Feasibility of ion exchange membranes to control pH changes during electro-osmotic consolidation of soft soils.

Évaluation de la faisabilité des membranes échangeuses d'ions pour contrôler les changements de pH lors de la consolidation électro-osmotique des sols doux

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ABSTRACT: Electro-osmosis is an established method of consolidating soft fine grained soils. The efficiency of electro-osmotic treatment is controlled by the electrical resistance of the soil-electrode system. Due to increase in soil resistance during treatment, its cost efficiency is reduced limiting the widespread use of this technique especially in developed nations. According to the Helmholtz-Smoluchowski model of electro-osmotic flow the zeta potential is directly proportional to the electro-osmotic permeability. One of the main causes of increased resistance is hydrolysis of water molecules around the electrodes. The acidification of the anode, in particular, reduces the negative surface charge of clay particles and, thus, the zeta potential. This paper studies the use of ion exchange membranes to assess their ability to prevent flow of hydrogen ions into the soil mass. The test with anion exchange membrane showed a more stable pH in the soil around the anode compared to a control test. Contrary to expectations, the cation exchange membrane used around the cathode reduced the hydraulic conductivity of the system such that little water was drained throughout the test, showing that drainage through the electrode will not be sufficient.

RÉSUMÉ : L'électro-osmose est une méthode établie pour consolider les sols fine. L'efficacité du traitement électro-osmotique est contrôlée par la résistance électrique du système sol-électrode. En raison de l'augmentation de la résistance du sol pendant le traitement, sa rentabilité diminue, limitant l'utilisation généralisée de cette technique, en particulier dans les pays développés. Selon le modèle Helmholtz-Smoluchowski d'écoulement électro-osmotique, le potentiel zêta est directement proportionnel à la perméabilité électro-osmotique. L'une des principales causes d'une résistance accrue est l'hydrolyse des molécules d'eau autour des électrodes. L'acidification de l'anode, en particulier, réduit la charge superficielle négative des particules d'argile et donc le potentiel zêta. Cet article étudie l'utilisation de membranes échangeuses d'ions pour évaluer leur capacité à empêcher l'écoulement d'ions hydrogène dans la masse du sol. Le test avec la membrane d'échange d'anions a montré un pH plus stable dans le sol autour de l'anode par rapport à un test de contrôle. Contrairement aux attentes, la membrane d'échange de cations utilisée autour de la cathode a réduit la conductivité hydraulique du système de telle sorte qu'une petite eau a été drainée tout au long de l'essai, montrant que le drainage à travers l'électrode ne suffira pas.

KEYWORDS: electro-osmosis; consolidation of soft soils; ion exchange membrane; pH control; soil resistance;

1 INTRODUCTION.

When subjected to loading, clay soils will consolidate and will undergo significant settlement which can have detrimental effects on structures. Due to the low permeability of clay, primary consolidation takes longer time to achieve. The consolidation period can be further expedited by electro-osmosis (Bergado et al., 2000). Electro-osmotic treatment has been extensively tested and it has proven to have clear benefits to consolidation of cohesive soils. However, certain problems have prevented the widespread use of electro-osmotic consolidation especially in developed nations.

One of the most the most widely used theories to model electro-osmotic flow is the Helmholtz-Smoluchowski model. The rate of water flow is controlled by the balance between the friction between the liquid and the capillary wall of soil pores and the electrical force causing water movement (Mitchell and Soga, 2005). In this model, the electro-osmotic permeability of the soil, k_e, is calculated by,

$$k_e = \zeta D n/\eta \qquad (1)$$

where ζ is the zeta potential, D is the relative permittivity, n is the porosity, and η is the viscosity. According to double layer theory, the slip plane in electrokyneticc processes is located a small distance away from the clay surface. The zeta potential refers to the electric potential caused by the clay particle’s surface charge at the slip plane. According to this model the capacity of electro-osmosis to transport water is directly proportional to the zeta potential of the soil, which is closely related to the resistance of the soil.

