

Enhanced Electrokinetic Removal of Phenanthrene from Clay Soil by Periodic Electric Potential Application

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ABSTRACT

Electrokinetically enhanced in-situ flushing using surfactants has the potential to remove polycyclic aromatic hydrocarbons (PAHs) from low permeability clay soils; however, previous research has shown that the applied electric potential produces complex physical, chemical, and electrochemical changes within clay soils that affect mass transfer and overall efficiency. This article presents the results of a laboratory investigation conducted to determine the contaminant mass removal by using a periodic voltage application. The periodic voltage effects were evaluated by performing four different bench-scale electrokinetic tests with the voltage gradient applied continuously or periodically, under relatively low voltage (1.0 VDC/cm) and high anode buffering (0.1 M NaOH) as well as high voltage (2.0 VDC/cm) and low anode buffering (0.01 M NaOH) conditions. For all the tests, kaolin soil was used as a representative clay soil and it was spiked with phenanthrene, a representative PAH, with a target concentration of 500 mg/kg. A nonionic polyoxyethylene surfactant, Igepal CA 720, was used as the flushing solution in all the tests. The voltage was applied according to a cycle of five days of continuous application followed by two days of “down time,” when

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the voltage was not applied. The results of these experiments show that considerable contaminant removal can be achieved by employing a high, 2.0 VDC/cm, voltage gradient along with a periodic mode of voltage application. The increased removal was attributed to increased phenanthrene solubilization and mass transfer due to the reduced flow of the bulk solution during the down time as well as to the pulsed electroosmotic flow that improved flushing action.

Key Words: Electrokinetics; Electroosmosis; Electrokinetic remediation; Phenanthrene; PAHs; Soils; Clays; Surfactants; Sorption; Solubilization; Remediation.

INTRODUCTION

Polycyclic aromatic hydrocarbon (PAH) contamination exists at numerous sites throughout the United States and worldwide. In particular, former manufactured gas plant (MGP) sites have become a high priority for remediation because these sites are often highly contaminated with PAHs and pose a substantial risk to human health and the environment.^[1] Since PAH contaminants are persistent and hydrophobic, they are exceptionally challenging for cleanup efforts, and conventional remediation techniques, such as thermal, stabilization and solidification, and bioremediation methods, are often inefficient or costly, especially when the contaminants are located within clayey and/or organic soils. An innovative remediation technique, electrokinetically enhanced in-situ flushing, has great potential to remediate PAH-contaminants in clayey soils. In essence, electrokinetically enhanced in-situ flushing is a combination of the electrokinetic and the in-situ flushing remediation techniques, and these methods are integrated because the electrokinetic transport mechanism of electroosmosis greatly improves flow and soil-solution-contaminant interaction in low permeability clayey soils.^[2] Moreover, since PAHs are hydrophobic, surfactants are used as flushing solutions to accomplish PAH removal by micellar solubilization.

Compared to most conventional remediation technologies, the electrokinetic method is relatively safe, easy to implement, and economical, but the contaminant mass transport mechanisms and the physical, chemical, and electrochemical processes that are involved are complex and are not well understood. In around 1914, Helmholtz and Smoluchowski presented one of the first theories concerning electroosmosis,^[3] and, although their theory is more applicable for soils with fairly large pores, it is still widely accepted. Helmholtz-Smoluchowski (H-S) theory basically states that the electroosmotic flow velocity (v_{eo}) is directly proportional to the applied voltage gradient (E_z), zeta potential (ζ), and dielectric constant (D) of the fluid, and it is inversely proportional to the fluid viscosity (η)^[3,4]:

$$v_{eo} = -\frac{D\zeta E_z}{\eta} \quad (1)$$

The zeta potential depends on the interfacial chemistry between the liquid and solid phases,^[5] and West and Stewart^[6] define it as the electric potential at the junction between the fixed and mobile parts in the double layer. The zeta potential is



thought to be a function of many parameters including the types of clay minerals and ionic species that are present as well as the pH, ionic strength, and temperature.^[7]

