

ELECTROKINETIC SOIL REMEDIATION: IMPACT OF AQUEOUS PHASE PROPERTIES ON  
SOIL SURFACE CHARGE AND ELECTROOSMOTIC EFFICIENCY

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## INTRODUCTION

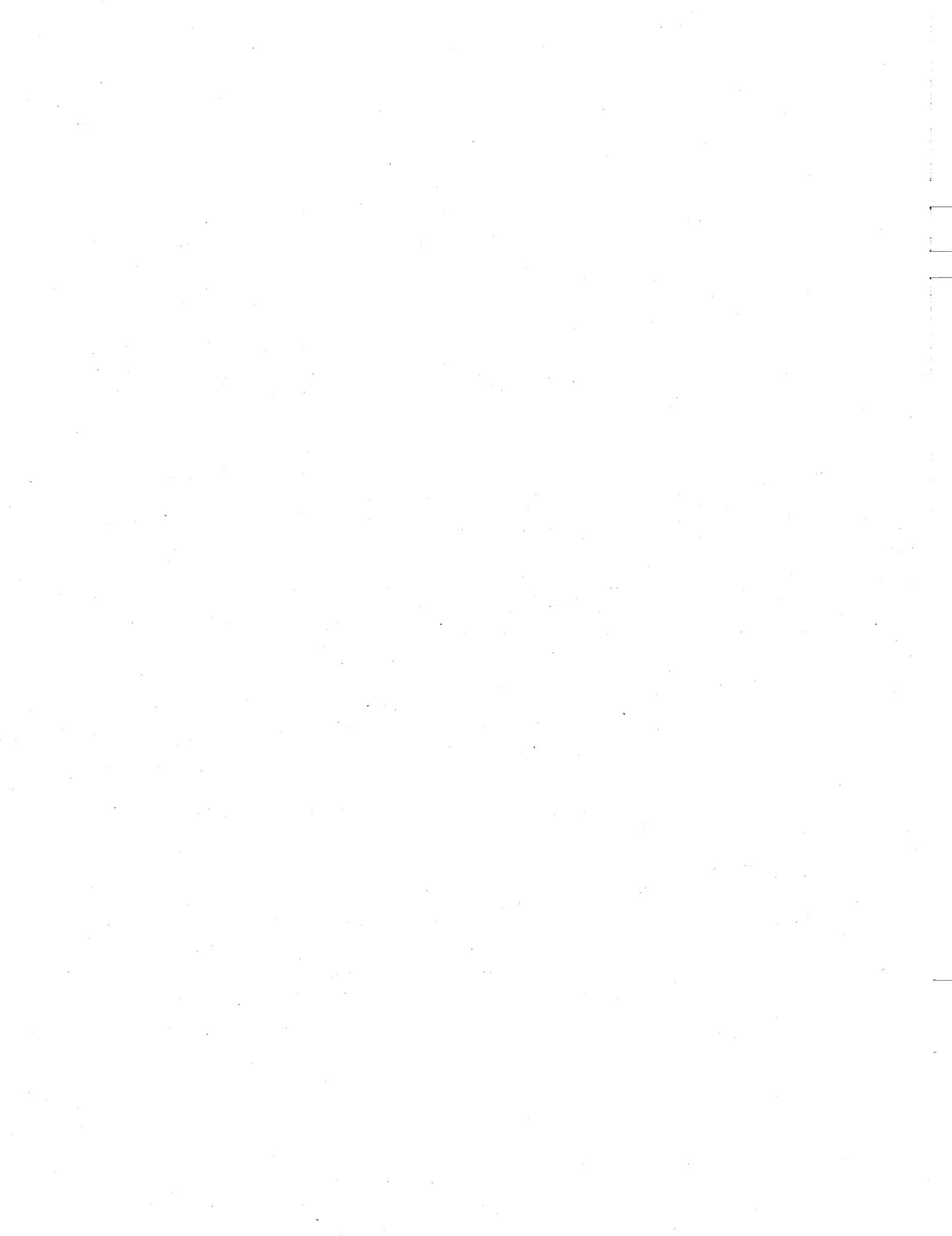
The *in situ* remediation of a contaminated soil is an exercise in mass transfer limitations. The challenge is to mobilize the contaminant and transport it to a treatment/collection zone or to deliver nutrients, microorganisms, or destruction chemicals to degrade the contaminant where it resides. For soils with high hydraulic permeabilities, mobilization or treatment solutions can be hydraulically delivered to the contaminated zones. Mobilized contaminants and degradation products can be removed in the same manner. However, pressure driven hydraulic delivery/removal in low permeability soils, such as clays, is impractical.

