

Effect of Soil Type on Electrokinetic Removal of Phenanthrene Using Surfactants and Cosolvents

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Abstract: Numerous sites have been contaminated with polycyclic aromatic hydrocarbons (PAHs), and these sites pose a significant risk to public health and the environment because PAHs are often toxic, mutagenic, and/or carcinogenic. Furthermore, these sites are often difficult or costly to remediate because PAHs are hydrophobic and highly resistant to degradation. The in situ flushing process using surfactants and/or cosolvents has shown great promise for sites possessing uniform and high-permeability soils, but it is generally ineffective for sites containing heterogeneous and/or low-permeability soils. Thus, for difficult soil conditions, electrokinetics can be integrated with the in situ flushing process to improve soil-solution-contaminant interaction. This investigation was conducted to evaluate the effects of two different low-permeability soils, kaolin and glacial till, on electrokinetically enhanced flushing. Each soil type was used in three bench-scale electrokinetic experiments, where each test employed a different flushing solution, deionized water, a surfactant, or a cosolvent. The results indicated that the contaminant was more strongly bound to the glacial till than the kaolin, and this was attributed to its higher-organic content. The glacial till also generated a greater electrical current and electro-osmotic flow, and this was probably a result of its higher-carbonate content and more diverse mineralogy. Based on the contaminant mass remaining in the soil, it was apparent that the surfactant or cosolvent solution caused contaminant desorption, solubilization, and/or migration in both soils, but additional research is required to improve PAH removal efficiency.

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Introduction

Polycyclic aromatic hydrocarbon (PAH) compounds have been found to be toxic, mutagenic, and/or carcinogenic (Clar 1964; Harvey 1991), so it is important to prevent the transport of these pollutants into the environment by remediating the source zones where high concentrations of PAHs exist. The United States Environmental Protection Agency (USEPA) estimates that 3,000 to 5,000 former manufactured gas plant (MGP) sites are located across the United States, and many of these contaminated sites contain substantial quantities of PAHs (USEPA, 2000). Since there are so many former MGP sites and they exist in a broad range of different geographical areas, the site conditions and the types of soils that are present at these sites may vary considerably. In situ flushing with surfactants/cosolvents has shown the ability to remediate PAH-contaminated soils that have a fairly high-hydraulic conductivity (Fu and Luthy 1986; Ganeshalingam et al. 1994; Roote 1997), but this remediation technique is often ineffective for heterogeneous and/or low-permeability soils, espe-

cially when the hydraulic conductivities are less than about 10^{-5} cm/s in magnitude (Roote 1997). PAH sorption may predominate in soils with large quantities of organic matter and/or clay/silt-sized particles because organic matter contains substances with similar hydrophobic characteristics and clay/silt-sized particles have large surface areas as well as electrical charges associated with them (Johnston 1996). Consequently, innovative techniques are needed to remediate PAHs from low-permeability clayey soils, and electrokinetically enhancing the in situ flushing process with surfactants/cosolvents has great potential.

Basically, electrokinetics involves the installation of electrodes into wells and the application of a low-electric potential across the predetermined anode (positive) and cathode (negative) electrodes. The electric potential induces a number of physicochemical processes including the phenomenon of electro-osmosis, which can transport a solution through clayey soils at a flow rate much higher than a conventional hydraulic gradient (Casagrande 1949). Surfactants/cosolvents can substantially increase PAH desorption and solubilization, and the increased flow rate due to electro-osmosis greatly improves soil-solution-contaminant interaction. If PAH desorption and solubilization occur, the contaminant-laden solution should migrate by electro-osmosis towards the electrodes, where the solution can be removed from the wells and treated using bioremediation or other conventional wastewater treatment techniques (Abdul et al. 1992; Joshi and Lee 1995; Pinto and Moore 2000; Lee et al. 2001).

The objective of this paper is to present a laboratory investigation that was performed to evaluate the effects of soil type on the removal of PAHs by electrokinetics. Bench-scale electrokinetic experiments were conducted using two diverse soils, kaolin and glacial till, that were spiked with phenanthrene as a represen-

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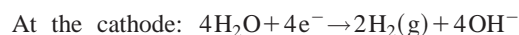
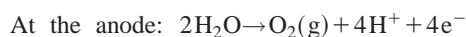
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tative PAH. Deionized water, a surfactant (3% Tween 80), and a cosolvent (40% ethanol) were tested as flushing solutions. The measured parameters during the tests included the electric current, cumulative electroosmotic flow, and cumulative mass removal, and, at the conclusion of the experiments, the soil was extruded and the hydrogen ion concentration (pH) values and residual phenanthrene concentrations were measured along the length of each soil specimen. The results were analyzed to assess the effects of soil composition on PAH desorption, solubilization, and electrokinetic remedial efficiency.

Background

Although a comprehensive review of the physicochemical processes that are involved in electrokinetics is beyond the scope of this paper, a brief overview is presented herein to facilitate an understanding of electrokinetic treatment. Initially, it should be recognized that under an electric potential, the electrolysis of water occurs at the electrodes according to the following reactions:



Thus, the electrolysis reactions cause an acidic solution to be generated at the anode and an alkaline solution to be generated at the cathode. The primary contaminant transport mechanisms that occur during electrokinetics are electromigration, electro-osmosis, and electrophoresis. Electromigration describes the transport of ionic species present in the pore fluid. This process is largely responsible for generating the electrical current, and it includes the migration of H^+ and OH^- towards the oppositely charged electrode. Moreover, under an electric potential, electro-osmotic flow is produced because the locally existing excess ions migrate in a plane parallel to the particle surface towards the oppositely charged electrode, and, as they migrate, they transfer momentum to the surrounding fluid molecules via viscous forces (Eykholt 1992). Electro-osmosis depends on the net amount of ionic migration towards an electrode location, and, in low-permeability clayey soils, the net ion migration may be high and it could significantly affect the decontamination process. The following Helmholtz-Smoluchowski (H-S) equation is often used to estimate the average electro-osmotic flow velocity (v_{eo}) (Eykholt and Daniel 1994):

$$v_{eo} = - \frac{D\varepsilon_0\zeta}{\eta} E_x$$

According to this equation, the flow velocity is proportional to the electrical gradient (E_x), zeta potential (ζ), and dielectric constant (D), and it is inversely proportional to the viscosity (η). The (ε_0) term represents the permittivity of vacuum ($8.854 \times 10^{-12} \text{ C/V m}$), and the dielectric constant and viscosity are properties of the pore fluid. The zeta potential depends on the zero point of charge (ZPC), which refers to the pH at which the net charge on the particle surface is zero. Generally, when the pH is below its ZPC, a soil has a positive zeta potential and the electro-osmotic flow occurs towards the anode. Conversely, when the pH is above the ZPC, the soil has a negative zeta potential and the electro-osmotic flow occurs towards the cathode. Alternately, the electro-osmotic flow velocity is given by

$$v_{eo} = K_e E_x$$

where K_e is referred to as the electro-osmotic conductivity. Finally, electrophoresis is the migration of charged colloids, but, in

a compact soil system, electrophoresis is less important since larger colloid-sized particles are typically restrained from movement.