The pH at which the net total clay particle surface charge is zero is known as the point of zero charge (PZC or pH_{pzc}), and various methods, such as titration, electrophoretic mobility measurement, or flocculation measurement, are used to determine this value.^[8] Generally, the mineral surface of a low acid buffering clayey soil may become protonated under low pH conditions, and a solution that has a pH below the pH_{pzc} would cause the mineral surface and the zeta potential to become more positively charged than a solution with a pH above the pH_{pzc} . Consequently, by H-S theory, the electroosmotic flow towards the cathode could reduce, cease or even reverse when pH is lowered from values above the pH_{pzc} to values below the pH_{pzc} .^[5]

During electrokinetics, electrolysis reactions occur at the electrodes generating H^+ ions at the anode and OH^- ions at the cathode. The electromigration of H^+ and OH^- and other ions into the soil towards the oppositely charged electrode could result in the adsorption of ions to the mineral surface, which affects the charge on the mineral surface and the zeta potential. In addition, chemical reactions between migrating ions could produce changes in the conductivity of the pore solution, and this may affect the voltage gradient at local regions along the soil profile.^[9] Moreover, changes in pH may increase mineral dissolution,^[10] which could increase the amount of ions in solution, ion migration, and electroosmotic flow. Low pH solutions may cause clay flocculation, which may produce a more open clay structure^[11] with a greater hydraulic conductivity. From H-S theory, it is evident that the variations in zeta potential and voltage gradient occurring at local regions will generate a nonuniform electroosmotic flow rate along the soil profile, and this could result in differences in pore pressure and/or cause consolidation in some soils.^[12] To address the problem of pH changes caused by the electrolysis reaction at the anode, several investigators have employed various buffering solutions, and these solutions appear to sustain or increase electroosmotic flow.^[13–15]

Due to the complex transport and physico-chemical processes, the electrokinetic process can be difficult to analyze, and the situation is exacerbated when surfactant solutions are used to remove PAHs. As the surfactant concentration increases in a dilute aqueous solution, a concentration known as the critical micelle concentration (CMC) is reached where the surfactant molecules begin to aggregate into tiny (1–10 nm diameter) structures called micelles.^[16] The interior of the micelle provides a hydrophobic region where PAH molecules may reside, and, as the surfactant concentration increases above the CMC, due to micellar solubilization, PAH solubility will increase considerably. One problem with surfactant solutions is that they may possess a low dielectric constant,^[17] which, by H-S theory, will reduce the electroosmotic flow rate compared to water.

Of the three main surfactant types, nonionic surfactants may be the best for the electrokinetically enhanced in-situ flushing process. This is because they are good solubilizers, they are relatively nontoxic,^[18] they do not strongly adsorb to clay soils like cationic surfactants, and they should not oppose the electroosmotic flow towards the cathode like anionic surfactants. However, as with all surfactants, nonionic surfactant molecules are amphiphilic (partly hydrophobic and partly hydrophilic) and attracted to interface locations, and several investigators have



found that surfactant sorption to interfaces may continue at concentrations that are substantially above the CMC.^[19-21] Since PAHs typically adsorb to organic substances, and surfactants are organic, solubilized PAH molecules may partition to sorbed surfactant molecules. In addition, some nonionic surfactants, such as the polyoxyethylene surfactants, have molecules that may acquire charges. These charged surfactant molecules may occur due to hydrogen bonding with the oxyethylene group^[22-24] or by the formation of complexes with cations, such as Na^+ .^[25] If sorbed surfactant molecules at the mineral surface become protonated due to hydrogen bonding, the mineral surface and zeta potential may become more positively charged, and, consequently, the electroosmotic flow towards the cathode will reduce. Furthermore, the CMC of the surfactant, the aggregation number, or the amount of micelles that are present may also be affected by the electrolyte concentration or by changes in the pore pressure.^[17]