One method of transporting solutions and compounds in low permeability soils is the application of an electric current to the soil in a process called Electrokinetic Soil Remediation (ESR). This form of remediation utilizes the response of charged molecules and particles to an applied voltage gradient to effect the movement of pollutants. Driving the remediation are the electrokinetic phenomena of electroosmosis, ion migration (electromigration), and electrophoresis. As depicted in Figure 1, most soil particles, including clays, carry a negative surface charge. When the soil is immersed in an electrolyte, the particles attract cations, creating a positively charged boundary layer (referred to as the *charged double layer*) next to the surface of the soil particles. Application of a voltage difference across a section of soil causes movement of the ions and associated water within the double layer toward the cathode (electron source). The remainder of the pore fluid moves in the same direction as the double-layer fluid due to viscous drag interactions. This net flow of pore fluid due to an applied voltage gradient is termed "electroosmosis" (EO). EO can be utilized to remediate contaminated soils *in situ* by flushing out the pore fluid and contaminants (or to deliver nonionic nutrients, surfactants, etc.).

The ions in the bulk pore fluid also respond to the applied voltage gradient with the anions being driven to the anode and cations driven to the cathode. This movement of aqueous ions and ion-complexes in response to the voltage gradient is referred to as ion migration or electromigration. Electromigration can be used to recover ionic contaminants from soil even in unsaturated soils (1). Larger charged molecules and particles also move due to an applied voltage gradient (electrophoresis). Substances which fall into this latter category include cationic or anionic surfactant molecules and micelles, clay particles, and polyelectrolytes. The degree to which each electrokinetic phenomenon occurs depends on the properties of the soil/pore fluid matrix including the degree of saturation, ionic strength of pore fluid, types of ions/charged particles present, pH of pore fluid, temperature, porosity of soil, soil composition (% clay, type of clay, etc.), and the surface charge of the soil particles. In this paper, the effect of pore fluid properties on the surface charge of clays and the resultant effect on electroosmosis in saturated clays will be examined.

When a charged particle is suspended in an electrolyte, ions with a charge opposite to that of the particle will concentrate in the charged double layer. The velocity of the particle ( $v_p$ ) when placed in an electric field is dependent on the viscosity of the fluid ( $\eta$ ), the applied voltage gradient ( $E$ ), and the zeta potential ( $\zeta$ ), or surface charge, of the particle as described by Smoluchowski's classic equation (2):

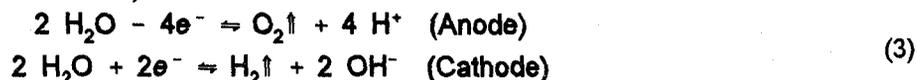
$$v_p = \frac{\epsilon \zeta E}{\eta} \quad (1)$$



Similarly, when a packed bed of clay particles is saturated with an electrolyte and exposed to a voltage gradient, the electroosmotic volumetric flow rate ( $q_{eo}$ ) resulting from the movement of solvated ions concentrated outside the stationary layer is described by the Helmholtz-Smoluchowski equation (2):

$$q_{eo} = \frac{-\varepsilon \zeta i}{\eta \lambda_o} A n = \frac{-\varepsilon \zeta E}{\eta} A n \quad (2)$$

where  $i$  is the bulk current density in the sample and  $\lambda_o$ ,  $A$ , and  $n$  are the bulk conductivity, total cross-sectional area, and porosity of the sample, respectively. The  $\zeta$  of most charged particles is dependent on solution pH, ionic strength, types of ionic species, temperature, and type of mineral. According to equation (2), the electroosmotic flow rate observed in packed beds of charged particles should also be a function of these same parameters. Investigators of electrokinetic soil remediation processes have observed the development of often dramatic pH, conductivity, temperature, and species concentration gradients. The pH gradients arise from electrolysis reactions which occur at the powered electrodes (shown below for unreactive electrodes):



The anode region becomes acidic (pH as low as 2) while the cathode region is basic (pH as high as 12). Unfortunately, models for electrokinetic soil remediation processes have only recently included the  $\zeta$  as a variable (3,4). Probst et al. incorporated  $\zeta$  as a fitting parameter, constant over the entire sample, while Eykholt introduced  $\zeta$  as a function of pH. Recently, Jacobs et al. mentioned the inclusion of pH and ionic species/concentration effects on  $\zeta$  in future versions of their model (5).

