

Development of pore pressures by nonuniform electroosmosis in clays

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Abstract

A theory is presented for the development of nonuniform pore pressures during electrokinetic treatment caused by local deviations in the electric field intensity and soil surface chemistry. The electric field intensity and surface (zeta) potential are the driving parameters for electroosmosis in any local soil region; when these parameters vary with space, there is a nonuniform driving force that must be balanced by a decrease or increase in local pore pressure. The theory is derived for the case of a rigid capillary, and is based on the assumptions of incompressible flow, negligible consolidation, the Helmholtz–Smoluchowski equation, and constant hydraulic conductivity. Comparisons of the theory with laboratory measurements made by Eykholt in 1992 are presented for one-dimensional electroosmotic flow through saturated kaolinite plugs. Measurements of the net electroosmotic flow rate, pore pressure and electrical potential profiles, and hydraulic conductivity, can be used to assess, at least qualitatively, the relative contributions to electroosmosis in soil regions along the profile. The k_{e0} profile simulations provided here did not correlate well with measured chemical profiles. Future success of the simulation strategy will likely depend on two factors: accurate electric field measurements and electrokinetic characterization of soil sections. © 1997 Elsevier Science B.V.

Keywords: Electroosmosis; Pore pressure; Kaolinite; Electrokinetic testing

1. Introduction

It is possible for pore pressures to develop within a saturated and freely draining soil as a result of nonuniform electroosmotic driving forces. For instance, consider a soil plug prepared in a rigid tube with freely draining ends, with no initial excess pore pressure within the soil and no net hydraulic gradient. If an electric field is applied across the soil and if there are nonuniformities in the local electric field intensity and/or surface chemistry, pore pressures will develop within the soil. The electric field intensity and surface (zeta) potential are the driving parameters for electroosmosis in any local

soil region; when these parameters vary with space, there is a nonuniform driving force (local fluid momentum) that must be balanced by a decrease or increase in local pore pressure. This can happen when the net pressure drop is zero and when there is no consolidation of the porous media. The magnitude of the pressure increases with increasing spatial nonuniformity in the driving force and with decreasing hydraulic conductivity. The purpose of this paper is to reveal the fundamentals and possible utility of this novel phenomenon. This discussion will be focused on the theory and laboratory measurements of one-dimensional electroosmotic flow through saturated kaolinite.

2. Background and theory

2.1. Early electroosmosis experiments

One important result shown by Esrig [1] was that excess pore pressures (negative or positive) could be developed in an incompressible material during electroosmosis if the voltage drop was nonlinear, even if the boundaries were freely drained. Mise [2] measured pore pressures in a saturated kaolinite with freely draining boundaries as low as -29 kPa. He suggested that the high negative pore pressures were due to an imbalance of pH in the soil (ranging from pH 2 to 12). He based this conclusion on his observations that the electroosmotic flow for kaolinite at pH 10 was nearly five times greater than the flow for kaolinite at a pH near 2. Sample pore pressure profiles from Mise [2] and Esrig [1] are shown in Fig. 1. It is interesting to note that the maximum suction developed in the Boston clay was much less than that of kaolinite, most likely due to the lower charge dependency on pH of the Boston clay. Casagrande [3] had carefully measured pore pressures developed during closed-boundary electroosmosis experiments—and had also observed nonuniform pore pressure profiles. These indepen-

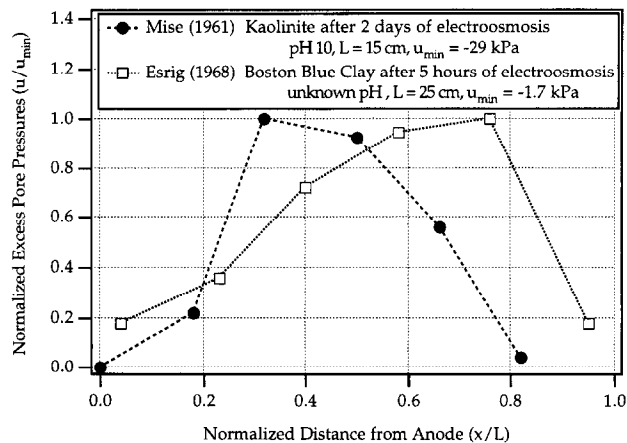


Fig. 1. Sample normalized excess pore pressure profiles (suctions) from electroosmosis experiments on freely drained clays: experiments of Mise [2] and Esrig [1].

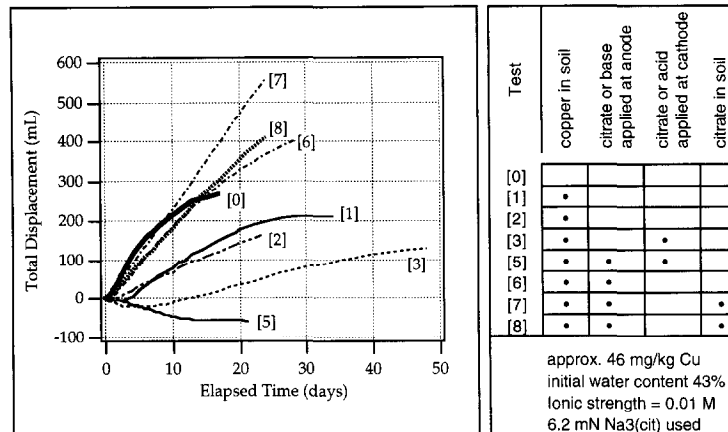


Fig. 2. Impact of system chemistry on records of electroosmotic flow toward the cathode in copper kaolinite specimens [4,5]. Note: 5.0V dc was applied across 20cm specimens ($A = 20 \text{ cm}^2$), 5.5 V dc for test 0.

dent results of Casagrande, Mise and Esrig can be used to suggest that pore pressures will develop if the driving forces for electroosmosis are nonuniform within the sample.