1.1 *Hydrolysis of water molecules at the electrodes*

The application of an electric field induces movement of water across the soil but also generates electrochemical reactions at the electrodes that negatively affect the performance of the electro-osmotic consolidation. The main reaction is the hydrolysis of water molecules (Acar et al. 1990). As water decomposes, hydroxide ions are produced at the cathode and hydrogen ions are produced at the anode, as shown in Eqs. 2 and 3.
At the anode (oxidation):

$$2H_2O \rightarrow O_2(g) + 4H^+ + 4e^-, \qquad E^o = 1.229V \qquad (2)$$

At the cathode (reduction):

$$4H_2O + 4e^- \rightarrow 2H_2(g) + 4OH^-, \qquad E^o=-0.828V \qquad (3)$$

The generation of H^+ at the anode causes low pH over time. The pH drops are associated with a reduction of the absolute value of the zeta potential and an increase in soil resistance, decreasing the electro-osmotic flow during direct current application (Rabie et al. 1994, Tuan et al. 2008). Change in the clay properties, both physical and chemical were reported by Mitchell (1991) and Lo et al. (1991) due to pH and zeta potential. Aziz et al. (2006) reported that the pH gradient in the soil sample might change the particle aggregation. For kaolinite, as the pH of the sample decreases from 10 to 3, the absolute value of the zeta potential decreases from 90 to 20 mV, this implies that the physical state of the soil particles changes from dispersed to coagulated (Mahmoud et al. 2010). On the other hand, high concentrations of OH^- cause precipitation of metallic ions in the soil, which reduces the porosity. Hu et al, 2015 showed that the impact of change in pH can be mitigated by intermittent current. Hu et al. 2016 also showed that the impact of change in pH can be mitigated by having a metal electrode made of copper.

1.2 *Ion-exchange membranes*

In order to surpass the adverse effects of hydrolysis and pH change at the electrodes electro-osmosis can be enhanced with the use of electro-dialysis (ED). This process uses an ion exchange membrane (IEM) to prevent the flow of charges ions. Two types of membranes can be used: anion exchange membranes (AEMs) that allow only anions to flow through, and cation exchange membranes (CEMs) that only allow cations to flow through. A sample picture of an ion exchange membrane is shown in Figure 1. The configuration of the electro-osmotic process combined with both membranes is shown in Figure 2**.**

Figure 1. Sample ion exchange membrane

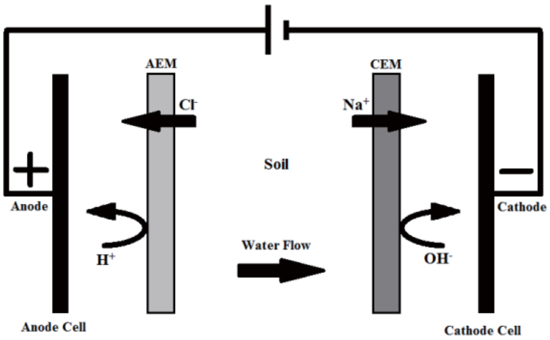

Figure 2. Schematic of electro-osmotic treatment of soil using ion exchange membranes

This study examines the use of an AEM alone to assess its effect on the electro-osmotic process and quantify them apart from a CEM. Later experiments will test the CEM alone and then both combined to evaluate which arrangement provides the best results.

2 MATERIALS AND METHOD

The study consisted of two electro-osmosis tests. Test 1 was used as a control. After preparation, the sample was connected to a power supply and 15 volts of DC were applied. During this time, an overburden pressure was maintained to prevent crack formation. 2800g of weight were applied on a plastic cover that roofed the sample, distributing the load evenly across the top. This was based on the ability of the wet sample to take load without failing. Water was drained through a drainage pipe connected to the cathode reservoir. After 40 hours the samples were disconnected and prepared for pH measurements. During the test, settlement and current were measured at regular intervals. pH measurements were also taken for the drained water. Test 2 introduced an anion exchange membrane at the anode. For these tests, the anode reservoir was filled with deionized water to allow for hydrolysis to occur.

Table 1. Soil Properties.

Soil Composition (by weight)	*Value*
Brown Kaolin (%)	50
Rock flour (%)	50
Liquid Limit (%)	33.5
Plastic Limit (%)	16.9
Soil pH	6.13
Water content (%)	37.5

2.1 *Soil sample*

Sample soil preparation consists of first mixing brown kaolin clay and rock flour. The mixture is mixed with water to a moisture content of 37.5%. The mixed sample is allowed to rest for 24 hours inside a vacuum oven to remove entrapped air. After this period the sample is placed in the testing chamber and loaded to allow of normal consolidation to occur. Properties of the used samples are shown on Table 1.

