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Effect of Calcium Chloride on the Electrokinetic Characteristics of Organic Soil

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The electrochemical properties of the organic soil treated with calcium chloride were investigated. The Electrokinetic (EK) injection technique was used by applying a constant electrical potential of 60V across the specimens. Two EK tests (DW-DW system, and Ca-DW system) were performed to assess the efficiency of EK treatment. Developing the weak HCl acid in the anode compartment changed the ease of H^+ ion migration and consequently influenced the electroosmotic flow (EOF) rate. The changes in the electrical potential across the EK cell, voltage gradient, current density, and EOF were measured and the results are presented accordingly. Electrical potential profiles and pH profiles indicate that the depolarization technique enhances the backward migration of hydrogen ions from the cathode to the anode. Besides the electrical potential gradients along the EK cell for the Ca-DW system was observed to be much smaller than DW-DW system.

Keywords: Electrokinetic injection, Calcium Chloride, Soil improvement, Organic Soil, depolarization technique.

1. INTRODUCTION

Organic soils are found in many places around the world [1]. Organic soil is a mixture of finely divided particles of organic matter, in some instances visible fragments of partly decayed vegetable matter and shells are also present in the organic matter [2, 3]. In Malaysia, peat has been identified as one of the major soil group. Peat as a soil with highly organic matter covers approximately 8.11% of the land or 3 million hectares.

When fluid is in contact with solid, the interfacial charge distribution between these two surfaces is changed into the structure of electrical double layer (EDL). This includes a mobile diffuse layer and an adsorption layer. Zeta (ζ) potential is defined as the potential at the interface (shear plane) between these two layers. The sign and magnitude of the ζ potential is dependent on the interfacial chemistry of both solid and liquid phase [4]. This potential is also affected by the thickness of the DDL, ion exchange capacity, and size of ion radius [5]. The electrokinetic (EK) phenomena results from the presence of this potential [6-8]. The rate of electroosmotic flow (EOF) is controlled by the coefficient of electroosmotic permeability of the soil, k_e, which is a measure of the fluid flux per unit area of the soil per unit electric gradient. The value of k_e is a function of the soil porosity, the viscosity of the pore fluid, the soil electrical permittivity, and the ζ potential. The coefficient of electroosmotic permeability is presented by Equation 1.

Equation 1: $$q=\frac{\varepsilon\zeta}{V_t}n\frac{E}{L}A=k_e i_e A$$

Where, ζ = Zeta potential, V_t = Viscosity of the pore fluid, n = Soil porosity, ε = Soil electrical permittivity, A = Gross cross-sectional area perpendicular to water flow, L = Length, i_e = Applied electrical gradient, k_e = Coefficient of electro-osmotic conductivity, and q = Flow rate. Hydraulic conductivity is considerably affected by the pore size and distribution in the medium, but k_e based on the Helmholtz-Smoluchowski theory is dependent mainly on ζ potential.

The movement of cationic agents such as calcium chloride into soil masses without disturbing the soil structure can be easily governed by the principles of EK [9-14]. When cations are injected through the soil samples the ions migrate into soils through the processes of electro-migration and osmotic advection. The injection of calcium chloride causes a series of reactions in both cathode and anode chambers which is called depolarization technique [15, 16]. This technique can significantly contribute to the soil remediation process (e.g. soil improvement, soil decontamination) and could provide more uniform effects than the traditional method [16]. The technique consists of supplying hydroxide ions at the anode to counterbalance the hydrogen ions generated from the reactions caused by electrolysis [16, 17]. This not only prevents the development of acid environments in the soil mass but also encourages hydroxide ions, which are generated at the cathode, to migrate backwards to the anode. As a consequence, the improvement area should be extended towards the anode [12].

The main objective of this study is to inject calcium chloride reagents into the organic soil mass in order to evaluate its electrical and mechanical enhancement during the EK process.

2. MATERIAL AND METHODS

2.1. Material

Organic soil samples were collected and sealed to maintain soil moisture in accordance with the British Standard Institution (BS) methods of test for soils (BS 1377-1:1990) from Kg Jawa Klang, Selangor, Malaysia. The containers for the disturbed soil were capable of being sealed to prevent any loss or gain of the moisture. Precautions were taken to avoid any kind of jolting during the transportation of the soil.

