

Surfactant-enhanced electrokinetic remediation of polycyclic aromatic hydrocarbons in heterogeneous subsurface environments

Richard E. Saichek and Krishna R. Reddy

Abstract: Polycyclic aromatic hydrocarbon (PAH) contamination exists at numerous sites and poses a substantial risk to public health and the environment. Electrokinetic remediation technology has the potential to treat PAH-contaminated soils, but the effect of soil heterogeneities such as layers, lenses, and mixtures of different soils on the electrokinetic process has not been adequately studied. This study evaluates surfactant-enhanced electrokinetic remediation under heterogeneous soil conditions. A series of bench-scale experiments was conducted using two soils (sand and kaolin) spiked with a representative PAH compound (phenanthrene) in a two-dimensional electrokinetic test apparatus under various layered, lens, or mixed soil configurations. In addition, the homogeneous sand and kaolin soils were each tested alone for comparison purposes. All the experiments employed the same nonionic surfactant (5% Igepal CA-720) flushing solution and a low (0.05) hydraulic gradient. The results showed that the surfactant flushing under the low hydraulic gradient alone was sufficient for complete removal of the contaminant from the homogeneous sand profile, whereas the electroosmotic flow generated by the application of a DC 2.0 V/cm electric potential in a periodic mode considerably enhanced the removal efficiency for the homogeneous and heterogeneous soil profiles containing kaolin. The voltage gradient varied spatially and temporally through the soil profiles and affected the electroosmotic flow and contaminant removal.

Key words: clays, electrokinetic remediation, electroosmosis, flushing, heterogeneity, polycyclic aromatic hydrocarbons (PAHs), phenanthrene, soils, sorption, solubilization, surfactants.

Résumé : De nombreux sites présentent une contamination aux hydrocarbures aromatiques polycycliques (HAP) et cela pose un grand risque pour la santé publique et l'environnement. La technologie de restauration électrocinétique peut traiter les sols contaminés aux HAP, mais l'effet de l'hétérogénéité du sol, représenté par des couches, des lentilles et des mélanges de différents sols, sur le procédé électrocinétique n'a pas été suffisamment étudié. Cette étude évalue la restauration électrocinétique améliorée par des surfactants sous des conditions de sols hétérogènes. Une série d'expériences en laboratoire a été effectuée sur deux types de sols (sable et kaolin) auxquels on a ajouté un composé représentatif des HAP (phénanthrène) dans un appareil d'essai électrocinétique bidimensionnel sous diverses configurations de sols : en couches, en lentilles ou mélangés. De plus, les sols homogènes de sable et de kaolin ont chacun été testés seuls à des fins de comparaison. Toutes les expériences utilisaient la même solution de lessivage rapide comportant un surfactant non ionique (Igepal CA-720 5 %) et un faible gradient hydraulique de 0,05. Les résultats montrent que le lessivage rapide du surfactant sous un faible gradient hydraulique seul était suffisant pour enlever complètement le contaminant du profil de sable homogène, alors que l'écoulement par électroosmose généré par l'application d'un potentiel électrique de CC 2,0 V/cm de manière périodique a amélioré considérablement l'efficacité d'élimination dans les profils de sols homogènes et hétérogènes contenant du kaolin. Le gradient de tension variait dans l'espace et dans le temps dans les profils de sols et affectait l'écoulement par électroosmose et l'élimination du contaminant.

Mots clés : argiles, restauration électrocinétique, électroosmose, lessivage rapide, hétérogénéité, hydrocarbures aromatiques polycycliques (HAP), phénanthrène, sols, sorption, solubilisation, surfactants.

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Introduction

Polycyclic aromatic hydrocarbon (PAH) contamination of soils and groundwater is a formidable problem, and many studies have been conducted to develop innovative remediation

technologies and assess contaminant fate and transport (Luthy et al. 1997; Li et al. 2000; USEPA 2000). One of the most promising remediation techniques for PAHs is in situ soil flushing with chemically engineered flushing agents, such as surfac-

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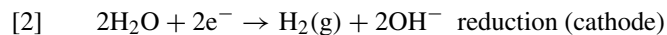
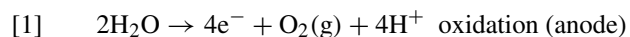
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tants and (or) cosolvents (Sabatini et al. 1995; National Research Council 1997). Although the in situ flushing process is promising for PAH removal, homogeneous soils with a low organic content and a high permeability are generally the best candidates for treatment. Conversely, low contaminant removal and tailing often occur when the in situ flushing process is used under heterogeneous subsurface conditions with layers, lenses, or mixtures of organic and (or) low permeability soils (Fountain et al. 1995). This low removal and tailing behavior is attributed to the movement of the flushing solution, which tends to flow along paths of high permeability, whereas the contaminant transport from organic or low permeability soil regions is controlled mainly by diffusion.

Electrokinetic remediation can be integrated with the in situ flushing technique by placing electrodes in the injection and extraction wells and by applying a low voltage gradient. The voltage gradient induces electroosmotic flow, which has the potential to improve contaminant removal from organic or low permeability argillaceous soils. Gray and Mitchell (1967), Eykholt (1992), Acar and Alshawabkeh (1993), Eykholt and Daniel (1994), and Acar et al. (1995) have outlined the different factors and processes that affect electrokinetic remediation.

During electrokinetics, the electrolysis of water occurs at the electrodes, generating oxygen gas and hydrogen (H^+) ions (low-pH solution) at the anode (eq. [1]) and hydrogen gas and hydroxyl (OH^-) ions (high-pH solution) at the cathode (eq. [2]):



The electric potential induces several contaminant transport mechanisms, such as electromigration, electroosmosis, electrophoresis, and diffusion. Electromigration refers to the transport of ionic species in the pore fluid; this is the main mechanism by which the electrical current flows through the soil. Electromigration also includes the movement of H^+ and OH^- ions produced by electrolysis toward the oppositely charged electrode. Electroosmosis describes the bulk movement of the pore fluid, and electroosmotic flow is produced because excess ions migrating toward the oppositely charged electrode transfer momentum to the surrounding pore fluid molecules (Eykholt 1992). Lastly, electrophoresis describes the transport of colloidal-sized particles through the pore fluid, and diffusion refers to the transport of species due to concentration gradients.

The Helmholtz–Smoluchowski (H–S) equation is often used to estimate the average electroosmotic flow velocity (v_{eo}) (Eykholt and Daniel 1994; Mitchell 1993):

$$[3] \quad v_{eo} = -\frac{D\varepsilon_0\zeta}{\eta} E_x$$

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

(8.854×10^{-12} F/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 soil particle surface is zero. When the pH is above the ZPC, the soil particles usually have a negative zeta potential and the electroosmotic flow occurs toward the cathode. Conversely, when the pH is below the ZPC, the soil particle surfaces generally have a positive zeta potential and the electroosmotic flow occurs toward the anode (reverse electroosmotic flow) (Shapiro and Probstein 1993). The H–S equation suggests that in addition to the pH, many other factors might affect the electroosmotic flow. For instance, the surface charge of the soil particles and the zeta potential are affected by changes in the ionic strength, dielectric constant, and viscosity. Furthermore, the electrical gradient may not be uniform through the soil, and hence, the electroosmotic flow is generally not uniform spatially or temporally (Eykholt and Daniel 1994).

It should be noted that contaminant transport occurs primarily through the pore fluid, so the electrokinetic remediation process is not effective unless the contaminants are soluble or are converted to a soluble form. Hence, surfactants were combined with the electrokinetic technique to increase PAH solubility through micellar solubilization (Myers 1988). The critical micelle concentration occurs when the surfactant molecules begin to aggregate into colloidal-sized structures (micelles). The micelles possess an interior lipophilic region where PAH molecules partition and accumulate, which greatly increases the solubility of PAH contaminants.

Many other studies have used surfactant-enhanced electrokinetics for the remediation of various hydrophobic organic compounds (Pamukcu 1994; Ko et al. 2000), but these studies have not adequately investigated the effects of heterogeneous soil conditions. Pamukcu (1994) identified variations between clay-rich and granular-soil specimens, but the effects of soil profiles, such as layers, lenses, and soil mixtures, were not addressed. Therefore, the main objective of this investigation was to conduct controlled laboratory experiments to determine how the electrokinetically enhanced in situ flushing process affected different PAH-contaminated heterogeneous soil profiles, particularly with respect to layers, lenses, and mixtures of soils with widely different permeabilities. The tests were performed using a specially designed and fabricated bench-scale two-dimensional (2-D) electrokinetic apparatus for both the homogeneous and heterogeneous soil conditions. For all the experiments, a common PAH compound, phenanthrene, was selected as the representative contaminant.