Although the electrokinetically enhanced in situ flushing technique has great potential, the effectiveness of the process can be highly dependent on soil-solution-contaminant chemistry. By observing the H-S equation, it can be seen that changes in the surface charge of the soil particles (zeta potential) and changes in the pore fluid properties (such as dielectric constant and viscosity) influence the electro-osmotic flow. In addition, the electrical gradient may not be uniform through the soil, so the electro-osmotic flow is generally not uniform spatially or temporally (Eykholt and Daniel 1994). Therefore, the average electro-osmotic conductivity (K_e) through the soil commonly varies with time, and, as a result of these physicochemical changes, the electro-osmotic flow may cease or even reverse in direction. Furthermore, soils may be extremely variable and complex substances, both structurally and compositionally (Mitchell 1993), and contaminant chemistry, desorption, and solubilization reactions, as well as the mass transport mechanisms that occur during electrokinetics may significantly complicate the process.

The electrolysis reactions greatly affect the remediation process because the ionic products (H^+ and OH^-) may electromigrate and/or they may be transported by electro-osmotic advection towards the oppositely charged electrode location. Thus, an acidic (H^+) front of solution may move from the anode towards the cathode, and/or an alkaline (OH^-) front of solution may move from the cathode towards the anode. The rate of electromigration may also be affected by ionic mobility, and, since hydrogen ions are smaller and have a greater mobility than hydroxyl ions, the acidic front generally moves faster through the soil. The reaction kinetics, or the rate of the electrolysis reactions at the electrodes, may also affect the generation and movement of the hydrogen and/or hydroxyl ions. Incidentally, for low-acid buffering clayey soils such as kaolin, the inflow of H^+ ions has the effect of causing the mineral surface charge to become more positive, which, by H-S theory, decreases the electro-osmotic flow towards the cathode. Shapiro and Probstein (1993) and Schultz (1997) have found that the addition of a pH buffer to the anode reservoir helps to counteract or neutralize the electrolysis reaction at the anode, and the result is a higher and more sustained electro-osmotic flow and greater contaminant removal. Since the pH buffering technique would complicate the comparison of the different soil types, it was not employed in this present investigation; however, a companion study using kaolin soil was performed to assess the effect of using a pH buffering solution at the anode (Saichek 2002).

There have been a number of laboratory studies performed to evaluate the electrokinetic remediation process and contaminant transport by electro-osmosis for soils contaminated with various organic compounds. In several investigations, the compounds were relatively soluble compared to PAHs and high-removal efficiencies were obtained by using ordinary purging solutions such as distilled or tap water (Acar et al. 1992; Bruell et al. 1992; Shapiro and Probstein 1993; Schultz 1997). The study conducted by Bruell et al. (1992) is of particular interest because they employed several different organic compounds with a range of aqueous solubilities and conducted experiments and used calculations to predict contaminant removal from kaolin by electro-osmosis. These researchers determined that an organic chemical with a relatively high-aqueous solubility and low adsorption, such as benzene, toluene, trichloroethylene, or m-xylene, could be easily

Table 1. Properties of Soils Tested

Property	Kaolin	Glacial till
Mineralogy	Kaolinite 100% Muscovite: trace Illite: trace	Quartz: 31% Feldspar: 13% Carbonate: 35% Illite: 15% Chlorite: 4–6% Vermiculite: 0.5% Smectite: trace
Particle size distribution (ASTM D 422)		
Gravel (%)	0	0
Sand (%)	4	20
Silt (%)	18	44
Clay (%)	78	36
Specific gravity (ASTM D 854)	2.6	2.7
Hydraulic conductivity [cm/s]	1.0×10^{-8}	8.8×10^{-8}
Organic content (%)	Near 0	2.8
pH (ASTM D 4972)	4.9	8.2
Cation exchange capacity [meq/100 g] (ASTM D 9081)	1.0–1.6	13–18
USCS classification (ASTM D 2487)	CL	CL

removed by electro-osmosis, but a chemical with a low-aqueous solubility and high adsorption, such as hexane or isooctane, was transported at a much slower rate (Bruell et al. 1992). The sorption of an organic compound to soils is often described by a linear isotherm $C_s = K_d C_w$, where C_s is the concentration of solute (phenanthrene) sorbed to the soil, C_w is the concentration of the solute in the aqueous solution, and K_d is the soil-solution distribution ratio or partition coefficient (Ko et al. 1998b). This equation is often valid over a limited range, particularly when C_w is low (Li et al. 2000). Assuming a linear isotherm, Bruell et al. (1992) predicted that a 90% removal of benzene (approximate solubility = 1,780 mg/L and experimental $K_d = 0.89$) from kaolin could be accomplished in 314 days using 2.01 pore volumes of water, while a 90% removal of isooctane (approximate solubility = 2.4 mg/L and experimental $K_d = 24$) from kaolin would require 4,731 days and 30.2 pore volumes of water.

Previously, electrokinetic experiments were performed at the University of Illinois at Chicago (UIC) to remediate a phenanthrene-contaminated glacial till soil using various cosolvents, but these experiments were only moderately effective at PAH desorption, solubilization and removal (Li et al. 2000). Subsequently, a series of batch tests were conducted to investigate PAH desorption and solubilization from two types of clayey soils, kaolin and glacial till, using a variety of surfactants, a cosolvent, and a surfactant-cosolvent mixture (Saichek 2002). These batch tests provided an assessment of the ability of the surfactant/cosolvent solutions to remove PAHs from the soils, but the mass transport and removal mechanisms that occur during batch tests and those that occur during electrokinetics can be quite different. Thus, Reddy and Saichek (2002) conducted a series of electrokinetic experiments using the best surfactant and cosolvent solutions as determined from the batch tests to evaluate PAH removal from a soil by electrokinetics. This earlier study, however, was limited to only one type of soil, namely, kaolin. Additional research conducted to investigate the effect of soil type on electrokinetic removal of PAHs using surfactant and cosolvent solutions is presented in this paper.

Experimental Methodology

Materials

The soils that were selected for this investigation were kaolin and glacial till, and Table 1 shows that the mineralogy and physical and chemical properties of these soils differ significantly. As seen in the table, kaolin basically consists of the clay mineral kaolinite whereas glacial till is largely composed of quartz, carbonates, feldspars, illite, and other clay minerals. The particle-size distribution shows that kaolin has a greater percentage of clay-sized particles, and glacial till has a considerable amount of larger, sand, and silt-sized particles. Clearly, both soils have a very low-permeability, and they are far below the 10^{-5} cm/s magnitude that is considered appropriate for in situ soil flushing (Roote 1997). For this investigation, one of the greatest differences between these two soils is the organic content. Kaolin is virtually non-organic while glacial till has a relatively high-organic content of 2.8%. Kaolin also has a somewhat lower-cation exchange capacity than glacial till. Kaolin is often used in electrokinetic research because it has been studied extensively, it has a low-organic content, consistent and uniform mineralogy, it is fairly nonreactive, and it has a low-cation exchange capacity (Eykholts 1992). Thus, kaolin is a good control soil for laboratory electrokinetic testing because the amount of experimental variation as a result of soil heterogeneity is minimized. In contrast, glacial till is a highly variable soil with a relatively high-organic content, complex mineralogy, and wide range of particle sizes, but, since field soils are often quite heterogeneous, glacial till is more representative of the soil conditions commonly found at contaminated sites. In other words, although testing with kaolin soil is beneficial for analyzing electrokinetic variables, such as the effects produced by the flushing solution or voltage gradient, it is insufficient for assessing the effects caused by soil heterogeneities, such as the presence of different minerals and organic matter.