2.2. Tests on copper kaolinite

A series of electroosmosis tests on copper kaolinite were performed by Eykholt [4] and also reported by Eykholt and Daniel [5]. The electroosmosis was found to be quite sensitive to chemical features of the system. A summary of the records of electroosmotic displacement for several of the electrokinetic tests is shown in Fig. 2. The most dominant effect was that of pH, but copper and citrate also had significant effects. The electrokinetic flow was greatest in cases in which the pH in the soil was highest, in the case when the kaolinite was free of copper, and in the case in which citrate had been added to the kaolinite. Adding acid or citrate at the cathode had a negative effect on electroosmotic flow toward the cathode. In tests on kaolinite prepared with copper and without citrate, the flow was much less than that of other cases. The flow was typically slow or even negative (toward anode) during the early stages of testing for these cases. The only exception was test 6, a test in which citrate was added solely to the anode reservoir. The flow response for this test was roughly equivalent to the case without copper. The flow was greatest for the tests with copper, initial citrate, and citrate treatment at the anode (tests 7 and 8).

Pore pressures developed as a result of nonuniformities in the electric field and surface chemistry during these electroosmosis tests. The pressures were generally negative (suctions) and the profiles were similar in shape to the result shown by Esrig [1] and displayed in Fig. 1. The minimum pore pressure (maximum suction) for each test is plotted against the corresponding flow rate in Fig. 3. The pore pressures were generally less than $\pm 0.5 \text{ kPa}$ at the beginning of testing but fell to nearly -30 kPa in the case of the highest flow rate. The minimum pore pressures clearly decreased with flow rate for specimens prepared with copper and for flow toward the cathode. Pore

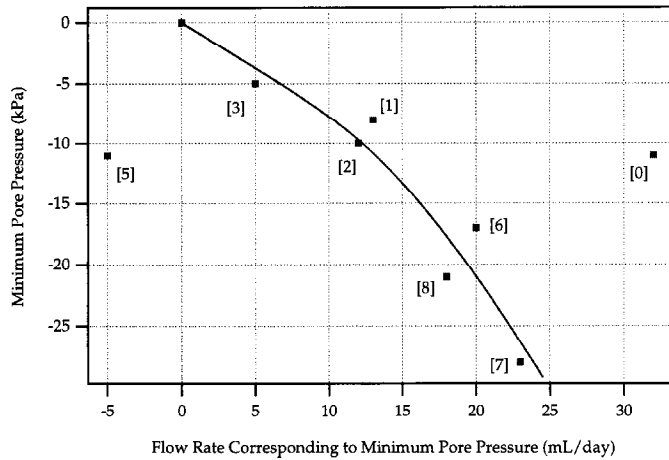


Fig. 3. Range in minimum pore pressure (maximum suction) corresponding to electroosmotic flow rate for a range of tests on copper kaolinite plugs of varying chemistry (see caption and key for Fig. 2). Trend curve shown for specimens prepared with copper and for flow toward cathode.

pressures were less for specimens prepared without copper and for flow toward the anode (tests 0 and 5, respectively).

Pore pressure profiles for one kaolinite specimen (test 0) are shown in Fig. 4. Pressure measurement at one port was impaired by a leak, but the general trends for pressure development can also be inferred from the profile of final water contents, shown in Fig. 5. Significant consolidation occurred in the zones of greatest suction, and the shapes of the water content and pore pressure profiles were similar. Here the consolidation was induced by the electroosmosis-induced suctions. However, the pore pressures developed by the nonuniform electroosmosis would not dissipate if the electroosmotic conditions remained the same, implying somewhat of an equilibrium condition [6]. This means that, although pore pressures were not uniform, the general

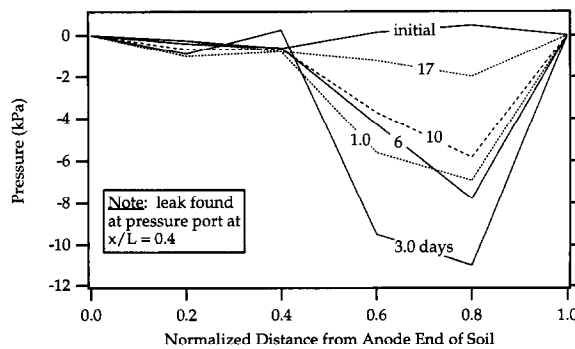


Fig. 4. Nonuniform pore pressures developed along kaolinite specimen from nonuniform electroosmosis (no copper present, test 0).