2.2. Electrokinetic Setup

A diagram of the EK apparatus which used in this study is presented in Figure 1. The EK cell consisted of an acrylic tube, 150 mm long and with a 69 mm diameter, where the soil was molded, and connected at both ends to acrylic cylindrical chambers of the same diameter. Sampling ports of 1 mm diameter were placed along the soil chamber for extraction of pore fluid. The holes were sealed to prevent any leakage during the sampling. As for electrode, graphite was held inside the electrolyte chambers. A diagram of the apparatus used in this study is presented in Figure 1. The apparatus was designed following the criteria given by Burnotte et al. (2004).

The electrical circuitry of the system was based on a laboratory multi-stage variable power supply with an adjustable range of voltage and current. This voltage regulation unit was placed to force the electrical carriers through the tube as a result of applying a constant stable DC voltage level. As the electrons travel from the negative output of the power supply to the cathode and absorb on the surface of the anode electrode, an electrical current is formed from the anode to the cathode. The accumulation of the negative and positive charges on the cathode and the anode relatively will cause the movement of contrasting charged ions through the electrolyte solution. The same phenomena can be seen in similar electrochemical processes such as electrolysis or electroplating.

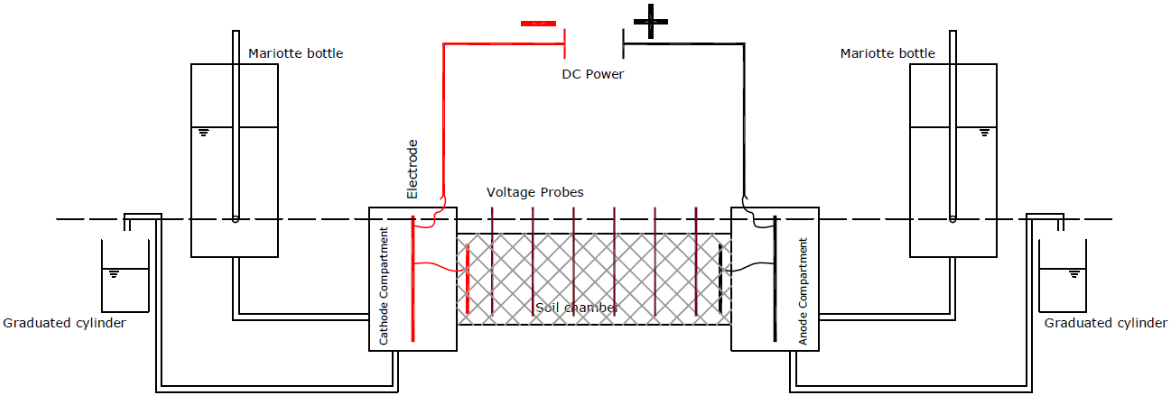


Figure 1. Schematic diagram of the EK apparatus .

3. RESULTS AND DISCUSSION

3.1. Physicochemical Properties of Soil Sample

Organic soil environment is a good candidate for the EK phenomena due to a very wet soil mass, high surface electrical charge, high Cation Exchange Capacity (CEC) at the natural soil pH, high specific surface area and presence of hydrated ions [18-21]. The physicochemical properties of the organic soil sample is presented in Table 1

Table 1. Physicochemical properties of the organic soil sample

Parameter	Standard	Values
Moisture content: %	ASTM D2216	141-158
In situ (natural) bulk unit weight: kN/m^3	BS 1337	9.86–11.25
Classification	ASTM D5715	Fibrous
Organic content: %	ASTM D2974	56
Hydraulic conductivity: m/s	ASTM D2434-68	5.35×10^{-6}
CEC	Gillman and Sumpter (1986)	51
Soil pH	BS 1337	5.63

The average CEC of organic soil was determined as 51 meq 100 g^{-1} by the ammonium acetate method at the pH equal to 7. As stated in the literature [22, 23] the average CEC of kaolinite at pH of 7 is 10 meq 100 g^{-1} which is much smaller than organic soil. This means higher capability of organic soils to hold cations at a given pH value. Mineralogical analysis of the soils showed the presence of kaolinite as a main clay fraction in organic soil.

3.2. Electrokinetic Behavior of Organic soil

As mentioned, two EK experiments were performed to assess the efficiency of EK treatment. In experiment 1, the traditional EK technique was applied (here called DW-DW system). However, the second test was aimed to inject $CaCl_2$ from the anode (Ca-DW). Both experiments were prformed within the 7 day curing time. Calcium chloride solution (1.0 mol/L.) at a pH of 2.8 was continuously supplied to the anode reservoir during the second EK experiments. Details of the experiments are summarized in Table 2.