A neutrally charged contaminant, phenanthrene (98% pure, $C_{14}H_{10}$; Molecular Weight = 178.2), was selected as the representative PAH compound, and it has an aqueous solubility of 1.1 mg/L

Table 2. Electrokinetic Testing Program

Test number	Soil type	Purging solution	K_d^a (mL/g)	Voltage gradient [VDC/cm]	Approximate test duration (days)
1	Kaolin	Deionized water	Not determined	1	188
2	Kaolin	3% Tween 80	2.9	1	231
3	Kaolin	40% Ethanol	11	1	245
4	Glacial till	Deionized water	210 ^b	1	168
5	Glacial till	3% Tween 80	10	1	229
6	Glacial till	40% Ethanol	20	1	236

^aSaichek (2002).

^bLi et al. (2000).

and a $\log K_{ow}$ of 4.57 at 25°C (Schwarzenbach et al. 1993). Besides the baseline tests that used deionized water, one surfactant, namely, 3% Tween 80 [polyoxyethylene (20) sorbitan monooleate] solution and one cosolvent, namely, 40% ethanol (C_2H_5OH) solution were used. Table 2 lists the K_d values and test durations and summarizes the variables and the number of tests conducted for this study. The K_d value for deionized water and kaolin soil was not determined due to the low solubility of phenanthrene in water.

Electrokinetic Reactor

The electrokinetic reactors used in this study were similar to those used in previous electrokinetic research at UIC (Reddy et al.

1997; Reddy and Parupudi 1997; Reddy and Shirani 1997). A schematic diagram of the electrokinetic reactor and the entire test setup is shown in Fig. 1. The reactor simulates one-dimensional (1D) contaminant transport under the combined influences of electrical, hydraulic, and chemical gradients.

The reactor consisted of a cell, two electrode compartments, an anode electrode reservoir, a cathode sample bottle, a power supply, a multimeter (Protek Model B-845), and peripherals, such as C-Flex tubing (Cole Parmer Instrument Company), wiring, and stands. For all the electrokinetic experiments, the power supplies were either Protek DC models 3006 or 3033 or a Hewlett Packard DC model 6205B. The reactor cell was made of plexiglass and it had a 6.2 cm inside diameter and a 19.1 cm length, so its volume was approximately 577 cm³. Each electrode compartment was

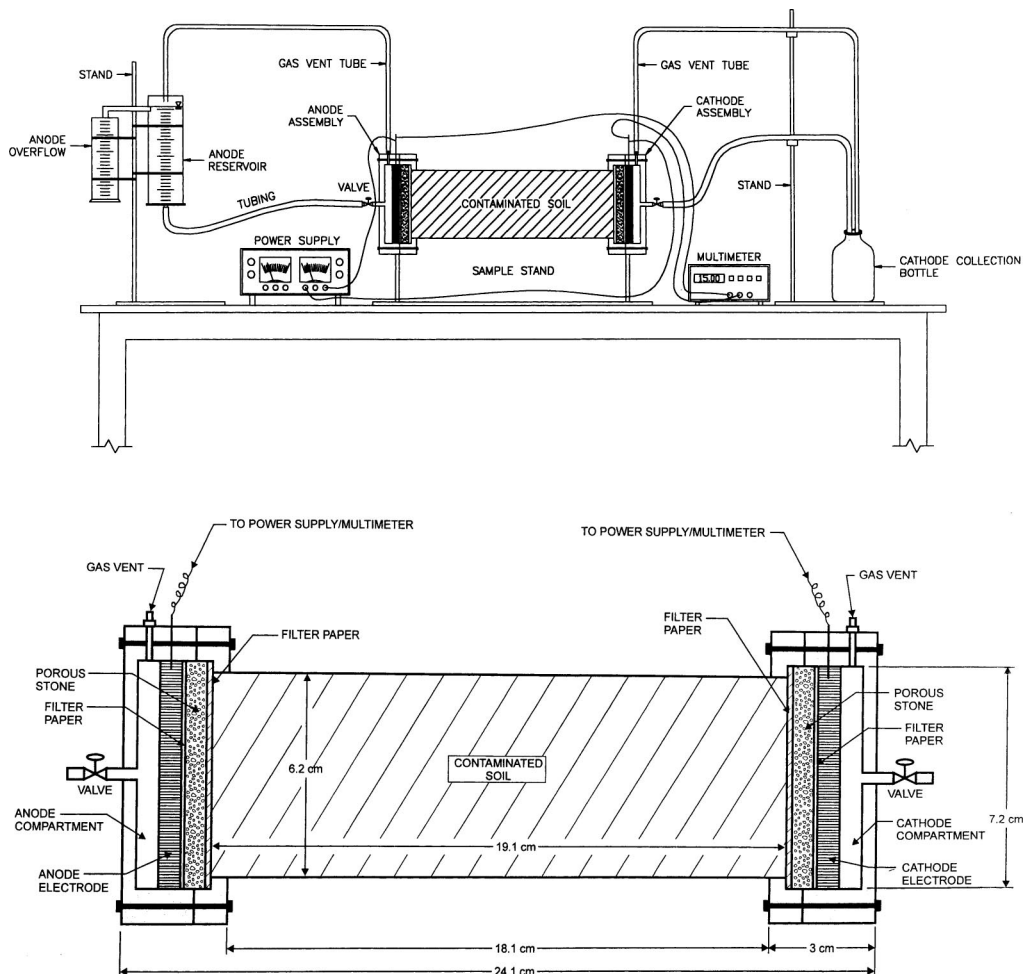


Fig. 1. (top) Overall schematic of electrokinetic test setup and (bottom) details of electrokinetic test cell

also made of plexiglass and contained Whatman filter paper, a porous stone, and a slotted graphite electrode. The #1 Whatman filter paper retains particles with diameters greater than 11 μm and the porous stone retains particles with diameters greater than 250 μm , and both the filter paper and the porous stone were used to prevent soil particles from entering into the anode reservoir or cathode sample bottle. The filter paper was placed between the soil and the porous stone, and both were placed in front of the electrode. Gas vents were provided in the electrode compartments to allow gases resulting from the electrolysis reactions to escape.

Testing Procedure

For all the electrokinetic tests, the soils were spiked with phenanthrene at a target concentration of 500 mg/kg (mass of phenanthrene/mass of dry soil), which represents the typical PAH concentrations that are found near source zones at contaminated sites (USEPA 2000). Approximately 1.5 kg of glacial till soil and 1.1 kg of kaolin soil was spiked for each electrokinetic test. Initially, the phenanthrene required to yield the target concentration was measured and then completely dissolved in about 500 mL of hexane. Hexane was used because phenanthrene has an extremely low solubility in water. The hexane-phenanthrene mixture was subsequently mixed with the measured amount of soil, and additional hexane was put in so that the soil-hexane-phenanthrene mixture could be easily stirred and blended homogeneously. The mixtures were stirred with stainless steel spoons, and all mixing operations were performed within glass beakers. The motivation for this mixing technique was to ensure that the phenanthrene would be distributed evenly throughout the soil. The soil-hexane-phenanthrene mixture was then placed beneath a ventilation hood for nearly a week until the hexane completely evaporated and the contaminated soil was dry. Occasional stirring was necessary during the drying period to increase the rate of drying and further ensure uniform phenanthrene distribution. A sample was taken to determine the actual initial concentration of phenanthrene in the soil, since a portion of the contaminant may volatilize along with the solvent, hexane. The initial mass of dry soil that was placed into the reactor varied slightly from test to test, but it was approximately 800 g for the kaolin tests and around 1,000 g for the glacial till tests.

