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Laboratory study of electrokinetic effects in complex natural sediments

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Abstract

The electrokinetic response to the application of direct current potential fields is examined in four sediments: natural and undisturbed glacial till, reconstituted glacial till, pure kaolinite and pure montmorillonite. Till samples contain abundant calcite and expandable smectite clays. The presence of calcite in till samples buffers the sediment and prevents the development of the low pH conditions seen in pure clay systems. Electroosmotic flow in undisturbed till is equivalent in both horizontal and vertical directions. The volume of electroosmotically driven flow in reconstituted till is relatively independent of the amount of clay minerals present. Electroosmotic efficiency of these sediments is an inverse function of the amount of smectite present. Pure montmorillonite samples exhibit color changes, shrinkage cracks, water loss and an increase in Fe(II) content upon application of a potential field. © 1997 Elsevier Science B.V.

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1. Introduction

The application of low-level direct current (DC) electric fields to fine-grained sediment produces several interrelated effects, in particular the electroosmotically induced flow of water from anode to cathode. Yeung, 1994 reviewed both the theoretical and practical aspects of electrokinetic processes in porous media. Recent literature contains numerous studies that use electroosmotic flow and the associated low pH fronts in the remediation of a variety of contaminants (e.g. Acar et al., 1994; Bruell et al., 1992; Cabrera-Guzman et al., 1990; EPRI, 1994; Hamed et al., 1991; Lageman et al., 1989; Pamukcu and Wittle, 1992; Probstein and Hicks, 1993; Shapiro and Probstein, 1993).

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Application of an electric field to saturated porous media induces several other effects besides electroosmosis. One effect is oxidation of water at the anode yielding O_2 gas and H^+ ions and reduction of water at the cathode yielding H_2 gas and OH^- ions. Production of H^+ ions at the anode causes an acid front to migrate with the electroosmotic flow towards the cathode. The acid front is the primary means by which metals are mobilized in electroosmotic treatment systems. If the media are sufficiently permeable and their surfaces carry little or no surface charge, electric conduction is accomplished by ionic migration (e.g. Runnels and Larson, 1986; Runnels and Wahli, 1993). Shapiro and Probstein (1993) maintain ion migration and electroosmotic flow are both necessary to explain their results in kaolinite systems.

The recent body of experimental work that uses electroomosis as a remediation scheme has almost exclusively used kaolinite as the fine-grained sediment (e.g. Acar et al., 1990; Acar et al., 1994; Bruell et al., 1992; Eykholt and Daniel, 1994; Gray and Mitchell, 1967; Pamukcu and Wittle, 1992; Segall and Bruell, 1992; Shapiro and Probstein, 1993). Some studies use water contents above the liquid limit of kaolinite (Acar et al., 1992; Bruell et al., 1992; Segall and Bruell, 1992). Other solid media used in experimental studies include quartz sand (Runnels and Larson, 1986; Runnels and Wahli, 1993), dredge spoils (Segall et al., 1980), illite (Gray and Mitchell, 1967), montmorillonite (Pamukcu and Wittle, 1992) or mixtures of these minerals (Pamukcu and Wittle, 1992; Segall and Bruell, 1992; Thomas and Lentz, 1990; Gray and Mitchell, 1967). The montmorillonite study (Pamukcu and Wittle, 1992) used water contents of 271%, well above the liquid limit. The illite study (Gray and Mitchell, 1967) applied electric fields for short periods of time only.

Although kaolinite is a common naturally occurring mineral, often becoming dominant in warm, humid climates, it seldom occurs in a pure state. Kaolinite is more commonly associated with other, more surface active clay minerals. For example, large amounts of fine-grained sediment found in glaciated terrains in the north central United States and throughout the world contain almost exclusively the surface active clays of the smectite and illite groups. Ancillary minerals that occur in naturally formed fine-grained sediment will also affect the response of the sediment to the application of an electric field. This is particularly true of calcite which has a large buffering capacity that tends to counteract the effects of cathodically produced acidity (Grundl and Michalski, 1995). The presence of significant amounts of granular silicate minerals (quartz, feldspars, etc.) will affect the electrokinetic response by decreasing the resistance to the flow of water through the sediment as a whole.

