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INFLUENCE OF ELECTROKINETIC PROCESSING OF A TROPICAL SOIL ON THE PHS OF THE ELECTROLYTES

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Abstract: The pH values of different anolytes and catholytes during electrokinetic (EK) processing of a tropical residual soil were investigated in laboratory. Four opened-anode and opened-cathode systems with different types of catholytes and anolytes were examined. Aluminium chloride, calcium chloride and phosphoric acid were used as electrolytes besides distilled water. Compressed soil samples, up to 90% of the maximum dry density at the optimum moisture content were subjected to a DC electrical potential of 30 V for 168 hrs. The pH values of the anolytes and catholytes were monitored continuously. The investigation showed that the pH values varied with time depending upon their initial values, the types of anolytes and catholytes and the systems employed. The measured pH values of the electrolytes were different from the theoretical values because of low efficiency of the EK experimental set up and complex electrochemical processes.

Keywords: *Electrokinetics, Residual Soil, Anolyte, Catholyte, Electrochemical*

Abstrak: Kajian ke atas nilai-nilai pH anolit dan katolit semasa pemprosesan elektrokinetik ke atas satu tanah baki tropika dilakukan di makmal. Empat sistem anod-terbuka dan katod-terbuka diaplikasikan dalam kajian ini dengan menggunakan katolit dan anolit yang berlainan jenis. Di samping air suling, bahan-bahan kimia lain yang digunakan sebagai elektrolit adalah aluminium klorida, kalsium klorida dan asid fosforik. Sampel-sampel tanah yang telah dimampatkan ke tahap 90% ketumpatan kering maksima pada kandungan lembapan optima dikenakan arus terus 30 V selama 168 jam. Nilai-nilai pH elektrolit dipantau sepanjang ujikaji. Kajian menunjukkan nilai-nilai pH berubah mengikut masa bergantung kepada nilai-nilai asal, jenis anolit dan katolit serta jenis sistem yang digunakan. Nilai-nilai pH yang diukur berbeza dari nilai-nilai teori disebabkan oleh faktor kecekapan peralatan ujikaji EK dan tidakbalas elektrokimia yang kompleks.

Katakunci: *Elektrokinetik, Tanah Baki, Anolit, Katolit, Elektrokimia*

1. Introduction

Tropical residual soils are generally heterogeneous and partially saturated. It is difficult to relate the properties of a residual soil directly to its parent rock. It is also rarely possible to extrapolate from one experience in one area to predict conditions in another even if the underlying hard rock geology in the two areas is similar (Blight, 1997). Taha et al. (1997) found that residual soils rely much of their properties from the bond strengths or the internal structural components of the weathered rock materials.

The strengths of residual soils are significantly reduced upon saturation due to the collapse of capillary stresses and increased in pore water pressures (Sridharan, 1988; Ahmad, 2004). It is worthwhile noting that the effectiveness of additives to increase shear strength was limited to small soil volume due to slow and restricted ion migration (Glendinning and Rogers, 1996). Thus, laboratory experiments to investigate the feasibility of combining electrokinetic (EK) processing with chemical addition to increase ion diffusion were performed in this study. Changes in strength of the EK-treated samples were anticipated as shown by Ahmad et al. (2004).

During EK processing, oxidation and reduction take place at the electrodes as electrons are transferred in and out of the system during the course of EK processing (Murayama and Mise, 1953; Gray and Mitchell, 1967; Lo et al., 1991; Mitchell, 1993; Shang and Ho, 1998) in addition to water transport between the electrodes. Such phenomena result in ion diffusion, ion exchange, development of osmotic and pH gradients, dessication by heat generation at the electrodes, mineral decomposition, precipitation of salts or secondary minerals, electrolysis, hydrolysis, physical and chemical adsorption, and fabric changes (Mitchell, 1993). Some of the changes may be beneficial while others retard the efficiency of electrokinetics. Electrolysis of water at the anode and the cathode produces oxygen and hydrogen, respectively, which can be represented by the following equations;

$$2H_2O - 4e^- \rightarrow 4H^+ + O_2 \uparrow \qquad \text{(anode)} \qquad (1)$$

$$2H_2O + 2e^- \rightarrow 2(OH)^- + H_2 \uparrow \qquad \text{(cathode)} \qquad (2)$$

Although the main objective of the EK experiments was to study the effects of EK processing on the strength of the treated soil, it is essential to note that pH values of electrolytes do affect the subsequent electrochemical reactions during the course of EK processing. It is also worthwhile noting that a pH value has significant impacts on chemical equilibria in dissolution or precipitation aqueous-phase reactions and in adsorption reactions in pore fluid, and on the fabric and engineering characteristics of the soil. Hence, this paper discusses laboratory observations on the changes of pH values of the electrolytes during 168 hrs of EK processing.

