

Acid/Base Distributions in Electrokinetic Soil Processing

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The development of pH gradients in the electrokinetic processing of soils is investigated. An analytical model, based on the Nernst-Planck equations, is presented to evaluate the acid/base distributions and the flow patterns generated in electro-osmotic flow. One-dimensional laboratory experiments with Georgia kaolinite demonstrated the validity of the predictions of the analytical model. Effects of the pH gradients on the efficiency of the process and soil properties are discussed. Results of studies are reviewed based on this new understanding of the acid/base distributions.

Electro-osmosis has been of interest to geotechnical engineers for 50 years as an electrochemical processing technique initiated by applying an electrical gradient across a soil mass to generate water flow. The technology has been used successfully to improve the geotechnical properties of fine-grained deposits by dewatering and consolidating (1-4). Studies are being conducted at Louisiana State University to investigate the feasibility of using electrokinetic processing to decontaminate soils from organic and inorganic contaminants. It is essential to investigate the theoretical basis of electrochemically generated material gradients and any subsequent chemistry that may occur in the medium for the practical use of such methods in the decontamination of soils.

Electrokinetic processing of soils or similar porous media by use of a low DC current results in development of electrical, hydraulic, and chemical gradients across the saturated strata. If a uniform concentration of ions is assumed to initially exist throughout a specimen, the application of an electrical potential will create a uniform electric field gradient. Subsequently, the process will result in the movement of ions and associated water molecules under the direct influence of and also because of coupling effects generated by those gradients. Figure 1 presents a schematic diagram of the process and development of those gradients in time. Initially, a constant current and constant hydraulic potential difference are assumed to be applied across a saturated, homogeneous specimen.

Presently available theoretical descriptions of electro-osmosis disregard the existence of any chemical gradients and reactions. However, the existence of a current in the soil implicitly necessitates faradaic reactions at the electrode boundaries. A review of previous studies indicate that those electrochemical effects may significantly affect the results of the process (5). Formation of chemical gradients will depend on the extent of electrolysis and the coupled chemical reac-

tions between the soil and electrolyte products. The importance of pH gradients in electro-osmosis has been noted by several investigators who have recorded the time rate of changes in pH of the pore fluid and mostly at the electrodes (6-12). The general trend is that the pore fluid gets acidic (pH = 1-4) at the anode and basic at the cathode (pH = 10-13). In assessing the chemistry of the medium (e.g., the adsorption and desorption of species on soil substrate), prediction of the development of pH gradients therefore becomes essential.

This paper reviews an analytical model and presents results of subsequent laboratory tests conducted to predict those gradients. Results of studies are reviewed based on this understanding of pH gradients.

ELECTROCHEMICAL REACTIONS AT ELECTRODES

In the absence of all but traces of electrolyzable solutes in the pore fluid (i.e., metal ions, Cl^- , organic matter or pollutants, dissolved oxygen) and for the case of inert electrodes, the approximation of 100 percent faradaic efficiency may be taken for water electrolysis. The primary electrode reactions would then be, at the anode,



and, at the cathode,



The production of H^+ ions at the anode decreases the pH at this electrode by Reaction 1, and the OH^- ion concentration at the cathode leads to a rise of pH. Twice as many water molecules are electrolyzed at the cathode than at the anode for the same quantity of electricity, leading to a chemical gradient of molecular water insignificant at current densities used in experiments. Two supplemental ionic species are generated as a consequence of Reactions 1 and 2 and in addition to migration of existing anions and cations in the pore fluid of the specimen. Those species can complicate further the net transfer of hydrated water or followup chemical gradients during the process or both. In other words, the ions generated in the medium by electrolysis, together with the ionic species available in the pore fluid, may carry a portion of the current depending on concentrations and types.

A variety of theories and models has been proposed to explain the electro-osmotic flow of water (e.g., Hemholz-Smoluchowski, Schmid, and Spiegler friction models), but

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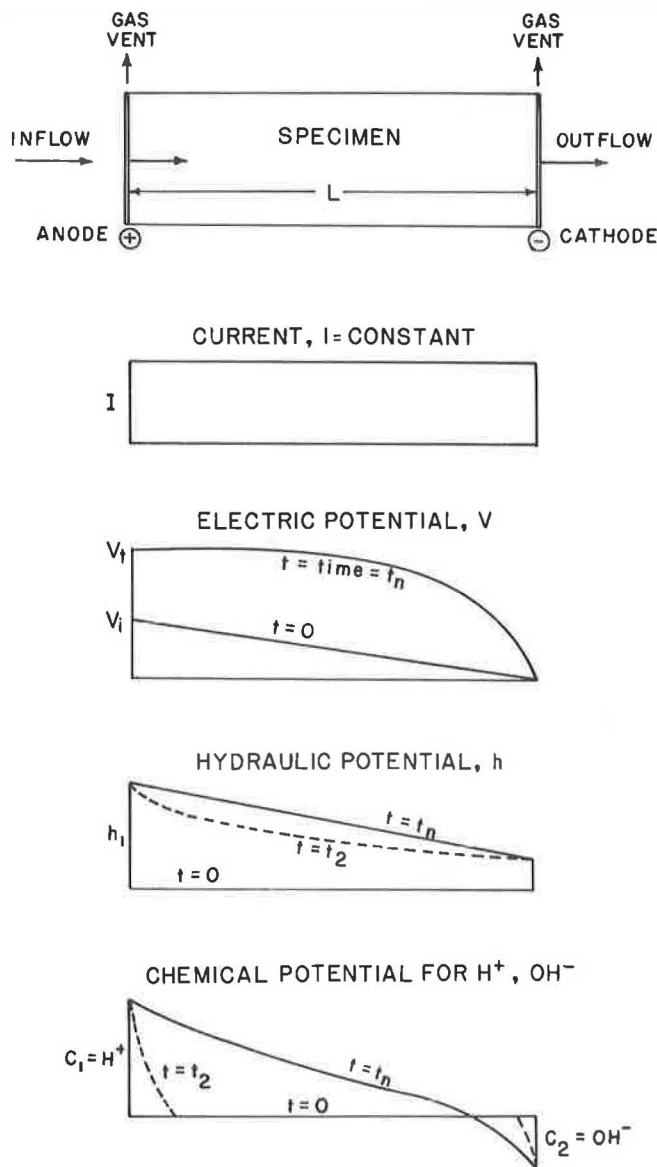


FIGURE 1 Schematic diagram of potential gradients in electro-osmosis (5).

none of those appears to have sufficient generality to account for the full range of behavior found in clay-water-electrolyte systems (13). Those models also largely disregard the electrode product chemistry in the medium and attempt to explain how the electro-osmotic coefficient of permeability, k_e , empirically relating the total flow of water, Q , to the electrical potential gradient in the system i_e could be predicted from the characteristics of the clay mineral, the pore fluid, and the pore sizes in the medium. The physical basis for the water transport can be summarized as follows:

1. Cations that transport their hydrated water sheath toward the cathode (less the transport of the solvated water by the anions to the anode);

2. Moving cations impart a dragging force on the solvent molecules as they move toward the cathode;
3. Displacement of water molecules by colloidal particles that move toward the anode by electrophoresis; and
4. Miscellaneous chemico-osmotic effects as a consequence of electrolysis.