2.2 *Membrane Preparation*

For the anion exchange membrane (AEM), it was prepared for use by soaking it in a 5% NaCl solution for 12 hours. This allowed the membrane to hydrate and expand. After this, the membrane was placed at the anode between the electrode and the soil. Membrane properties are listed in Table 2.

Table 2. Anion exchange membrane properties

Functional Group	*Quaternary*
Ionic Form	*Chloride*
Thickness (mm)	*0.45±0.025*
Electrical Resistance (Ohm.cm2)	*<40*
Total Exchange Capacity (meq/g)	*1.3±0.1*
Water Permeability (ml/hr/ft2) @5psi	*<3*

2.3 *Testing chamber*

Figure 3 shows a schematic diagram and dimensions of the rectangular testing chamber. The initial soil cell dimensions were 100mm x 80mm x 40 mm. A small drainage tube in the cathode reservoir allowed for drainage of removed water.

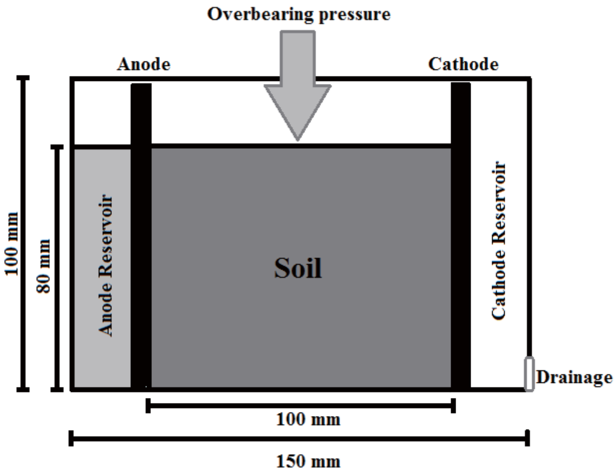

Figure 3. Schematic of testing cell.

3 RESULTS AND DISCUSSION

3.1 *pH*

The variations of pH in the soil bed are shown in Figure 4. As the hydrolysis proceeds, hydroxide ions are produced at the cathode, whereas at the anode protons are produced, this results in a pH gradient across the soil (Yoshida 2000, Yuan and Weng 2003). The acid front near the anode and base front near the cathode migrate towards each other. The acid front moves faster than the base front due to the higher mobility of H^+ than OH^-, and therefore low pH dominates the chemistry across the soil except for a small region close to the cathode (Alshawabkeh & Bricka, 2000). The control tests reflects this phenomena. The pH around the anode drops to 3.9 and rises to 9.5 at the cathode, indicating that hydrolysis has occurred affecting the soil pH as expected. The pH at the center of the sample is acidic compared to the original, showing that the acidic front dominates.

Test 2 combines electro-osmosis with an anion exchange membrane to prevent the flow of hydrogen ions into the soil near the anode and reduce the change in pH. The pH of Test 2 near the anode decreased to 5.0, even with in the presence of the membrane. This might be due to the exchange capacity of the membrane. As hydrolysis takes place, the membrane prevents the passage of H^+ ions into the soil. However, eventually the membrane is depleted and ions can pass more freely. The membrane used had a low hydraulic permeability, thus passage of ions from the anode reservoir would still be partially thwarted even after depletion. The pH at the cathode is actually higher than that of the control. Since the membrane prevented the flow of hydrogen ions into the soil bed, the zeta potential of clay particles was better maintained. This is evidenced by the lower resistance of Test 2 as shown in Figure 5. Consequently, the current throughout the test is higher (Figure 6) and hydrolysis occurs at a greater rate. This slightly greater generation of hydroxide ions increases the pH at the cathode to 10.1. At the center of the soil bed the pH for Test 2 is higher than the control, even higher than the initial pH. Since the hydrogen ions are trapped in the anode reservoir, the basic front generated at the cathode can migrate towards the anode and increases the pH of the soil. This further shows that the membrane prevented over acidification of the soil.