2. Experimental Procedures

2.1 Sample Preparation

A granite residual soil was obtained at depths between 2 m and 3 m below the ground surface within the compound of the Universiti Teknologi Malaysia at Skudai, Johor. The soil was air-dried under laboratory condition. Figure 1 illustrates the soil particles distribution. A distinctive feature of the granitic soil is that it is a mixture of sand, silt and clay in varying proportions (Ting and Ooi, 1976). Only soil particles passing 2.00 mm sieve was used in the EK experiments.

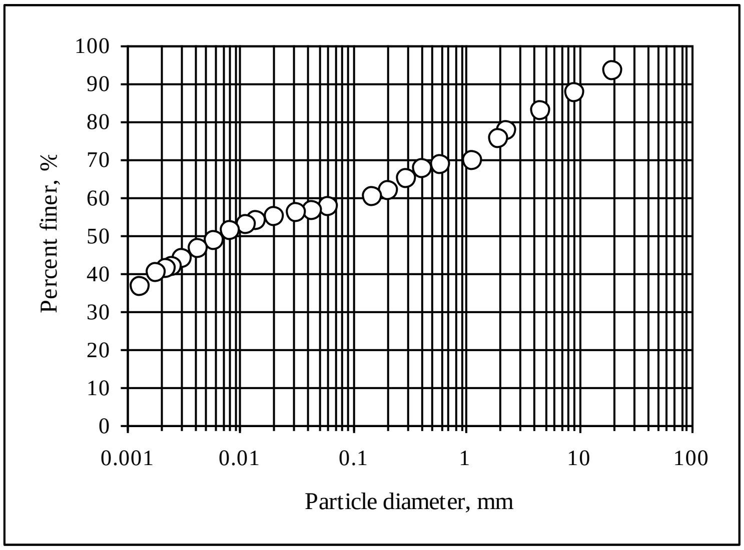

Figure 1: Grain size distribution of residual soil used in this study.

Figure 2 illustrates the compaction curve with the maximum dry density and optimum moisture content of 1415 kg m^{-3} and 33%, respectively. The procedures to perform the Standard Proctor compaction tests were in accordance with guidelines by Head (1990). Soil samples with a dry density of 90% of the maximum dry density and the corresponding optimum moisture content were used for sample preparation for EK treatments. Every mixture of soil and distilled water prepared for each of the EK treatments was poured into a 10 cm diameter soil compartment. After the required quantity of 666 g was obtained, the mixture was compressed using a triaxial test loading frame until a predetermined thickness of about 5 cm so that a bulk density of 1695 kg m^{-3} and a dry density of 1274 kg m^{-3} were obtained. Then, each sample was subjected to saturation.

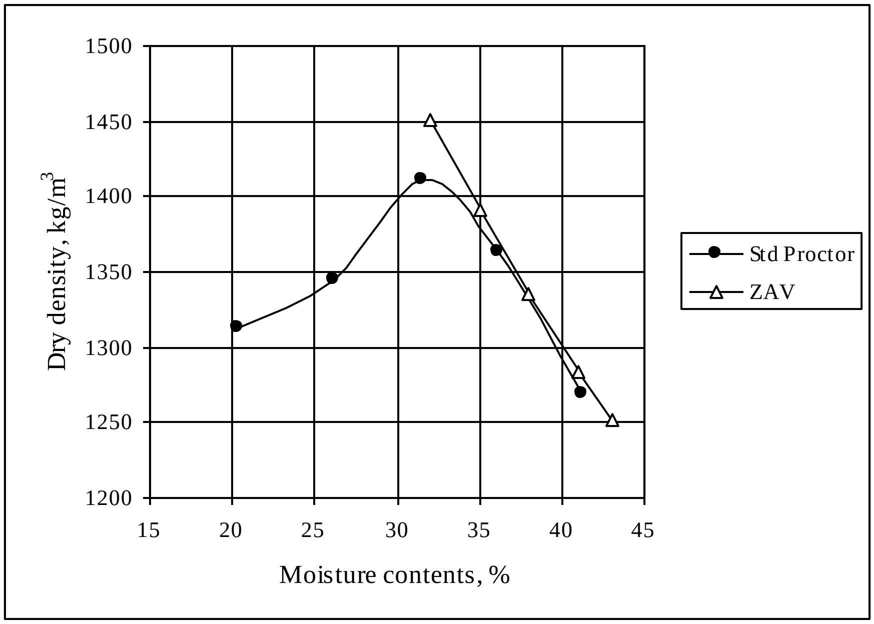

Figure 2: Compaction curve to determine the maximum dry density and optimum moisture content.