After the phenanthrene-contaminated soil was dry, it was thoroughly mixed with a measured amount of deionized water in a glass pan, so that the soil water content would simulate field conditions. The target water content for the kaolin soil was 35%, and the target water content for the glacial till was 20%. The moist soil was then placed into the reactor soil chamber in layers, and each layer was tamped into the chamber using an aluminum pestle so that the amount of void space was minimized. Once the soil was fully packed into the chamber, the reactor assembly was completed, the peripheral equipment was attached, the anode and cathode compartments as well as the anode reservoir were filled with solution, and a constant, 1 VDC/cm, voltage gradient was applied for the required time duration. Initially, at the start of testing, the cathode compartment was filled with deionized water and the anode compartment and reservoir were filled with the selected flushing solution.

During the testing, the electrical current and the inflow volume and effluent volume at the anode and cathode were measured periodically. Samples of the effluent were taken so that the phenanthrene concentration could be measured. The tests were run until the current greatly decreased, the effluent volume significantly reduced, or it appeared that the phenanthrene concen-

tration in the effluent had reached a steady-state condition. At the conclusion of testing, the soil was extruded from the test apparatus and divided into sections to analyze the spatial distribution of the pH as well as the residual phenanthrene remaining in the soil. The soil samples were sectioned into five parts approximately every four centimeters along the length of the reactor soil chamber. Representative samples were taken from each soil section for the determination of moisture content, soil pH, and phenanthrene concentration. Soil pH measurements were determined using a soil to water ratio of 1:1 as described in ASTM Method D 4972. Generally, 10 mL of deionized water was added to 10 grams of soil, and the pH was measured using a Digi-Sense digital pH meter that was calibrated using standardized pH solutions. Soil water contents were determined using ASTM Method D 2216.

Chemical Analysis

To determine the phenanthrene concentration in the soil, a dry representative soil sample weighing 10 g was thoroughly mixed with about 10 g of Na_2SO_4 (Fisher Scientific), and the mixture was placed into a Whatman cellulose extraction thimble. The phenanthrene was then extracted using a Soxhlet apparatus consisting of a 250 mL flask, a Soxhlet extraction tube, and a bulb-type Allihn condenser. The procedure is outlined in USEPA Test Method 3540C (USEPA 1986). The solution used in the Soxhlet extraction process was 190 mL of a 1:1 mixture of hexane and acetone (Fisher Scientific), and the process was operated for at 4–6 cycles/h for at least 24 h. After the extraction was completed, the volume of the solvent remaining in the Soxhlet extraction tube and flask was measured, and high-pressure liquid chromatography (HPLC) analysis was performed on a sample of the liquid. The soil was usually highly contaminated with phenanthrene, so the solvent-phenanthrene liquid samples obtained from the Soxhlet extraction were directly analyzed using the HPLC. In addition to the soil analysis, the liquid effluent samples from the electrokinetic tests containing surfactant/cosolvent-phenanthrene were directly analyzed using the HPLC.

A Hewlett-Packard Model 1100 HPLC equipped with an Alltech Econosphere reverse-phase C18 column (250 \times 4.6 mm, 5 μm particle size) and a diode array ultraviolet detector was used. The detector wavelength was set at 254 nm. Before injection into the HPLC, the samples were filtered through a 0.22 μm particle retaining Cameo 13F Teflon, polytetrafluoroethylene, membrane. Each sample was injected via a manual injector with a 20 μL sample loop. A mixture of water and methanol 25:75 was used as the mobile phase at a constant flow rate of 1.0 mL/min. The HPLC was calibrated using standards prior to performing chemical analyses.

Quality Control

Throughout the electrokinetic testing, the plexiglass reactors and reservoirs were either specifically constructed for these tests, or they were thoroughly washed using an acid cleaner and detergent and visually inspected to ensure cleanliness. The electrodes, tubing, and connecting pins or hose clamps were all new for each test. Furthermore, all the glassware, such as vials and sample bottles, used in the electrokinetic tests were new from the manufacturer and certified to be clean. All of the testing equipment, such as the multimeters, power supplies, and pH and electrical conductivity meters, were in good condition and were calibrated. A conscious effort was made to ensure that the chemicals used as solvents or during test operation were new from the manufacturer

and that they were fresh and of high-grade purity. The deionized water was tested to verify that it had an ionic conductivity near zero.

The calibration standards for the phenanthrene analyses by HPLC were prepared in two different concentration ranges, and each series contained at least four standard solutions that covered an order of magnitude in concentration or more. The linearity of the calibration graph was always checked to make sure that the regression coefficient (R^2) was close to one, and sample blanks, without contamination, were injected regularly to ensure that the system remained uncontaminated. Duplicate standard samples were commonly injected to certify a uniform response, and to ensure that the calibration graph and the baseline remained stable. The syringe was rinsed with solvent several times between sample injections to reduce contamination carryover.

After the electrokinetic tests were completed, the cumulative mass of phenanthrene collected in the effluent samples and the residual mass of phenanthrene remaining in the soil were added to determine the total measured mass. This total measured mass of phenanthrene subsequent to testing was then divided by the initial mass of phenanthrene present in the soil prior to testing to compute the mass balance. The initial mass was computed from the mass of soil placed into the reactor times the initial phenanthrene concentration. Relatively good mass balances ($\pm 10\%$) were found for the experiments, demonstrating that the phenanthrene losses were not significant and the testing procedures and quality control were adequate. Discrepancies in the mass balance may be caused by uneven contaminant distribution within the soil, detection limitations in the chemical analyses, or contaminant adsorption to the electrokinetic equipment, such as the plexiglass chambers, the electrodes, porous stones, tubing, and/or sample bottles. Volatilization of phenanthrene along with the solvents during the extraction procedures may have also caused mass balance differences.