A laboratory research program consisting of batch tests and one-dimensional (1-D) bench-scale electrokinetic tests was conducted previously (Saichek 2002). These previous 1-D electrokinetic experiments illustrated the effects of different operating parameters, including the soil type, surfactant type and concentration, pH, voltage gradient, and periodic voltage application. The earlier efforts were incorporated into the present 2-D experiments, which employed a 5% nonionic surfactant solution and a DC 2.0 V/cm voltage gradient with a periodic

Table 1. Properties of soils.

| Property | Kaolin | Sand |
|---|---|----------------------|
| Mineralogy | Kaolinite: 100%; Muscovite: trace; Illite: trace | Quartz: 100% |
| Particle size distribution (ASTM D 422) (%) | | |
| Gravel | 0 | 0 |
| Sand | 4 | 100 |
| Silt | 18 | 0 |
| Clay | 78 | 0 |
| Specific gravity (ASTM D 854) | 2.6 | 2.65 |
| Hydraulic conductivity (cm/s) | 1.0×10^{-8} | 3.4×10^{-3} |
| Cation exchange capacity (mequiv/100 g) (ASTM D 9081) | 1.0–1.6 | NA |
| pH (ASTM D 4972) | 4.9 | 7.3 |
| Organic content (%) (ASTM D 2974) | Near 0 | Near 0 |
| USCS classification (ASTM D 2487) | CL | SP |

Note: NA, not applicable.

Table 2. Initial soil conditions*.

| Soil profile | Dry mass of sand (g) | Dry mass of kaolin (g) | Bulk density (g/cm ³) |
|---------------------------------------|-------------------------|---------------------------|--------------------------------------|
| Homogeneous sand | 3104 | 0 | 1.552 |
| Homogeneous kaolin | 0 | 2684 | 1.342 |
| Top kaolin, bottom sand | 1500 | 1800 | 1.650 |
| Kaolin lens | 2820 | 250 | 1.535 |
| 10% kaolin and 90% sand mixture | 2947 | 328 | 1.638 |

*Volume of soil chamber is 2000 cm³.

mode of application.

Experimental methodology

Materials

Kaolin (VWR Scientific Products) and fine sand (U.S. Silica F-110, U.S. Silica Company) were used in this research; the physical and chemical properties of these soils are summarized in Table 1. The kaolin was used to simulate a typical clayey soil encountered at contaminated sites.

Phenanthrene (C₁₄H₁₀, 98% pure, Aldrich Chemical Company) has a molecular weight of 178.2 and is a grayish-white crystalline powder. It has an approximate aqueous solubility of 1.1 mg/L and a log *K*_{ow} of 4.57 at 25 °C (Schwarzenbach et al. 1993).

A 5% nonionic octylphenol polyoxyethylene surfactant (Igepal CA-720) was used as the flushing solution. The chemical formula is C₈PE₁₂, where C represents the alkyl chain length (-CH₂-), P represents a phenol ring (-C₆H₆-), and E represents an ethoxylate group (CH₂CH₂O) (Yeom et al. 1995). This particular surfactant and its concentration were selected primarily because of its compatibility with the electrokinetic process and its success in previously conducted batch tests and 1-D electrokinetic experiments (Saichek 2002).

Electrokinetic apparatus

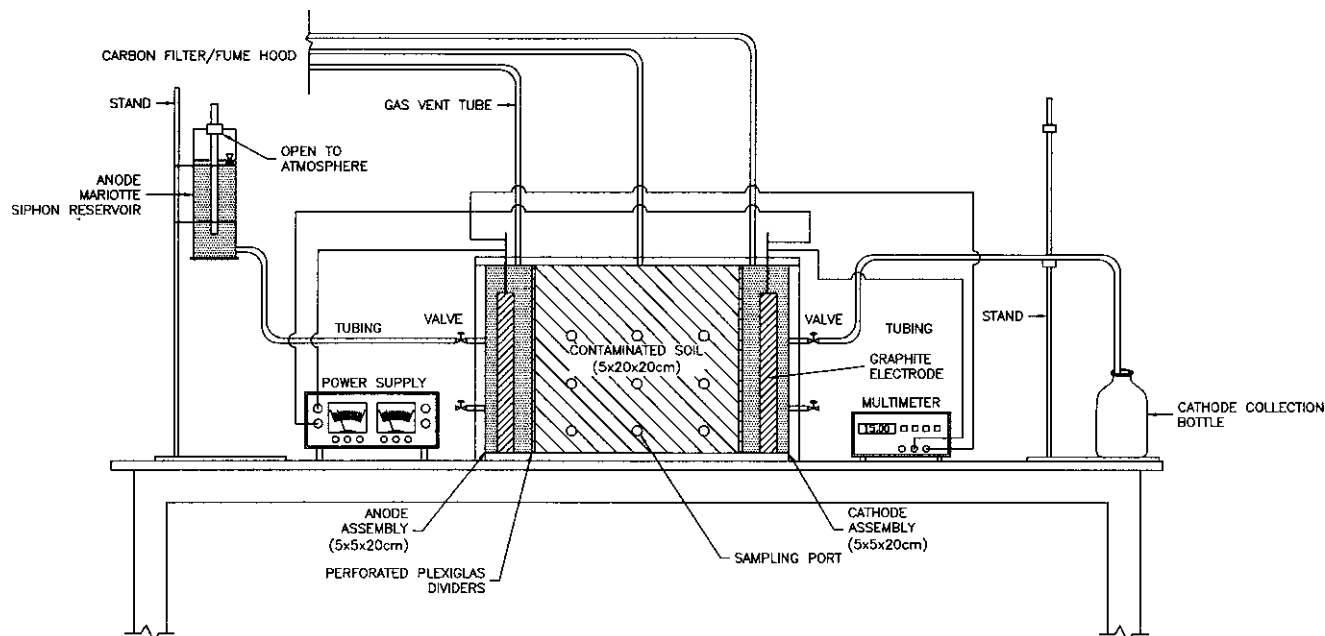
A 2-D electrokinetic apparatus (Fig. 1) was used to simulate contaminant transport. The 2-D apparatus consisted of a Plexiglas™ soil chamber, two electrode compartments, an anode reservoir, a cathode bottle, a power supply, a multimeter, and peripherals such as tubing, wiring, and stands. The soil chamber measured 20.0 cm in length, 5.0 cm in width, and 20.0 cm in height, and each electrode compartment measured 4.7 cm in length, 5.0 cm in width, and 20.0 cm in height. The electrodes consisted of 1.3-cm-diameter and 20.0-cm-long EG-3 graphite rods (EDM Graphite Corp.) that were sealed into the electrode chamber by using recessed rubber O-rings. The anode reservoir was constructed using a Mariotte siphon design to maintain a low and constant hydraulic head. A perforated Plexiglas™ divider covered with Whatman #1 filter paper separated the soil from the electrode compartment, and the filter paper was employed to inhibit the migration of colloidal particles into the electrode compartments. Three gas vents were included to allow the gas that developed during the electrolysis reactions to escape. The top and bottom of the Plexiglas™ cell were removable.

Nine sampling ports were included at approximately 5-cm intervals in the horizontal and vertical directions to measure the electrical potential variations within the soil profile. Each sampling port consisted of a rubber septum held in place by an aluminum fitting. Stainless steel probes were inserted through the rubber septa to measure the electrical potential at each port position.

Testing program

Five different 2-D experiments were conducted with the phenanthrene-spiked soils. Initially, baseline comparison tests were conducted by performing two separate experiments using homogeneous soil profiles. Specifically, one baseline test used only sand, whereas the other used only kaolin. Because sand has a high hydraulic conductivity, an electric potential was not required to produce adequate flow. In other words, electrokinetics was not applied to the homogeneous sand test; this test was simply conducted as an in situ soil flushing experiment using a low (0.05) hydraulic gradient. Conversely, because of the much lower hydraulic conductivity of kaolin, the test employing the homogeneous kaolin soil profile did not generate any outflow after application of the low hydraulic gradient, so the flow in this test was due to electrokinetics and the transport mechanism

Fig. 1. Schematic of 2-D electrokinetic test apparatus.



of electroosmosis. In addition to the two homogeneous baseline tests, three heterogeneous soil profiles were tested. The first profile consisted of a kaolin layer overlying a sand layer. The second profile consisted of a circular lens of kaolin (approximately 5 cm in diameter) in the center of a sand layer. The third profile consisted of a soil mixture of 10% kaolin and 90% sand.