The crystal structure of minerals within the smectite and illite groups is that of an octahedrally coordinated layer sandwiched between two tetrahedrally coordinated layers. Iron occurs in all these minerals. In smectites, small amounts of iron can be found in the tetrahedral layer or as an inner layer cation; however, the primary repository for iron is in the central octahedral layer (Scott and Amonette, 1988; Sherman and Vergo, 1988). The oxidation state of octahedral iron is variable and is a function of exterior redox conditions (see Scott and Amonette (1988) and Stucki (1988) for reviews of oxidation and reduction, respectively).

Reduction of octahedral Fe(III) to Fe(II) causes a net increase in the surface charge of the mineral and causes changes in several macroscopic properties of smectite minerals.

As iron is reduced, the surface area and swelling pressure decreases (Gates et al., 1993; Stucki et al., 1984; Egashira and Ohtsubo, 1983), particle size increases (Stucki and Tessier, 1991), and cation fixation increases (Khaled and Stucki, 1991). Octahedral Fe(III) reduction also causes cracks or micropores to appear and the hydraulic conductivity to increase (Shen et al., 1992). Color changes from grey in the oxidized state to green (most commonly), yellow or blue in the reduced state have been noted in smectite minerals (Komadel et al., 1990; Rozenson and Heller-Kellai, 1976a,b).

The primary intent of this study is to investigate electroosmotic flow in a sediment–water system taken from a glacial till in southeastern Wisconsin. The effect on electroosmotic flow due to the presence of calcite and variable amounts of granular silicates was investigated. In addition, undisturbed samples of the till were taken in both vertical and horizontal orientations to determine the effect of spatial orientation on electroosmotic flow. Lastly, the unusual response of montmorillonite (a smectite mineral) to the application of an electric field was investigated. The clay mineralogy of the till is dominated by a mixed layer illite/smectite phase and also contains significant amounts of carbonate minerals and granular silicates.

2. Methods

Electroosmotic flow: Laboratory scale column experiments were performed in vertically oriented, plexiglass columns with an internal diameter of 7.6 cm. Sediment samples were between 5 and 6 cm in length, and water flow was from top to bottom. Perforated, spring-loaded Plexiglass end plates held the sample in place. Perforated graphite sheet electrodes (Alfa AESAR) extended over the entire cross-sectional area of the column at both ends. The anode was placed at the top of the column, therefore electroosmotic flow was from top to bottom. Electrical contact was made by a copper wire bolted to the center of each electode with a nylon bolt. Silicone sealant over the bolt served to isolate the wire from contact with liquid. Constant hydraulic head differences on the columns of between 8 and 71 cm were maintained throughout each experiment by means of a vertically adjustable constant head tank. Both ends of the column were open to the atmosphere to allow evolved gases (from the electrolysis of water) to escape. Effluent water dripped through a funnel and was collected in a 10 ml graduated cylinder and periodically measured to determine flow rate. Based on control experiments, evaporative loss was insignificant. De-aerated tap water was used as a pore fluid in all experiments. Air-dried sediment was brought to a water content sufficient to produce a thick paste and manually placed in the column. Water content varied from 15% to 74% depending on the sediment. Undisturbed samples were used as collected from the field with no addition of water.

Experiments were run for periods of between 100 and 400 h (4 to 17 days) at constant voltage and hydraulic head while effluent volume and amperage were monitored over time. All experiments were performed at electric field strengths of 80 V/m using Protex (Model 3015) dual DC power supplies. Field strengths were determined from total potential drop across the circuit. No attempt was made to determine the potential distribution within the sediment column itself. Amperage was measured with a standard multimeter.

At the end of each experiment, columns were disassembled and the sediment sliced into one centimeter sections for an analysis of sediment pH and water content. Sediment pH was determined with a glass electrode in a 1:1 mix (by weight) of deionized water and sediment. Water content was determined by weight loss after air drying at 23°C to a constant weight.

Sediment characterization: Reconstituted till samples were collected from the Oak Creek Till formation as auger drill cuttings from a site on the University of Wisconsin – Milwaukee campus. Samples were taken from between 2 and 15 meters in depth. Each sample was air dried and broken until the sediment passed through a 600 micron sieve. Grain size analysis was determined by Stokes Law settling velocities (Klute, 1986). The percentage of clay in some of the trials was decreased by the addition of extra material from the silt and sand fraction of previously separated samples. Percent carbonate was determine by weight loss after reaction with 10% hydrochloric acid. Clay mineralogy was determined by X-ray diffraction analysis of the 001 peak of ethylene glycol solvated samples (Soil Science Society of America, 1994). Grain sizes less than 0.2 μm were used for X-ray analysis. Powdered kaolinite samples were obtained commercially (Aldrich Chemical) and used directly with no further processing. Powdered montmorillonite samples were obtained commercially as Wyoming bentonite (Volclay) and used with no further treatment.