2.2 Electrokinetic Experiments

The soil compartment containing compacted and saturated sample was then connected to electrolyte compartments. The schematic diagram of the EK experiment is illustrated in Figure 3. Each EK cell consisted of a soil compartment connected to electrolyte chambers on both ends. The diameter and length of each soil compartment were 10 cm and 5 cm, respectively. Each electrolyte compartment with the diameter and length of 10 cm and 4 cm, respectively, was connected to Mariotte bottle. The bottles functioned as reservoirs supplying electrolytes and at the same time maintaining zero hydraulic gradients. The zero hydraulic gradients were to ensure the fluid flows during the course of the experiments were due to EK processing.

In addition to distilled water, the electrolytes used in this study were 1.0M aluminium chloride, 1.0M calcium chloride and 1.0M phosphoric acid. Since different anolytes and catholytes were prepared for the EK processing, which depend upon the ion types (anions or cations) to be injected into the soil, codes were used to designate the utilised fluids. Table 1 tabulates the codes assigned to each EK treatment system. The left and right terms of the codes indicate the anolyte and catholyte, respectively.

The EK treatment period of 168 hours (one week) was in line with the soil decontamination experiments performed by Taha et al. (1994). Titanium meshes were used as electrodes due to its high resistance to corrosion (Berkeley and Pathmanaban, 1990). A constant voltage of 30 V was applied to each system. On an average, 12 experiments for each system were conducted to study the effects of different electrolytes on the strength of the EK-treated sample. Only two sets of EK experiments were performed at a time due to limited EK cells and DC power supplies.

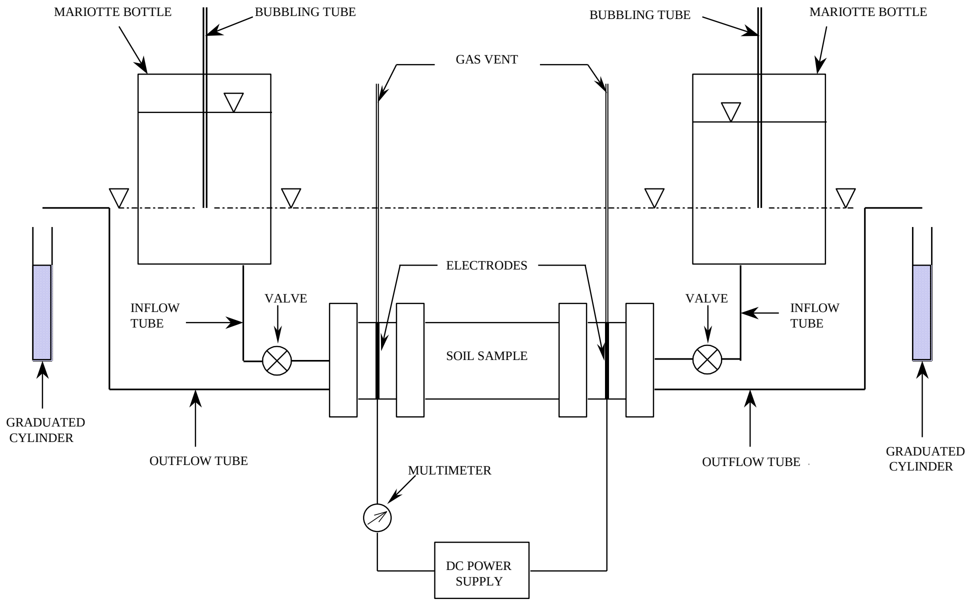

Figure 3: General layout of the EK experiment.

Table 1:Codes for EK treatment systems.