The rates at which micelles are created and dissipate are considered to be very rapid,^[17] and the partitioning of the PAH between the aqueous and micellar phases is also generally assumed to be a fast process.^[26] However, Yoem et al.^[27] and Patterson et al.^[28] suggest that the mass transfer is limited due to the diffusion of the PAH from the soil matrix. Thus, in addition to the surfactant effects discussed earlier, micellar solubilization further complicates electrokinetic remediation because it is a rate-limited process.^[26-28] It is important to note that the rate of the electrolysis reactions may also vary with time.^[29] Moreover, these changes greatly affect the remediation process because they are linked to other parameters such as the charge on the mineral surface, the conductivity of the pore solution, as well as to the electrolyte concentration or the pore pressure, which may affect the CMC of the surfactant, the aggregation number, or the amount of micelles that are present.^[17] Thus, under an applied electric potential, the soil-solution-contaminant system is in a dynamic state undergoing many kinetic, or time dependent, physical, chemical, and electrochemical reactions, which are much more complex than those occurring during the in-situ flushing process under a hydraulic gradient alone.

A detailed laboratory investigation at the University of Illinois at Chicago (UIC) has been undertaken to develop an electrokinetically enhanced in-situ flushing method for PAH-contaminated clay and/or organic soils.^[30] An extensive literature review as well as series of batch tests and bench-scale 1-D electrokinetic experiments were conducted to assess the effects of using different surfactants, electrolyte concentrations, soil types, and voltage gradients to enhance PAH remediation.^[30] Although this study provided valuable information and a better understanding of the electrokinetically enhanced remediation process, the overall amount of contaminant removal was low.

It was postulated that applying the electric potential in a periodic manner, or disconnecting the voltage periodically, would increase micellar solubilization and enhance remedial efficiency. A series of bench-scale electrokinetic experiments were conducted using a clay soil, kaolin, spiked with a representative PAH, phenanthrene. A nonionic surfactant, that was proven to be effective from previous investigations, was used as the flushing solution. The tests were conducted with a continuously or periodically applied voltage gradient. The test results were analyzed to determine the beneficial effects of periodic voltage application on remedial efficiency.



EXPERIMENTAL METHODOLOGY

Materials

The soil chosen for this research was kaolin, and its mineralogy and properties are shown in Table 1. Kaolin basically consists of the mineral kaolinite, and it has a hydraulic conductivity of around 10^{-8} cm/s, which is far below the 10^{-5} cm/s magnitude that is considered appropriate for in-situ soil flushing.^[31] This soil has been previously used in electrokinetic research at UIC and in other studies because it has a low organic content, a consistent, uniform mineralogy, it is fairly nonreactive, and it has a low cation exchange capacity.

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 and a $\log K_{ow}$ of 4.57 at 25°C.^[32]

A nonionic octyl phenol polyoxyethylene surfactant, which has the trade name of Igepal CA-720, was used for all the experiments, and NaOH was also used to counteract (buffer) the electrolysis reaction at the anode. It should be noted that most surfactants are biodegradable,^[18] and, for ethoxylate nonionic surfactants, decreasing the number of oxyethylene units in the hydrophilic group and increasing the linearity of the hydrophobic group generally enhances biodegradation.^[33] In addition to biodegradability, it is also important to ensure that the surfactant is compatible with the flushing technique and the subsurface environment, so advection and biodegradation are controlled and microbial activity does not overwhelm the process or biofoul and clog pore spaces and/or the injection/extraction wells.^[34]

The selection of the surfactant and its concentration were based on a series of batch and bench-scale electrokinetic experiments conducted in a previous investigation.^[30] In this previous investigation, the batch tests were conducted using individual soil–solution (1:5) slurries placed on a mechanical shaker table. The

Table 1. Properties of the soil (kaolin) tested.

Property	Result
Mineralogy	Kaolinite 100% Muscovite: trace Illite: trace
Particle size distribution (ASTM D 422) (%):	
Gravel	0
Sand	4
Silt	18
Clay	78
Specific gravity (ASTM D 854)	2.6
Hydraulic conductivity (cm/s) at porosity = 46%	1.0×10^{-8}
Organic content (ASTM D 2974) (%)	Near 0
pH (ASTM D 4972)	4.9
Cation exchange capacity (ASTM D 9081) (meq/100g)	1.0–1.6
USCS classification (ASTM D 2487)	CL



results indicated that the contaminant removal was greater in the batch tests than the electrokinetic tests due to the different contaminant mass transport and removal mechanisms. In particular, soil–solution–contaminant interaction was probably much greater during the batch tests.