Undisturbed samples of the Oak Creek Till were collected from a fresh slump face of the shoreline bluff of Lake Michigan at the same horizon as the reconstituted samples. Samples were collected by shaving back the bluff face for one meter with a shovel and manually pushing the experimental columns into the sediment. A 12 cm long aluminum sleeve surrounded the columns to provide support and to aid in inserting the columns. After sample collection, the sleeve was peeled off, and the sample trimmed to length with a spatula. The ends were sealed and the samples transported to the laboratory.

Ferrous iron content of montmorillonite was determined after extraction in an anaerobic chamber for one hour in 0.5 M HCl. The extract was spectrophotometrically analyzed for the presence of Fe(II) at 562 nm after the addition of the complexing agent ferrozine (3-(2-pyridyl)-5,6-diphenyl-1,2,4-triazine-4′,4″-disulfonic acid monosodium salt) (Stookey, 1979). The spectrophotometer was calibrated against standard solutions of ferrous ammonium sulfate. Ionic composition of influent pore water was analyzed by flame atomic absorption following American Public Health Association (1989) procedures.

3. Results

Sediment characteristics: The bulk characteristics for all sediment used in this study are given in Table 1. Reconstituted till, kaolinite, and montmorillonite samples were mixed with enough water to achieve a textually consistent, thick paste using a water similar in composition to groundwater in the area (Table 2). In all cases the sediment was kept below the liquid limit. Undisturbed till samples were used directly from the field. As is typical of glacially deposited sediment, undisturbed till was very poorly

Table 1
Bulk characteristics of sediments used in this study. Clay-sized particles are < 2 μm, silt-sized particles are between 2 and 20 μm and sand-sized are between 20 and 600 μm. Weight percentages in till samples sum to more than 100% because some of the carbonate grains are clay sized

Sediment	percent				
	clay	silt	sand	carbonate	pH
undisturbed till	40	48	12	39	8.2
reconstituted till	41	47	12	37	7.8
kaolinite	100	0	0	0	5.5
montmorillinite	100	0	0	0	8.8

sorted and highly variable. Pebbles as large as 2 mm, coarse sand, and occasional mm thick silty layers were encountered.

Based on X-ray analysis on the clay fraction of the till, the clay minerals were dominantly illite and an illite/smectite mixed-layer phase. The mixed-layer phase was approximately 84% smectite with the ratio of mixed layer to illite phases approximately 0.8:1.0. Therefore, the clay fraction of the till contained approximately 40% smectite. This accounts for the remarkably low hydraulic conductivity of the till. Grundl and Michalski (1995) reported the hydraulic conductivity of reconstituted till as 6.5×10^{-8} cm/s.

Electroosmotic flow was investigated in all four sediment types. All experiments were conducted at the same field strength and with the same pore fluid. The electroosmotic flow results are discussed by sediment type. For ease of comparison, all figures are plotted on the same time scale. Of necessity, flow rate and amperage scales vary from figure to figure. Table 3 is a data summary of all flow experiments.

Flow behavior in undisturbed till: Four horizontally oriented and five vertically oriented columns were assembled and a hydraulic head applied. No background hydraulic flow for periods of up to 43 h was observed prior to the application of an electric field. Upon application of an electric field, an electroosmotically driven flow of

Table 2
Chemical composition of influent pore water used for all experiments

Ion	concentration	
	mg/l	mmol/l
Ca^{2+}	37	0.92
Mg^{2+}	10	0.41
Na^{+}	5.8	0.25
K^{+}	3.8	0.10
HCO_3^-	150	2.46
Cl^-	12	0.34
SO_4^{2-}	28	0.29
NO_3^-	0.7	0.01
pH	6.8	–

Table 3
Summary of electroosmotic flow data. Numbers in parentheses are standard deviations expressed as percentage of the mean (relative standard deviation). pH values are representative values for the bulk of the column at the end of electroosmotic processing