Thus, as a result of electro-osmosis and prevailing electrode reactions, as is illustrated in Figure 2, there will be a movement of cations to the cathode and anions to the anode. Figure 2 depicts qualitatively the amount of water molecules carried by each species depending on their hydration numbers. Hence, the rate of movement, v_i , of each species will depend on the ionic current carried by the species, on the chemical gradients of species produced or removed, and on any local hydraulic and electrical potential gradients present in the system. The hydraulic gradients are either externally imposed on the system or may be internally generated owing to chemical/electrical interactions of the species present or produced with the porous media.

Experimental evidence indicates that the water flow is orders of magnitude (100 to 4,000 moles/Faraday) greater than that possible from transport of the waters of hydration (possibly 1 to 15 moles/Faraday). In addition, physical chemistry models for ionic motion through solvents do not support the existence of any sustained or appreciable drag beyond the immediate hydration sphere for homogeneous systems (open space). Therefore, it is difficult to understand how the large quantity of water flow in porous systems can be explained by basis 1. The analytical model developed by Acar et al. (14) and detailed next does not require a complete quantification of all the contributory factors to electro-osmosis because the Nernst-Planck equations are able to account for all the components of species of transport regardless of the actual phenomenology that produce them.

ANALYTICAL MODEL

It is assumed that constant current and hydraulic potential difference are applied across a water-saturated and homogeneous specimen of clay. It is necessary to assess the product distributions generated by the electrolysis to estimate the boundary conditions generated by the electrode reactions. Acar et al. (5) demonstrated that for currents of the order of milliamperes used in electro-osmosis there will be an ample amount of H_2O flow to sustain the electrolysis and that local convection will be present at electrodes producing gases.

In electro-osmosis the water flow rate q_e is related empirically to the current by (13)

$$\begin{aligned}
 q_e &= k_e(\text{cm}^2/\text{V sec})i_e(\text{V/cm})A(\text{cm}^2) \\
 &= k_e(\text{cm}^3/\text{amp sec})I(\text{amp}) \\
 &= \frac{k_e}{\sigma} I
 \end{aligned} \tag{3}$$

where σ is the conductivity of the pore fluid in mhos/cm, k_e is given in L/amp sec, I in amp, and k_e is the electro-osmotic

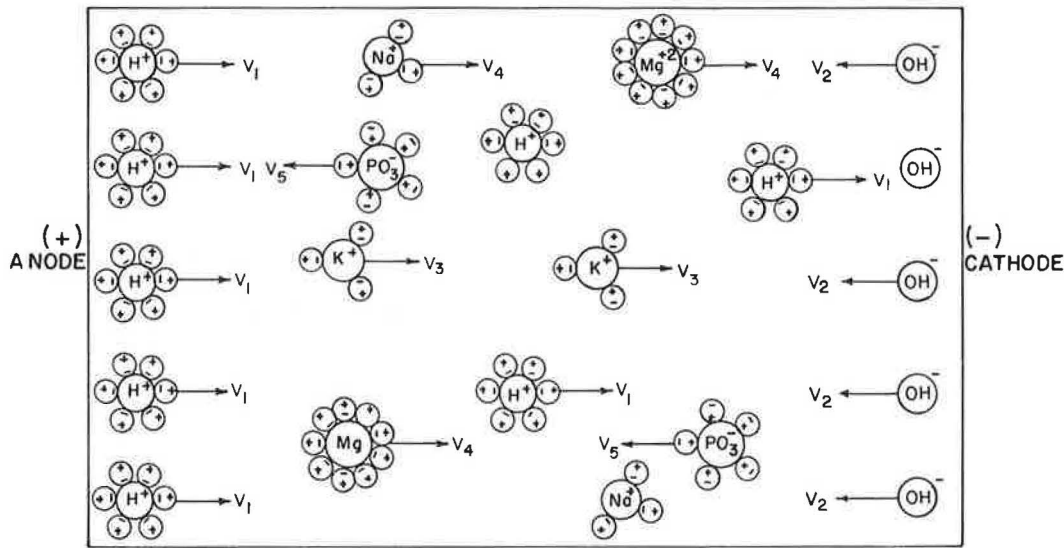


FIGURE 2 Movement of cations and anions in an electric field.

coefficient of permeability. Here, k_i values range between 0 to 1.0×10^{-3} L/amp sec for soils.

If the applied current is I , 2 moles of H_2O needs $4F$ coulombs at anode (Equation 1), and then the rate at which H_2O is lost

$$R_{H_2O}(\text{mole/sec}) = \frac{I(\text{amp})}{(2)(96485(\text{amp sec/mole}))} = I \times (5.18 \times 10^{-6}) \text{ moles/sec} \quad (4)$$

Considering an incremental element at the anode, the instantaneous steady state pH will be estimated as follows:

$$Q_{H^+} = \text{rate of } H^+ \text{ production} = 2 \times R_{H_2O} = (1.036 \times 10^{-5})I(\text{moles/sec}) \quad (5)$$

The net steady state concentration will then be

$$\begin{aligned} \text{molar concentration} &= \frac{Q_{H^+}(\text{moles/sec})}{q_e(\text{L/sec})} \\ &= \frac{(1.036 \times 10^{-5})(\text{moles/amp/sec})}{k_i(\text{L/amp/sec})} \\ &= \frac{1.036 \times 10^{-5}M}{k_i} \end{aligned} \quad (6)$$

For maximum k_i of 1.0×10^{-3} L/amp sec, Equation 6 renders a maximum pH of 2.0 at the anode, which is in conformity with recorded values in previous studies. Interestingly, as the efficiency of the process decreases (smaller k_i values), the pH at the anode will also decrease. Similarly, at the cathode (Equation 2), 4 moles of H_2O need $4F$ coulombs of electrical charge to produce 4 moles of OH^- ion, and, hence, the $[OH^-]$ ion concentration of the solution at the electrode will have a pH of 12.0.