When electroosmosis is relied upon to transport contaminants (as with uncharged contaminants with or without nonionic surfactants), the time required to remediate a site is proportional to the electroosmotic flow rate - assuming that the contaminant in the pore fluid is in equilibrium with the sorbed contaminants. Therefore, based on equation (2), variations in  $\zeta$  and  $E$  directly impact the remediation time. Even when electromigration is the desired transport process, the amount of electroosmosis must be factored into the remediation scheme. While  $E$  can be independently controlled at the electrodes,  $\zeta$  is determined solely by the subsurface conditions which may be dramatically affected by the remediation process. For this reason, it is critical that the  $\zeta$  of the soil be evaluated based on the expected conditions during the remediation as well as based on depth and position at the site.

## METHODOLOGY

The zeta potentials of small particles in dilute suspensions have been routinely measured using instruments which range from relatively simplistic manually operated optical electrophoresis devices to more involved automated light scattering devices. These instruments allow for the rapid determination of zeta potential as a function of solution properties with a high degree of control over these properties. Therefore, a wide range of variables can be investigated in a reasonable amount of time. Conversely, bench-scale electroosmosis experiments in compressed clay samples suffer from little control over variables such as pH, conductivity, and types of ionic species both as a function of position in the sample and of time. As a result, it is difficult to distill  $\zeta$  information from bench-scale data, although the larger scale data is required to more fully evaluate the process under field conditions.

The effect of pH, ionic strength, clay type, and ionic species on the zeta potential was evaluated using an automated microelectrophoresis instrument (ZetaSizer 4, Malvern Instruments). Dilute suspension (0.1 g/L) samples of kaolinite, bentonite, and a local silty clay soil were analyzed. Bench-scale electroosmosis experiments were performed with 3" diameter kaolinite clay samples of 1" or 4" length. The samples were placed between electrolyte reservoirs in which platinum electrodes were immersed. The pH and conductivity of the electrolyte was kept constant as was the electric current through the sample. A constant fluid level in the reservoirs was maintained by gravity overflow to a receiving container. The electroosmotic flow rate was determined from the weights of the inflow and outflow bottles for each

reservoir. The voltage gradient across the sample was measured using platinum mesh electrodes pressed into the ends of the sample cell.

## RESULTS

The variation of zeta potential with pH for the kaolinite, bentonite, and soil samples in 0.01M KCl is shown in Figure 2. It is apparent that the zeta potentials of bentonite and the soil sample were relatively insensitive to pH. However, the zeta potential of kaolinite was found to be a strong function of pH, ranging from -50 mV under basic conditions to approximately 0 mV at pH = 2.0. Equation (2) predicts that the electroosmotic flow rate-voltage gradient ratio ( $q_{\text{os}}/E$ ) is proportional to the zeta potential. As a result, the flow/voltage ratio should be pH dependent for packed beds of kaolinite. In Figure 3, the flow/voltage ratio for a 4" long packed kaolinite bench-scale sample is plotted alongside the dilute suspension kaolinite zeta potential data (absolute value), both as functions of pH. As predicted, the flow/voltage ratio displays the same pH dependence as the zeta potential. For the same voltage gradient, the electroosmotic flow rate was about 3 times greater at pH=5.0 than at pH = 2.8. The zeta potential results suggest even more dramatic increases in flow at higher pHs.

The effect of various cations, anions, and ionic strength on the zeta potentials of bentonite and kaolinite was also investigated. Changes in ionic strength (KCl) did not greatly alter the zeta potential of either kaolinite or bentonite. More significant changes were observed when the concentrations of the +2 cations  $\text{Pb}^{2+}$ ,  $\text{Ca}^{2+}$ , and  $\text{Cu}^{2+}$  were increased. For example, the magnitude of the zeta potential of bentonite was reduced by 1/3 when the  $\text{Pb}^{2+}$  concentration was increased to 100 ppm in 0.01M KCl. This same concentration of  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$ , or  $\text{Ca}^{2+}$  (in 0.01M KCl @ pH=4) was sufficient to reverse the sign of the charge on kaolinite, indicating that the direction of electroosmotic flow would be reversed. Reduction of the background electrolyte concentration from 0.01 to 0.0005M KCl resulted in kaolinite charge reversal at 10 ppm  $\text{Pb}^{2+}$ .

## CONCLUSIONS

Zeta potential results indicate that the electroosmotic efficiency (flow/voltage ratio) in bentonite should be relatively insensitive to pH and ionic strength variations. The zeta potential of kaolinite, however, was found to be quite sensitive to pH. The electroosmotic efficiency for kaolinite was found to be equally sensitive to pH. Zeta potential results further indicate that the electroosmotic efficiency as well as the direction of electroosmosis in kaolinite will be impacted dramatically by the presence of metal cations. These results suggest that zeta potential measurements could be used to study the impact on electroosmotic efficiency of initial site conditions as well as conditions expected during an electrokinetic remediation process.