Results and Analysis

Current

Fig. 2 shows the current in the kaolin and glacial till soils for the three different solutions, deionized water, 3% Tween 80, and 40% ethanol. The current values follow the same trend in all six tests. Initially, or within hours after applying the voltage, the current reaches a peak value. Then, for about a week, the values decrease rapidly, and, over the next few weeks, the rate of decrease gradually declines. Finally, after approximately 50 days, the current attains a relatively stable or long-term value that basically indicates the electrical conductivity characteristics of the solution during electrokinetics. By comparing the results for the two soils in Fig. 2, it is obvious that for all three solutions the long-term current values are approximately ten times higher in the glacial till than in the kaolin, and this reflects that a consistently larger amount of ion solubilization was occurring during the glacial till tests. Clearly, the changes in electrical conductivity that resulted from using different types of solution were minor compared to the changes in conductivity produced when using different types of soil. Generally, the long-term current values in glacial till were observed to fluctuate slightly more than in kaolin, and this is attributed to the more diverse mineral composition and possibly non-uniform mineral dissolution. In the baseline deionized water and 3% Tween 80 tests, the current in the glacial till soil remained fairly high and may have even slightly increased after about 100

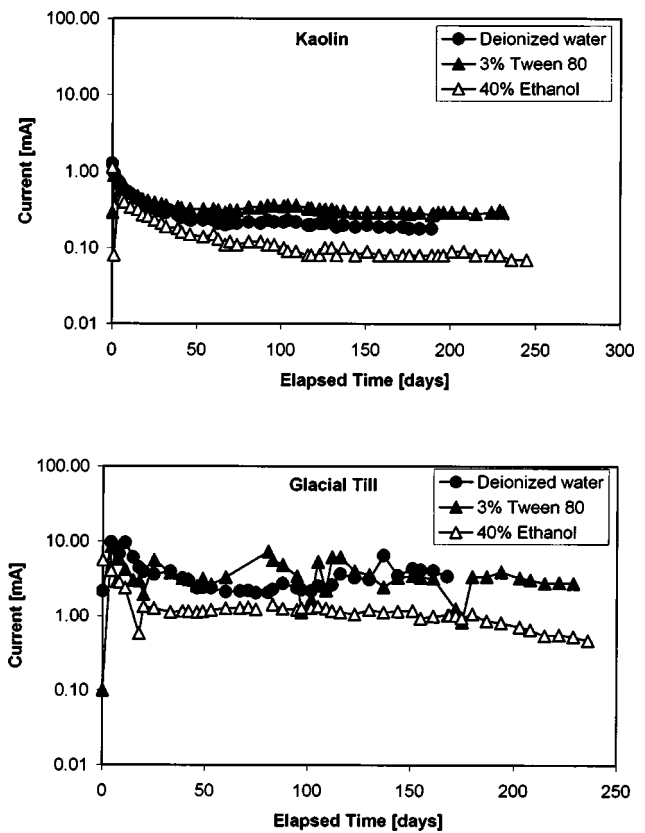


Fig. 2. Comparison of current in kaolin and glacial till soils

days. Apparently, compared to the kaolin soil, the presence of salts and carbonates and a higher amount of mineral dissolution slightly increased the electrical current and conductivity in the glacial till soil.

Grundl and Michalski (1996) found that the current increased over time in electrokinetic tests conducted with glacial till, and Pamukcu (1994) showed current values that fluctuated, increased, and decreased in different tests conducted with field soils. Therefore, it seems that with heterogeneous field soils such as glacial till, the long-term current may be highly correlated to the mineralogy, and in some instances it is possible for the current to increase over time. It should also be recognized that the electrolysis reaction at the anode causes an increase of H^+ ions, which are then transported through the soil specimen by electromigration and electro-osmosis (Acar et al. 1995). The movement of this acid front through the soil may increase mineral and salt dissolution and thereby increase ion solubilization and electrical current.

As shown in Fig. 2, the kaolin soil test using the nonionic surfactant, 3% Tween 80, had a slightly higher long-term current value than the baseline deionized water test. There is evidence that nonionic surfactants may possibly acquire an ionic charge (Rosen 1989; Edwards et al. 1994; Ko et al. 1998b), and, therefore, the sorption or presence of monomers and/or micelles may change the solution chemistry or the charge on the soil surface, so there is an increase in ion solubilization and a higher electric current results. In the glacial till soil, the 3% Tween 80 solution had a long-term current value that was nearly the same as deionized water, and this may be due to the greater number of ions in solution. Hamann et al. (1998) showed that at high ion concentrations, the conductivity of an electrolyte could actually decrease because there are a greater number of interionic interactions. In addition, it is likely that more surfactant sorption occurred in the

glacial till soil due to its higher-organic content, and, consequently, a lower number of surfactant micelles were present in solution, and this led to a reduction of ion solubilization. In either soil, glacial till or kaolin, the results show that the 40% ethanol flushing solution had a lower long-term current than the other two solutions, and this is attributed to its lower dielectric constant and the reduced amount of ion dissociation.

Electroosmotic Flow

As mentioned earlier, electromigration is the transport mechanism that fundamentally drives the electro-osmotic flow, but phenanthrene is an uncharged compound, and the surfactant and cosolvent were also nonionic or uncharged, so electro-osmosis was deemed to be the primary mechanism responsible for contaminant transport. Essentially, the surfactant and/or cosolvent were necessary for enhancing phenanthrene desorption and solubilization, but electro-osmosis was required to increase soil-solution-contaminant interaction and, after the phenanthrene had been solubilized, electro-osmosis would be the most important mode of contaminant transport.

The soil porosity of the kaolin (46%) and the glacial till (30%) can be used along with the total volume of the reactor (577 cm³) to estimate the size of a pore volume for the kaolin (265 mL) and the glacial till (170 mL) soils. Similarly, the dry mass of soil that was placed into the cell (approximately 800 g for kaolin and 1,000 g for glacial till) can be used along with the K_d values to estimate the number of pore volumes that would be required to solubilize the contaminant mass. These calculations indicate that over 1,200 pore volumes of deionized water would be necessary to remove the phenanthrene from the glacial till soil, whereas significantly lower-pore volumes (59 pore volumes for 3% Tween 80 or 118 pore volumes for 40% ethanol) were calculated for the surfactant or the cosolvent. As shown in Table 2, lower K_d values were measured for the kaolin soil, and the number of pore volumes reduced to 9 and 33 for the 3% Tween 80 and 40% ethanol solutions, respectively. Fig. 3 shows that for both soils the cumulative electro-osmotic flow volume was much less than that required based on the K_d values to remove phenanthrene. However, it should be noted that the mass transport and removal mechanisms that occur during hydraulic flushing and those that occur during electrokinetics can be quite different.

As previously mentioned, the electro-osmotic conductivity K_e is related to the electro-osmotic flow velocity v_{eo} by $v_{eo} = K_e E_x$. For the electrokinetic tests, the K_e was computed from the following equation:

$$K_e = \left(\frac{Q}{t} \right) \left(\frac{1}{A} \right) \left(\frac{L}{\Delta E} \right)$$

where Q = cumulative electro-osmotic flow in cm³; t = elapsed time in seconds; A = cross-sectional area of the electrokinetic reactor (approximately 30.19 cm²); L = distance between the electrodes; and ΔE = difference in voltage. As observed in Table 2, the electrical gradient (E_x) = ($\Delta E/L$) was equal to 1 VDC/cm for all six tests. In contrast to the electro-osmotic flow velocity, the hydraulic flow velocity is given by $v = k i$, where k is the hydraulic conductivity and i is the hydraulic gradient ($\Delta h/L$) or pressure head loss per unit length (Holtz and Kovacs 1981).