This deliberation is for an aqueous solution where the decomposition of water is the primary result and thus for an anode that does not decompose. Several types of electrodes (aluminum, steel, iron, graphite, bronze, copper, platinum, gold) are used in processing studies. The electrolyzed products of some of those electrodes will introduce other ions in conjunction with the H^+ and OH^- ions and thus can change the chemistry generated at the boundaries. Those ions will complicate the chemistry further by diffusion into the specimen or precipitating or both, depending on the pH of the pore fluid.

MASS TRANSFER IN THE SYSTEM

The total material flux into an incremental element of thickness dx , q_{tc} , is composed of three components:

$$q_{tc} = q_{cc} + q_{ch} + q_{ce} \quad (7)$$

where

q_{cc} = material influx due to chemical gradients,
 q_{ch} = material influx due to hydraulic gradients, and
 q_{ce} = material influx due to electrical gradients.

The concentration of the material (solute), C_j , is defined as the mass of solute per unit volume of solution. The mass of solute per unit volume of porous media is, therefore, (nC_j) , where n is the porosity of the medium (the volume of voids over the total volume of the element). The total mass transfer caused by electrical and material gradients in an electrochemical system, in general, is described by the Nernst-Planck equations (15)

$$q_{tc} = \left[-D_j \frac{\partial C_j}{\partial x} + V_x C_j - \frac{zF}{RT} D_j C_j \frac{\partial \phi}{\partial x} \right] n \quad (8)$$

where

- z = charge on the ion,
- F = Faraday's constant (96,485 coulombs),
- R = universal gas constant,
- T' = temperature ($^{\circ}\text{K}$),
- ϕ = electrical potential,
- D_J = diffusion coefficient,
- x = the flow direction,
- V_x = average seepage velocity = v/n , and
- v = discharge velocity.

The material (solute) flux owing to chemical gradients is given by Fick's First Law:

$$q_{cc} = -D_x \frac{\partial C_J}{\partial x} n \quad (9)$$

where D_x is called the longitudinal dispersion coefficient in a saturated porous media and is composed of two components (16):

$$D_x = \alpha_x V_x + D^* \quad (10)$$

The first term represents the dispersion of the species caused by the average linear seepage velocity in the pores of the medium, and the second term describes the diffusion of the chemical in the pores. Here, α_x is the longitudinal dispersivity dependent on the size and frequency of the pores in the medium (fabric). In fine-grained soils, the contribution of the first term is negligible because of very low seepage velocities, and, hence, the longitudinal dispersion coefficient may be taken equal to the diffusion coefficient (16). The molecular diffusion coefficient D^* in the pore fluid is related to the diffusion coefficient in the free solution by

$$D^* = \rho D_0 \quad (11)$$

where ρ depends on porosity and tortuosity of the medium and varies between 0.13 to 0.49 (17).

The solute flux caused by hydraulic gradients (convection) is directly related to the seepage velocity and, hence, Darcy's law:

$$q_{ch} = \left(k_x \frac{\partial h}{\partial x} \right) n C_J \quad (12)$$

where k_x is the hydraulic conductivity of the medium and h is the hydraulic potential.

Those expressions show that the material flux depends on the diffusion gradients, the convective flow conditions, and the migration contributions of species, respectively. The average seepage velocity of species will be taken as linear, uniform, and equal to the average macroscopic fluid velocity. The migration contribution presented in Equation 8 represents all the ionic species in the medium. For conditions where a dilute aqueous electrolyte is slowly passed through an electro-osmotic cell at a small but constant electrical current, the migration term will be nonlinear in concentration if the electric field $\partial\phi/\partial x$ is not constant or if the species in question carry a significant but varying fraction of the current

anywhere in the bulk solution. Migration effects are usually avoided in electrochemical cells by providing an excess of an inert and supporting electrolyte.

One further simplifying assumption will be made in the following derivation. The electrical field ($\partial\phi/\partial x$) is assumed to be constant in time across the specimen. This assumption may not entirely be valid, because the electrical field in electro-osmotic experiments depends on the concentration gradients imposed by the generated H^+ and OH^- ions and, hence, the specific conductance of the pore fluid in time and space. However, this assumption will be considered valid to provide a first-order approximation to chemical gradients.

These conditions will simplify the total material flux as

$$q_{ic} = \left[k C_J - D^* \frac{\partial C_J}{\partial x} \right] n \quad (13a)$$

$$k = -\frac{zF}{RT} D^* \frac{\partial \phi}{\partial x} + k_x \frac{\partial h}{\partial x} = -k_m + k_h \quad (13b)$$

where k is a constant with units of $[L/T]$ representing the velocity of the pore fluid. The first term represents the contribution to the flow of water molecules caused by, for example, the migration of H^+ ion and its hydrated water molecules under an electric potential gradient, and the second term k_h depicts the contribution to flow caused by the induced or applied hydraulic gradients as a consequence of the electro-osmosis phenomena.

The mass balance across the element requires

$$\nabla q_{ic} = -R \frac{\partial C}{\partial t} n \quad (14)$$

where $(\partial C/\partial t)$ is the rate of mass change, A is the area, and R is called the retardation coefficient, a term representing the adsorption and desorption of different species on clay surfaces or any interactions between the different species leading to precipitation or other chemical reactions or both,

$$R = 1 + \rho_d k_p / n \quad (15)$$

where ρ_d is the dry bulk density of the soil and k_p is the partition coefficient.

