

Review

Probable electrokinetic phenomena in tropical peat: A review

Afshin Asadi^{1*}, Hossein Moayedi², Bujang B. K. Huat² and Alireza Parsaie³

¹Department of Civil Engineering, Isfahan Science and Research Branch, Islamic Azad University, Isfahan, Iran.

²Department of Civil Engineering, Universiti Putra Malaysia, 43400 UPM Serdang, Selangor, Malaysia.

³Department of Civil Engineering, Khorasgan Branch, Islamic Azad University, Isfahan, Iran.

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Peat is unconsolidated superficial deposits with high non-crystalline colloid (humus) content, constituting the subsurface of wetland systems. Electrokinetic techniques are innovative ground improvement methods for soft soils. Peats have noticeable qualities to make a suitable environment for utilization of electrokinetic techniques, i.e. (i) the saturated mass is a good environment, (ii) the high charge and high specific surface area of the humus increases the presence of cations for a water momentum in an electro-osmotic phenomenon, (iii) the surface charge may cause electro-osmosis to occur, (iv) the decomposition processes affect the electro-osmotic behavior, (v) the resistivity may affect the electro-osmotic behavior. Introducing cations as a bridge between clay and humus surfaces may stabilize the peat from a geotechnical view point. The expectations of this review have to be proven by conducting some electro-osmotic experiments.

Key words: Electrokinetic phenomena, humus, peat.

INTRODUCTION

In recent years, several Electrokinetic (EK) experimental studies have been conducted to find out the feasibility of these techniques on different type of mineral soils (Ozkan et al., 1999; Azzam and Oey, 2001; Alshawabkeh and Sheahan, 2003; Asavadorndejaja and Glawe, 2005). In the case of peat, these processes have not been studied yet. This paper aims to provide a critical review of the fundamentals of electro-kinetics, probable transport in peat, and the possible role of organic matter and mineral portions in EK phenomena.

Based on the American Standard for Testing and Material (ASTM), peat is a soil having organic content of more than 75%. The brownish, fibrous, and partially decomposed peat is termed *fibric* and *hemtic*, and highly humified, black, and powdery peat is termed *sapric*. The variations in peat arise from the variety of plants whose residues contribute to peat formation, and from the environmental conditions in which humification takes place. Alteration in the mineral content, increasing

pressure of overburden, physical transport, geothermal changes, and microbial activities are among the variables which affect the course of humification and produce the diversity observed in peat. The decomposition processes of organic soils are chemical, biological and enzymes. Four types of organic matter exist: (i) humins, (ii) humic acids, (iii) fulvic acids, and (iv) yellow organic acids (Edil and Fox, 2000; Huat, 2004).

The total peat land in the world amounts to about 30 million hectares. In Malaysia, some 3 million hectares of the country's land area is covered with peat. Peats are extremely soft and geotechnically problematic (Huat, 2004). The most chemically active fraction of peat is colloids. Humus is the main colloidal portion of a peat and the mineral portions may be silicate clays, non-crystalline silicate clays, and iron or aluminum oxide.

Most peats have a net negative charge due to negative charges on organic matter and layer silicates, however, some quaternary nitrogen compounds carry positive charges, which can alter the behavior of predominantly negatively charged peat colloids. In summary, in organic matter, non-crystalline silicate clays and iron or aluminum oxide, and gain or loss of H⁺ from functional groups make pH-dependent charges, whereas in crystalline

*Corresponding author. E-mail: afshin.asadi@yahoo.com. Tel: 00983116624961.

silicate portions of a peat; isomorphic substitution leaves a permanent net negative charge (Stevenson, 1994).

Peats have a large surface area (approximately 200 m²), high negative charge, high CEC (100 to 300 cmol⁺/kg) and high water holding capacity (4 to 5 times its mass) (Edil and Fox, 2000). The bulk densities of peats are in the range of 0.8 to 1.2 mg/m³ (Huat, 2004). In Malaysia, the depth of peat ranges from less than 1 m up to 25 m, depending on location (Hooijer, 2006). The high temperatures (up to 32°C) of the tropics have previously been cited as a reason for rapid decomposition processes (Mathuriau and Chauvet, 2002). Tropical peat typically develops at a rate of between 2 and 5 mm per year. The mean annual rainfall in the region ranges from 1,500 mm to over 2,500 mm with approximately 1,750 mm near the coast to 2,750 mm in the inland areas (Yule and Gomez, 2008).

EK phenomenon is defined as the physicochemical transport of charge, action of charged particles, and effects of applied electric potentials on formation and fluid transport in a porous media. The EK phenomena include electro-osmosis, streaming potential, electrophoresis, and sedimentation potential. Electro-osmosis and electromigration play a key role in soil improvement (Acar and Alshwabkeh, 1993; Barker et al., 2004).