Testing procedure

For all the 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 found near source zones at contaminated sites (USEPA 2000). Approximately 4.0 kg of soil was spiked for each test. Initially, the mass of phenanthrene required to yield the target concentration was measured and then completely dissolved in about 500 mL of hexane. Hexane was used instead of water because phenanthrene has extremely low solubility in water. The hexane-phenanthrene mixture was subsequently mixed with the measured amount of soil. Additional hexane was added so that the soil-hexane-phenanthrene mixture could be stirred easily. The mixtures were stirred with stainless steel spoons, and all mixing operations were performed in glass beakers. The soil-hexane-phenanthrene mixture was then placed in a ventilation hood for nearly a week until the hexane completely evaporated and the contaminated soil was dry. The initial concentration of phenanthrene in the soil was then determined.

The phenanthrene-contaminated kaolin soil was subsequently mixed with a measured amount of deionized water in a glass pan. The target water content for the kaolin soil was 35%. The moist soil was then placed in the 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 peripheral equipment was attached to complete the assembly of the apparatus. The cathode compartment was filled with deionized water, and the anode compartment and reservoir were filled with the surfactant solution (5% Igepal CA-720). The periodic DC-voltage gradient was then applied for the designated time duration. The periodic voltage was cycled for 5 d on and then 2 d off.

The electrical current and the volume of effluent were routinely measured, and aliquots of the effluent solution were collected for chemical analysis and the determination of contaminant mass removal. The electrical potential (voltage) value from the cathode to each of the nine ports was also measured using a multimeter to examine the spatial variation of electrical potential through the soil. The tests were run until the applied current greatly decreased through the soil or it appeared that the phenanthrene concentration in the effluent had reached a steady state condition. After the tests were completed, the soil was extruded and divided into nine sections that corresponded to the nine port positions and then divided along the vertical and horizontal directions, where each section was about 7 cm × 7 cm × 5 cm. 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 by Mitchell (1993). Generally, 10 mL of deionized water was added to 10 g of soil, and the pH was measured using a Digi-Sense digital pH meter that was calibrated using standardized pH solutions. Water contents were determined using ASTM D 2216.

Chemical analysis

For the chemical analysis of the soil, a Soxhlet extraction procedure was followed; this 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 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 gas chromatograph (GC) 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 Hewlett-Packard GC model 6890. Saichek (2002) provided the details and parameters concerning the operation of the GC.

A liquid–liquid extraction procedure was adopted to extract the phenanthrene from the aqueous surfactant–cosolvent solution into methylene chloride (dichloromethane) (Fisher Scientific GC Resolv grade). The extraction procedure first consisted of placing 15 mL of methylene chloride into a clean, empty 40-mL clear or brown glass vial. Then, a 5-mL sample of the effluent surfactant–cosolvent–phenanthrene solution was placed in the vial along with the methylene chloride. The vials were placed on a rotary shaker table at 250 rpm for 24 h. Since phenanthrene has a high solubility in methylene chloride, the contaminant was extracted during the shaking process from the surfactant–cosolvent solution into the methylene chloride. Moreover, the greater density of the methylene chloride solvent causes it to sink and form a separate liquid phase beneath the aqueous surfactant–cosolvent solution. Thus, after mechanical shaking, a 1.0-mL aliquot of the methylene chloride – phenanthrene solution was removed from beneath the surfactant solution by using a Hamilton glass 1-mL syringe, and the extracted methylene chloride – phenanthrene solution was placed in a 2-mL Target auto-sampler vial with a Teflon screw cap for injection by GC analysis. Between samples, the syringe was flushed approximately eight times using two flasks of methylene chloride to avoid cross-contamination.

Quality control

The external calibration standards for the phenanthrene analyses by GC 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. Sample blanks were injected to ensure that the system remained uncontaminated. Duplicate standard samples were also injected to certify reproducibility of the results and to ensure that the calibration graph and the baseline remained stable. The syringe was rinsed with solvent several times between sample injections.

An overall mass balance was conducted to account for the initial mass of phenanthrene spiked into the soil. The mass balances were accurate to within 73% to 90% of the initially spiked mass, and three of the five tests had mass balances accurate to within 85% of the initially spiked mass. Discrepancies in the mass balance were attributed primarily to uneven contaminant distribution within the soil or the volatilization of phenanthrene along with the solvents during the Soxhlet extraction procedure.

Results and analysis

Hydraulic flushing in sand

For the homogeneous sand test, the electric potential application was not necessary because sufficient flow was generated by the low (0.05) hydraulic gradient. Figure 2 shows the cumulative volume and the mass removed during the flushing test through the sand profile. Approximately 10 L of surfactant solution were flushed through the sand during an interval of approximately 19 d; this test had a high flow rate of about 526 mL/d. It is evident that PAHs do not bind strongly to the silica surface of sand particles, especially when there is a low organic content (Luthy et al. 1997); consequently, the surfactant solution rapidly removed the phenanthrene from this sandy soil in approximately 10 d. No residual mass of phenanthrene was detected in the exhumed sand samples.

Electrokinetically enhanced flushing in clays and heterogeneous soils

Electric current

Dry clay particles commonly have a negative surface charge that is balanced by cations or anions in the form of salt precipitates, and when the dry clay particles come into contact with water (or surfactant solution), the salt precipitates dissolve into solution, thereby releasing ions (Mitchell 1993). These mobile ions in solution are largely responsible for producing the electrical current under electrokinetics, but typically a reduction in current is observed over time. This is because the mobile ions electromigrate toward the electrodes, where they concentrate, react with the electrode, or become neutralized by oppositely charged ionic species (Eykholt 1992; Pamukcu 1994; Grundl and Michalski 1996). The electrolysis reactions, which produce H^+ ions at the anode and OH^- ions at the cathode, usually cause additional variations in the current. These ions tend to migrate toward the oppositely charged electrode, and they may increase the current, exchange with ions and affect the charge on the soil particle surface, and (or) cause salt or mineral precipitation–dissolution. However, if H^+ and OH^- ions react to form water within the soil, a steady state condition may occur, where the electromigration of these ions will not generate much current or electroosmotic flow (Dzenitis 1997).

Figure 3 shows the variation in electrical current with elapsed time for the various soil profiles. For the homogeneous kaolin test, the low (0.05) hydraulic gradient was applied (without voltage) for approximately 1.6 d before the voltage gradient was applied. After the voltage (2.0 V/cm gradient) was applied, the current quickly reached a maximum level of about 160 mA, but the current values decreased considerably after the second day of voltage application. The high 160-mA current resulted from the initial conductivity of the soil, but the migration of the mobile ions toward the electrodes resulted in a reduction in current over time. After approximately 20 d, relatively stable and lower current values between approximately 4 and 12 mA were maintained. It should be noted that in the homogeneous kaolin test the current increased after about 100 d because NaOH solution

Fig. 2. Cumulative volume of surfactant solution and cumulative mass of phenanthrene removed during the sand test.