The gradient operator ∇ in one-dimensional conditions renders

$$\left(\frac{\partial q_{ic}}{\partial x} \right) = -R \left(\frac{\partial C}{\partial t} \right) \quad (16)$$

When Equations 8–10 and 13 are substituted in Equation 16,

$$D_x C_{,xx} - k C_{,x} = R C_{,t} \quad (17)$$

where $C_{,xx}$, $C_{,x}$, $C_{,t}$ represent partial derivatives in space and time. If the experiments were conducted with a constant hydraulic potential gradient across the specimen, or if it were assumed that the total flow caused by water molecules being transported through the migration of H^+ ions is constant throughout the system, then k simplifies to V_x ,

$$D_x C_{,xx} - V_x C_{,x} = R C_{,t} \quad (18)$$

Equation 18 can be further nondimensionalized by taking

$$X = x/L \quad (19a)$$

$$C^* = 1 - \frac{C}{C_i} \quad (19b)$$

$$P = V_x L / D_x \quad (19c)$$

$$T = D_x t / R L^2 \quad (19d)$$

where L is the length of the specimen and C_i is the initial concentration of the specific species in the bulk solution. In solute transport, P is often called the Peclet number and T is the nondimensional time. When Equations 19 are substituted in Equation 18, the nondimensional form is obtained:

$$C_{,xx}^* - P C_{,x}^* = C_{,T}^* \quad (20)$$

Equation 20 must be solved with appropriate boundary conditions for the initial conditions and process rate to have a first estimate of the pH gradients in electrochemical processing of soils.

The species generated at the inlet and the outlet is different. A constraint exists at the boundary; therefore, when they meet at a location, the following neutralization reaction occurs:



A computer program (DIFFUSE) has been written in FORTRAN based on the given formalism (14).

PREDICTIONS OF THE ANALYTICAL MODEL

Figure 3 presents different pH gradients predicted by the model. Figure 3a presents the case when the pH at the anode and cathode are 2.0 and 12.0, respectively, and when the initial pH of the porous medium is 7.0. The front presented is for diffusion only, and, hence, the acid-base front meets in the middle. A neutralization reaction will occur when those fronts meet. Figure 3b depicts the case when the specimen is initially acidic with a pH of 5.0. Here, the OH^- ion front moves through the specimen. Figure 3c presents the case when the convective flux provides a P value of 30. The acid front moves farther toward the cathode in time and is expected to flush the specimen eventually. The three cases presented indicate that the pH gradient would be a function of

1. The pH values established at the electrodes by the rate of electrolysis: extreme values occur at low k_i (see Equation 6) and, hence, high electrolyte concentrations of productions (see Equation 3);

2. The initial pH of the porous medium;

3. Whether the flows would be governed by solely diffusion of the chemical or by the advection of the bulk fluid flow (P value); and

4. Any adsorption/desorption and precipitation of H^+ and OH^- ions: the effects are included in the retardation coefficient R given in Equation 15.

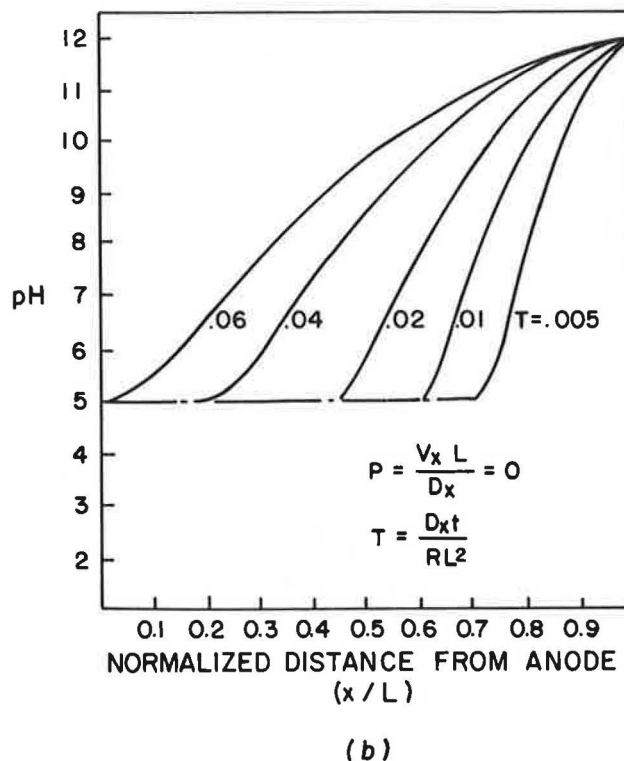
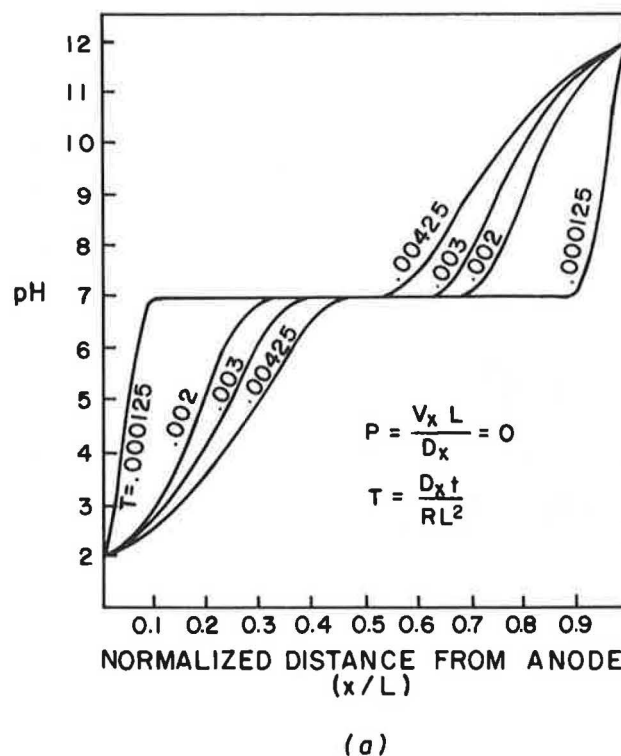


FIGURE 3 pH gradients predicted by the model (5). (a) Diffusive flux only: pH_i (initial) = 7.0, $pH_{inl} = 2.0$, $pH_{out} = 12$; (b) diffusive flux only: $pH_i = 5.0$, $pH_{inl} = 5.0$, $pH_{out} = 12$; and (c) diffusive and convective flux: $P = 30$, $pH_{inl} = 2.0$, $pH_{out} = 12$.

FIGURE 3 (continued on next page)

TABLE 2 SUMMARY OF CHEMICAL ANALYSES OF THE SUPERNATANT

Ion	Molecular Weight	Concentration* (mg/L)
Anion		
SO_4^{-2}	96.1	14.8
Cl^{-1}	35.5	1.6
F^{-}	19.0	0.2
Cation		
Na^{+}	23.0	12.7
K^{+}	39.0	0.4
Mg^{+2}	24.3	0.1
Ca^{+2}	40.0	3.8

* All the ionic species in the system were not analyzed.

length) was removed after consolidation. The sleeve was cleaned, trimmed, and weighed to determine the percent of saturation. The "average water content" in the clay prior to testing was determined by averaging three samples from the top and bottom trimmings.