Electro-osmosis is defined as a fluid movement with respect to a solid wall as a result of an applied electric potential gradient. Reuss (1809) was the first to discover that water flow could be induced through a capillary by an external electric field (Das, 2008). Several theories have been proposed for electro-osmosis including Helmholtz-Smoluchowski theory, Schmid theory, Spiegler friction model, Buckingham π theory, and ion hydration theory (Gray and Mitchell, 1967). The Helmholtz-Smoluchowski theory is one of the earliest and still widely used models of electro-osmosis.

The theory is based on the assumption of fluid transport in the soil pores due to transportation of excess positive charges in the diffuse double layer towards the cathode. The rate of electro-osmotic flow is controlled by the coefficient of electro-osmotic 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 assumed to be a function of the zeta potential (ζ) of the soil-pore fluid interface, the viscosity of the pore fluid (η), soil porosity (n), and soil electrical permittivity (ϵ). The coefficient of electro-osmotic permeability is given by,

$$k_e = \frac{\epsilon \zeta}{\eta} n$$

While hydraulic conductivity, k_h , is significantly by the pore size and distribution in the medium, k_e according to Helmholtz-Smoluchowski theory is dependent mainly on n and ζ . The value of k_e has been assumed to be constant during the electrokinetic process as long as there is no change in the concentration of ions or pH of

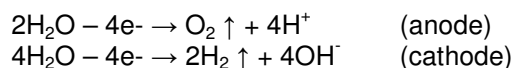
the pore fluid (Gray and Mitchell, 1967). Based on the Helmholtz-Smoluchowski, the ζ and the charge distribution in the fluid adjacent to soil surface play key roles in determining the electro-osmotic flow. The ζ can be measured by microelectrophoresis, the measurement is very direct (Hunter, 1981). The magnitude and sign of the ζ is dependent on the interfacial chemistry of both liquid and solid phase (Eykholt and Daniel, 1994; Vane and Zang, 1997; Yukselen and Erzin, 2008). This potential is also influenced by ion exchange capacity and size of ion radius (Fang and Daniels, 2006). The thickness of the double layer affects the magnitude of ζ (Hunter, 1981).

The Helmholtz-Smoluchowski theory assumes that the pore radii are relatively large compared to the thickness of the diffused double layer and all the mobile ions are concentrated near the soil-water interface. These assumptions are valid as long as soils with large pores are saturated with water. In dealing for small capillaries or unsaturated soils, where the thickness of electric double layer and the water layer radius are of the same order of magnitude, the Helmholtz-Smoluchowski Equation is no longer applicable. The most widely used electro-osmotic flow equation for the under unsaturated subsurface system is proposed by Casagrande (1949):

$$Q = K_e i_e A$$

where, Q is the electro-osmotic flow rate, in m³s⁻¹, k_e is the coefficient of electro-osmotic conductivity, in m²Vs⁻¹, i_e is the applied electrical gradient, in Vm⁻¹ and A is the gross cross-sectional area perpendicular to water flow, in m². In dealing for small capillaries or unsaturated soils, Smoluchowski Equation is no longer applicable.

The application of direct current through the soil specimen induces three mechanisms. The first mechanism is related to reduction and oxidation (i.e. redox) reactions taking place at the electrodes. However, chemically inert and electrically conducting materials such as graphite, coated titanium, or platinum could be used as electrodes to prevent dissolution of electrode and generation of undesirable corrosion produced in the acidic and basic environments. Electrolysis reactions at the electrodes are the second mechanism to take place. Oxidation of water at the anode generates an acid front, while reduction at the cathode produces a base front as described by the following electrolysis reactions;



Within the first few days of processing, electrolysis reactions drops the pH at the anode and increase it at the cathode, depending upon the total current applied (Acar et al., 1990; Acar and Alshwabkeh, 1993).

While the acid generated at the anode advances through the soil toward the cathode by ionic migration

and electro-osmosis, the base developed at the cathode initially advances toward the anode by diffusion and ionic migration. However, the counter flow due to electro-osmosis retards the back-diffusion and migration of the base front. The advance of this front is slower than that of the acid front because of the counteracting electro-osmotic flow and also because the ionic mobility of H^+ is higher than OH^- . Geotechnical reactions in soil pores significantly impact electrokinetic phenomena and can enhance or retard the process. The last mechanism to take place is ion migration. A combination of these three mechanisms could result in physico-chemical reactions including precipitation, dissolution, sorption, and complication reactions in the process (Acar et al., 1990; Alshawabkeh and Acar, 1992; Probst and Hicks, 1993). Using EK techniques to improve peats entails evaluating probable EK phenomena in peats, which provides an excellent context for this study.