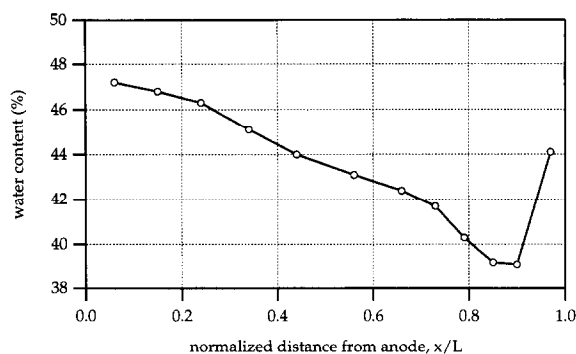


Fig. 5. Changes in water content along kaolinite specimen by consolidation from nonuniform electroosmosis (initial water content 45.5%, no copper present, test 0).

nature of the pore pressure profile will be maintained as the driving forces which caused the nonuniformity are maintained.

A more quantitative reasoning for the development of these nonuniform pore pressures will be discussed in context of the theory and modeling results. Experimental details of these tests have been described by Eykholt [4]. The principal contribution of this work is to extend the theory of electroosmotic pore pressure development for cases of nonuniform chemistry (reflected by local variations in k_{eo}). However, the key equations are also reduced to exhibit consistency with earlier work.

2.3. Theory of nonuniform electroosmosis and pore pressure development

Anderson and Idol [7] used a spatial average modification of the Helmholtz–Smoluchowski equation to describe electroosmotic flow velocity in a constant diameter capillary with a nonuniform electric field intensity E_x and a nonuniform zeta potential ζ . Eykholt and Daniel [5] and Shapiro et al. [8] applied this relationship for the electroosmosis velocity (\bar{v}_x) and flow rate (q_{eo}) in a clay plug in terms of the phenomenological coefficient k_{eo} ,

$$\bar{v}_{eo,x} = \frac{q_{eo}}{A} = \langle k_{eo}(x) E_x(x) \rangle, \quad (1)$$

where the quantity in the brackets, $\langle k_{eo}(x) E_x(x) \rangle$, denotes a spatial average over the length of the clay plug with cross-sectional area A .¹ Assumptions used for the derivation of this equation include those of the Helmholtz–Smoluchowski equation and are discussed by Anderson and Idol [7] and by Eykholt [4].

The pore pressures in an incompressible porous material of constant fluid density can be estimated through the use of a volumetric flow rate balance, and the coupling can be

¹ Sign conventions: $E_x = -dV/dx$ (positive for potential loss dV from anode to cathode), ζ is negative and k_{eo} is positive for negative surface charge, x increases from anode to cathode. See Eq. (15) for the relationship between ζ and k_{eo} .

described by the theory of irreversible thermodynamics [9–11]. The bulk flow rate is balanced by the hydraulic and electrokinetic contributions,

$$\frac{q}{A} = -\frac{k_h}{\gamma_w} \frac{dP}{dx} + k_{eo} E_x, \quad (2)$$

where k_h is the hydraulic conductivity (m s^{-1}), γ_w is the unit weight of water, and P is the pore pressure. If k_h is constant, the flow rate balance may be expressed in terms of the pressure gradient, and Eq. (1) can be substituted to obtain

$$\frac{dP}{dx} = \frac{\gamma_w}{k_h} \{k_{eo} E_x - \langle k_{eo} E_x \rangle\}. \quad (3)$$

This expression can be integrated over the length to obtain the pressure at any point, $P_{(x)}$, in terms of the pressures at the boundaries. An imposed hydraulic pressure gradient ($\Delta P_{\text{imposed}}$) can be superimposed to obtain

$$P_{(x)} - P_{(0)} = \frac{\gamma_w}{k_h} \left\{ \int_0^x k_{eo} E_x dx - \langle k_{eo} E_x \rangle x \right\} + \{\Delta P_{\text{imposed}}\} \frac{x}{L}. \quad (4)$$

If either electrode boundary is closed to flow and no external hydraulic pressures are imposed ($\Delta P_{\text{imposed}} = 0$), the solution becomes

$$P_{(x)} - P_{(0)} = \frac{\gamma_w}{k_h} \int_0^x k_{eo} E_x dx. \quad (5)$$

With constant k_{eo} with distance x , Wan and Mitchell [6] and others [1,3] have shown that the pressures can be defined by

$$P_{(x)} - P_{(0)} = \frac{\gamma_w k_{eo}}{k_h} \int_0^x E_x dx = \frac{\gamma_w k_{eo}}{k_h} (V_{(0)} - V_{(x)}). \quad (6)$$

The following solutions for pressures at the electrodes (Eqs. (7) and (8)) apply for the cases of closed anode and closed cathode, with the other electrode open to flow (uniform k_{eo}):

$$P_{(0)} = -\frac{\gamma_w k_{eo}}{k_h} (V_{(0)} - V_{(L)}) \quad (\text{anode closed, } P_{(L)} = 0); \quad (7)$$

$$P_{(L)} = +\frac{\gamma_w k_{eo}}{k_h} (V_{(0)} - V_{(L)}) \quad (\text{cathode closed, } P_{(0)} = 0). \quad (8)$$

These trends for uniform k_{eo} and E_x are shown in Fig. 6. Cases for pore pressure development with the nonuniform product $k_{eo} E_x$ and closed boundaries can be found through integration of Eq. (5).