Electrokinetic Test Setup

The electrokinetic test setups used in this study were similar to those used in previous electrokinetic research at UIC.^[35–37] A schematic diagram of the electrokinetic cell and the entire test setup is shown in Fig. 1. The test setup simulates 1-D contaminant transport under the combined influences of electrical, hydraulic, and chemical gradients.

The test setup consisted of a cell, two electrode compartments, an anode electrode reservoir, 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 electrokinetic cell was constructed with a 19.1 cm long Plexiglas tube with a 6.2 cm inside diameter (cross-sectional area = 30.2 cm²). The electrodes were slotted and composed of graphite. Each electrode compartment was also made of Plexiglas, and it contained #1 Whatman filter paper and a porous stone 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. The distance from the soil interface to the electrode was less than a centimeter, and measurements revealed that the voltage drop over this distance was negligible. Gas vents were provided in the electrode compartments to allow gases resulting from the electrolysis reactions to escape.

Testing Program

This investigation included the performance of four different electrokinetic tests that varied in buffering concentration, voltage gradient, and/or the mode of voltage application, which was either continuous or periodic. The periodic voltage application consisted of a cycle of five days of continuous voltage application followed by two days of “down time,” where the voltage was not applied in order to allow time for the mass transfer, or the diffusion of the contaminant from the soil matrix, to occur and also to balance the dual objectives of generating high electroosmotic flow while providing adequate time for mass transfer and contaminant removal. Table 2 shows the details of other test variables. All four tests used the same kaolin soil and 5% Igepal CA-720 surfactant solution. The Tests A and B were performed using a 0.1 M NaOH buffering concentration and a 1.0 VDC/cm voltage gradient, while Tests C and D were conducted using a 0.01 M NaOH buffering concentration and a 2.0 VDC/cm voltage gradient. The Tests A and C were conducted using a continuous mode of voltage application, while the Tests B and D were conducted with a periodic mode of voltage application.