Table 2. Summary of small EK tests

Test No.	Test	Chemical solution		Grout	Voltage
		Cathode	Anode	Concentration	(V)
1	DW-DW	DW	DW	Pure water	60
2	Ca-DW	DW	Ca	147.05 gr/L	60

DW-DW: Electroosmosis without cationic reagents.
Ca-DW: Electroosmosis with supplying of 1 mol/L calcium chloride as Anolyte.

Figure 3 also showed a schematic view of the EK apparatus during the EK process. Due to Hydrogen ions released in the anode, thousands of the tiny bubbles produced and accumulated within the anode compartment (Fig. 3.a). After 5 days treatment time, the liquid color in anode compartment altered to black in the rest of the treatment time. This is attributed to reaction between hydrogen ions (H^+) and chloride ion (Cl^-) that is supplied from the calcium chloride solution (1 mol/L.). The results of such interaction is a weak hydrochloride acid (HCl), in anode compartment.

(a) (b)

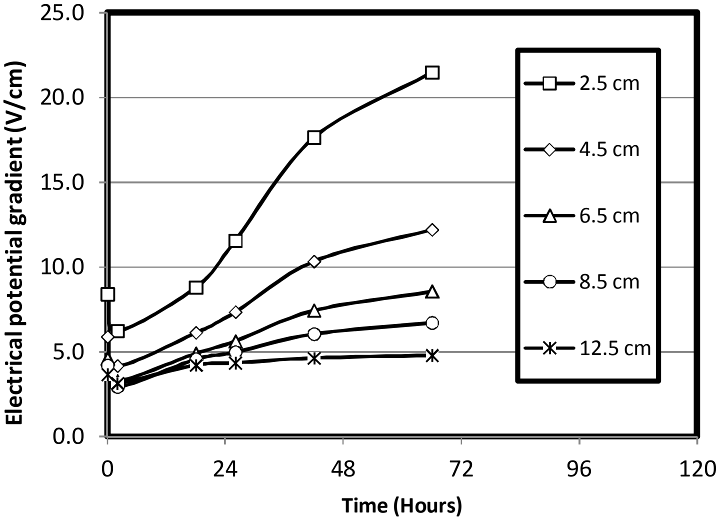
Figure 3. Tiny bubbles produced in the Anode, (a) in 1 day (b) After 5 days treatment time.

3.3.3. Distribution of current density and voltage gradient

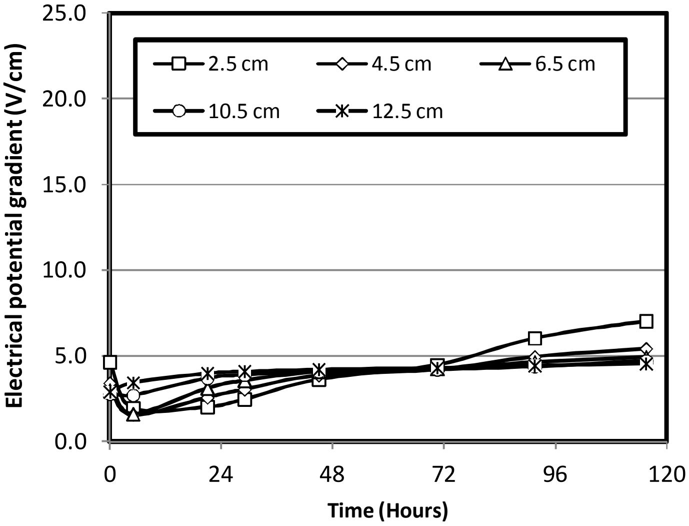
As showed in Figure 4, the variation of electrical potential gradient for DW-DW experiment was occurred in a wider range than Ca-DW system. For instant, in DW-DW system and at 2.5cm distance away from anode electrode the electrical potential gradient was started from 8.40V/cm continued with a sharp decreasing to 6.24 within first hour and finally rise up to the 21.48 v/cm within 72 hours. While in Ca-DW experiment the variation was measure between 4.64v/cm at the first hour to the 7.04 after 120 hours.

According to Hausmann (1990), greater soil particle surface will result in higher moisture film transfer. He also noted that another factor affecting this phenomenon is electrical potential applied [24]. Electrical potential profiles provide an indirect assessment of the chemical changes in the ionic compositions of the pore fluid [25]. On the other hand, the high resistivity zone, demonstrated by a sharp drop in the electrical potential, not only indicates uniformity of the ionic composition but also identifies the location of the precipitation zone [26]. Figure 4 presents the development of electrical potential profiles across the specimens during the experiments.