Sediment type	number of replicates	total eo flow (ml)	total pores volumes	peak flow rate (ml/h)	peak current (mA)	pH	initial water (%)
undisturbed till							
vertical	4	91(65)	1.2(71)	0.4(29)	7.5(9)	7.0–8.0	16
horizontal	5	37(40)	0.8(68)	0.4(21)	9.4(14)	7.0–8.0	16
reconstituted till	6	99(23)	1.2(27)	0.9(10)	6.7(16)	6.8–7.0	28
montmorillinite	5	103(16)	0.6(26)	3.4(12)	63(17)	2.0–2.5	74
kaolinite	3	81(43)	0.7(46)	1.0(15)	3.1(21)	2.5–4.0	34

water was observed. The flow of water slowly diminished over time and eventually stopped. The same general behavior was observed in all columns for both horizontal and vertical orientations. Figs. 1 and 2 are plots of typical flow behavior in the horizontal and vertical orientations respectively. The total amount of water passed through the sediment columns varied from 14 to 155 ml which corresponded to between 0.13 and 2.25 pore volumes. Peak flow averaged 0.4 ml/h in both the horizontal and vertical orientations.

Flow behavior in reconstituted till: Reconstituted till had the same general flow behavior as undisturbed till (Fig. 3). Electroosmotic flow rate slowly decreased over time and stopped in a similar manner. Although the peak flow rate was higher (averaging 0.9 ml/h), the total amount of water passed, both in terms of total volume and number of pore volumes, was the same (Table 3).

A series of additional experiments was conducted using reconstituted till in which the percent clay was sequentially lowered and the resulting electroosmotic response ob-

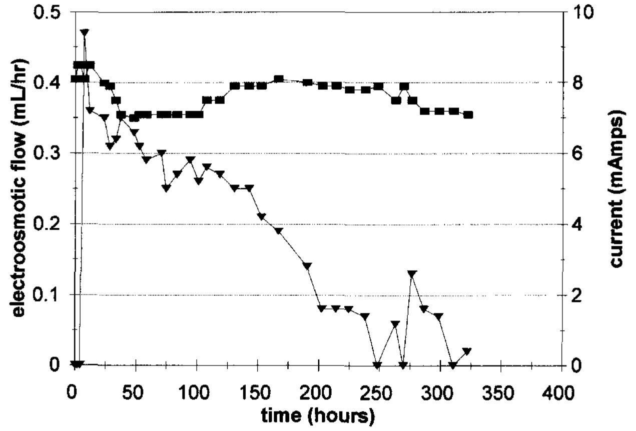

Fig. 1. Electroosmotic flow rate and current vs. time for a representative experiment in an undisturbed till sample collected in the horizontal orientation. The time axis is in hours since application of electric potential. ▼ = electroosmotic flow rate. ■ = current. Total number of pore volumes passed in this experiment was 0.8.

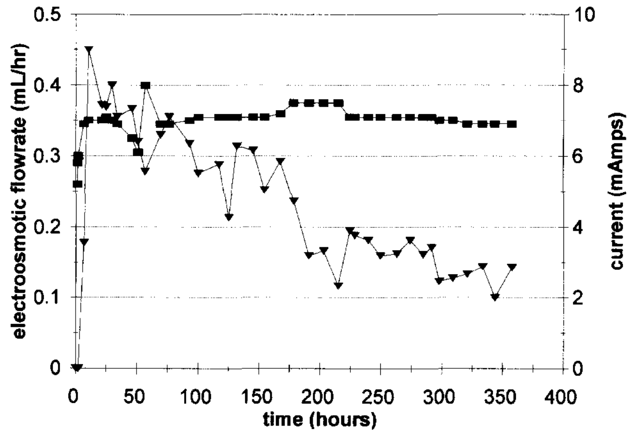

Fig. 2. Electroosmotic flow rate and current vs. time for a representative experiment in an undisturbed till sample collected in the vertical orientation. The time axis is in hours since application of electric potential. ▼ = electroosmotic flow rate. ■ = current. Total number of pore volumes passed in this experiment was 1.12.

served. The experiments were performed at a constant field strength of 80 V/m using the same pore fluid as all other experiments. The electroosmotic flow behavior was essentially the same for clay contents that range from 41% (pure till) to 13% (Fig. 4). There was no backgound hydraulic flow in any of the columns and all observed flow was electroosmotically driven. In Fig. 4 there are also data for the silt and sand fraction of the reconstituted till. The electroosmotic response was quite similar to sediment with larger amounts of clay present; however, this fraction contained only 2% clay and as such had a significant hydraulically driven flow of water. Background hydraulic flow