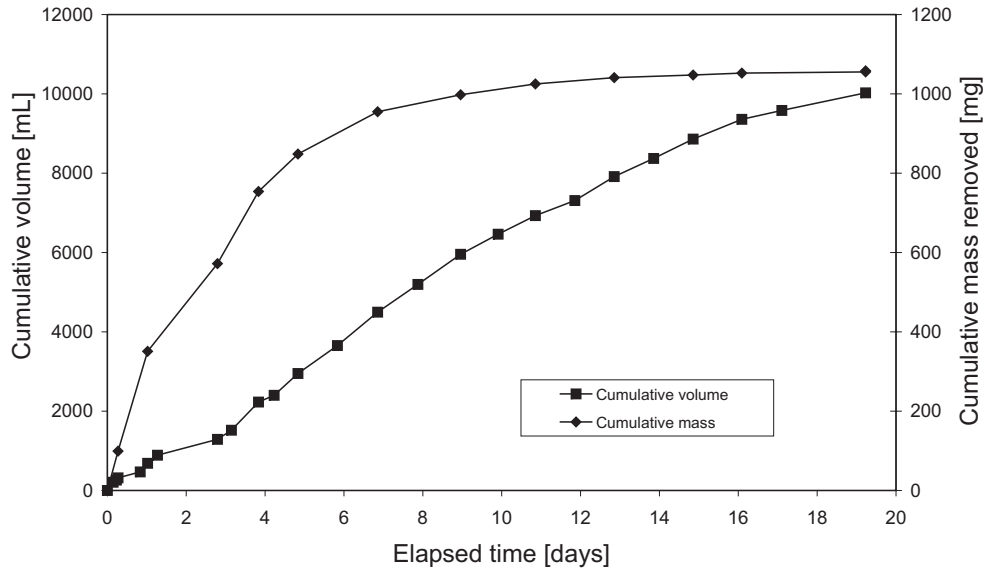
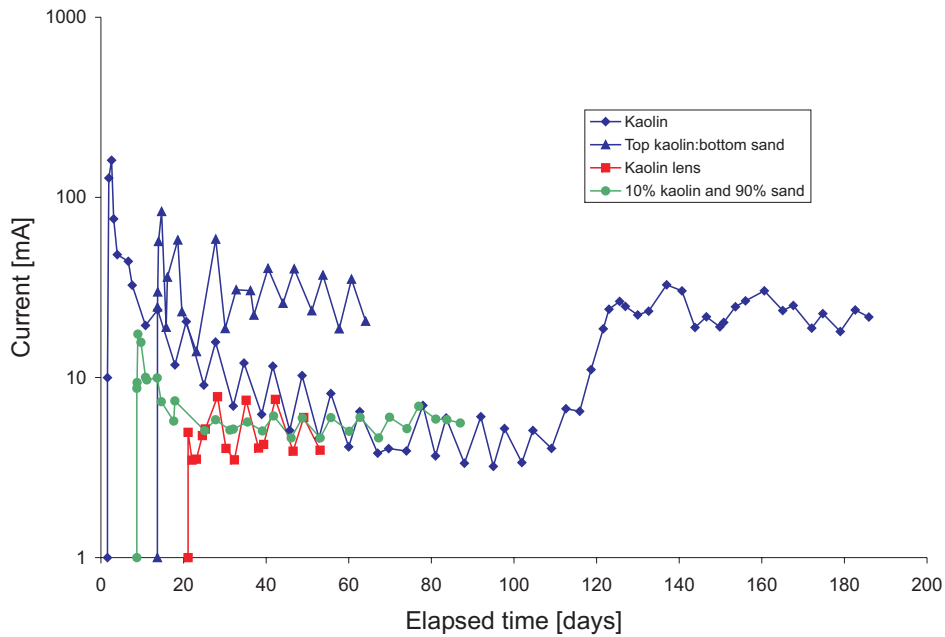


Fig. 3. Current measured during electrokinetic tests.



was introduced to induce electroosmotic flow. The homogeneous kaolin test was the only test where NaOH was added; the procedure and reasons for adding this solution will be explained later in the text under the topic of electroosmotic flow.

For the soil profile consisting of a kaolin layer overlying a sand layer, the 0.05 hydraulic gradient was maintained for approximately 14 d prior to the application of voltage. After the voltage was applied, the current quickly rose to just over 80 mA during the first day (Fig. 3), which was about half the initial current of the homogeneous kaolin test. By the follow-

ing day, however, the current in the top kaolin with bottom sand (layered) test had diminished, and over the next week or so it varied between about 20 and 60 mA. Over the long term, this test sustained higher current values than those measured in the homogeneous kaolin test; this is attributed to the greater flow velocity and fluid circulation that occurred owing to the presence of the higher hydraulic conductivity sand layer. Apparently, the greater flow or circulation allowed additional mineral or salt dissolution and ion solubilization from the upper kaolin region of the soil profile.

The kaolin lens test was started using the 0.05 hydraulic gradient for approximately 21 d prior to applying the voltage gradient. Since the soil in this test was composed mostly of sand, very little current was produced after the voltage application. The small current that did result was most likely due to the dissolution of minerals and salts that were present in the kaolin soil because, as seen in the tests discussed earlier, the initial current was approximately proportional to the mass of kaolin present. There were fewer mobile ions in the kaolin lens test, so the current remained consistently low and varied between about 4 and 8 mA.

The voltage gradient was applied to the 10% kaolin and 90% sand test after approximately 9 d of flushing with the 0.05 hydraulic gradient. As shown in Fig. 3, the current reached a maximum value of approximately 17 mA near the start of voltage application, and as in the kaolin lens experiment, the small amount of kaolin used in the 10% kaolin and 90% sand test resulted in relatively low current values that ranged from about 4 to 7 mA. This supports the earlier hypothesis that the current is a largely a result of the dissolution of minerals and salts that were present in the kaolin soil.

The fluctuating current pattern that can be observed in all the electrokinetic tests is a result of the periodic voltage application. Typically, the current decreased during the 5-d period of continuous voltage application as the mobile ions migrated toward the electrodes. Then the applied voltage was suspended for 2 d, and it is postulated that additional mineral dissolution and (or) ion solubilization occurred. When the voltage was reapplied, current that was measured was often substantially higher than current that was measured before the “down time”. The increase of conductivity may be partly explained by studying what happens at the molecular scale. Schwarzenbach et al. (1993) observed that a stagnant boundary layer of solution normally surrounds a saturated soil particle and this comparatively stagnant layer limits the diffusion of molecules into the faster flowing bulk solution. Thus, when the voltage was not applied and the flow rate diminished, greater diffusion and molecular interaction may have occurred between the inner stagnant layer and the bulk solution, thereby increasing mineral dissolution, ion solubilization, and solution conductivity. In addition, Mohamedelhasen and Shang (2001) reported that current intermittence causes a charge redistribution (depolarization) of the electrical diffuse double layer, which may have contributed to the current increase after the down time.

Voltage

It should be noted that DC 40 V was applied across the electrodes, so if a uniform voltage gradient existed through the soil, the voltage would have dropped by DC 2 V/cm from the anode to the cathode. However, the voltage gradient through the soil profiles was usually not uniform; it was often much lower than the voltage gradient applied across the electrodes. Saichek (2002) illustrated that after about 100 d, the voltage gradient from the ports adjacent to the cathode to the cathode region was approximately DC 6.0 V/cm (DC 30 V per 5 cm); therefore the

voltage gradient through the remainder of the soil, which was the majority of the soil profile, was approximately DC 0.7 V/cm (DC 10 V per 15 cm). According to the H-S equation, voltage variations greatly impact the electroosmotic flow along the soil profile.

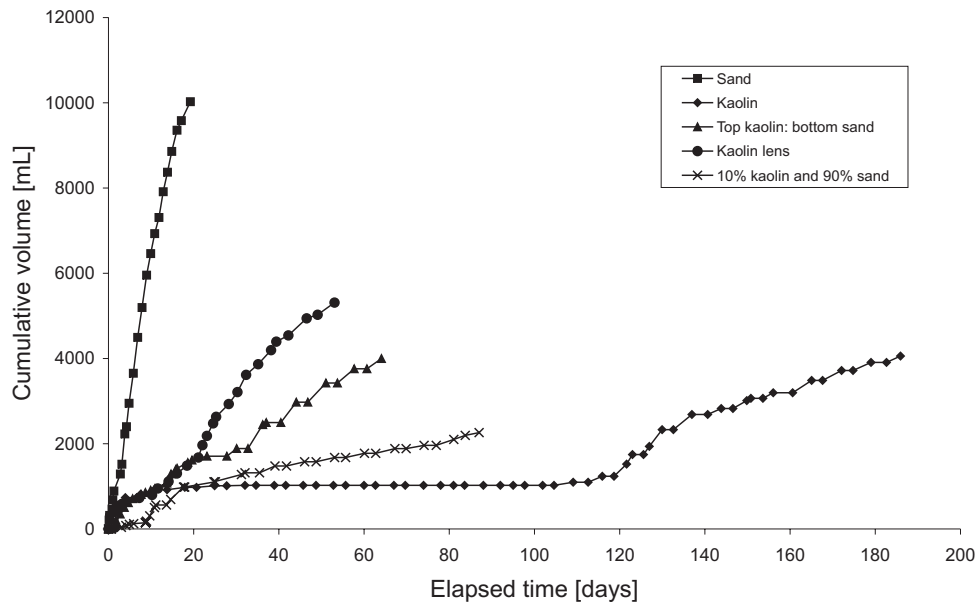
The ports nearest the cathode usually experienced larger voltage fluctuations; this was attributed to the lower conductivity of the solution near the cathode, which resulted from the pH change caused by the electrolysis reaction at the cathode. Metallic cations typically become neutralized or precipitate as hydroxide species and salt solubility may decrease under high pH conditions. The lower conductivity of the solution near the cathode most likely resulted in a greater influx of ions during the down time because ions would tend to diffuse into the cathode region owing to the concentration gradient. Hydrogen and hydroxyl ions tend to have a higher mobility because they associate or dissociate with water molecules. Compared with the rest of the soil profile, the cathode region resulted in a greater increase in conductivity and, therefore, when the voltage was reapplied, a larger drop in voltage occurred near the cathode relative to the remainder of the soil profile. Apparently, regions near the middle and toward the anode end of the soil profile maintained a high and relatively stable conductivity during the periodic voltage application because the voltage fluctuations for the ports in those regions were smaller than the column of ports nearest to the cathode.