Lefebvre and Burnotte (2004) also reported that chemical treatments can reduce the electric potential drop at electrodes [27]. The variation of voltage gradient (Fig. 5) and current density (Fig. 6) versus time presented for both DW-DW and Ca-DW. During the first 24 hours, the voltage gradient increase with increasing via time and then steadily decreases until the end for Ca-DW, whereas the voltage gradient decreases sharply with time from the 24 hours to the end for DW-DW. The amount of voltage gradient by Ca-DW is about 1.45 times greater than DW-DW (Fig. 5). On the other hand, the variation of current density distribution with time shows a similar trend during DW-DW test with Ca-DW experiment (Fig. 6).



(a)



(b)

Figure 4. Development of electrical potential profiles across the specimen, (a) DW-DW system, (b) Ca-DW system. (Distances are from the anode)

Current density is a measure of the density of flow of a conserved charge [28]. Usually the charge is the electric charge, in which case the associated current density is the electric current per unit area of cross section, but the term current density can also be applied to other conserved quantities. It is defined as a vector whose magnitude is the current per cross-sectional area. A study on the influence of current density and pH on electrokinetic by Hamed and Bhadra (1997) showed that tests with higher current densities resulted in higher flow rates [29]. This study was later expanded by performing several EK tests by Alshawabkeh and Bricka (2000). Alshawabkeh and Bricka (2000) stated that high current levels generate more acid (e.g. more acid will work for the EK process) however it increases the total ionic concentration that will decrease the overall EOF [30]. The observed result in this study is in contrary with the reported result by both researches conducted by Hamed and Bhadra (1997) and Alshawabkeh and Bricka (2000).