Code	Anolyte	Catholyte
DW-PA	Distilled water	1.0M phosphoric acid
DW-DW	Distilled water	Distilled water
Al-DW	1.0M aluminium chloride	Distilled water
Ca-DW	1.0M calcium chloride	Distilled water

The pH values of the electrolytes were determined every 12 hours by extracting the fluids through the outlets provided on the end caps of the electrolyte compartments. A portable pH meter model Hanna HI 8424 was used. The top tips of the bubbling tubes of the Mariotte bottles were plugged using clay dough to prevent fluid in the bottles from flowing into the electrolyte compartments during the extraction of the electrolytes. The extracted fluids were poured back into the respective electrolyte compartments through the gas vents installed on the electrolyte compartments after the completion of pH determinations.

3. Results and Discussion

Figure 4 illustrates the variations of selected pH values of the electrolytes resulted from the employed systems. Generally, the pH values varied with time depending upon the initial values, electrolyte types and systems used.

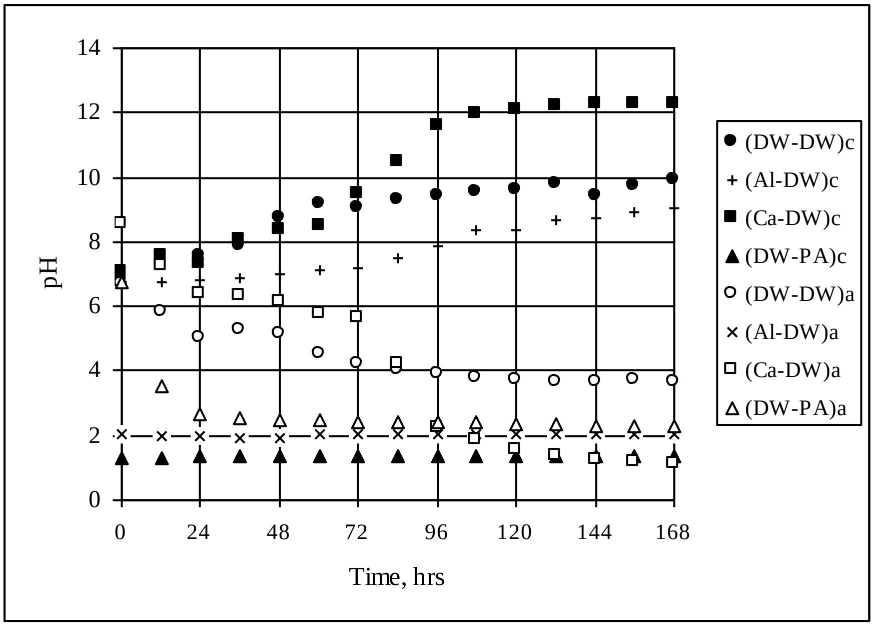

Figure 4: Changes in pH values of anolytes and catholytes over time.
Note: Subscripts a and c designate anolyte and catholyte, respectively.

3.1 DW-DW System

For the DW-DW system, the pH values of the anolyte decreased steadily from 6.90 to 3.84, whereas the pH values of the catholyte increased from 6.80 to 10.00. The pH values of the anolyte and catholyte of the DW-DW system changed at a relatively low rate, and the magnitudes of changes were also relatively small. These observations were due to the low efficiency of the experimental set-up that affected the electrolysis in addition to complex electrochemical reactions as mentioned previously. Some of the changes due to the reactions may be beneficial while others retard the efficiency of electrokinetics. It is worthwhile noting that maintaining contact between the electrodes and the soil is one of the most important factors in electrokinetic processing, which might be the reason for the current density fluctuation (Shang and Lo, 1997). Although the electrodes used in this study were installed in electrolytes to facilitate constant maximum contact with the soil, the formation of gas bubbles on the electrodes and soil resulting from the electrolysis of water contributed to the reduction of the effective area. Consequently, the efficiency of the EK system was reduced.

The low efficiency of the system was evident as the measured pH values of the anolyte were higher than the theoretical values. Theoretically, 96,500 Ampere·second (A·s) will produce 1.0 mole of H^+ and OH^- as a result of electrolysis of water. For the volume of 320 mL anolyte, about 2.78 x 10^{-3} mole L^{-1} of H^+ would be produced in the DW-DW system for the first 24 hrs of EK processing assuming a constant current of 1.0 mA. Since the current readings were recorded for every 12 hours of processing, a linear variation was assumed. With such H^+ concentration, a pH value of approximately 2.55 was expected. Nonetheless, measurement made on the anolyte of the DW-DW system indicated that the pH value was 5.0 (see Figure 4).