A similar expression to Eq. (3) can be obtained from a momentum balance on an incompressible, nonuniformly charged capillary of radius a [4]:

$$P_{(z)} - P_{(0)} = \frac{8 \varepsilon F (\kappa a)}{a^2} \left\{ \langle \zeta_z E_z \rangle z - \int_0^z \zeta_z E_z dz \right\} + \{\Delta P_{\text{imposed}}\} \frac{z}{L}. \quad (9)$$

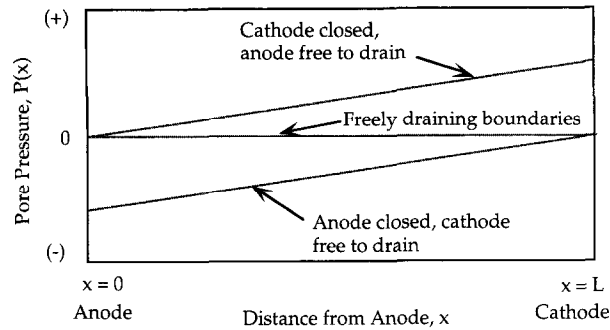


Fig. 6. Nature of pore pressure development during electroosmosis for linear potential drops, uniform k_{eo} , and various drainage conditions.

The parameter ε is the permittivity of the liquid (constant for low frequency, constant temperature), κ is the inverse Debye length, ζ_z is the zeta potential as a function of distance z , and E_z is the electric field intensity as a function of z . Note that the pressure predicted from Eq. (9) is independent of fluid viscosity. The function $F(\kappa a)$ is the Rice and Whitehead electroosmosis correction factor, explained below.

One limitation of the Helmholtz–Smoluchowski equation is that it is limited to relatively thin double layers (large values of κa). Rice and Whitehead [12] have presented a modified solution for electroosmotic flow in a uniform capillary, appropriate for low ζ ($|\zeta| < 25$ mV):

$$v_{eo,z} = - \frac{\varepsilon \zeta E_z}{\eta} F(\kappa a), \quad (10)$$

where the correction factor $F(\kappa a)$ is defined as

$$F(\kappa a) = \left[1 - \frac{2}{\kappa a} \frac{I_0(\kappa a)}{I_1(\kappa a)} \right], \quad (11)$$

where I_0 and I_1 are modified Bessel functions of zero and first order, respectively. The Rice–Whitehead correction can be used to consider the impact of ionic strength on the effectiveness of ζ . As the ionic strength or capillary radius increases (large values of κa), $F(\kappa a)$ approaches 1.0 and Eq. (10) approaches the Smoluchowski result. At low ionic strength, overlapping double layers may result, and $F(\kappa a)$ is reduced. Values of $F(\kappa a)$ are 0.11, 0.64, 0.81, 0.90 and 0.96 for κa values of 1, 5, 10, 20 and 50, respectively. A similar relationship was drawn for electroosmosis in a narrow slit by Burgreen and Nakache (as cited by Hunter [13]). Their correction factor for low ζ is

$$F(\kappa h) = \left[1 - \frac{\tanh(\kappa h)}{\kappa h} \right], \quad (12)$$

where $2h$ is the height of the slit. For a κh of 10, $F(\kappa h)$ is approximately 0.90.

While the incompressible capillary is a useful model, it may not be the best choice for advanced modeling of electroosmosis in porous media. Kozak and Davis [14]

criticized capillary tube models for electroosmosis in porous media. Tube models “are physically unrealistic for concentrated suspensions and porous media in which the flow more closely resembles flow over a suspended particle”. They developed a model which considers a packing of a ‘swarm’ of spheres. The characteristic flow could be described by a unit cell technique. They found that the Smoluchowski result was obtained for low $|\zeta|$, moderate porosity, and moderate values of κa . For instance, the Smoluchowski result was obtained up to a potential near 50 mV, for a porosity of 0.5 and κa of 50. The Rice–Whitehead correction factor may serve as a good approximation for the more exact result of Kozak and Davis [14]. For instance, for $\kappa a = 20$, unit porosity, the correction is ~ 0.83 , or 5% below the Rice–Whitehead correction. Therefore, so long as $|\zeta|$ is kept low, the capillary model should provide a reasonable estimate of the electroosmosis and pore pressure development.