A schematic diagram of the electro-osmosis cell and the test setup is presented in Figure 4. The glass sleeve containing the consolidated specimens was directly placed in the electro-osmosis cell. Filter paper was placed at the ends of the clay. Carbon electrodes were used for electro-osmosis. To allow flow, 30 to 40 3-mm holes were drilled in those electrodes. Constant current tests were conducted. The current, voltage, effluent pH, and flow were continuously monitored.

The current was turned off at the end of the test, and the glass sleeve was removed. The clay was extruded from the cell and dissected into ten 1-cm-wide sections. A water content sample was taken from each section, and the pH of the soil and the pore fluid was determined.

Determination of pH in Soil

The pH measurements were made by using combination pH electrodes and a pH meter. The meters were calibrated with pH buffers in the range of the measurements to be made.

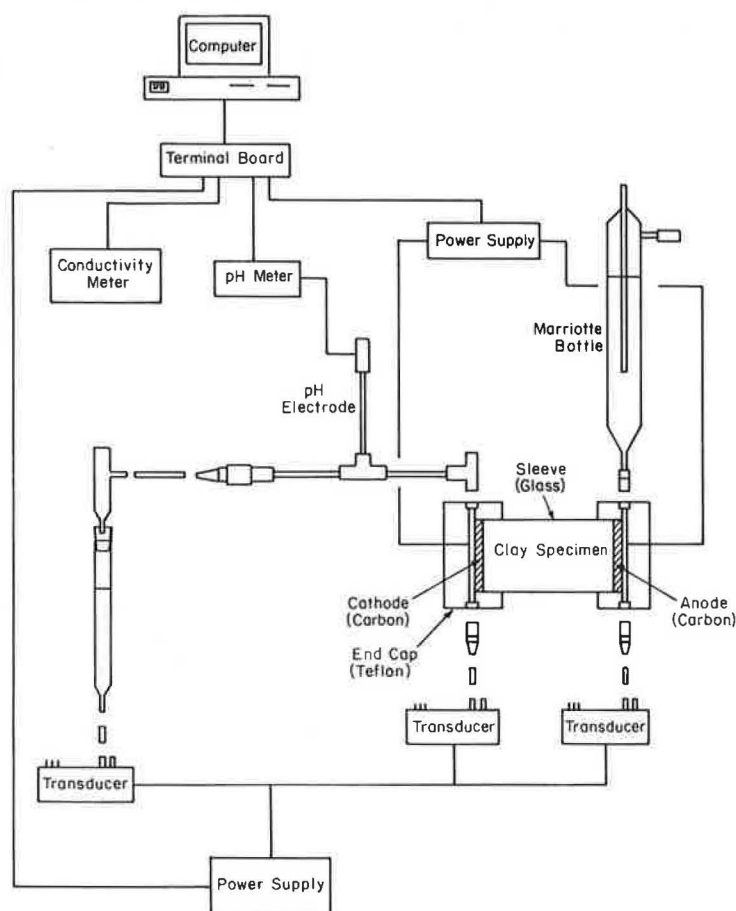


FIGURE 4 Schematic diagram of the test setup.

The pH was determined by two methods: (a) direct measurement of the pore fluid pH after its extraction from the clay by applying hydrostatic pressures to samples from each section by using compressed nitrogen gas and (b) direct measurement of the pH in the specimen. The clay specimen was dissected, as in the first method, and water content samples were taken. The combination pH electrode was immediately inserted directly into the wet clay slices. Putnam (18) demonstrated that in situ pH values thus recorded did not significantly vary for a wide range of water contents. Variations were recorded only at water contents more than 200 percent for the kaolinite used in this study.

ANALYSIS OF RESULTS

Coefficient of Electro-Osmotic Permeability, k_e

The coefficient of electro-osmotic permeability, k_e , varied between 0.80×10^{-5} to 3.0×10^{-5} cm²/V sec in tests conducted in this study. The flow and, hence, k_e , decreased with time of processing.

Coefficient of Water Transport Efficiency, k_i

Figure 5 compares the range of k_i values obtained in this study with previous studies. The initial k_i values were generally within the values obtained in previous studies, and a signifi-

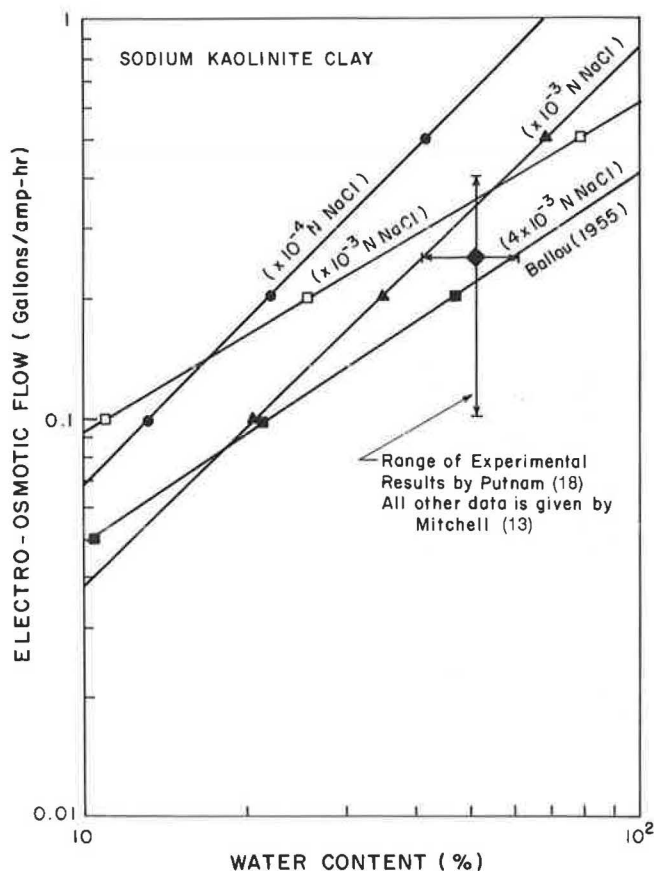


FIGURE 5 Comparison of k_i with previous studies.

cant variation was observed in time. Figure 6 presents the change of k_i with time in selected tests. All tests indicated that water transport efficiency decreases in time after the initial increase (18).

