two upper cell chambers in the sockets for the sample holder. The Ag/AgCl electrodes were inserted into the chambers from the opposite side of the sample holder until the tip of the electrode was 1 cm from the surface of the sample. Hereby, the two reference electrodes could measure the potential drop in the electrolyte over the poultice sample at a close distance from the sample surface. The lower chambers were filled until the CuCl₂ solution reached the lower part of the glass beads. Then, the upper chamber was filled with the intended solution (tap water or NaCl) for each experiment until half of the capillary tube was filled. After checking every socket to make sure the cell was not leaking, the setup was left for 30 min before applying the current to reach a stable pressure balance. It was checked that the solution in the capillary tubes was not moving. All together from filling the upper compartments to starting the experiment no more than 60 min passed.

2.3. Procedure for the EO experiments

In brief, when the potential gradient was applied to the working electrodes, the electroosmotic transport of water was observed in the capillary tubes. Crucial to the quality of the measurement is that the direction of the flow changes when reversing the polarity of the working electrodes, and that the rate of the flow is the same in both directions.

During each EO test, a total of 6 polarity changes were made. Three replicates were carried out for each type of poultice (the poultice was changed between each replicate). The process of changing polarity was to make sure that the rate of the EO was stable and only determined by the applied potential gradient. Each EO experiment with 6 changes of polarity lasted between 15 and 30 min.

The time of the water transport in the capillary tube to reach 10 cm was determined (in the capillary tube where the flow was in the direction of the open end of the tube). After changing the polarity, the same procedure was repeated for the other side. With the diameter of the capillary tube, the time for the solution in the capillary to move 10 cm, the potential gradient, and the size of the sample in the sample holder, the coefficient of EO permeability can be calculated.

At the end of each experiment, the cell was disassembled. The sample holder with the poultice was detached from the cell, and the poultice was taken out to measure its pH and conductivity. The pH and conductivity were also measured at the end of the test in the electrolyte solutions in the upper compartments.

2.4. Experiments conducted

EO experiments were conducted with eight different poultices based on different powder mixes (kaolinite with 0–80 % CaCO₃ by weight), see details in Table 1. Kaolinite powder manufactured by VWR International BVBA was used. The calcium carbonate used in this study was manufactured by VWR BVBA, Belgium.

The powder samples (kaolinite or kaolinite/CaCO₃) (Table 1) were mixed with different solutions to form a poultice. The weight ratio of the poultices was 1:1 by weight, e.g., in mixture K40TW, 40 g of kaolinite was added to 60 g of CaCO₃ together were mixed with 100 mL of solution. Selected characteristics (density, dynamic viscosity, pH, conductivity, and ionic strength) were measured in the solutions (Table 2). The density and dynamic viscosity measurements were done using a Viscosimeter PT100 Fungilab Vis-

<table>
<thead>
<tr>
<th>Mixture</th>
<th>Kaolinite (w%)</th>
<th>CaCO₃ (w%)</th>
<th>solution</th>
<th>electric current (l) (mA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>KTW</td>
<td>100</td>
<td>0</td>
<td>Tap Water</td>
<td>2</td>
</tr>
<tr>
<td>K40TW</td>
<td>40</td>
<td>60</td>
<td>Tap Water</td>
<td>2</td>
</tr>
<tr>
<td>K33.4TW</td>
<td>33.4</td>
<td>66.6</td>
<td>Tap Water</td>
<td>2</td>
</tr>
<tr>
<td>K25TW</td>
<td>25</td>
<td>75</td>
<td>Tap Water</td>
<td>2</td>
</tr>
<tr>
<td>K20TW</td>
<td>20</td>
<td>80</td>
<td>Tap Water</td>
<td>2</td>
</tr>
<tr>
<td>K0TW</td>
<td>0</td>
<td>100</td>
<td>Tap Water</td>
<td>2</td>
</tr>
<tr>
<td>KNaCl 0.1</td>
<td>100</td>
<td>0</td>
<td>0.1 M NaCl</td>
<td>2</td>
</tr>
<tr>
<td>KNaCl 0.5</td>
<td>100</td>
<td>0</td>
<td>0.5 M NaCl</td>
<td>2</td>
</tr>
</tbody>
</table>
Colead Pro instrument with the precision of ±1 % full scale range, with −10 °C to 150 °C temperature limit and resolution of 0.01 °C/−17.722°F. Regarding pH and conductivity, 12.5 mL from each solution was taken and tested by sensION MM374 pH meter.