After approximately 100 d, the NaOH solution caused the voltage gradient through the homogeneous kaolin test to resemble more closely a uniform voltage gradient of DC 2.0 V/cm, so it seems that supplementing the pore solution with mobile Na^+ and OH^- ions resulted in a more consistent electromigration and conductivity through the soil specimen. In the test with the kaolin layer overlying the sand layer, there was not much difference between the voltage values in the top and bottom halves of the soil chamber. This indicates that the voltage values were largely a function of the properties of the pore solution (conductivity and pH), and the pore solution chemistry was probably similar in both soils. Furthermore, the greater flow velocity and fluid circulation that occurred in the electrokinetic tests employing the higher hydraulic conductivity sand might have produced greater ion solubilization and ion mixing, which seem to delay the onset of a distinctive voltage pattern from anode to cathode. Compared with the tests with large relatively higher conductivity flow zones (the kaolin layer overlying the sand layer and kaolin lens tests), the 10% kaolin and 90% sand test had a lower electroosmotic flow and less flow circulation; this allowed the voltage values to become distinctly arranged and the voltage to drop near the cathode within a relatively short amount of time.

Electroosmotic flow

The cumulative volume measured during the five experiments is shown in Fig. 4. The sand test, which was conducted under a low (0.05) hydraulic gradient alone, is shown for comparison purposes. For about the first day, the hydraulic gradient

Fig. 4. Cumulative volume of surfactant solution measured during tests with different soil profiles.



was applied to the homogeneous kaolin test, but no flow occurred as a result of the low hydraulic conductivity of this soil. However, Fig. 4 illustrates that after voltage was applied there was a high rate of electroosmotic flow for approximately 10 d, when the flow gradually reduced and eventually stopped. This cessation of flow was apparently due to the depletion of mobile ions, or it could be a result of the electrolysis reactions and the effects of these reactions, such as the changes to the charge on the particle surface (zeta potential) and the development of a low-conductivity region near the cathode.

Other investigators, such as Eykholt (1992), Dzenitis (1997), and Hsu (1997), have found that nonuniform and nonlinear electric potentials commonly occur through the soil, and it seems that when the process is unaltered by the addition of chemical agents to the anode or cathode compartments an abrupt voltage drop typically occurs near the cathode. Eykholt (1992) found that adding an acid solution to the cathode compartment caused the conductivity of the pore solution to increase in the cathode region and the voltage drop became less steep. Eykholt (1992) also determined that the voltage drop was larger in regions where the pH was high and the quantity of free sodium and aluminum metals was low.

Dzenitis (1997) indicated that the relative conductivity along the soil profile is important and the soil profile from the anode to a region near the cathode has a conductivity that is relatively higher than the small region adjacent to the cathode. Moreover, Dzenitis (1997) estimated that the low conductivity and high electrical gradient near the cathode produced the greatest contribution to the electroosmotic flow. As mentioned earlier, the steep voltage gradient occurring near the cathode indicates a higher flow in that region. Dzenitis (1997) implied that this relatively small low-conductivity region near the cathode pulled the solution from the other regions, and this might cause the gener-

ation of low pore pressures. Moreover, these low pore pressures may consolidate clay soils and clog pore spaces, thereby reducing the electroosmotic flow (Eykholt 1997). Dzenitis (1997) also suggested that the combined low conductivity and high electrical gradient in the region near the cathode could eventually weaken electroosmotic flow because the double-layer thickness becomes greater and there are fewer mobile ions to generate flow through this region.

The high-conductivity solution near the anode could be a result of the low pH conditions, which may cause greater mineral dissolution (Carrol-Webb and Walther 1988) and may allow many metals to become more soluble. Incidentally, this is the reason why electrokinetics is commonly used to "acid wash" metallic contaminants from the soil (Acar et al. 1995; Reddy and Parupudi 1997; Reddy et al. 1997). Conversely, near the cathode, the H^+ ions may react with the OH^- ions generated by electrolysis to form water, so the pore solution adjacent to the cathode may have a lower conductivity. Furthermore, because the H^+ ion has a high mobility that is about twice the ionic mobility of the OH^- ion (Acar et al. 1995) and the electromigration of the OH^- ion opposes the direction of electroosmotic flow, it is reasonable for the reaction to occur near the cathode.

Shapiro and Probst (1993) found that when a pH control solution was added to the anode solution, a higher and more sustained electroosmotic flow was generated, and many other investigators such as Dzenitis (1997) and Schultz (1997) have verified this phenomenon. However, an excessively high current might result if the pH control solution is added at the start of the test when there is high conductivity due to the initial dissolution of salts that are associated with the dry soil particles. Consequently, for the present investigation it was decided to add the NaOH solution to control the pH at the anode in the homogeneous kaolin test after the current had subsided. It should

be noted that high current values could cause damaging effects to the process, such as soil heating and desiccation.

As shown in Fig. 4, about 30 d after the start of the homogeneous kaolin test, the amount of electroosmotic flow was negligible. Therefore, the anode compartment was filled with fresh surfactant solution combined with a 0.01 mol/L NaOH solution to increase the pH at the anode. This was then repeated a few times when the anode solution became acidic owing to the electrolysis reaction, but the flow was still negligible. Consequently, after approximately 90 d, the anode compartment was filled with a fresh surfactant solution combined with a more concentrated 0.1 mol/L NaOH solution. With this more concentrated pH control solution, the current increased substantially at approximately the 120-d elapsed time increment (Fig. 4). Over the duration of the kaolin test, the flow rate was low compared with the other tests, but this test demonstrated that the use of a pH control solution could revive the electroosmotic flow. Incidentally, Hsu (1997) observed that when NaOH was added to the anode reservoir, the sodium concentration greatly increased near the cathode. It appears that the Na^+ ions may slightly increase the pore solution conductivity near the cathode and the formation of water near the anode may lower the conductivity in the remainder of the soil profile, which helps to explain the more even voltage gradient that occurred across the soil at the later stages of the kaolin test.

Figure 4 shows that the flow through the top kaolin with bottom sand test was high during the period of time prior to the application of the voltage gradient, but it was gradually decreasing over time; this may have been because of the viscosity or other properties of the surfactant. Allred and Brown (1995) found similar reductions in hydraulic conductivity when using nonionic surfactants; this is another reason why enhancing the in situ flushing process with electrokinetics could be advantageous for increasing the flow. Because the flow reduction was not observed in the homogeneous sand test, it appears that the presence of kaolin may have been partially responsible for decreasing the flow. As observed in Fig. 4, the top kaolin with bottom sand test experienced a slight rise in the flow when the voltage was applied after approximately 14 d, and then the flow followed a step-like pattern that correlated to the periodic voltage application. The horizontal steps in the figure indicate that when the voltage was not applied during the down time, the flow due to the low hydraulic gradient became negligible compared with the electroosmotic flow. Nevertheless, it appears that because of the greater hydraulic conductivity of the sand layer, the top kaolin with bottom sand test had a substantially higher long-term electroosmotic flow rate than the homogeneous kaolin test, and over the duration of this layered test, the flow rate was approximately three times the amount measured in the homogeneous kaolin test.