PROBABLE ELECTROKINETIC MECHANISMS IN PEAT

Peat-water and probable electro-osmotic flow relationships

Peats generally have a very high water content, which can be in excess of 1500%, compared with mineral soils (sand, silt, and clay) whose values in the field may range between 3 to 100%. Peat soils tend to have a high water content due to their organic contents. The natural water content of peat increases with an increase in organic content (Huat, 2004). Since a saturated soil mass is needed to carry out the electro-osmotic flow, the peat's environment could give it a good sense of the purpose.

In electro-osmotic dewatering, the frictional drag is produced by the movement of hydrated ions. The quantity of these ions depends on the soil CEC. The CEC range of humus is from 100 to 300 $cmol^+/kg$, which is highest amid colloids. The mineral fractions of many tropical regions are dominated by kaolinite, aluminium oxides, and iron oxides. The CEC range of kaolinite and Al, Fe oxides is 5-10 and 2-6 $cmol^+/kg$ of soil, respectively. Therefore, humus is the key component to create a potential ability for a water momentum in electro-osmotic phenomena. Since humus is negatively charged, in electro-osmotic phenomena, the occurrence of a water flow from anode to cathode is expected.

Cations adsorption in peat is highly pH dependent, thus, a precise measure of CEC at soil pH is highly recommended for EK experiments. In fact, the main problem with the measurement of CEC at pH 7 is that it buffers the soil at pH 7, causing large overestimates of CEC for acidic soils (Gillman and Sumpter, 1986; Fang and Daniels, 2006).

There is a direct relationship between CEC and organic matter. CEC increases with an increase in organic

content. The quantity and quality of the charges on peat surface is related to the colloidal portion of peat and the degree of humification (Stevenson, 1994). Therefore, humified peat seems to be a good candidate for electro-osmotic phenomena. Since the CEC of peat soils are fully pH-dependent, a negative permanent charge could be observed at the cathode resulting in a consistent peat water flow from the anode to the cathode.

The retention of water by peat can be considered in terms of reactions of water molecules with the surfaces of peat particles. Water in peat could be classified as: (i) mechanically entrained, (ii) capillary water, and (iii) chemically bound water. From a practical viewpoint, the distinction based on the energy of the water in peat shows that only mechanically entrained and a part of the capillary water can (at least in principle) be removed by mechanical methods (e.g. vertical drains). Electro-osmotic dewatering is effective to extract not only the mechanically entrained and capillary water contents, but also the chemically bound water. Thus as a new idea, using the electro-osmotic technique and vertical drains (electrical vertical drains) could be a winning combination for dewatering peat.

Fibrous peat tends to have a higher mechanically entrained and capillary water content than chemically bound water. In contrast, in humified peat, chemically bound water is considerable. Since electro-osmotic technique is effective in extracting the chemically bound water as well, and since the rapid removal of water from humified peat appears to be difficult due to high disruption, electro-osmotic technique as a slow removal technique in humified peat could be more effective than using electro-osmotic technique in fibrous peat.

Although the water holding capacity of a fibrous peat is higher than a humified peat, but the higher CEC and higher pH of the humified peat by reason of having a higher charge may make a better condition for electro-osmotic phenomena (Asadi et al., 2009, 2011).

Probable electro-osmotic flow and depth relationships

The decomposition processes of organic soils are chemical, biological, and enzymes (Yule and Gomez, 2008). The activity of bacterial enzymes associated with carbon, phosphorus and nitrogen cycling was shown to be highest at the surface and declined markedly with increasing depth of peat (Yule and Gomez, 2008). The pH was found to decrease with increased depth of peat (Yule and Gomez, 2008). Decomposition tends to be most active in neutral to slightly alkaline conditions (Huat, 2004). As a result, higher degree of humification at the surface may make a better condition for electro-osmotic phenomena. Despite a higher degree of humification at the surface, the higher the intensity of rainfall in tropical regions, the higher the infiltration rate through the soil

(Huat et al., 2006). Thus, the cations Na^+ , K^+ , Ca^{+2} , Mg^{+2} , Fe^{+3} , and silica are removed from the topsoil due to leaching. As a result, there might be a tendency for an increase in electro-osmotic flow with depth. However, the degree of humification, and quality and quantity of the ions present in the peat environment are key factors that affect the intensity of electro-osmotic flow.