2.5. Characterization methods for the poultices

Different poultice characteristics were measured before and after the EO experiments. The poultice was dried in an oven at 105 °C for at least 24 h and milled to powder. The pH, ion content and conductivity in the poultices were measured. For this purpose, 5 g of the powder sample was suspended in 12.5 mL of distilled water, shaken for 8 h, and filtered through 0.45 μm nitrocellulose filters. The Cl− content was measured in the filtrates using high-resolution chromatography-IC-(Dionex ICS-100). The pH and conductivity were measured in the suspension before the filtration.

The zeta potential was measured on the poultices with kaolinite with different solutions before the EO experiments using a Zetasizer Nano Z, from Malvern Instruments, applying electrophoresis measurement (EPM), as was done in previous studies [19,20]. For this purpose, 1 g of powder was suspended in 25 mL of distilled water. The zeta potentials were measured in three replicates for each poultice.

3. Results and discussion

3.1. Electroosmotic volume flow

An EO flow was generated in the specimens by applying 2 mA of electric current. The flow rate ($J_e$, m/s) was calculated based on the volume of the transported water divided by the time of water transport in the determined length (10 cm) in the capillary tube multiplied by the cross area of the mixture. It was found that kaolinite mixed in tap water had the highest EO flow rate compared with the mixtures containing a percentage of CaCO3 (Fig. 3a). The flow rate for the specimen was the average of EO flow rate in 6 times of changing polarity. For instance, KTW had a flow rate of 4.54 (μm/s) and this was reduced significantly to 1.77 (μm/s) when in K40TW, 60% CaCO3 was added to the mixture. The reduction of the flow rate continued by adding more CaCO3 into the specimen. For instance, K25TW had the lowest EO flow rate (0.57 μm/s), being the concentration of CaCO3 up to 75%. It was found that by increasing the concentration of CaCO3 to 80% there was no EO flow in the system. K0TW with pure CaCO3 also did not have any EO flow response under the same applied current (2 mA). Considering electrical parameters in Table 3, we can see approximately similar values in the conductivity in these poultices and the only variable factor in the poultices was the concentration of CaCO3. These results showed the relation between the rate of EO flow and concentration of CaCO3 in the poultice mixture, i.e., by increasing the amount of CaCO3 in the poultice, the EO flow was reduced.

Fig. 3b represents the EO flow rate results for the kaolinite mixed with NaCl with two different concentrations, namely 0.1 and 0.5 M. It was found that the poultice mixed with a lower concentration of ions had a higher EO flow rate than the poultice with higher ion content, i.e., the flow rate for KNaCl0.1 was 0.495 (μm/s) and this rate reduced to 0.00775 μm/s for KNaCl0.5. This might be explained by the differences in the ion content in these two poultice mixtures. Having the information in Table 2, the ionic strength in KNaCl0.5 was higher in KNaCl0.1. By comparing the EO flow rate of KNaCl0.1 and KNaCl0.5 with KTW it was found that KTW had the highest rate of EO flow (4.54 μm/s), with the lowest ionic strength (Table 2). These results indicate the relation of EO flow rate with the ionic strength in the poultice mixtures, i.e., by increasing the ion content the EO flow rate decreased, consistently with what reported in [21]. This can be explained by the fact that by increasing the ionic strength, the thickness of the electric double layer (EDL) (1/K) decreases and, by decreasing the thickness of EDL, the zeta potential decreases [22], which corresponds with our measurements (Table 3). As shown in [23], zeta potential depends on the ionic content of the solution and in fact KNaCl0.5 had a lower zeta potential (~37.4 mV) than KNaCl0.1 (~41.3 mV), which is close to the range (~30 mV) for kaolinite measured by [24]. Consequently, the EO rate in KNaCl0.1 was higher.

3.2. EO permeability coefficient

The EO permeability coefficient ($L_{12}$) was calculated by dividing the flow rate by the potential gradient as shown in Eq. (3). The potential difference (V) was measured by Ag/AgCl electrodes as
Table 3

<table>
<thead>
<tr>
<th>Sample</th>
<th>KTW</th>
<th>KNaCl0.1</th>
<th>KNaCl0.5</th>
<th>K40TW</th>
<th>K33.4TW</th>
<th>K25TW</th>
<th>K20TW</th>
<th>K0TW</th>
</tr>
</thead>
<tbody>
<tr>
<td>Current Density</td>
<td>32.9</td>
<td>32.9</td>
<td>32.9</td>
<td>32.9</td>
<td>32.9</td>
<td>32.9</td>
<td>32.9</td>
<td>32.9</td>
</tr>
<tr>
<td>Resistance (kΩ)</td>
<td>22.9</td>
<td>2.7</td>
<td>0.7</td>
<td>18.4</td>
<td>19.2</td>
<td>20.3</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Resistivity (kΩ m)</td>
<td>0.02</td>
<td>0.0018</td>
<td>0.00052</td>
<td>0.01</td>
<td>0.01</td>
<td>0.014</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Conductivity (S/m)</td>
<td>0.07</td>
<td>0.5</td>
<td>2.1</td>
<td>0.08</td>
<td>0.08</td>
<td>0.07</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Zeta potential</td>
<td>–40.53</td>
<td>–41.33</td>
<td>–37.47</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Potential Drop (V)</td>
<td>45.5</td>
<td>5.2</td>
<td>1.3</td>
<td>36.9</td>
<td>38.4</td>
<td>40.9</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