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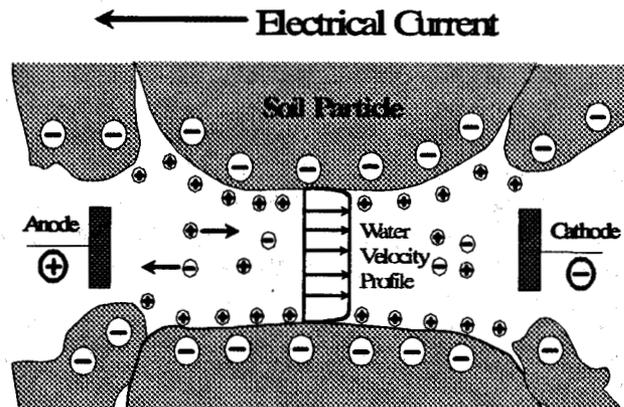


Figure 1. Illustration of Electrokinetic Processes in Soil Pore

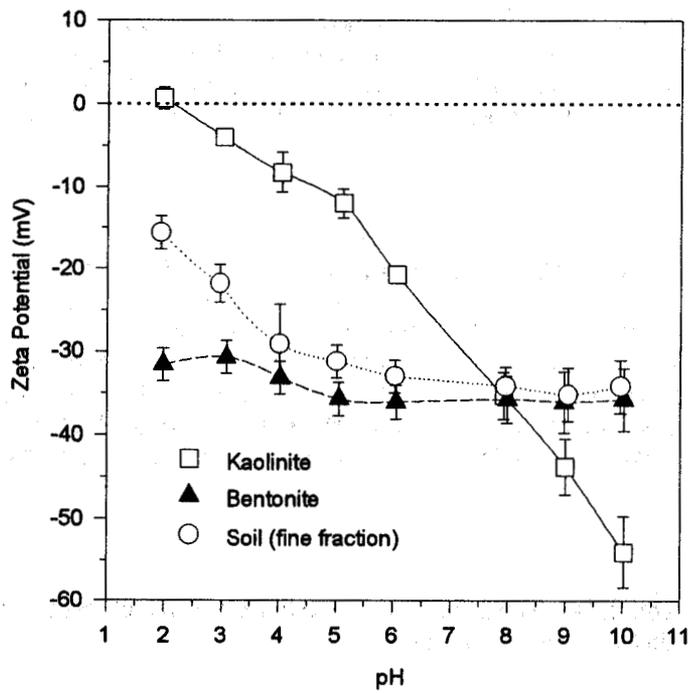


Figure 2. Variation of Zeta Potential with pH for Samples of Kaolinite, Bentonite, and a Silty Clay Soil. (25°C, 0.01M KCl, KCl-treated samples)

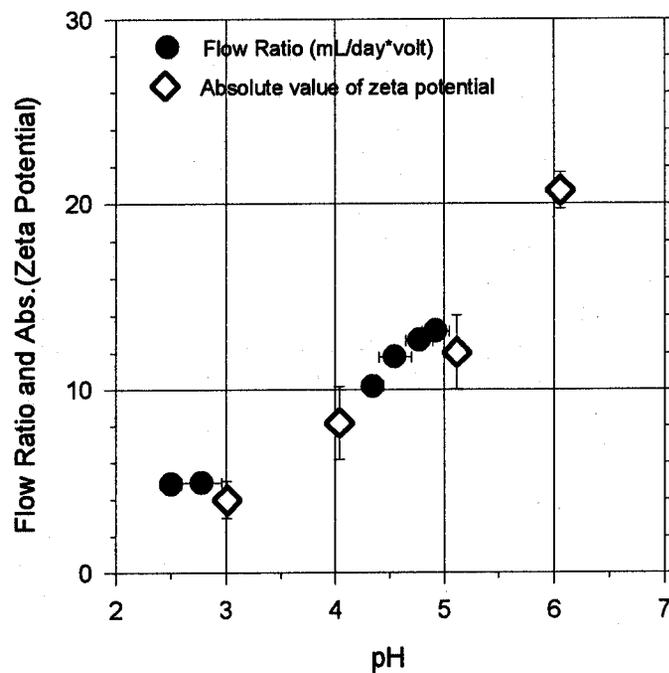


Figure 3. Variation of Flow-Voltage Ratio (mL/day\*volt) and Absolute Value of Zeta Potential (mV) with pH for 3" dia. Kaolinite Packed Column (4" length) and 0.1 g/L Kaolinite Suspension, respectively.

FOR MORE INFORMATION

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