SENSITIVITY OF PEAT TO PROBABLE ELECTROKINETIC PHENOMENA

In conventional geotechnical engineering; it is assumed that soil parameters such as specific gravity (G_s), liquid limit (LL), plastic limit (PL), and grain size characteristics are constant for a given soil under any environment conditions. However, results in various publications indicate that these parameters are not a constant for a given soil and change when environmental conditions change (Fang and Daniels, 2006). In essence, increasing the pH at the anode leads to greater inter-particle repulsion (and thus smaller particles) while low-pH conditions at the anode could favor aggregation (and thus larger particles). As the pH increases, the grain size distribution becomes skewed toward a finer distribution. Lower pH at the anode may cause thinning of diffuse double layer and flocculation of particles resulting in an increase in undrained shear strength, PL, and LL, while a higher pH at the cathode may cause more negative ζ , thickening of diffuse double layer, and dispersion of particles which results in a decrease in LL and undrained shear strength at the anode. As in peat soils, the charge is fully pH dependent, the sensitivity of peat seems to be more than the minerals by reasons of mentioned reactions. In addition, the CEC of peat soil is high therefore, the movement of ions away from the anode may cause thickening of diffuse layer at the cathode. Since humified peat has a higher quantity and quality of humus in comparison with fibrous peat, it would be more sensitive to pH than fibrous peat. In summary, humified peat sounds make many geo-environmental and -technical surprises under utilization of EK techniques.

PEAT SOIL STABILIZATION

In peats with lower organic content, clay-organic complexes and the formation of the stable aggregates are key components of peat stabilization. Several bonding forces may operate between humus and clay minerals including cation bridging, water bridging, anion exchange, ligand exchange, and Van der Waals (Stevenson, 1994). Since organic anions are normally repelled from negatively charged clay surfaces, adsorption of humus by clay minerals occur only when polyvalent cations are present on the exchange complex.

The main polyvalent cations responsible for the binding of humus to soil clays are Ca^{+2} , Fe^{+3} , and Al^{+3} . The divalent Ca^{+2} ion does not form strong coordination complexes with organic molecules and would be effective only to extend that a bridge linkage could be formed (Stevenson, 1994). In contrast, Fe^{+3} and Al^{+3} form coordination complexes with organic compounds and strong bonding of humus with clay could be possible through this mechanism.

Since the CEC of peat is high, and since the cations Na^+ , K^+ , Ca^{+2} , Mg^{+2} , and silica are removed from topsoil due to leaching, there is a probable higher presence of trivalent ions (Fe^{+3} and Al^{+3}) at the surface peat in tropical regions. Therefore, using the electromigration and injection of trivalent cations could be a winning combination in electro-strengthening of peat soil at the cathode area. In summary, cationic surfactants are expected to flocculate peat through a combination of charge neutralization and bridging, and may be effective dewatering agents. Several studies have been carried out to stabilize soft clays by ionic injection under electric fields (Ozkan et al., 1999; Alshawabkeh and Sheahan, 2003; Asvadorndeja and Glawe, 2005), thus it is due for finding a solution to peat stabilization under electric fields.

PEAT SOIL DECONTAMINATION

Peat has been used to scavenge heavy metals from industrial wastes widely. Organic matter has a key role in chelation of metals such as Fe, Zn, and Cu (Fuchsman, 1986). The pH gradient during EK remediation between the anode and the cathode due to electrolysis of water causes acidic pH at the anode and basic pH at the cathode. Such variations in pH activate changes in the physicochemical properties at the soil-liquid-contaminant interface and may alter the EK properties of a peat soil. Thus the study of surface charge characterizations of organic matter is recommended to understand the mechanism of adsorption and/or desorption of contaminants by peat. Therefore, utilization of electrophoresis in combination with electro-osmosis could be novel challenges to rise.

ENERGY EXPENDITURES

The economics of EK phenomena are governed by energy expenditures. The energy expenditures are determined based on soil electrical resistivity and the applied electrical potential. An increase in soil water content results in a decrease in electrical resistivity (Pozdnyakov et al., 2006). The usual limit of peat resistivity is 5 to 250 Ωm , which is higher than clay (8 to 70 Ωm). As a result, low energy expenditures during the EK experiments are expected. An increase in water content and temperature cause the resistivity of soils to

decrease. A humified peat has higher colloids and consequently a higher charge in comparison with a fibrous peat and as a result, the resistivity of a humified peat could be less than fibrous peat. Furthermore, humified peat is black in color and may attract higher temperature results in having a lower resistivity. In tropical areas, the resistivity of a decomposed peat may be less than cold regime areas because of its higher surface temperature and heavier rainfall.

CONCLUSIONS

Peats have noticeable qualities to make a suitable environment for the utilization of EK techniques. The saturated mass is a good sense of the purpose. The high CEC and high specific surface area could increase the presence of cations for a water momentum in electro-osmotic phenomena. The net negative surface charge may cause electro-osmosis to occur from anode to cathode. The humification processes would improve not only the quantity of the humus's surface charge, but also the quality of the charge which results in a better condition for EK experiments. The high resistivity may make low energy expenditure on processing.

Introducing cations as a bridge between clay and humus surfaces may stabilize the peat from a geotechnical view point. The predictive expectations of this study have to be proven by conducting some EK experiments.

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