Electrical Potential

Figure 7 presents an example of the voltages measured across the electrodes. The voltage steadily increases in each test and implies an increase in total "apparent" resistance and a decrease in "apparent" conductivity of the system.

The change in all voltages is a consequence of several phenomena. First, H^+ and OH^- ion concentration will steadily increase in the cell owing to the migration of the material fronts and will independently increase the pore fluid conductivity (lower resistance). Separately, any polarization at the electrodes owing to generation of gas bubbles, the decrease in porosity owing to any changes in water content across the cell, and depletion of ionic species will increase those "apparent" resistances. Further, the neutralization reaction at the front where H^+ and OH^- ions meet will result in forming of H_2O molecules decreasing the conductivity of the pore fluid. Figure 7 indicates that factors affecting the increase in resistance are more predominant.

pH Gradient Distributions

Figure 8 depicts a summary of some of the results of pH gradients determined for the 1.0 mA constant current tests

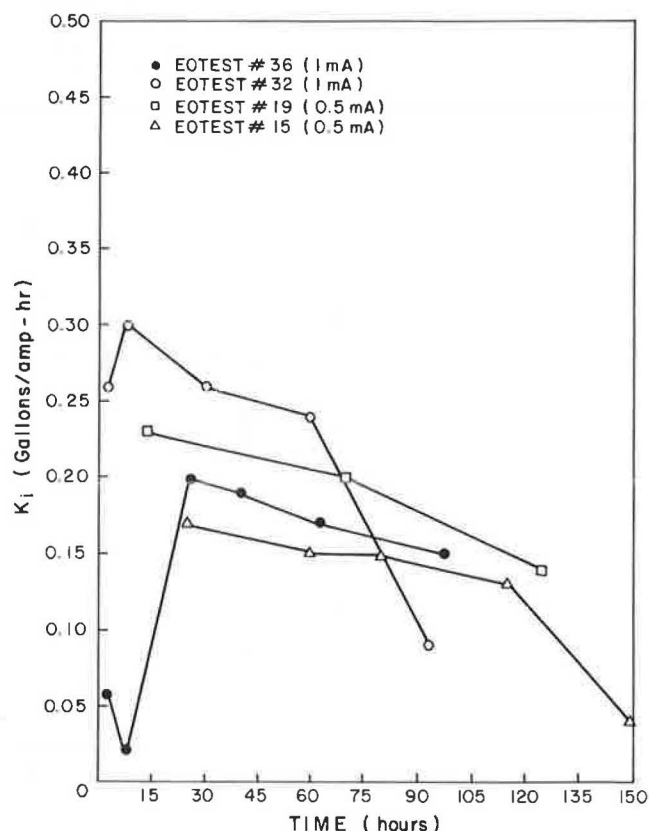


FIGURE 6 Change of k_i in time.

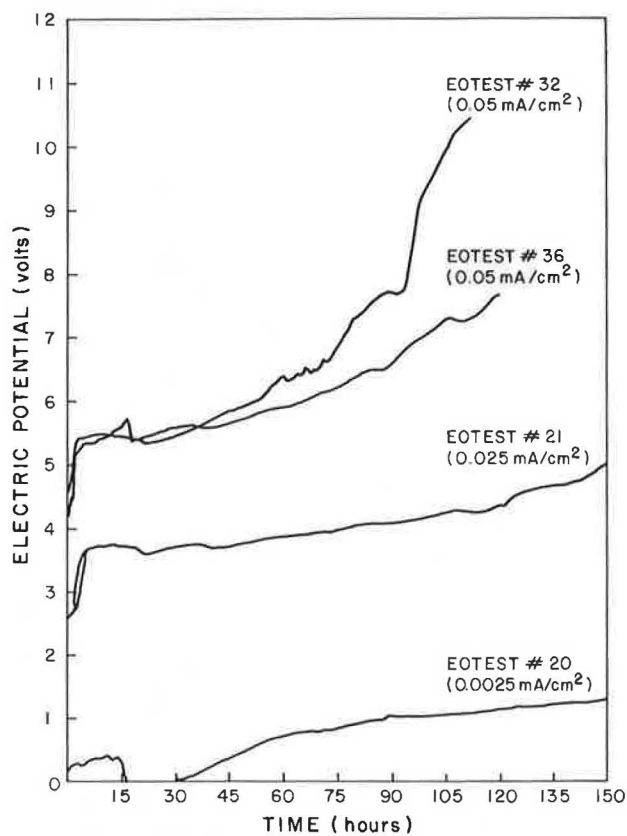


FIGURE 7 Change of voltage in time.

by using the in situ method of pH measurement. The acid front flushes over 75 to 85 percent of the clay specimen in a few hours, and the specimen becomes more acidic with time. The pH profiles obtained in those experiments conform with the predictions of analytical model. The change in pH becomes more pronounced at the discontinuity layer as the treatment time increases.

The movement of the hydrogen ion front through the specimen by diffusion is augmented by the transport of hydrogen ions owing to convection. In addition, water flow at the outlet will help remove some of the hydroxide ions generated from the cathode reaction.

Pore Fluid pH versus In Situ pH

Figure 9 presents a comparison of in situ and pore fluid pH values measured. The pore fluid pH is generally higher than the in situ pH. The difference was predominant in the case when the in situ pH was acidic. Identical values were obtained by both methods (18) in the case when the in situ value was basic. Those results demonstrate that the clay surfaces hold a major portion of H^+ ions by ion exchange equilibria.

Water Content Across the Cell

Figure 10 summarizes the changes in water content across the cell. The average water content line was determined by aver-