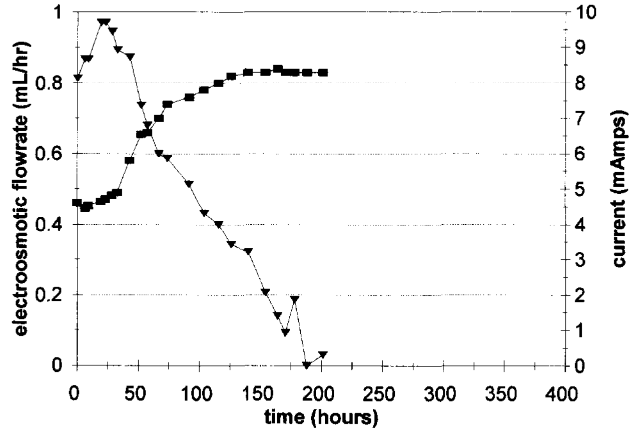

Fig. 3. Electroosmotic flow rate and current vs. time for a representative experiment in a reconstituted till sample. The time axis is in hours since application of electric potential. ▼ = electroosmotic flow rate. ■ = current. Total number of pore volumes passed in this experiment was 1.07.

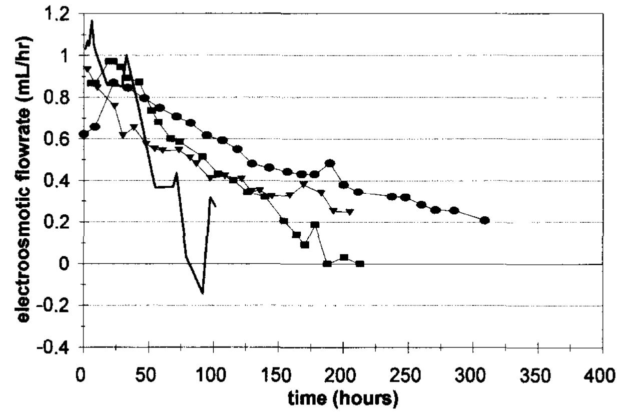

Fig. 4. Electroosmotic flow rate vs. time of reconstituted till with varying weight percentages of clay fraction present. ■ = 41 wt. % clay. ▼ = 21 wt. % clay. ● = 13 wt. % clay. – = the silt and sand fraction which contained 2 wt. % clay. Time axis is in hours since application of electric potential.

was approximately 6 ml/h. The electroosmotic flow depicted in Fig. 4 is the difference between the flow seen in a column with voltage applied and an identical control column that had no applied voltage. The erratic nature of the curve and the apparent negative flow at 92 h is due to the necessity of subtracting background hydraulic flow from a separate column. The extent of electroosmotically driven flow in all fractions, including the silt and sand fraction, increases with increasing field strength up to the maximum field strength tested of 120 V/m (data not shown).

Flow behavior in kaolinite: Kaolinite samples also had no background hydraulic flow. Electroosmotically driven flow appeared immediately after the application of an electric field and stopped after approximately one pore volume (Fig. 5 and Table 3).

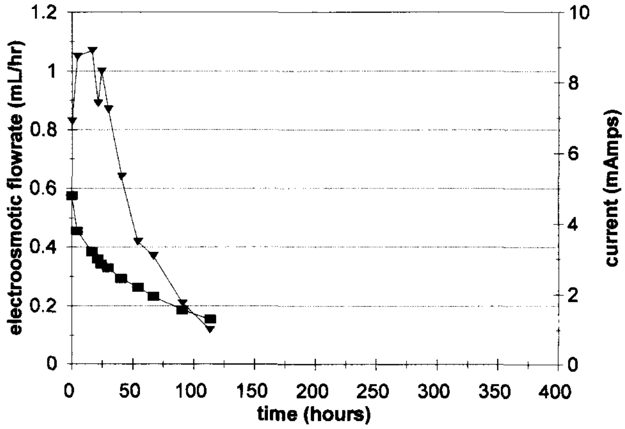

Fig. 5. Electroosmotic flow rate and current vs. time for a representative experiment in a kaolinite sample. The time axis is in hours since application of electric potential. ▼ = electroosmotic flow rate. ■ = current. Total number of pore volumes passed in this experiment was 0.50.