2.4. Unifying capillary model with phenomenological parameters k_{eo} and k_h

It is useful to unify the capillary model with the more commonly used equations expressed in terms of the phenomenological parameters k_{eo} (electroosmotic permeability) and k_h (hydraulic conductivity). The conversion requires the incorporation of three main elements: the effective porosity n_e for velocity terms, the tortuosity τ for changes in coordinate systems, and the assumptions of equivalent flows driven by electroosmosis or hydraulic gradient. Bear [15] defines the tortuosity as the square of the ratio of lengths of the specimen (x -coordinate) to that along the flow path (z -coordinate):

$$\tau = \left(\frac{L}{L_e} \right)^2 < 1.0. \quad (13)$$

The hydraulic-driven flow in a capillary is described by Poiseuille’s equation, and this can be related to Darcy’s law to yield

$$\frac{k_h}{\gamma_w} = \frac{a^2 n_e \tau}{8\eta}. \quad (14)$$

Electroosmotic flow from the capillary model can be related to k_{eo} to yield

$$k_{eo} = \frac{-\varepsilon \zeta_x n_e \tau}{\eta} F(\kappa a). \quad (15)$$

These relationships can be used to verify that Eq. (4) is equivalent to Eq. (9), providing a useful link between the phenomenological and more fundamental methods.

2.5. Use of electric potential and pore pressure profiles to infer changes in k_{eo}

Since nonuniform profiles of k_{eo} and E_x were shown to result in nonuniform pore pressure profiles, it is also possible to show how one might use measurements of electroosmotic flow and profiles of pore pressure and electric field to infer the nonuniform profiles of $k_{eo(x)}$. The nature of the electric potential and pressure profiles can be used to assess, at least qualitatively, the efficiency of electroosmosis in various

soil regions along the profile. Eq. (3) can be modified to include an imposed pressure gradient and rearranged to obtain

$$k_{\text{eo}(x)} E_x = \langle k_{\text{eo}} E_x \rangle + \frac{k_h}{\gamma_w} \left[\frac{dP}{dx} - \frac{\Delta P_{\text{imposed}}}{L} \right]. \quad (16)$$

Substituting Eq. (1) and rearranging, one obtains

$$k_{\text{eo}(x)} = \frac{\bar{v}(x) + \frac{k_h}{\gamma_w} \left[\frac{dP}{dx} - \frac{\Delta P_{\text{imposed}}}{L} \right]}{E_x}. \quad (17)$$

All right-hand-side terms are measurable or known at various values of x . For cases where the pressure profile dP/dx equals the average, imposed pressure gradient, the product $k_{\text{eo}} E_x$ is a constant over the profile. This solution (Eq. (17)) was derived with some significant assumptions, mainly that the value of hydraulic conductivity is independent of both the position along the specimen and the amount of electroosmosis. The derived expression for the pore pressure profile also relies on the following assumptions: incompressible flow, validity of the Helmholtz–Smoluchowski equation in each region, negligible surface conductivity, one-dimensional flow, and uniform boundary conditions. The electric field intensity E_x and the pore pressures must be measured sensitively over the profile, otherwise the inferred k_{eo} values will be largely an artifact of the measurement error. These errors may be the largest in regions where the gradients of pressure and voltage are lowest.

3. Modeling and test methods

Two different series of modeling simulations were performed, one based on an earlier capillary model discussed by Eykholt and Daniel [4,5], and the other based on Eq. (17) using experimental results of Eykholt [4]. The capillary model simulations were based on Eq. (9). Profiles for pH and E_x were determined from a finite difference electrokinetic transport model.

The general scheme of the model was to predict the changes in pH profile as a result of the electrokinetic treatment, using empirical relationships to indicate how electroosmotic driving parameters E_x and ζ would vary. Once the pH in the profile was estimated, values for ζ were determined from an empirical relationship, a fit to the streaming potential results of Lorenz [16]:

$$\zeta \text{ (mV)} = -38.6 + 281 e^{-0.48\text{pH}}. \quad (18)$$

The values for electrical potential were derived empirically, largely to fit experimental potential measurements. The spatial average product $\langle \zeta_x E_x \rangle$ was used to recalculate the flow rate, and the migration of acid and base was predicted by the advection–dispersion equation. The porosity, tortuosity and capillary radius were assumed to be 0.58, 0.67 and $0.2 \mu\text{m}$, respectively [4]. The Rice–Whitehead correction was considered negligible ($F(\kappa a) > 0.97$). The magnitude of pore pressures was very sensitive to the

assumption of capillary radius, but these conditions led to an equivalent hydraulic conductivity of $\sim 2.0 \times 10^{-8} \text{ m s}^{-1}$.

The other series of simulations was used to reveal how k_{eo} may vary spatially; this was based on Eq. (17) and experimental results for electroosmotic flow and profiles of pressure and the electric field. The experiment used was test 8, a kaolinite prepared with copper citrate and tested with anode reservoir conditioning of sodium citrate (also called EKCHEM-8 in ref. [4]). The average electroosmotic velocity, \bar{v} , for this test was $9.9 \times 10^{-8} \text{ m s}^{-1}$ and was relatively constant over the 23 days of testing. The applied $\langle E_x \rangle$ was 25 V m^{-1} over a 0.20 m plug (therefore, $k_{eo} = 4.0 \times 10^{-9} \text{ m}^2 (\text{V s})^{-1}$). The hydraulic conductivity measured for a similar specimen was $1.0 \times 10^{-9} \text{ m s}^{-1}$.