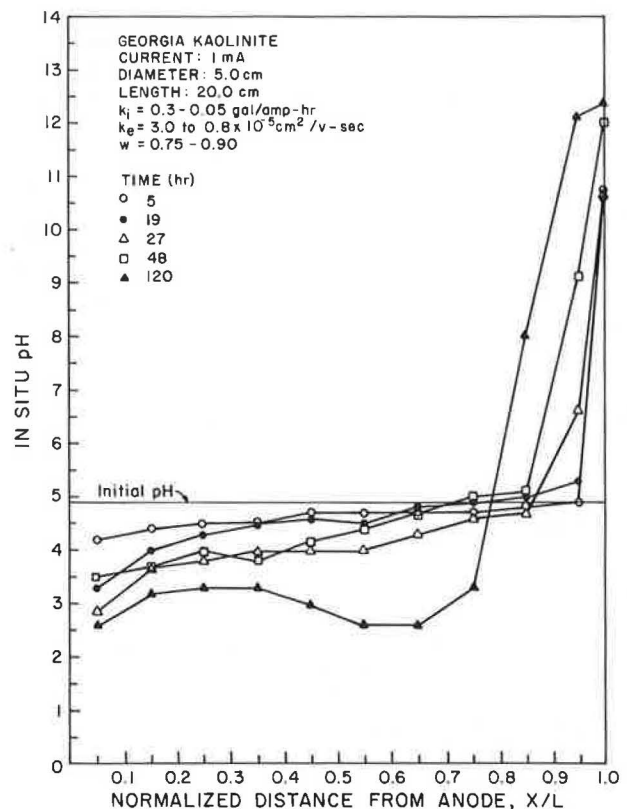
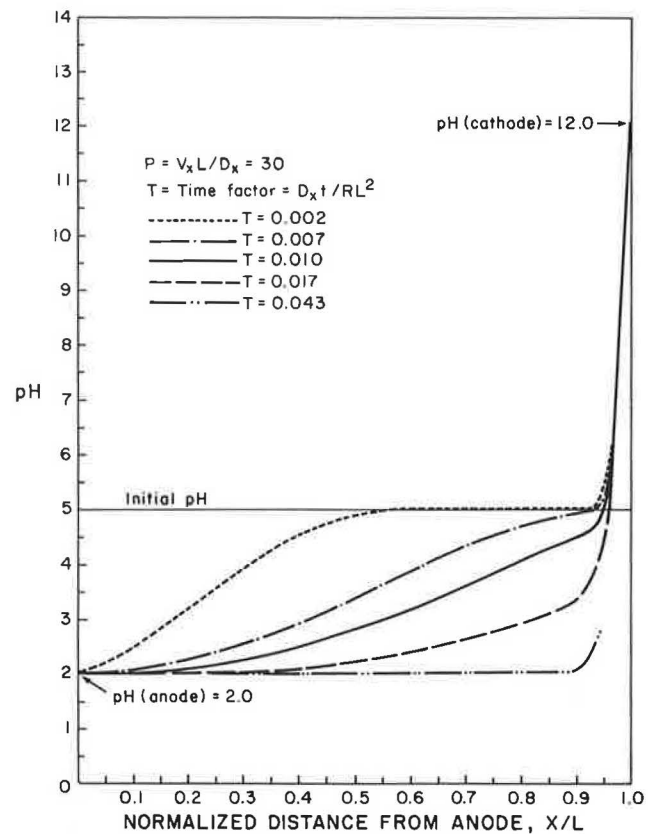


FIGURE 8 pH gradients across the cell.

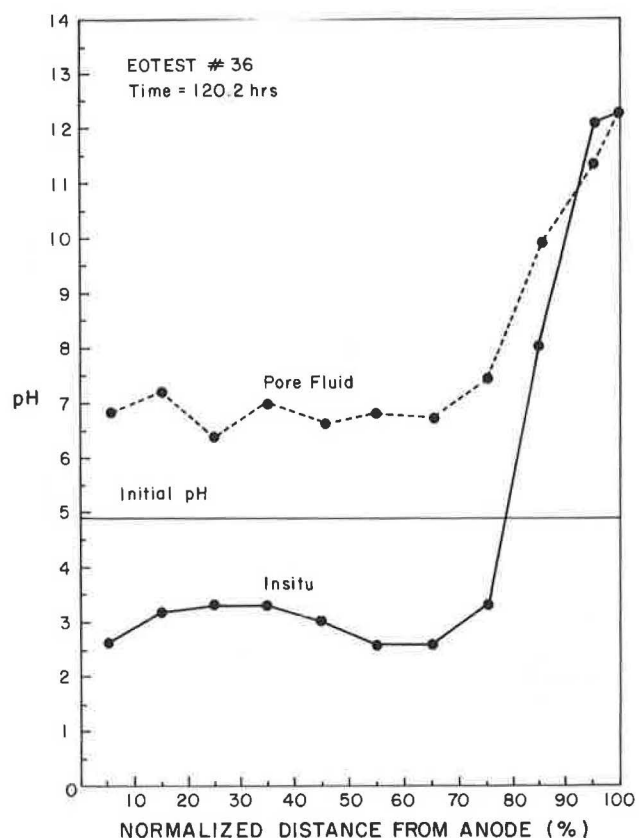


FIGURE 9 Comparison of in situ and pore fluid pH across the cell.

aging three water content samples from the top and bottom trimmings of the specimens after consolidation but before testing. The zero water content line represents a straight-line approximation of the water contents obtained from those trimmings. The zero hour curve indicates that variation in water content exists across the specimen after consolidation and is due to incomplete consolidation under the specified load.

Interestingly, a substantial decrease exists in the water content close to the anode, although open boundary conditions for pore fluid ingress prevail during testing. This decrease in water content implies either an increase in hydraulic potentials or consolidation. Hydraulic potentials may increase across the cell owing to an increase in the osmotic potential by soil chemistry caused by electrolysis products.

DISCUSSION

The interactions of the ions in the pore fluid and the ions generated at the electrodes with the minerals of the porous medium result in physicochemical changes leading to variations in engineering characteristics and mechanical behavior. On the basis of the current state of knowledge (13), the following physicochemical interactions would be expected owing to changes in pH:

1. Dissolution of the minerals beyond a pH range of 7–9;
2. Replacement of H^+ and OH^- ions by exchangeable ions on the clay surface;

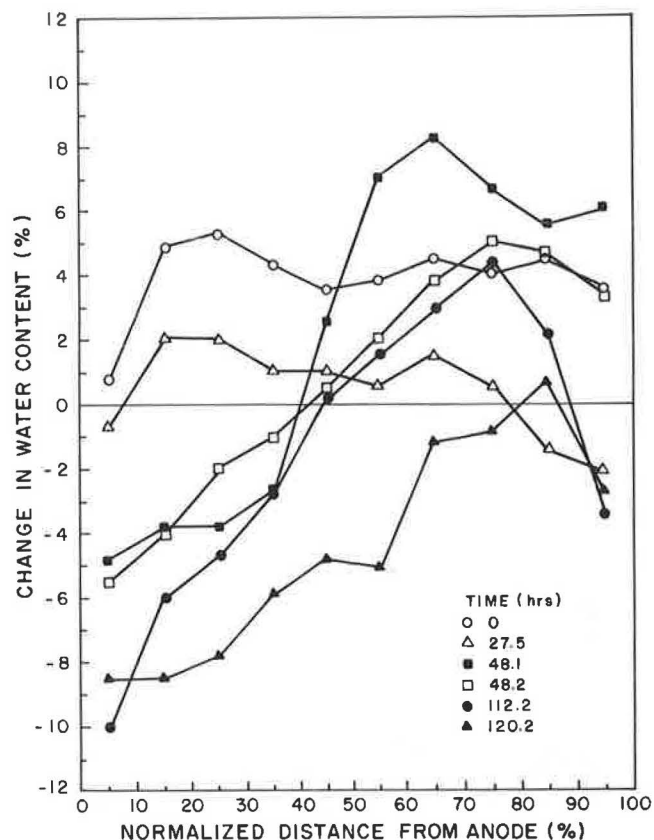


FIGURE 10 Change in water content across the cell.