The flow rate of the kaolin lens test was about one fifth of the flow rate of the homogeneous sand test, but it was substantially higher than the test with the kaolin layer overlying the sand layer profile (Fig. 4). As discussed earlier, the voltage was not applied until the test had been operating for approximately

21 d; Fig. 4 shows that the flow rate for the kaolin lens test noticeably increased at this elapsed time increment. In addition, in the kaolin lens test, similar to the top kaolin with bottom sand test, it can be observed that even before the voltage was applied, the flow produced by the hydraulic gradient was gradually reducing, and as mentioned before, this was probably caused by the surfactant solution and viscosity effects.

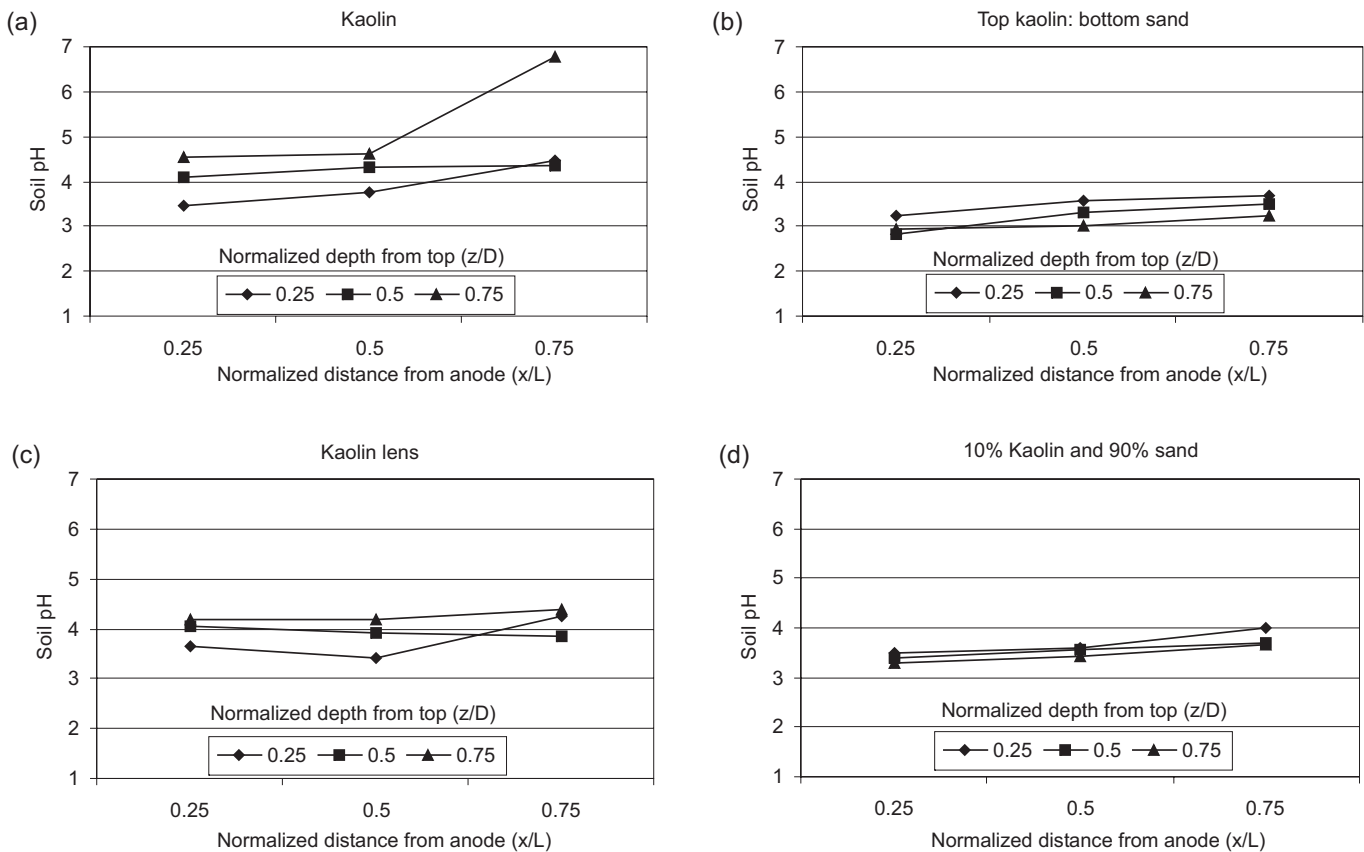
Typically, the hydraulic flow through well-graded soils is lower than through poorly graded soils because, when different size soil particles are placed together, the smaller particles fill or clog the gaps in the larger-sized particles, creating a tortuous flow path due to the tighter network with less open pore space (Mitchell 1993). Therefore, during the 10 % kaolin and 90% sand test, the kaolin particles filled in the pore spaces in the sand particles, and the effect was that the flow was substantially reduced through the soil profile. As observed in Fig. 4, the 10% kaolin and 90% sand test had the lowest flow of any of the heterogeneous tests, and the average flow rate of about 26 mL/d was only marginally better than that of the homogeneous kaolin test. At the start of the test, the flow due to the hydraulic gradient alone was extremely low, and the voltage was applied after approximately 9 d. Thus, after this time, a rise in the flow was observed; however, as the initial current slightly reduced to lower long-term values (Fig. 3), the flow rate also diminished.

Soil pH

Figure 5 shows the pH values that were measured in the soil sections after they were exhumed. Figure 5a illustrates that the pH in the homogeneous kaolin test was mostly acidic across the soil from anode to cathode, and this is attributed to the electrolysis reaction at the anode and the subsequent movement of H^+ ions toward the cathode by electromigration and electroosmosis. The soil section at the bottom of the apparatus nearest the cathode was an anomaly that had a pH that was substantially higher than the other soil sections, which may have been the result of the introduction of NaOH and the concentration of Na^+ ions near the cathode. Perhaps this anomaly occurred at the bottom of the apparatus because of the variation in the electroosmotic flow and pore pressure through the soil profile. It is important to note that the pH values in the soil profile were generally lower than the ZPC of kaolinite, which is estimated to be near 4.5 (Evangelou 1998), but the zeta potential may be a function of other factors, such as the ionic species that are present as well as the ionic strength of the pore solution. In addition, Lambe and Whitman (1969) reported that low pH conditions cause clay particles to flocculate and produce a more open structure, so this may have allowed greater flow movement through the low pH zone. As Dzenitis (1997) suggested, the soil regions, such as the one nearest the bottom of the reactor adjacent to the cathode, where the pH was higher and the zeta potential was probably more negative, could be largely responsible for pulling the electroosmotic flow toward the cathode.

All the other electrokinetic tests shown in Fig. 5 also had acidic solution through the soil profile from anode to cathode

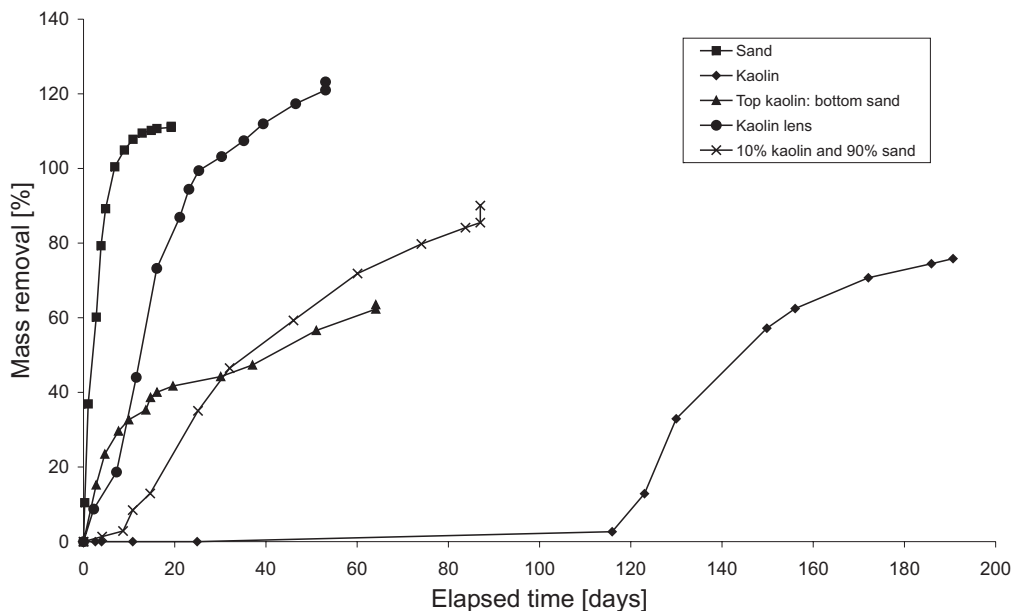
Fig. 5. Measured soil pH after electrokinetic testing with different soil profiles: (a) kaolin, (b) top kaolin, bottom sand, (c) kaolin lens, and (d) 10% kaolin and 90% sand.