The pore pressures in the soil and at the ends were measured by pressure transducers. Solid state, differential pressure transducers used in this study required a 5 V dc excitation voltage, and the output was a direct voltage in the order of millivolts. The transducers were supplied by Motorola Company (MPX series), and were calibrated before and after an experiment with columns of water at 25°C. The resulting calibration curves were linear, with a least-squares coefficient of correlation typically above 0.998. The sensitivity in the pressure measurements was near to $\pm 0.1 \text{ kPa}$. The pressure transducers and connected tubing were filled with deaired–distilled water, and the tubing was inserted into the soil. The pressure transducers were spaced evenly along the axis of the electrokinetic cell. Tubing from one of the electrode reservoirs was connected to all the reference ports, so the pressures were measured relative to the pressure in the electrode reservoir.

The electrical potential along the axis of the sample was measured. A stainless steel syringe needle was inserted into the pH port septa and used as a voltage probe. All voltages were measured relative to a platinum sensing electrode at each end of the soil by a Kiethly microvoltmeter/null-detector (Model 155) with an input impedance of $100 \text{ M}\Omega$. The uncertainty in each measurement was estimated to be lower than $\pm 5\%$ of the reading. However, there was no correction for polarization or the self-potential of the electrode. It is speculated that these potentials may be as high as $\pm 1.0 \text{ V}$. This is likely the greatest source of error toward the estimation of spatially dependent k_{eo} .

The test profile data of pressure and electric voltage were interpolated with a 100-point cubic-spline method using natural end-points. The interpolated voltage profile was differentiated to obtain the electric field intensity. Eq. (17) was then used to calculate k_{eo} profiles.

4. Results of modeling simulations, and discussion

Results of the capillary model to simulate nonuniform pore pressures developed during extended electroosmosis testing are shown in Fig. 7. The nonuniformity in E_x and ζ are severe, and thus the pressure profile is significant. The greatest suction occurs in the sections of the greatest changes in E_x and ζ . The general shape of the profile matches the experimental results shown in Figs. 1 and 4. This solution relies heavily on the predictions of the profiles of E_x and ζ , and these parameters were derived empirically for this simulation.

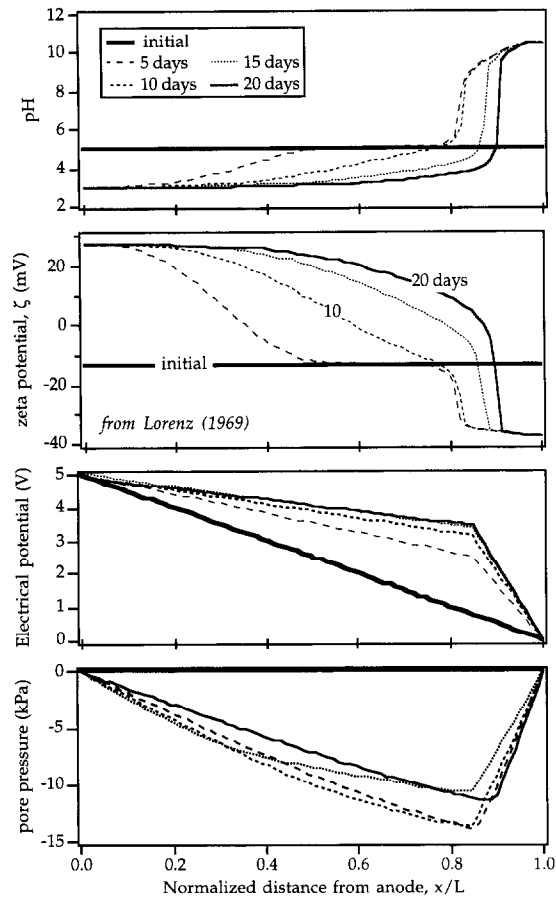


Fig. 7. Pore pressure profile simulations induced by nonuniform values of ζ and E_x , using capillary model of Eq. (9).

It would be useful to have experimental characterization of the changes in ζ vs pH for the range of chemical conditions expected, or to formulate more general and theoretical relationships for the changes in conductivity and surface chemistry with electrokinetic migration predictions. At this stage, however, these simulations may be useful only at the research stage. A researcher may compare simulations with profile measurements for pore pressures and chemical characterization as a measure of model testing. Eykholt [4] showed that, when flow direction was reversed toward the anode due to acid treatment at the cathode, profile pore pressures also reversed from negative (suction) to positive. A numerical electroosmosis model showed the same general trends in flow and pressure reversals.

The most useful application from the above relations may be the use of experimental pore pressure, potential, and flow data to reveal changes in pore chemistry during testing. If k_h is constant over the profile and there are accurate determinations of

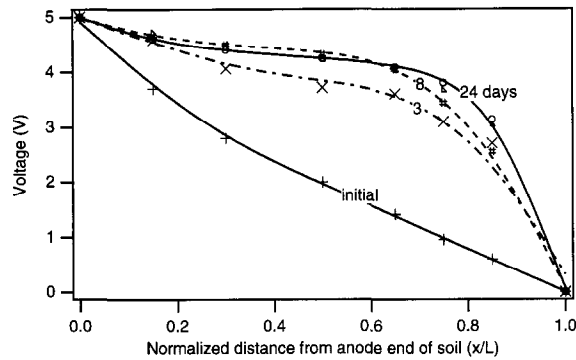


Fig. 8. Development of nonuniform electric potential profiles in copper-citrate treated kaolinite during electrokinetic testing (test 8). Smooth curves represent 100-pt. cubic spline interpolations. Soil length is 20 cm.

pressure and electrical potential profiles, Eq. (17) can be used to assess, at least qualitatively, the local changes in k_{eo} over the profile.