In addition, the system depended mainly on the electrolysis of water in the anode and the cathode compartments to generate ions, namely H^+ and OH^-, respectively as shown by Eqs. (1) and (2). These ions then initiated changes in pH of the anolyte and the catholye. Although the generation of these ions took place continuously throughout the electrokinetic processing, some of these ions involved in electromigration, i.e. the H^+ ions migrated toward the cathode and the OH^- travelled toward the anode. As a result, the pH values of the anolyte and the catholyte decreased and increased slowly with time, respectively.

3.2 Ca-DW System

Like the DW-DW system, the pH values of the anolyte and catholyte of the Ca-DW system decreased and increased with time, respectively, from 9.90 to 1.42 and from 6.68 to 12.00. The pH values of both the anolyte and the catholyte changed slightly with time for the first 60 hours of electrokinetic processing. The values then changed quite significantly for the next 36 hours after which the values became almost constant. Low efficiency and low rate of electrolysis might be the reason for the slight changes in the pH of the anolyte and catholyte. The electrolysis became intensive initiated by the generated H^+ and OH^-. The migration of Ca^{2+} from the anolyte compartment across the soil might be an additional factor which intensified the electrolysis.

3.3 DW-PA System

The pH values of the anolyte of the DW-PA system also decreased with time from 6.73 to 2.37, whereas the values of the catholyte increased slightly from 1.33 to 1.36 due to the high initial concentration of phosphoric acid. Unlike the DW-DW system, the pH values of the anolyte of the DW-PA system decreased rapidly within the first 24 hours of electrokinetic processing. The values then decreased slightly and became almost constant. This drastic change during the initial electrokinetic processing indicates rapid and intensive electrolysis of the anolyte to produce high quantity of H^+. The migrated anions from the catholyte (i.e., HPO_4^{2-} and $H_2PO_4^-$) toward the anode might be the reason for the intensive electrolysis of the anolyte. On the other hand, the increase in pH values of the catholyte was almost negligible. The H^+ ions in the DW-PA system were also continuously dissociated from phosphate species in the catholyte. At the same time, the H^+ combined with the generated OH^- to form water. Hence, the increase in pH of the catholyte was retarded and the low pH was restored. Such a condition obeyed the Le Chatelier principle of equilibrium (Ali, 1995).

3.4 Al-DW System

Unlike the other systems, the anolyte of the Al-DW system did not show any significant change in pH due to high initial acidity. On the contrary, the pH of the catholyte increased from 6.72 to 9.05. In the Al-DW system, it can be considered that changes in the pH values of the anolyte were very small due to significantly low initial pH indicating high concentration of H^+. Subsequently, the generation of H^+ from the electrolysis had a very minimum impact on the pH of the anolyte. On the other hand, the pH of the catholyte increased moderately after 72 hours of EK processing from 7.2 to the final value of about 9.0. The slight changes in the pH of the catholyte could be associated with the migration of H^+ toward the cathode. The H^+ then combined with the generated OH^- in the catholyte compartment to form water causing dilution of OH^- and evidence of moderate pH increase of the catholyte. In addition, the migrating OH^- toward the anode gave an impact on the pH of the catholyte by reducing the concentration of the OH^- in the catholyte compartment.

4. Conclusions

Four opened-anode and opened-cathode laboratory electrokinetic (EK) systems were employed to investigate the effects of EK processing on the strength of a granite tropical residual soil using different anolytes and catholytes. Aluminium chloride, calcium chloride and phosphoric acid were used as electrolytes in addition to distilled water. Since pH electrolytes do affect subsequent electrochemical reactions during the course of EK processing, changes in pH values were monitored. Major findings that can be drawn from this study are as follows.

i) The pH values varied with time depending on their initial values, the types of anolyte and catholyte, the employed EK systems as well as due to complex electrochemical processes.
ii) The measured pH values of distilled water used as both the anolyte and catholyte (DW-DW system) were higher and lower, respectively than the theoretical values.
iii) With distilled water as the anolyte, the pH values of 1.0M phosphoric acid as the catholyte (DW-PA system) were not significantly changed owing to the low initial pH value.
iv) With distilled water as the catholyte, the pH values of 1.0M aluminium chloride as the anolyte (Al-DW system) were not significantly affected due to the low initial pH value.
v) The pH values of calcium chloride as anolyte and distilled water as catholyte (Ca-DW system) decreased and increased, respectively because of electrokinetic processing.
vi) The measured pH values of the electrolytes were different from the theoretical values because of low efficiency of the EK system. The formation of bubbles on the electrodes due to electrochemical reactions reduced the effective contact area between electrodes and electrolytes.

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