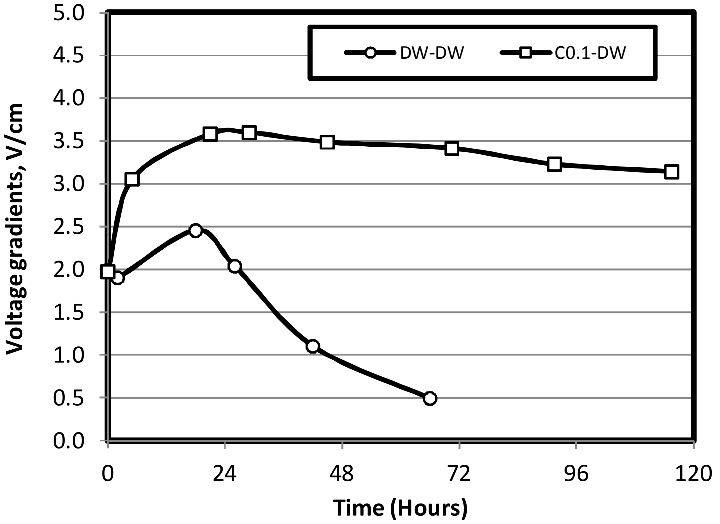


Figure 5. Development of voltage gradient across the cell

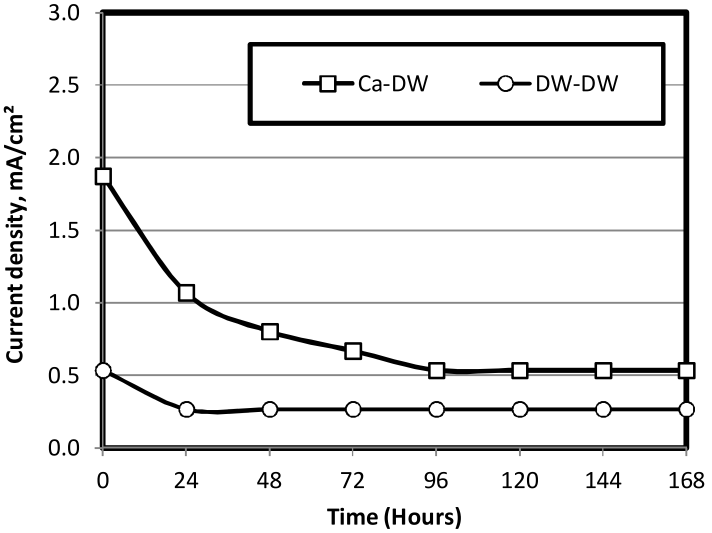


Figure 6. Development of current density across the cell

3.3.1. Electroosmotic Flows Characteristics

Figure 7 shows the plots of the cumulative volume of the effluent against elapsed time. The average flow rate was approximately 23 for both of the DW-DW and Ca-DW system. The net cumulative flow for Ca-DW system at the end of the 7 days treatment time was 156ml (Fig. 7). Eykholk (1994) is reported the reverse flows due to the presence of cationic reagents [4]. Such change in flow direction is attributed to the change in sign of ζ which caused by changing soil pH [4, 8, 31]. Other researchers also agreed that the pH at which polarity reversal of the ζ takes place depends on the physicochemical properties of the both soil and pore fluid [32, 33]. In addition, according to Gurtu (1977) the sign of charge in most cases can be changed by the addition of small quantities of certain active electrolytes in water [34]. It should be noticed that the pH level of the electrolyte has a direct effect on its electrical resistance. The more deflection from neutral pH, the more ionic electrolyte and less equivalent resistance it shows to the electrical current flow.

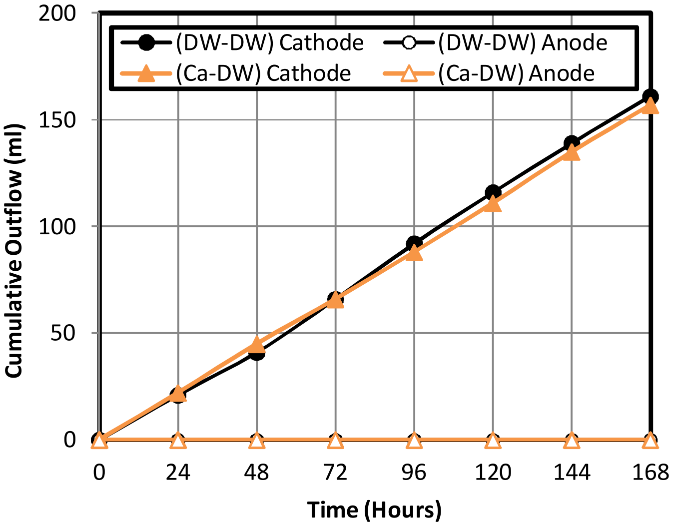


Figure 7. Volume of effluent (ml) versus time for DW-DW and Ca-DW

The presence of the cationic reagent changed the efficiency of the H^+ ion since it reacts with some of the available elements in the anolyte. In this study, when calcium chloride used as anolyte, the calcium ions (Ca^{2+}) are electrically injected into soils to replace with the monovalent ions while chloride ion (Cl^-) will react with the released hydrogen and producing the Hydrochloric acid (HCl). This means the hydrogen ions generated from the electrolysis at the anode, are prevented from migrating into soils. Preventing the distribution of acidic region decreases the total ionic concentration that in turn will affect the overall EOF.

The net flow for both of the Ca-DW and DW-DW systems was from anode toward the cathode. It seems that the electrolyte concentrations (1mol/L.) for both of the cation-based reagents was not enough to reverse the surface charge of the soils inside the EK box during the EK process. Definitely, the more concentrations of calcium chloride reverse the charge of colloids and consequently changing the EOF direction. It can be concluded that the colloidal surface charge reversal (e.g. reversing the EOF direction) under cationic reagents with higher valence occurs in a lower concentration. Another possibility is that the soil sample reached into its maximum CEC point (CEC is limited to 51 meq 100 g^{-1}) where there is no more exchangeable group in humus (e.g. phenolic hydroxyl, quinonic hydroxyl, and enolic hydroxyl groups) for the extra cations to be absorbed.

4. CONCLUSIONS

The current study explores the influence of injecting $CaCl_2$ thorough the organic soil by applying a constant electrical potential of 60 V across the specimens. Electrical potential profiles and pH profiles indicate that the depolarization technique enhances the backward migration of hydrogen ions from the cathode to the anode. Calcium ions are electrically injected into soils to replace monovalent ions while hydrogen ions, generated from electrolysis at the anode, are prevented from migrating into soils by continuous depolarization at the anode reservoir. However, hydroxide ions, generated at the cathode, are able to migrate into the soils. The injected calcium ions and hydroxide ions react with the dissolved silicates and aluminates in the clay fraction of the organic soil and eventually form the cementing agents-calcium silicates and/or aluminum hydrates.

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