This analysis was done for the test 8 data (see key and caption for Fig. 2). Profiles for voltage and pressure were measured routinely over the 24-day test, and these profiles for five representative periods are shown in Figs. 8 and 9, respectively. The voltage profiles became quite nonlinear within 3 days, then became slightly more nonlinear for the duration. The negative pore pressure profile developed early and then pressures seemed to dissipate for the duration. Since the flow rate was relatively constant, the magnitude and shape of the pore pressure profile depended primarily on the nonlinearity of the electric field and chemical variability.

Estimates for the effective k_{eo} over the profile, simulated by use of experimental data and Eq. (17), are shown in Fig. 10. The initial k_{eo} is relatively constant over the profile and matches fairly well with the bulk value of $4.0 \times 10^{-9} \text{ m}^2 (\text{Vs})^{-1}$. However, the simulation produces unrealistically high values of k_{eo} in the middle portion of the profile for later times. These k_{eo} profiles should correspond to changes in the chemistry

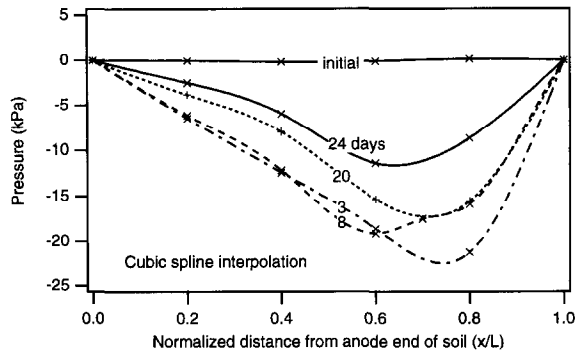


Fig. 9. Development of nonuniform pressure profiles in copper-citrate treated kaolinite during electrokinetic testing (test 8). Smooth curves represent 100-pt. cubic spline interpolations. Soil length is 20 cm.

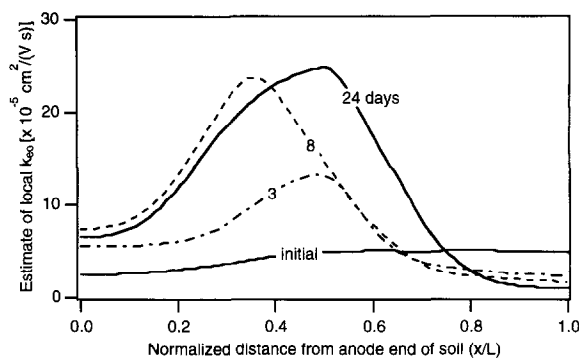


Fig. 10. Simulated development of nonuniform k_{ee} profiles in copper-citrate treated kaolinite, using experimental profiles of electrical potential and pore pressures.

along the profile. The final pH and copper profiles, two factors that are known to control k_{ee} , are shown in Fig. 11. The two profiles do not correspond very well to the final k_{ee} profile. For instance, one would expect that k_{ee} would be lowest (and even negative) for low pH and/or high copper concentrations, but be high at low copper concentrations and high pH [17].

While there is a general decrease of k_{ee} with increasing copper (x/L ranging from 0.6 to 0.9), any effects of the precipitate zone ($x/L = 0.9$) or large pH changes are not reflected in the k_{ee} simulation. In fact, the greatest changes in simulated k_{ee} occur in zones of moderately low pH—where one might expect k_{ee} to be null or slightly negative. This poor agreement between simulated k_{ee} and profiles of copper and pH may be due to errors in the measurements of pressure or voltage, fundamental variation from the theory (such as significant surface conductance effects), or chemical effects from other ionic species. The sensitivity to errors in E_x is discussed below, but further

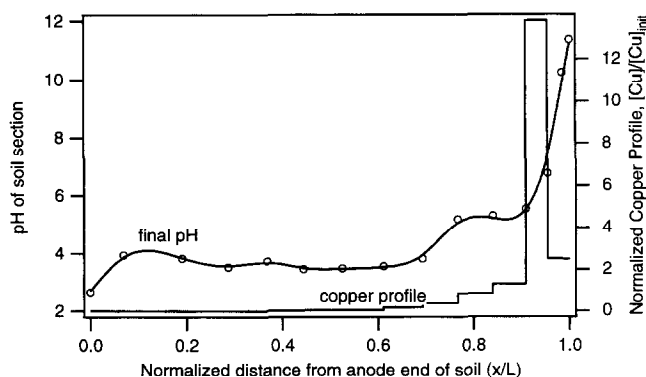


Fig. 11. Final experimental pH and copper profiles in copper-citrate treated kaolinite during electrokinetic testing (test 8). The simulated k_{ee} profile does not seem to correlate with these conditions.