due to the electrolysis reaction at the anode and the movement of H^+ ions toward the cathode. The uniform pH through these tests supports the hypothesis suggested earlier that the properties of the pore solution were similar in the kaolin and sand soils. Moreover, the low pH observed in these experiments indicates that the electroosmotic flow might have been improved by adding a pH control solution. The pH values in the kaolin lens test were slightly higher than the pH values measured in the top kaolin with bottom sand test or the 10% kaolin and 90% sand test, which was probably a result of the higher flow rate and (or) the different flow circulation patterns that existed. As mentioned previously, generally, when the flushing solution moves through the soil profile at a high flow rate, there will be less time for the H^+ ions to concentrate in the anode reservoir, so there may be less pH reduction through the soil. However, the top kaolin with bottom sand test had a higher flow rate than the 10% kaolin with 90% sand test (Fig. 4), and the pH values were slightly lower than in the 10% kaolin with 90% sand test. This might have been a result of the higher electrical current in the top kaolin with bottom sand test (Fig. 3), which could have corresponded to an increase of the electrolysis reaction rate at the anode and increased H^+ ion production.

Phenanthrene removal

Figure 6 shows the percent mass removal (cumulative mass removed normalized by the initial mass) with time, respectively, for the five tests. A high flow rate and high contaminant removal were achieved in the homogeneous sand test using hydraulic flushing alone; these results are shown again in Fig. 6 for comparison purposes. About 75% of the phenanthrene was removed during the homogeneous kaolin test. A large amount of electroosmotic flow occurred in the homogeneous kaolin test during the early stages of testing when the current was high (Figs. 3 and 4), but it is obvious from Fig. 6 that this initial effluent contained a negligible amount of phenanthrene. This is probably because the water used to establish the original soil water content was being flushed out during this early time interval, and the reaction kinetics between the soil–surfactant–contaminant was not facilitating adequate phenanthrene solubilization. The phenanthrene did not break through in the homogeneous kaolin test until approximately 120 d, when the NaOH solution reestablished the electroosmotic flow (Fig. 6). Apparently, phenanthrene solubilization was possible because of the presence of the surfactant solution as well as the additional reaction time provided by the periodic voltage application. Previous 1-D experiments demon-

Fig. 6. Cumulative mass of phenanthrene removed in tests with different soil profiles.

strated that the periodic voltage application and the high-voltage gradient were critical factors for generating phenanthrene removal from kaolin (Saichek 2002). This quasi-2-D homogeneous kaolin test verifies that substantial PAH removal from highly argillaceous soils can be accomplished by using electrokinetically enhanced in situ flushing with a surfactant.

Figure 6 illustrates that about 63% of the phenanthrene was removed from the top kaolin with the bottom sand test. This test resulted in a lower percentage of contaminant removal than the homogeneous kaolin test, which emphasizes that soil-layer heterogeneities might cause detrimental effects. The solution primarily flowed through the greater hydraulic conductivity sand layer, and it seems the contamination from the kaolin layer was released at a much slower rate. This behavior was evidenced by the detection of higher than initial phenanthrene concentrations in some of the residual kaolin soil samples, particularly the top three kaolin regions as well as a very high concentration in the center kaolin section. No phenanthrene was detected in the residual soil samples of the lower sand layer or in the kaolin regions to the right or left of the central kaolin section, so it is likely that the induced electroosmotic flow largely contributed to the migration and removal of phenanthrene from the kaolin layer.

The percent mass removal from the top kaolin with bottom sand test was approximately 38% after 14 d of testing using only hydraulic flow, suggesting that phenanthrene was being removed from the lower sand layer. When the hydraulic flow began to subside and the voltage gradient was applied, contaminant removal was enhanced by an additional 25%, probably from the kaolin layer. In addition, further improvement might have been possible if electrokinetic enhancement was applied for a longer duration or if a pH control was used along with the surfactant flushing solution. This experiment suggests that elec-

trokinetic enhancement may substantially improve contaminant removal from heterogeneous subsurface environments containing low hydraulic conductivity soil layers.

As observed in Fig. 6, a large amount of phenanthrene was removed during the kaolin lens test, and since the results were similar to the homogeneous sand experiment, it is evident that most of the contaminant mass was removed by simply flushing the soil profile with the surfactant solution under a hydraulic gradient alone. However, a close comparison of the results of the kaolin lens test with the homogeneous sand test reveals that the homogeneous sand test had contaminant concentrations that gradually reduced near the end of the experiment as less and less phenanthrene mass remained, whereas the kaolin lens test results show a sharp bend or upward shift that corresponds to the time of voltage application. This incongruity indicates that phenanthrene removal was probably enhanced by the voltage application. Furthermore, the sand was most likely remediated under the hydraulic gradient, as observed in the homogeneous sand test, so the additional phenanthrene mass that was removed was probably from the contaminated kaolin lens region. The phenanthrene concentration in the residual soil samples helped to confirm this hypothesis because the contaminant was not detected in any of the sand regions and phenanthrene was detected in the kaolin lens region, but at a much lower concentration than the initial concentration. This implies that although the remediation of heterogeneous soil profiles containing inclusions of soil of low hydraulic conductivity is difficult, electrokinetically enhancing the in situ flushing process was beneficial. The percent mass removal for the homogeneous sand test and the kaolin lens test exceeded 100% (Fig. 6), which was most likely caused by an underestimation of the initial phenanthrene concentration in the sand. During the extraction process for initial contaminant concentration, there was probably greater contam-

inant volatilization from the sand because the phenanthrene was weakly adsorbed to this soil.

As shown in Fig. 6, roughly 90% of the phenanthrene mass was removed from the 10% kaolin and 90% sand test. Moreover, phenanthrene was not detected in any of the residual soil samples. Therefore, it is evident that this test was highly successful, and it demonstrates that the electrokinetically enhanced in situ flushing process can be very promising for heterogeneous soil profiles containing well-graded, low-permeability soil mixtures.

Conclusions

The main conclusions drawn from this study were as follows:

- (1) For the homogeneous sand test, adequate flow was generated by the hydraulic gradient alone and electrokinetic enhancement was not required. Moreover, evidently the phenanthrene was weakly adsorbed to the sand particles because the hydraulic flushing of surfactant accomplished rapid removal of the contaminant from the homogeneous sand test. Conversely, because of the low hydraulic conductivity of kaolin, the same hydraulic gradient used in the homogeneous sand test did not generate any flow through the homogeneous kaolin test, and the flow through the kaolin was attributed to electroosmosis. Furthermore, the contaminant was difficult to remove from the kaolin soil because there may have been greater sorption or the contaminant was more easily trapped within the smaller clay particles, which have a much larger surface area.
- (2) In the homogeneous kaolin test, a pH control solution (NaOH) was added to the surfactant flushing solution, and this resulted in the movement of Na^+ ions toward the cathode due to electromigration and electroosmosis. The physico-chemical changes that occurred were responsible for substantially increasing the current and inducing a sustained electroosmotic flow. The pH control solution along with the periodic voltage application and the high DC 2.0 V/cm voltage gradient resulted in a contaminant removal efficiency of about 75% for the homogeneous kaolin test.
- (3) All the electrokinetic tests had a voltage gradient through most of the soil that was less than the uniform voltage gradient based on the voltage applied to the electrodes. This is important because the contaminant transport mechanisms, such as electromigration and electroosmosis, largely depend on the voltage gradient. For the heterogeneous profiles, the electrical current was higher when a greater percentage of kaolin was used; this was attributed to the dissolution of salts and minerals associated with the negatively charged clay particles.
- (4) In the electrokinetic tests, a region of low-conductivity solution formed near the cathode; this region was probably produced by the electrolysis reaction at the cathode, which

generates OH^- ions that may reduce cation mobility or neutralize cations by the formation of hydroxide species. This low-conductivity region might have contributed to weakening the electroosmotic flow because the voltage gradient increased near the cathode, where the double layer may be larger and there are less mobile ions. In addition, as a result of the electrolysis reaction at the anode and the migration of H^+ ions toward the cathode, low pH conditions existed in all the electrokinetic tests; this was detrimental for inducing flow toward the cathode.