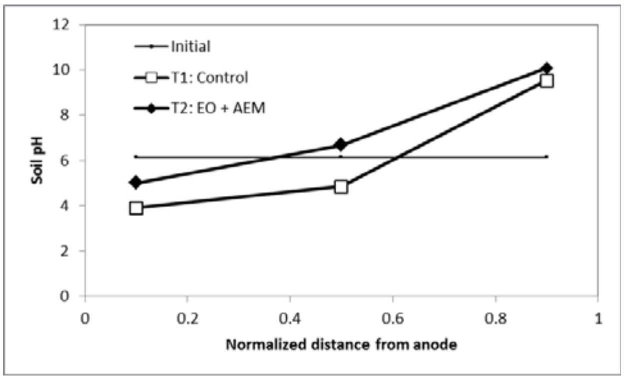

Figure 4. pH across soil bed after 40 hours of electro-osmotic treatment. (a) Test 1: control; (b) Test 2: electro-osmosis with anion exchange membrane

The pH of the drained water and the water in the anode reservoir were also measured. These values are shown in Table 3. The drained water pH corresponded with the pH of the soil near the electrodes. Both had high pH, with Test 2 showing the higher value. For Test 2, the anode reservoir was filled with deionized water up to a height equal to the soil to avoid creating a hydraulic gradient. The deionized water served as the source of water molecules for hydrolysis to take place. Because the membrane prevented the generated hydrogen ions from flowing into the soil, the pH of the water in the anode reservoir decreased intensely. The pH was found to be below 1. This indicated that the membrane succeeded in keeping the hydrogen ions from entering the soil bed. A yellowish coloration and faint smell also formed in the water. Because the membrane has an exchange capacity limit, once it depletes, hydrogen ions may pass through it into the soil. If the membrane was depleted during the test and hydrogen ions were allowed to migrate, this could explain the low pH of the soil at the anode in Test 2. While it is not as low as that of Test 1, the soil still shows more acidity than the initial value. In the future, drainage and replacement of the water in the anode reservoir could be beneficial to avoid acidification of the soil once the membrane depletes.

Table 3. pH measurements for drained water

Test 1: Control	
Drained water pH	10.17
Test 2: EO + AEM	
Drained water pH	10.79
Anode reservoir pH	0.5*

*The pH meter user had a minimum safe range of 1. Thus, the measurement obtained for the anode reservoir is below 1 but unreliable beyond that.

3.2 *Electrical resistance and current*

In accordance with the literature, the resistance of the soil increased as electro-osmosis was carried out. The resistance of the soil throughout testing was measured in one minute intervals for 40 hours. The results are shown in Figure 5. Both tests display an increasing resistance. However, Test 1 experiences a resistance 4.8 times greater than that of Test 2. The membrane does increase the resistance in Test 2 by a fixed amount; however the trends still show its positive effects.

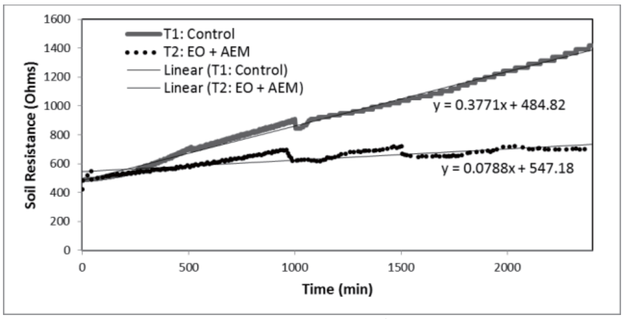

Figure 5. Soil resistance during 40 hours of electro-osmotic treatment. (a) Test 1: control; (b) Test 2: electro-osmosis with anion exchange membrane

Figure 6 shows the variation in current through the soil over time. According to Ohm's law, the current is directly related to the resistance, thus as resistance increases the current decreases. While the current is still high compared to the initial value, and although the rate at which it decreases is low, the current can be expected to reach very low values, and even zero, if electro-osmosis is continued. This study ended after 40 hours to study the immediate effects of a membrane. If the test was continued until current reached zero the membrane would have long been depleted and its effects likely nullified by the highly acidic water in the anode reservoir. Both Figures 5 and 6 show some jumps, especially at around 1000 minutes. These are probably due to a change in lab conditions, which have been known to affect precise measurements.