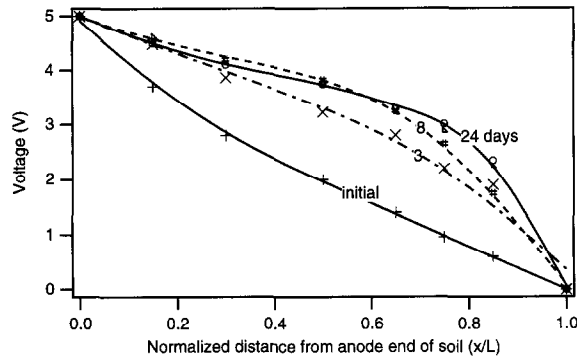


Fig. 12. Hypothetical 'corrected' voltage profile, considering positive bias by self-potential and polarization.

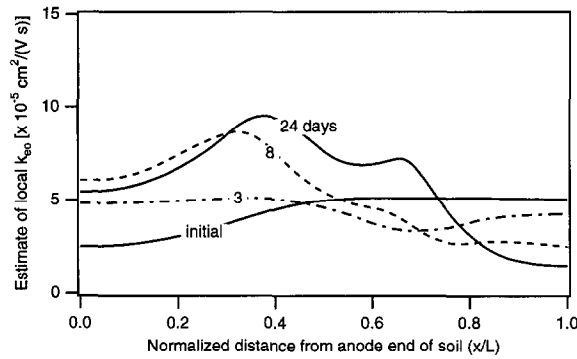


Fig. 13. Simulated development of nonuniform k_{e0} profiles in copper-citrate treated kaolinite, using 'corrected' voltage profiles.

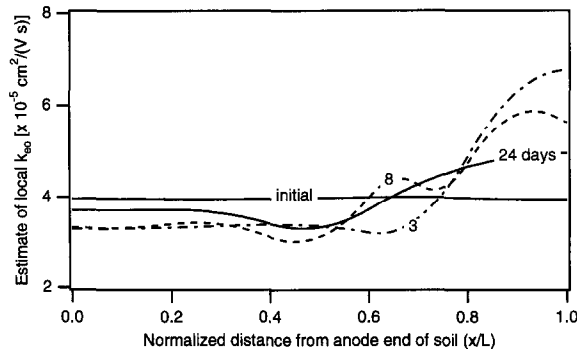


Fig. 14. Simulated development of nonuniform k_{e0} profiles in copper-citrate treated kaolinite, using linear voltage profile.

theoretical development and better chemical characterizations of sections are required before the other issues can be addressed.

The relative errors in simulated k_{eo} may be driven by inaccuracy in the measurement of the electric field, and the errors may be largest where E_x is small. It is possible that the electric field measurement is biased by the self-potential of the electrode and/or polarization effects. This bias may be as large as ± 1.0 V. The profile voltages shown in Fig. 8 were subtracted by no more than 0.8 V to obtain a purely hypothetical but more linear voltage profile, shown in Fig. 12. The resulting k_{eo} profile is shown in Fig. 13, and has changed dramatically from the prior simulation. The raw variation in the simulated k_{eo} profiles is smaller, but k_{eo} is higher in regions of higher E_x . However, the trends in k_{eo} still do not correspond with pH and copper profiles. If a linear voltage profile is enforced, the resulting k_{eo} profiles are somewhat correlated with pH. These profiles are shown in Fig. 14. While contrary to voltage measurements, this exercise reveals the sensitivity in the simulated k_{eo} profiles to electric fields.

5. Conclusion

Pore pressures will develop if there are nonuniform driving forces within the media. The pressures are typically negative relative to the hydrostatic pressure profile. Pore pressures will also develop if there is a variation in hydraulic resistance within the soil or at the boundaries. Theoretical equations, derived from a capillary model and from phenomenological flow coupling, can be used to simulate profiles of pore pressure or k_{eo} , provided that supporting experimental data are available.

The derived expression for the pore pressure profile relies on the following assumptions: incompressible flow, validity of the Helmholtz–Smoluchowski equation in each region, constant hydraulic conductivity, negligible surface conductivity, one-dimensional flow, and uniform boundary conditions. Sensitive measurements of the electric field are especially important, since the simulation of the k_{eo} profile is very sensitive to error in E_x . The nature of the pore pressure profile can be used to assess, at least qualitatively, the relative contributions to electroosmosis in various soil regions along the profile. These simulations require measurement of the net electroosmotic flow rate, pressure and electrical potential profiles, and hydraulic conductivity.

The utility of such simulations is questionable at this stage, especially if they are used for more complicated systems. The k_{eo} profile simulations provided here were not well correlated with measured pH and copper profiles. The success of the simulation strategy will likely depend on two factors: accurate electric field measurements and electrokinetic characterization of soil sections. Only in this way can the theory be well tested. New theoretical development, such as inclusion of surface conduction effects, is encouraged. However, confirmation in the form of measurements is essential.

It may be useful to monitor pore pressures as another monitoring technique in research studies. The nonuniformity of pore pressures implies nonuniform contributions to flow, or obstructions along the profile. Used as such, this technique may enable researchers to refine how soil and reservoir conditioning schemes may be employed for optimal electrokinetic treatment. However, at this stage, such inferences are still somewhat qualitative.

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