There were, however, marked differences between kaolinite and till in both current and pH response. Kaolinite had no buffer capacity on the time scales of these experiments, and the pore water was subject to large reductions in pH. Till samples contained abundant solid calcite which effectively buffered the pore water against drastic pH changes caused by production of H^+ ions at the anode. The pH in till samples is buffered to 7 within one centimeter of the anode and remained close to this value until the cathode was approached, at which point the pH abruptly rose to 11 or more. By contrast, the pH of kaolinite samples remained between 2.5 and 4 until the cathode was approached. Values of pH given in Table 3 are representative pH conditions found in the bulk soil column at the end of each experiment, excluding the centimeter closest to the cathode.

In kaolinite, the current decreased in conjunction with the decreasing flow of water. This is in marked contrast to both undisturbed and reconstituted till in which the current remained constant or rose as flow diminished (compare Fig. 5 with Figs. 1 and 2 and 3). The pH level in the unbuffered kaolinite systems is well below the typical PZC for kaolinites (e.g. Lorenz, 1969; Stumm and Morgan, 1981). Other workers have noted the parallel drop in electric and hydraulic conductivities in kaolinite systems and suggest ion starving (Hamed et al., 1991) or the reversal of surface charge as pH conditions change (Eykholt and Daniel, 1994; West and Stewart, 1995) as the cause.

Flow behavior in montmorillonite: The flow and current response of montmorillonite was substantially different from those of any of the previously discussed sediments (see Fig. 6). The montmorillonite system was a much more conductive medium than undisturbed till, reconstituted till or kaolinite. Note that in Fig. 6 both current and flow rate scales are much larger than in previous figures. In montmorillonite, the flow rate and current rapidly diminished in a parallel manner during the course of the experiment; however, both were initially much higher than observed in previous sediments. There was still approximately 10 mA of residual current passing after

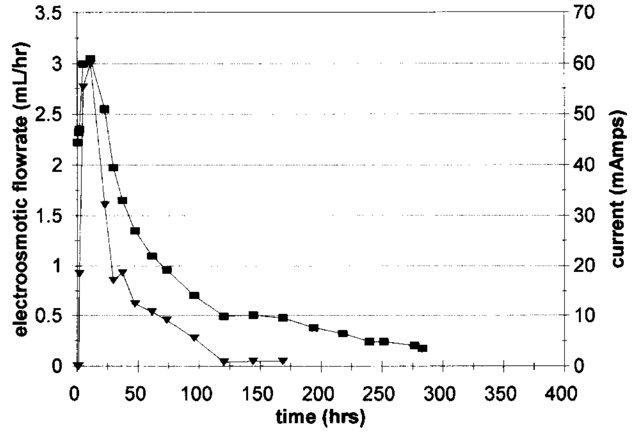

Fig. 6. Electroosmotic flow rate and current vs. time for a representative experiment in a montmorillonite sample. The time axis is in hours since application of electric potential. ▼ = electroosmotic flow rate. ■ = current. Total number of pore volumes passed in this experiment was 0.55.

cessation of electroosmotic flow. This equals or exceeds the maximum amount of current passed in any of the other sediments. Moreover, this residual current only slowly diminished over the next 200 h. Electroosmotic flow and current were decoupled in montmorillonite.

4. Discussion

Undisturbed till: Within the reproducibility limits of the data, the results of experiments conducted on undisturbed till show no difference in flow behavior between horizontally and vertically oriented samples. This is true in terms of both peak flow rate and total amount of water passed (Figs. 1 and 2 and Table 3). The high relative standard deviation (roughly 70%) of flow measurements in the undisturbed samples is a reflection of the previously mentioned natural variability of these sediments. The fact that electroosmotic flow is essentially isotropic suggests that, on a microscopic scale, these sediments may have a flocculated clay fabric. In flocculated clay fabrics individual clay platelets or platelet groups are oriented edge to face instead of face to face. This tends to cause isotropic flow behavior (Goldman et al., 1990). A wide variety of depositional environments can result in a flocculated clay fabric (Holtz and Kovacs, 1981). This is encouraging for electroosmotic remediation techniques such as the 'lasagna' technique (Brodsky and Ho, 1994) that rely upon the vertical movement of water towards intervening porous zones.

Reconstituted till: The physical nature of the reconstituted till differs from undisturbed till in three important respects. First, all material coarser than medium sand was removed; second, the water content was higher (Table 3); and third, the sediment was mixed with water and inserted into the columns by hand. The resulting sediment was macroscopically more uniform. In general, the flow results were more reproducible, reflecting the sample's macroscopic heterogeneity.