Fig. 3 shows a comparison of the cumulative electro-osmotic flow produced during the six electrokinetic tests performed using the kaolin and glacial till soils. The trend of the cumulative electro-osmotic flow somewhat correlated with the electric current in that the experiments exhibited a little more flow during the

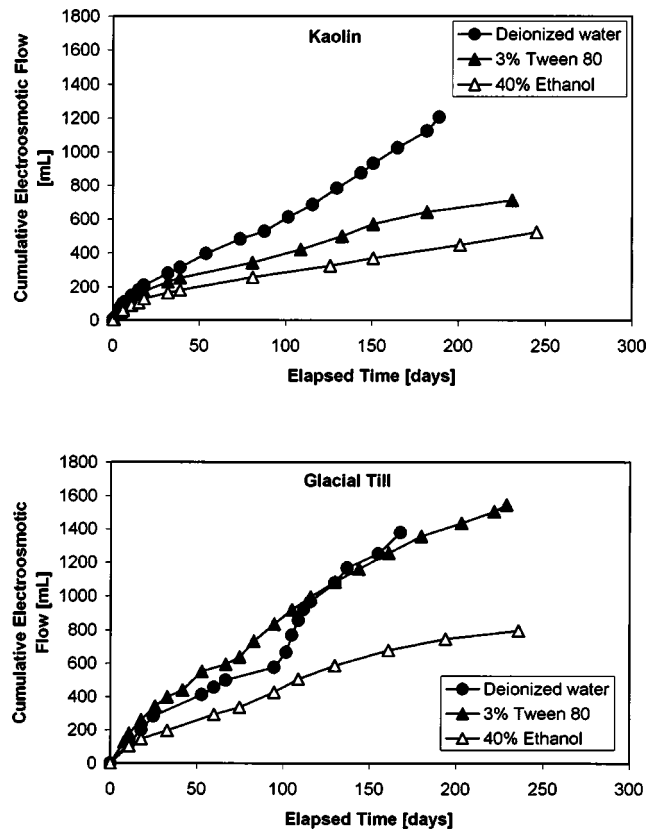


Fig. 3. Comparison of electro-osmotic flow in kaolin and glacial till soils

first week when the current was high, and then the flow rate slightly decreased as the current reduced. Comparing the two soils, it is apparent that the higher conductivity and ionic migration in the glacial till resulted in a significantly higher-cumulative electro-osmotic flow for all three solutions. Average electro-osmotic conductivity (K_e) values of 2.46×10^{-6} and 3.15×10^{-6} , 1.18×10^{-6} and 2.59×10^{-6} , and 0.82×10^{-6} and 1.29×10^{-6} cm²/(s volt) were computed for the deionized water, 3% Tween 80, and 40% ethanol solutions in the kaolin and glacial till soils, respectively. Since the electrical gradient (E_x) = ($\Delta E/L$) was equal to 1 VDC/cm for all six tests, these same K_e values were equal to the electro-osmotic flow velocity with units of cm/s. To compare these electro-osmotic flow velocity values to the fluid velocity produced by an hydraulic gradient, the hydraulic conductivity values for kaolin and glacial till, 1×10^{-8} and 8.8×10^{-8} , (from Table 2) respectively, can be used. For instance, the lowest-electro-osmotic flow velocity, 0.82×10^{-6} cm/s, occurred in the test using the 40% ethanol solution in the kaolin soil, and the approximate hydraulic gradient for this test would be $v/k = 0.82 \times 10^{-6} / 1 \times 10^{-8} = 82$, or a pressure head of about 15.7 m for a 19.1 cm length of soil. This large head loss suggests that solution transport occurred mainly as a result of electroosmosis.

It should be recognized that water is a highly polar substance with a large dielectric constant, so ion dissociation occurs more easily in water than in a lower-polarity and lower-dielectric constant solution such as 40% ethanol (Hamann et al. 1998). According to the Helmholtz-Smoluchowski theory (H-S theory), the electro-osmotic flow is proportional to the dielectric constant of the fluid, the zeta potential, and the electric-field strength, and inversely proportional to the fluid viscosity. By H-S theory, water, which has a high-dielectric constant and low viscosity, should

produce a greater electro-osmotic flow than a 40% ethanol solution, which has a lower-dielectric constant, or a surfactant solution, which may have a much higher viscosity. It is also useful to observe that the electro-osmotic flow is directly proportional to the zeta potential, which is partially a function of the charge on the mineral surface and may be affected by changes in pH (Eykholt and Daniel 1994; Vane and Zang 1997).

The largest difference in cumulative electro-osmotic flow between the two soils occurred with the 3% Tween 80 solution, where, after approximately 160 days, the flow in the glacial till experiment was more than double the amount in the kaolin test. In the kaolin soil, the 3% Tween 80 surfactant appears to inhibit or hinder electro-osmotic flow compared to deionized water, but, in glacial till, it seems that the 3% Tween 80 had very little effect on electro-osmotic flow, and the flow was nearly the same, and at times greater, than the flow measured in the deionized water test. In kaolin, the surfactant solutions lower the electro-osmotic flow because it seems that the monomers at the soil-solution interface affect the diffuse double layer region and/or ionic migration in that region. Moreover, it should be remembered that nonionic surfactant monomers may acquire charges or sorb to the surface of the mineral and/or become protonated (Rosen 1989), and this could cause the mineral surface to become more positive, thereby changing the zeta potential, which by H-S theory, could reduce the electro-osmotic flow. In other words, nonionic surfactant monomers may increase the mineral surface charge, and, subsequently, reduce the electro-osmotic flow, and this appears to be the case in the kaolin soil. Glacial till, however, has a high-buffering capacity, so the H^+ ions may combine with other species that are present, such as carbonates. Consequently, the surfactant monomers that are sorbed to the mineral surface in glacial till may not become protonated or attract H^+ ions, and the mineral surface charge and zeta potential could remain negatively charged. The mineral surface could even become more negatively charged when micelles are present if the micelles attract H^+ ions away from the mineral surface, and this could help to increase the electro-osmotic flow.

The high acid buffering capacity of glacial till is probably responsible for the higher-cumulative electro-osmotic flow in the baseline deionized water and 40% ethanol tests. Kaolin has a low-acid buffering capacity so the high H^+ concentration generated due to the electrolysis reaction at the anode leads to the formation of an acidic front that is transported through the soil specimen by electromigration and electroosmosis (Acar et al. 1995). As the acid solution migrates into the kaolin, the charge on the mineral surface increases, thereby changing the zeta potential, and, subsequently, the electro-osmotic flow in the region near the anode reduces. Conversely, in glacial till, carbonate minerals are present that buffer the acid generated at the anode, and this keeps the pH high, the zeta potential relatively unchanged, and the electro-osmotic flow is basically unaffected by the electrolysis reaction at the anode. The lower flow of the 40% ethanol compared to the baseline tests in both soils can be attributed to the significantly lower dielectric constant for ethanol, and, according to H-S theory, the electroosmotic flow velocity is directly proportional to the dielectric constant.