3. Precipitation of salts and metal ions in high pH environments leading to cementitious products or dissolution of such products at very low and very high pH environments;

4. Changes in the structure of the soil owing to variations in repulsive forces on clay surfaces; and

5. Complications of physicochemical interactions owing to the corrosion products produced at the electrodes.

A review of the previous studies indicates that all those phenomena have been observed in electrochemical processing (5). Esrig and Gemeinhardt (8) and Gray and Schlocker (19) are the only previous studies where pH measurements were reported across the cell in tests conducted with open electrodes at both ends. Esrig and Gemeinhardt conducted experiments that studied the rate at which electrokinetic stabilization takes place in an illitic soil with a pH of about 2.0. The cathode compartment was kept dry during testing. Gray and Schlocker studied electrochemical alteration of clays. In those tests the cathode compartment also was buffered to a maximum pH of 8.0. The original pH of the soil was about 6.0, and the cathode compartment contained a large volume of pore fluid. The results of those studies are summarized in Figure 11. In those tests the base front advances gradually into the cell, similar to the predictions presented in Figure 3b.

The model and experimental studies presented here indicate that different flow and boundary conditions employed in experiments will result in different pH gradients across the cell, leading to significantly different interactions. Therefore, it is essential to monitor and specify the flow conditions and the electrochemical products formed at the boundaries in electrochemical processing of soils.

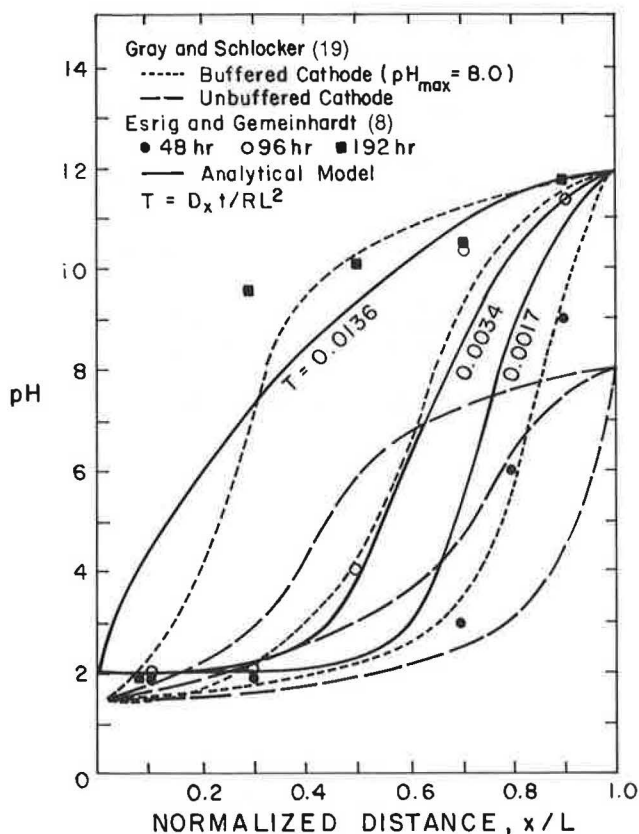


FIGURE 11 Comparison of pH gradients reported in previous studies.

The limitations of the assumptions used in present theories and models in electrochemical processing of soils are that they fail to explain all of the physicochemical effects. It is not yet well established how the chemistry relates to the mechanical behavior, although the studies indicate a strong influence exists on the water flow and soil-pore fluid interactions. An understanding of the chemical interactions in the pore fluid and perception of how diffusion, convection, and migration effects can be better quantified are needed. Further, the acid-base front generated at the electrodes will meet in the specimen accompanying a neutralization reaction, releasing an energy of 10 to 15 kcal/mole. It is yet to be understood how this energy release might affect the observed electro-osmotic flow.

Recent studies by Lockhart (12) indicate that the efficiency of processing is a function of the pH generated at the anode. The most interesting conclusion is that k_i is not usually proportional to the concentrations of ions present, nor to the zeta potential. Those results further substantiate that, as postulated in the analytical model presented here, the electro-osmotic dewatering is a direct current process where the water flow is only a consequence of transport by hydrated metal ions (mechanism a) or drag forces (mechanism b).

CONCLUSIONS

The following conclusions are made:

1. Electrochemical processing of soils has the potential to be used as a method of decontamination, an efficient pumping

mechanism, or as an opposing gradient to flows from storage facilities.

2. The theory and model presented provide the rational basis in developing a better understanding of the electrochemistry associated with the process.

3. pH gradients lead to the physicochemical interactions in the soil and dominate the ion flow associated with the applied current in a low ionic strength media.

4. The presented analytical model and experimental results indicate that different flow and boundary conditions in electrochemical processing will result in different pH gradients, leading to different soil-pore fluid interactions.

5. Acid generated at the anode moves into the specimen by both diffusion and convection in open flow conditions.

6. Tests indicate that the efficiency of the process and water flow decrease with time of processing. Specimens consolidate under open flow arrangements in electro-osmosis.

The relationship of the chemistry generated by the electrodes, and the observed mechanical behavior, flow, and physicochemical changes, are not yet well understood. The potential use of electrokinetic processing of soils can be enhanced if the fundamental understanding of those issues is developed.

ACKNOWLEDGMENTS

This study is funded by the Board of Regents of the State of Louisiana under the Research Enhancement and Development Program by Grant LEQSF-RD-B-10(86-89). The funds provided by this agency are gratefully acknowledged. Harold Olsen is acknowledged for his valuable suggestions in this study.

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Publication of this paper sponsored by Committee on Physicochemical Phenomena in Soils.