From the flow experiments in reconstituted till, there are several interesting results. The first is the negligible effect of variable clay content on electroosmotic flow which is essentially identical for sediment that ranges from 2% to 41% clay (Fig. 4). This stands in sharp contrast to the hydraulic behavior of sediment that contains even minor amounts of clay minerals. Only two to three weight percent of swelling clay is sufficient to lower the hydraulic conductivity by two or three orders of magnitude and any sediment containing over 33% swelling clay behaves essentially as a pure clay with very low hydraulic conductivity (Goldman et al., 1990).

To the extent that the reconstituted sediments represent real sediments, these results have important consequences for electroosmotic processing of contaminated aquifers. Usually aquifers contain small, variable amounts of silts and clay minerals. This is an important factor in causing aquifer heterogeneity. Based on the results seen in Fig. 4, electroosmotic processing could be used to 'smooth out' aquifer heterogeneities with the concomitant increase in the ability to flush aquifers clean. This may be more important in a practical sense than the ability to move contaminants out of otherwise impermeable aquitards. This is especially true in light of the current regulatory movement in the United States towards allowing contamination to remain in isolated, highly impermeable sediments.

In till samples, which contain calcite and in which the clay phase is largely smectite, the response is more complicated than in kaolinite in that electroosmotically driven flow of water and current flow are decoupled. The structurally derived surface charge of the clays in such sediment is essentially pH independent. Moreover, in these well-buffered tills, the pH does not decrease. Therefore a lowered or reversed surface charge does not simultaneously cause the current and electroosmotic flow to stop. Instead, a complicated set of reactions between pore fluids and solids is likely to conspire to stop electroosmotic flow. The probable dissolution and subsequent precipitation of carbonate minerals and metal oxide coatings, ion exchange reactions, and partial dehydration of the clays all likely contribute to the decreasing ability of the sediment to transmit water.

Montmorillonite: An obvious, visible reaction front passed through montmorillonite as electroosmotic processing was applied. The front was marked by a sharp pH drop, an increase in the ferrous iron content of the clay, a decrease in water content, a visible color change, and the development of shrinkage cracks. The shrinkage cracks were laterally discontinuous, were both parallel and perpendicular to the axis of the column and were as large as 4 mm in width and 3 cm in length. Cracks appeared within 8 to 12 h after electroosmotic processing started. An interesting feature was that the cracks were not filled with pore fluid in spite of the presence of a hydraulic head on the column and the continuing presence of electroosmotic flow through the clay. Electroosmotically driven water moved through the clay, not through the cracks.

After 36 to 48 h the reaction front stopped within a centimeter of the cathode where high pH conditions were encountered. Further electroosmotic processing served to sharpen the front and eventually caused a millimeter thick layer of the clay at the reaction front to turn dark olive green. The magnitudes of the changes that occurred across the reaction front at the end of an experiment are given in Table 4.

Destructive analysis of the clay after the experiment indicated that the Fe(II) content of the clay increased as the front passed (Table 4). Possibly this was due to reduction of octahedrally bound Fe(III) within the crystalline structure of the clay. Reduction of structural iron was further supported by the appearance of the color green. This is consistent with previous work on chemical reduction of smectite which commonly causes the color to change to green (Komadel et al., 1990; Rozenson and Heller-Kellai, 1976a,b). These color changes arise from intervalence electron transfer between Fe(II) and Fe(III) in adjacent octahedral sites (Lear and Stucki, 1987).

Reduction of octahedral Fe(III) to Fe(II) has also been reported to cause a net increase in the surface charge (Lear and Stucki, 1989). Additional surface charge causes

Table 4
Properties of montmorillonite at the end of electroosmotic processing when the reaction front stabilized near the cathode. The green layer is very thin, approximately 1 millimeter. There was insufficient sample material for an accurate water content. Fe(II) values are given in mg/kg of wet clay

Sample location	color	pH	Fe(II) (mg/kg)	percent water
before reaction front passes	grey	9.0	240	72–74
after reaction front passes	white	1.7–1.9	876	65–69
at reaction front	green	7.8–9.3	4564	–