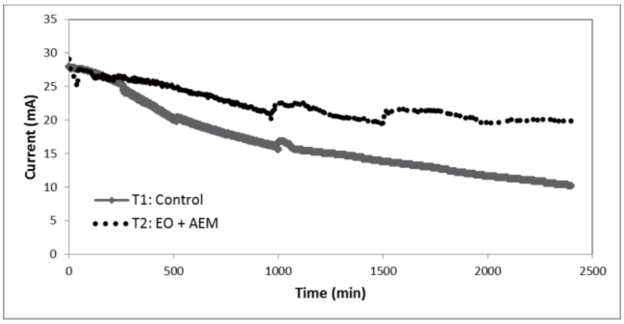

Figure 6. Current through the soil during 40 hours of electro-osmotic treatment. (a) Test 1: control; (b) Test 2: electro-osmosis with anion exchange membrane

3.3 *Settlement*

A settlement gauge was placed on the center of the soil bed to measure the settlement of the sample as electro-osmosis was applied. Figure 7 shows the settlement as a function of time. The application of a direct current induced settlement on both samples. Test 2 showed increased settlement due to the use of the anion exchange membrane. Both tests show an initial high settling rate that plateaus after about 18 hours. Following this, settlement continues but at a much lower rate. Because the membrane prevented the flow of hydrogen ions into the soil bed, the absolute value of the zeta potential was not as affected and the resistance in Test 2 did not increase as rapidly as Test 1. This allowed for a higher current and, thus, higher electro-osmotic flow, leading to increased consolidation.

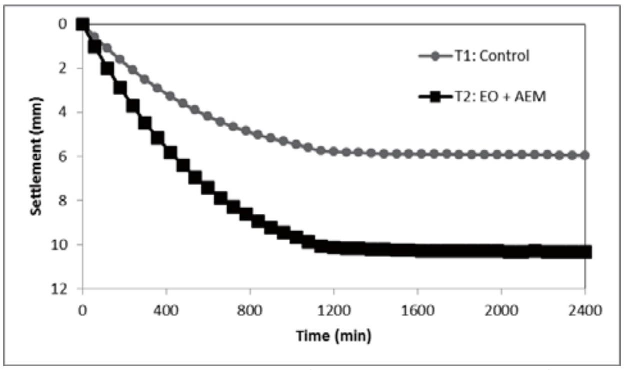

Figure 7. Settlement at the center of soil bed during 40 hours of electro-osmotic treatment. (a) Test 1: control; (b) Test 2: electro-osmosis with anion exchange membrane

4 CONCLUSIONS

The efficiency of electro-osmotic consolidation is significantly affected by the changes in pH in the soil, especially around the electrodes. In an effort to optimize the method to allow its commercial use, many studies have been done. This study asses the possibility of use of anion exchange membranes at the anode to isolate hydrolysis of water around the anode and prevent the flow of hydrogen ions into the soil. Two tests were performed to analyze the effects of the membrane. During these tests, the resistance, current, and settlement of the soil samples were measured. After the tests, the pH through the soil and in the drained water was also measured.

The membrane showed very positive results in all respects when compared to conventional electro-osmotic treatment. The pH of the soil around the anode did not decrease as much as with in the control test. It still decrease compared to the initial value. This is likely due to depletion of the exchange capacity of the membrane. The resistance of the soil was shown to increase at a slower rate for the test with the membrane. This further affirms that the membrane produced a positive effect. The increased settlement of Test 2 was also very positive. The use of a membrane allowed for consolidation beyond that obtainable with simple electro-osmosis.

The use of membranes should be investigated further with respect to electro-osmotic consolidation. The use of an cation exchange membrane should be investigate as well as its coupled effect with the anion exchange membrane. Especial attention should be given to drainage of water during treatment. Depending on the hydraulic permeability of the cation exchange membrane used, drainage through the electrode, as was the case in this study, might not be possible. Additionally, the capacity of a membrane to prevent the flow of ions before it becomes depleted should be taken into account and investigated. While membranes might provide a significant improvement to the electrical properties of the soil, if its effects are too short it might not be sufficient to help popularize electro-osmotic consolidation. Despite using the membrane, the resistance of the soil still increased. This demonstrates the acidification of the soil around the anode is not the only force reducing electric efficiency.

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