- (5) The heterogeneous soil profiles were difficult to remediate using surfactant flushing alone because the flushing solution prefers to travel along flow paths with greater hydraulic conductivity. Consequently, the contaminant remains in zones of low permeability. The hydraulic flow through 10% kaolin and 90% sand mixture was substantially lower than that of the other heterogeneous tests because, when the different-sized soil particles were used together, the smaller particles filled or clogged the open gaps in the larger-sized particles, thereby forming a tighter network with less pore space and lower permeability. In general, the application of electric potential improved the flow through all the heterogeneous electrokinetic tests, which was clearly observed as a rise in the cumulative electroosmotic flow at the time of voltage application. The improvement was particularly beneficial for the soil profiles with the kaolin layer overlying the sand layer and the 10% kaolin and 90% sand mixture.

Overall, the results of this laboratory investigation indicate that the electrokinetically enhanced flushing process can improve the mass removal of phenanthrene from heterogeneous soil profiles containing layers, lenses, or mixtures of high and low hydraulic conductivity soils.

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References

- Acar, Y.B., and Alshawabkeh, A.N. 1993. Principles of electrokinetic remediation. *Environ. Sci. Technol.* **27**(13): 2638–2647.
- Acar, Y.B., Gale, R.J., Alshawabkeh, A.N., Marks, R.E., Puppala, S., Bricka, M., and Parker, R. 1995. Electrokinetic remediation: basics and technology status. *J. Hazard. Mater.* **40**: 117–137.
- Allred, B., and Brown, G.O. 1995. Surfactant-induced reductions of saturated hydraulic conductivity and unsaturated diffusivity. *In* Surfactant enhanced subsurface remediation — emerging technologies. Edited by D.A. Sabatini, R.C. Knox, and J.H. Harwell. ACS Symposium Series 594, American Chemical Society, Washington, D.C. pp. 217–229.
- Carrol-Webb, S.A., and Walther, J.V. 1988. A surface complex reaction model for the pH-dependence of corundum and kaolinite dissolution rates. *Geochim. Cosmochim. Acta*, **52**: 2609–2623.

- Dzenitis, J.M. 1997. Steady state and limiting current in electroremediation of soil. *J. Electrochem. Soc.* **144**(4): 1317–1322.
- Evangelou, V.P. 1998. Environmental soil and water chemistry, principles and applications. John Wiley and Sons, Inc. New York, N.Y.
- Eykholt, G.R. 1992. Driving and complicating features of the electrokinetic treatment of contaminated soils. Ph.D. thesis, Department of Civil Engineering, University of Texas, Austin, Tex.
- Eykholt, G.R. 1997. Development of pore pressures by nonuniform electroosmosis in clays. *J. Hazard. Mater.* **55**: 171–186.
- Eykholt, G.R., and Daniel, D.E. 1994. Impact of system chemistry on electroosmosis in contaminated soil. *J. Geotech. Eng.* **120**(5): 797–815.
- Fountain, J.C., Waddell-Sheets, C., Lagowski, A., Taylor, C., Frazier, D., and Byrne, M. 1995. Enhanced removal of dense non-aqueous phase liquids using surfactants; capabilities and limitations from field trials. *In* Surfactant enhanced subsurface remediation — emerging technologies. Edited by D.A. Sabatini, R.C. Knox, and J.H. Harwell. ACS Symposium Series 594, American Chemical Society, Washington, D.C. pp. 177–190.
- Gray, D.H., and Mitchell, J.K. 1967. Fundamental aspects of electroosmosis in soils. *J. Soil Mech. Found. Div., Am. Soc. Civ. Eng.* **93**(SM6): 209–236.
- Grundl, T., and Michalski, P. 1996. Electroosmotically driven water flow in sediments. *Water Res.* **30**(4): 811–818.
- Hsu, C. 1997. Electrokinetic remediation of heavy metal contaminated soils. Ph.D. thesis, Department of Civil Engineering, Texas A & M University, College Station, Tex.
- Ko, S., Schlautman, M.A., and Carraway, E.R. 2000. Cyclodextrin-enhanced electrokinetic removal of phenanthrene from a model clay soil. *Environ. Sci. Technol.* **34**(8): 1535–1541.
- Lambe, W.T., and Whitman, R.V. 1969. Soil mechanics. John Wiley and Sons, New York, N.Y.
- Li, A., Cheung, K.A., and Reddy, K.R. 2000. Cosolvent-enhanced electrokinetic remediation of soils contaminated with phenanthrene. *J. Environ. Eng.* **126**(6): 527–533.
- Luthy, R.G., Aiken, G.R., Brusseau, M.L., Cunningham, S.D., Gschwend, P.M., Pignatello, P.M., Reinhard, M., Traina, S.J., Weber, W.J., Jr., and Westall, J.C. 1997. Sequestration of hydrophobic organic contaminants by geosorbents. *Environ. Sci. Technol.* **31**(12): 3341–3347.
- Mitchell, J.K. 1993. Fundamentals of soil behavior. John Wiley and Sons, Inc., New York, N.Y.
- Mohamedelhasen, E., and Shang, J.Q. 2001. Effects of electrode materials and current intermittence in electro-osmosis. *Ground Improv.* **5**(1): 3–11.
- Myers, D. 1988. Surfactant science and technology. VCH Publishers Inc., New York, N.Y.
- National Research Council. 1997. Innovations in ground water and soil cleanup. National Academy Press, Washington, D.C.
- Pamukcu, S. 1994. Electrokinetic removal of coal tar constituents from contaminated soils. Electric Power Research Institute Final Report, EPRI TR-103320, Project 2879-21.
- Reddy, K.R., and Parupudi, U.S. 1997. Removal of chromium, nickel, and cadmium from clays by in-situ electrokinetic remediation. *J. Soil Contam.* **6**(4): 391–407.
- Reddy, K.R., Parupudi, U.S., Devulapalli, S.N., and Xu, C.Y. 1997. Effects of soil composition on removal of chromium by electrokinetics. *J. Hazard. Mater.* **55**(1–3): 135–158.
- Sabatini, D.A., Knox, R.C., and Harwell, J.H. 1995. Emerging technologies in surfactant-enhanced subsurface remediation. *In* Surfactant enhanced subsurface remediation — emerging technologies. Edited by D.A. Sabatini, R.C. Knox, and J.H. Harwell. ACS Symposium Series 594, American Chemical Society, Washington, D.C. pp. 177–190.
- Saichek, R.E. 2002. Electrokinetically enhanced in-situ flushing for HOC-contaminated soils. Ph.D. thesis, University of Illinois at Chicago, Chicago, Ill.
- Schultz, D.S. 1997. Electroosmosis technology for soil remediation: laboratory results, field trial, and economic modeling. *J. Hazard. Mater.* **55**: 81–91.
- Schwarzenbach, R.P., Gschwend, P.M., and Imboden, D.M. 1993. Environmental organic chemistry. John Wiley and Sons, Inc., New York, N.Y.
- Shapiro, A.P., and Probststein, R.F. 1993. Removal of contaminants from saturated clay by electroosmosis. *Environ. Sci. Technol.* **27**(2): 283–291.
- USEPA. 1986. Test methods for evaluating solid waste. Vol. 1A: laboratory manual, physical/chemical methods, SW-846. 3rd ed. Office of Solid Waste and Emergency Response, Washington, D.C.
- USEPA. 2000. A resource for MGP site characterization and remediation. EPA/542-R-00-005. Washington, D.C.
- Yeom, I., Ghosh, M.M., Cox, C.D., and Robinson, K.G. 1995. Micellar solubilization of polynuclear aromatic hydrocarbons in coal tar-contaminated soils. *Environ. Sci. Technol.* **29**(12): 3015–3021.