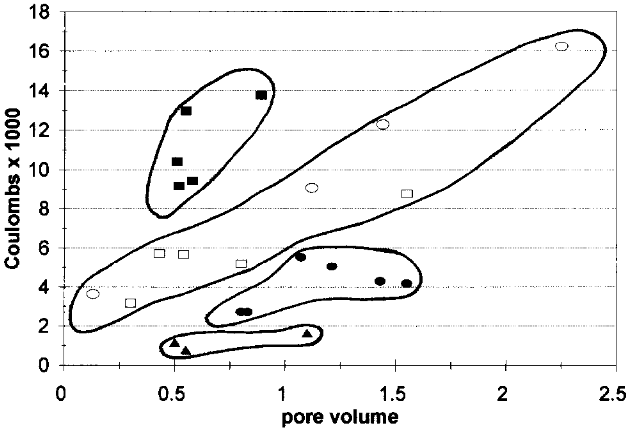

Fig. 7. Amount of electricity used vs. number of pore volumes of water passed at the end of each experiment. ■ = montmorillonite. ○ = undisturbed till, vertical orientation. □ = undisturbed till, horizontal orientation. ● = reconstituted till. ▲ = kaolinite

interlayer cations to be more strongly attached to the surfaces inducing inner sphere type surface complexing and causes the collapse of parallel clay layers (Wu et al., 1989). At the same time, waters of hydration are expelled, clay layers tend to rotate to a face-to-face orientation (Stucki and Tessier, 1991), and the swelling pressure decreases. The nearly 10% loss in water content and the appearance of shrinkage cracks observed in the montmorillonite columns are all consistent with structural reduction of iron in the clay. Similar decreases in swelling pressure and the appearance of shrinkage cracks were reported for chemically reduced smectites (Shen et al., 1992; Lear and Stucki, 1989). Grundl and Michalski (1995) reported shrinkage cracks in reconstituted till samples following electroosmotic processing at 100 V/m which may be due to the same phenomenon.

The type of clay mineral present in a sediment has a large effect on the response to the application of an electric current. This is depicted in Fig. 7 in which the total amount of electricity used (coulombs) is plotted versus the total amount of water passed at the end of each experiment. In Fig. 7, the efficiency of a given sediment is exemplified by the extent to which each field can be considered as a linear function of coulombs versus pore volume. The slope of each linear field represents the efficiency of that sediment. Note that each sediment type falls within a well-defined field. Kaolinite was the most efficient at generating electroosmotic flow and montmorillonite (a smectite) was the least efficient. Till samples, which contain lesser amounts of smectite, have intermediate efficiencies.

Electroosmotic efficiency is a balance between the driving force and the resistance to flow in a given sediment. In this study, in which the initial fluid composition was not changed, variations in the driving force were largely a function of the solids present. Resistance to flow was a complicated and time variant function of the changes induced in the sediment as a result of electroosmotic processing. The changes include at least the pH induced dissolution and precipitation of solids, changes in surface charge, changes in water content and clay fabric, as well as a variety of homogeneous reactions that contribute to the buffer capacity and ionic speciation within the aqueous phase. At what point these changes will cause the flow resistance to overcome the driving force depends on subtle differences in the water content, mineralogy, and fabric of the initial sediment. The lateral extent of each field along the x-axis in Fig. 7 represents the variability in the initial sediment. The high variability in the undisturbed samples (open symbols) with respect to reconstituted and pure clay samples (filled symbols) is evident.

5. Conclusions

Based on this study, the electrokinetic response of natural sediments is complex and time variant. The presence of calcite and montmorillonite is particularly important to the electrokinetic response of the sediment. Montmorillonite reacts directly to the application of an electric field and this causes changes in the fundamental character of the clay. Montmorillonite should not be considered as a solid that simply serves to provide a charged surface for the generation of electroosmotic flow but rather as a reactive mineral. The presence of calcite in a system causes it to be well buffered, and the migrating low pH front seen in simple kaolinite–water systems is absent. Attempts to model the electrokinetic behavior of real systems must take into account the initial mineralogy of the sediment, in particular the effect that montmorillonite and calcite have on the system.

Electroosmotic flow is equivalent in an undisturbed glacial till in both horizontal and vertical orientations. For sediment of this type, electrodes placed horizontally are just as effective at moving water through a clay body as vertically oriented electrodes. An encouraging result for the future of electrokinetic remediation is the fact that electroosmotic flow may be possible in sediment with as little as 2% clay. The possibility of being able to ‘smooth out’ heterogeneities in aquifer conductivity due to spatially variable clay content holds promise for enhanced remediation of contaminated aquifers by electroosmotically assisted pump-and-treat techniques.

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