Cumulative Mass Removal

Fig. 4 shows the cumulative mass of phenanthrene removed by the three different flushing solutions during the electrokinetic tests performed using the two soils, kaolin and glacial till. The results show that for all six tests each of the solutions produced very

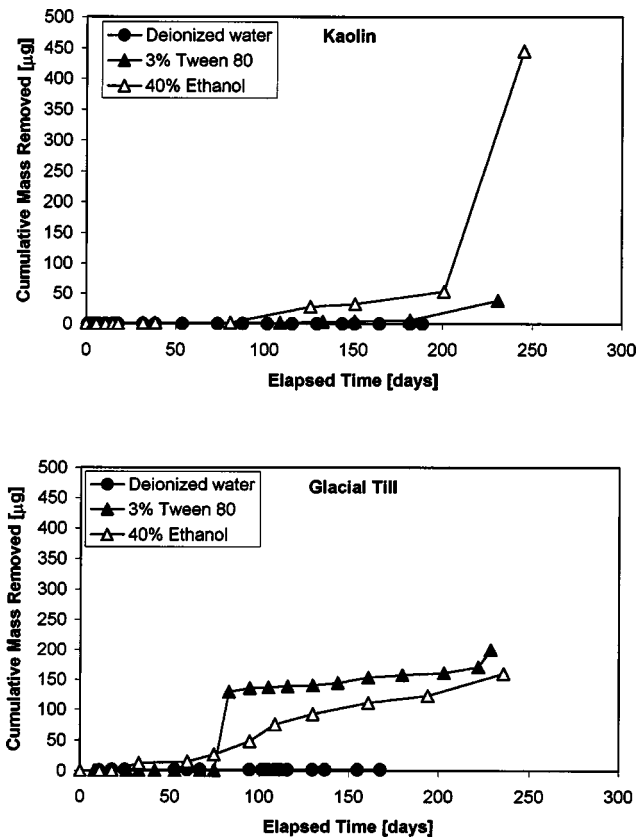


Fig. 4. Comparison of phenanthrene mass removal from kaolin and glacial till soils

low-contaminant mass removal. The highest-cumulative mass removed was about 450 μg of phenanthrene, and this was measured in the test using 40% ethanol in kaolin soil. However, compared to the initial mass of roughly 400,000 μg this amount of mass was almost negligible. Although there was not much mass removal in any of the tests, the results show that some solubilization occurred in the tests using surfactants/cosolvents, but, since the solubility of phenanthrene is so low in deionized water, no phenanthrene was detected in the effluent when this flushing solution was used. PAHs such as phenanthrene have a tendency to bind or associate with organic matter because organic matter often contains hydrophobic sites and characteristics that are similar to PAHs (Means et al. 1980; Chiou et al. 1998; Gillette et al. 1999). Therefore, since glacial till has a higher-organic content, it was expected to be more difficult to remove phenanthrene from glacial till. This expectation was reinforced when the 40% ethanol flushing solution was used, because, as shown in Fig. 4, a significantly higher removal resulted from the kaolin than the glacial till soil. It should be mentioned that at the conclusion of each electrokinetic experiment, the solution in the cathode compartment was analyzed, and, as seen in the 40% ethanol in kaolin test, occasionally this final sample caused a peak in phenanthrene mass. This peak in mass is probably because some phenanthrene concentrated in the solution contained in the cathode compartment and it did not flow out to the effluent sample bottle.

As seen in Fig. 4, the 3% Tween 80 flushing solution removed significantly more phenanthrene mass from glacial till than kaolin. The electro-osmotic flow of the 3% Tween 80 solution in glacial till was more than double the amount in the kaolin test, and the extra soil-solution-contaminant interaction could have

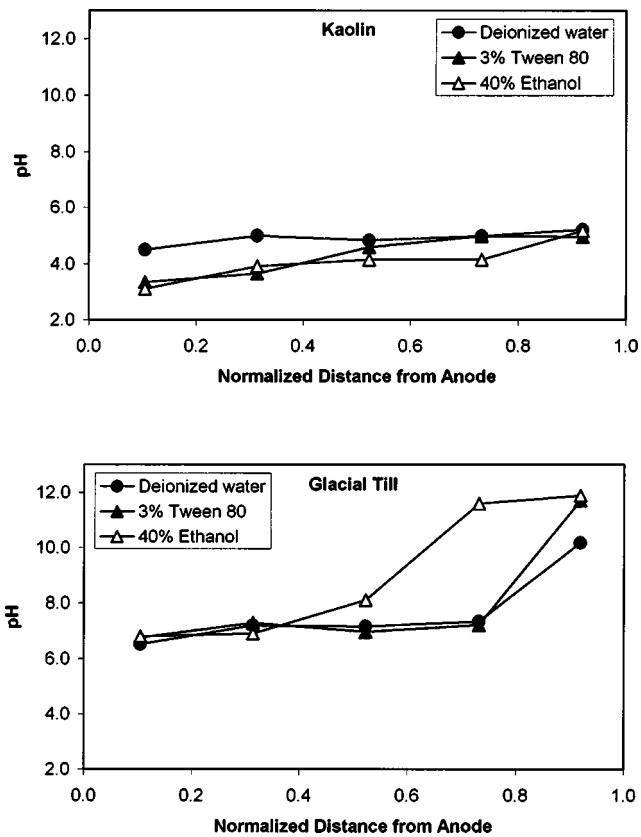


Fig. 5. Comparison of pH in kaolin and glacial till soils after electrokinetic remediation

been responsible for the increased removal. Furthermore, it is important to recognize that both the tests employing the 3% Tween 80 solution had a low amount of contaminant removal compared to the results from the batch tests (Saichek 2002), so there may not have been sufficient soil-solution-contaminant interaction and/or the kinetics, or reaction rate, may require extra time for solubilization or micellization (Grimberg et al. 1995; Yoem et al. 1996; Patterson et al. 1999). Moreover, although the Tween 80 concentration was significantly above the critical micelle concentration investigators have found that surfactant sorption may continue well beyond this point (Pennell et al. 1993; Adeel and Luthy 1995; Ko et al. 1998a), and the contaminant may then partition to the sorbed surfactant.

Comparison of pH

Fig. 5 compares the pH profiles in kaolin and glacial till soils at the conclusion of the electrokinetic experiments. For all three solutions, the results clearly show that glacial till had a high-acid buffering capacity, because the pH in the glacial till was well over 6.0 near the anode. Conversely, kaolin has a low-acid buffering capacity, so the electrolysis reaction at the anode generated a high concentration of H^+ ions, and, for all the solutions, the pH was near 4.0 near the anode. Moreover, the H^+ ions in the kaolin soil migrate into the soil due to electromigration and electro-osmotic flow, so the pH conditions for the kaolin tests are acidic along the length of the profile. In glacial till, the H^+ ions generated at the anode are buffered due to the high-carbonate content, so there is a minimal amount of H^+ migration, but, as seen in the figure, OH^- , which is generated by the electrolysis reaction at the cathode, electromigrated into the soil and raised the pH near the cathode

for all the solutions. The electro-osmotic flow in all the experiments was directed from the anode towards the cathode, so OH^- electromigration counteracts the electro-osmotic flow. Thus, when the 40% ethanol solution was used, there was a lower amount of electro-osmotic flow to counteract OH^- electromigration, and, as seen in the figure, this allowed the OH^- ions to move further into the glacial till. The electro-osmotic flow for the 3% Tween 80 and deionized water tests were similar in glacial till, so the pH profiles were also similar.

Generally, when the electro-osmotic flow reduces, it allows the concentration of ions generated by the electrolysis reactions to increase. These ions will then move towards the opposite electrode due to electromigration, but, depending on the direction, electro-osmosis may hinder or aid ion transport. In kaolin, the 3% Tween 80 and 40% ethanol tests had a lower-electro-osmotic flow than deionized water, so this allowed the H^+ concentration near the anode to increase in these tests. The low pH exacerbates the situation because it can increase the charge on the mineral surface, which changes the zeta potential and further lowers the electro-osmotic flow. In contrast, the greater electro-osmotic flow produced by deionized water in the kaolin test allowed additional inflow of high-pH solution and less time for the electrolysis reaction at the anode to concentrate the H^+ ions, therefore, the pH near the anode was slightly higher in this test.