**Fig. 4.** Electroosmotic permeability coefficient in (a) kaolinite and CaCO₃ mixtures with tap water and (b) kaolinite poultice mixed in 0.1 and 0.5 M NaCl solutions.

shown in Fig. 1, then divided by the length of the poultice sample to get the potential gradient \( V (\nabla \psi) \) in (V/m). Results showed that the poultice with pure kaolinite mixed in tap water had the largest value of EO permeability coefficient, compared with the poultices containing CaCO₃ (Fig. 4a). For instance, in KTW, the EO coefficient was \( 8.49 \times 10^{-9} \) m².V⁻¹.s⁻¹, which was close to the range of EO permeability coefficient \( (k_e) \) reported in [12]. By adding 80% of CaCO₃, the coefficient value considerably decreased to \( 0.438 \times 10^{-9} \) m².V⁻¹.s⁻¹. According to these results, beyond 80% of CaCO₃, EO permeability coefficient tended toward zero. For poultices K20TW and K0TW, we could not measure the coefficient since there was no EO water flow. The results indicated that this added amount of CaCO₃ hindered the EO permeability.

Fig. 4b, represents the EO permeability coefficient in kaolinite poultice mixed with NaCl concentrations. The EO permeability coefficient value for KNaCl0.1 with 0.1 M of NaCl was \( 8.04 \times 10^{-9} \) m².V⁻¹.s⁻¹ and \( 5.13 \times 10^{-9} \) m².V⁻¹.s⁻¹ for KNaCl0.5 with 0.5 M NaCl. In literature, reported values for EO permeability coefficient \( (k_e) \) in fine-grained soils are between \( 10^{-9} \) and \( 10^{-9} \) m².V⁻¹.s⁻¹ [12]. Accordingly, also in this case, there is a relatively good consistency of the measured values with literature data.

Comparing the data in Fig. 3a related to KTW with the data in Fig. 4b related to KNaCl0.1 and KNaCl0.5, it was found that EO permeability decreased when the mixing solution contained a higher concentration of NaCl. This might be due to the higher amount of ions in the solution and, therefore, a lower resistivity (Table 3). As shown in [25], a high degree of conductivity negatively affects the EO process. Moreover, at the same time, as reported in [24], sodium has a low mobility in kaolinite. These results agree with previous studies, such as [23] that established that the higher the
ionic strength, the lower the thickness of the double layer and the lower EO flux.

3.3. Characteristics of poultice and solution after the test

The level of pH and electric conductivity of the solution in the upper chambers remained stable. A small sample from the solution after changing the polarity each time was taken for one of the tests to study if there might be any difference in the pH of the solution. The same procedure was repeated for the poultice sample after finishing the test (6 polarity changes). The results for conductivity values for the poultice specimens are presented in Table 4. It was found that the conductivity values remained relatively stable before and after the test. Only the poultice KNaCl0.5 had a slight difference in the conductivity, which might be due to the ion’s migration during the test. Results showed that effects from the electrode reactions were successfully separated from the upper compartments. The experiment seemed to have no significant effect on the level of pH during and after the test (Fig. 5), meaning that the pH values did not considerably change during the test.

4. Conclusion

The electroosmotic water flow was investigated in different kaolinite and CaCO₃ poultice mixtures under application of a direct current. Results showed that pure kaolinite mixed in tap water had the highest EO permeability efficiency compared with the poultices with calcium carbonate mixtures, and the EO water flow considerably reduced when 60 % of calcium carbonate was added to the mixture. At 80 % calcium carbonate, the EO flow stopped. Also, there was no EO water flow in a pure calcium carbonate mixture. These results proved that it is possible to design a mixture of calcium carbonate and kaolinite where an EO water flow is hindered as is desired in, e.g., electro-desalination. Furthermore, the ionic strength had a reverse effect on the EO flow. A poultice with kaolinite mixed with 0.5 M NaCl had a lower rate of EO flow than the poultice mixed in 0.1 M NaCl, yet both these poultices had a lower EO flow compared with the mixture of kaolinite with tap water. This implies that, for conservation purposes, applying a poultice containing between 60 % and 80 % calcium carbonate not only hinders drying the mixture during the desalination process but also can buffer the acidification due to the electrode processes.

References