Residual Phenanthrene Distribution

Fig. 6 shows a comparison of the residual phenanthrene distribution in the different soils, kaolin and glacial till, at the conclusion of the electrokinetic experiments. Since phenanthrene has such a low solubility in deionized water, the tests using this flushing solution did not show any phenanthrene migration, and the slight variability was most likely due to small differences in the initial contaminant distribution. It was encouraging, however, that the profiles showed evidence of some phenanthrene migration towards the cathode with both the 3% Tween 80 and 40% ethanol solutions. PAHs are often associated with organic matter and glacial till had a greater organic content, so the phenanthrene removal from glacial till would be more difficult. Comparing the two soils in Fig. 6, it can be seen that in the section nearest the anode, both the 3% Tween 80 and the 40% ethanol solubilized less phenanthrene from the glacial till than kaolin. Although organic material dissolution may increase under high-pH conditions (Laor et al. 1998), and phenanthrene could subsequently bind or complex with the dissolved organic matter, Figs. 5 and 6 indicate that the high-pH region in the glacial till did not result in greater phenanthrene removal. In both kaolin and glacial till, the 3% Tween 80 and the 40% ethanol tests had cleaner soil sections near the anode, and this is probably due to the greater amount of soil-solution-contaminant interaction, or flushing action, and the higher-electro-osmotic flow that traveled through this region. In addition, the low pH in this region could have caused clay particle flocculation, whereby the soil formed a more open structure that allowed additional soil-solution-contaminant interaction (Lambe and Whitman 1969).

As seen in Fig. 6, in kaolin or glacial till, the 3% Tween 80 and 40% ethanol experiments resulted in some contaminant desorption and solubilization near the anode. For both the kaolin and glacial till tests using the 3% Tween 80 flushing solution, the phenanthrene concentration was less than the initial concentration in the two soil sections nearest to the anode, but it was significantly higher than the initial concentration in the soil in the

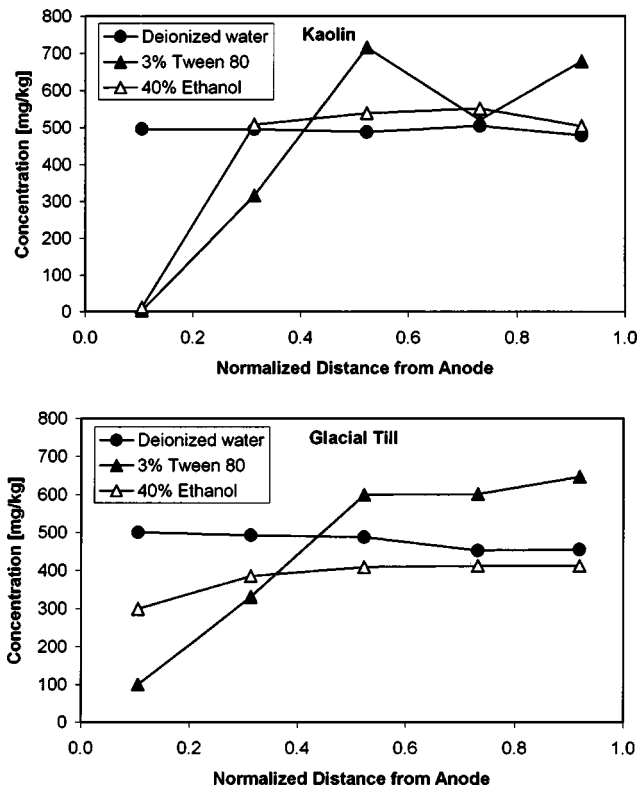


Fig. 6. Comparison of residual phenanthrene concentrations in kaolin and glacial till soils after electrokinetic remediation

middle section and section or sections nearest to the cathode. For the 3% Tween 80 flushing solution in kaolin, the fourth section from the anode had a concentration that was close to the initial phenanthrene concentration, and the concentration in this region was lower than the middle section and the section nearest the cathode. Due to the variation in pH or electrical gradient, significant pore pressures may result (Eykholt and Daniel 1994; Eykholt 1997), so it is possible that the flow and, consequently, the contaminant distribution, was uneven through this soil section. For both the kaolin and glacial till tests using the 40% ethanol solution, a lower than initial phenanthrene concentration resulted in the soil section nearest the anode, but this contaminant mass seems to have been distributed fairly evenly throughout the remainder of the soil profile. Thus, it seems that for both the 3% Tween 80 and 40% ethanol solutions, a greater amount of soil-solution-contaminant interaction took place near the anode, and this produced phenanthrene desorption and solubilization. The contaminant-laden solution then migrated towards the middle sections, but it appears that changes in the soil and/or solution chemistry in this region caused the contaminant to sorb, become trapped, or precipitate back onto the soil particles.

Summary and Conclusions

The objective of this laboratory investigation was to examine the distribution of phenanthrene under different soil conditions and to assess phenanthrene removal using electrokinetics combined with surfactants/cosolvents. The experiments employed two clayey soils, kaolin and glacial till, to compare the effects caused by the different soil types. The parameters measured during testing included the electric current, the cumulative electro-osmotic flow,

and the cumulative mass removal, and, at the conclusion of testing, the pH and residual contaminant concentration in the soil were measured. The following conclusions can be drawn from this study:

1. Generally, PAHs bind and associate with organic matter, and, since glacial till has a higher-organic content, phenanthrene seemed to be more difficult to remove from glacial till. Furthermore, phenanthrene and organic matter association was even more evident considering that a higher amount of electro-osmotic flow and soil-solution-contaminant interaction occurred in the glacial till experiments.
2. Compared to kaolin, glacial till has a more diverse mineralogy and chemistry, and it appears that the presence of salts and carbonates as well as a higher amount of mineral dissolution in the tests conducted with glacial till resulted in significantly higher long-term electric current values. Moreover, the small changes in electrical current that resulted from using different types of flushing solutions were minor compared to the changes in current that resulted from using different types of soil.
3. The high carbonate content in glacial till results in a large acid buffering capacity that is advantageous for counteracting the electrolysis reaction at the anode and, consequently, increasing the electro-osmotic flow. The reduction in H^+ concentration due to carbonates appears to be particularly beneficial when nonionic surfactants are present, because the surfactants molecules may adsorb to the mineral surface and become protonated at high- H^+ concentrations. The sorbed and protonated surfactant molecules cause the mineral surface to become more positively charged and this results in a lower electro-osmotic flow. The acid buffering capacity of glacial till prevents high- H^+ concentrations, and the glacial till test using 3% Tween 80 had more than double the flow of the kaolin test using 3% Tween 80. Furthermore, the higher flow in glacial till as compared to kaolin was probably responsible for removing more phenanthrene when the 3% Tween 80 flushing solution was employed.
4. Significant phenanthrene desorption, solubilization, and migration occurred when the 3% Tween 80 and 40% ethanol flushing solutions were used, but it appears that changes in the soil and/or solution chemistry in regions further towards the cathode caused the contaminant to sorb, become trapped, or precipitate back onto the soil particles. Thus, although the results are promising, further research is necessary to optimize the electrokinetically enhanced in situ flushing process for PAH-contaminated soils.

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