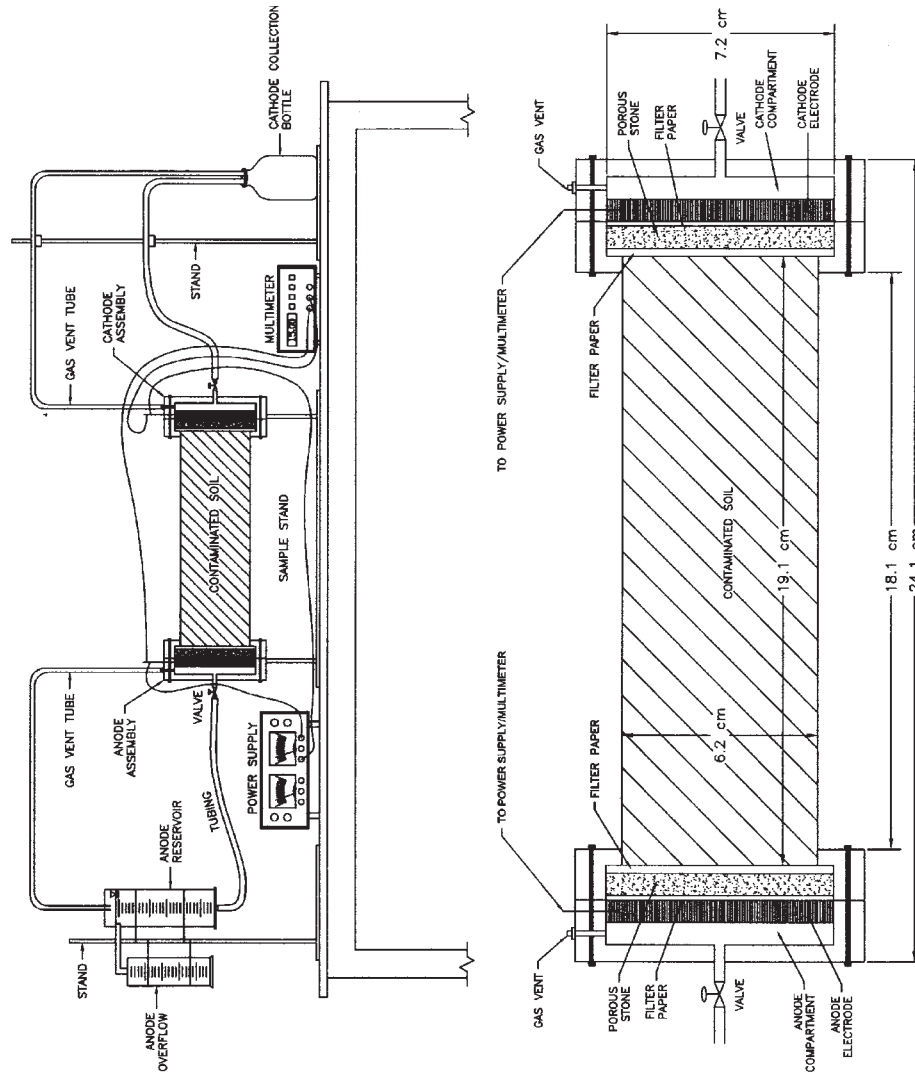


Figure 1. Schematic of electrokinetic test setup.



Table 2. Electrokinetic testing program.

Test designation	Soil type	Purging solution	Buffering solution	Voltage gradient (VDC/cm)	Voltage application
A	Kaolin	5% Igepal CA-720	0.1 M NaOH	1	Continuous
B	Kaolin	5% Igepal CA-720	0.1 M NaOH	1	Periodic
C	Kaolin	5% Igepal CA-720	0.01 M NaOH	2	Continuous
D	Kaolin	5% Igepal CA-720	0.01 M NaOH	2	Periodic

Testing Procedure

For all the electrokinetic tests, the soil was spiked with phenanthrene at a target concentration of 500 mg/kg (mass of phenanthrene/mass of dry soil), which was to represent the typical PAH concentrations found near source zones at contaminated sites.^[1] Approximately 1.1 kg soil was spiked for each electrokinetic test and this mass included soil for the determination of the initial contaminant concentration. 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 a low solubility in water. The hexane–phenanthrene mixture was subsequently mixed with the measured amount of soil and additional hexane was added so that the soil–hexane–phenanthrene mixture could be easily stirred and blended homogeneously. 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. 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.

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%. The moist soil was then placed into the electrokinetic cell in layers, and each layer was tamped into the cell using an aluminum pestle so that the amount of void space was minimized. Once the soil was fully packed into the cell, the electrode compartments/reservoirs were connected, the peripheral equipment was attached, the anode and cathode compartments as well as the anode reservoir were filled with solution, and the constant or periodic DC 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 surfactant/buffering solution.

During the testing, the electrical current and the inflow volume and effluent volume at the anode and cathode were measured periodically, and samples of the effluent were taken so that the phenanthrene concentration could be measured. The anode reservoir was graduated to determine the inflow volume, and the outflow was measured by pouring the effluent into a graduated cylinder. The tests were operated until substantial reductions occurred in the current or effluent volume, and



measurements of the phenanthrene concentration in the effluent had stabilized. 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 phenanthrene remaining in the soil. For all tests, the soil samples were sectioned into five parts approximately every four centimeters along the length of the electrokinetic cell.

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 D 4972. 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 method D 2216.

Chemical Analysis

For the analysis of the phenanthrene in the soil, a dry representative 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 as described in USEPA test method 3540C.^[38] 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 performance 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 not diluted and were directly analyzed using the HPLC. In addition to soil analysis, the liquid effluent samples from the electrokinetic tests containing surfactant-phenanthrene were directly analyzed using the HPLC.

A Hewlett-Packard Model 1100 HPLC equipped with an Alltech Econosphere reverse-phase C18 column (250 × 4.6 mm, 5 μm particle size) and a diode array UV 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 (PTFE), 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

All the testing equipment, such as the multimeters, power supplies, and pH meters, were in good condition and were calibrated, and a conscious effort was made to ensure that the chemicals used as solvents or in analyses were fresh and high-grade (HPLC) purity. The deionized water was tested to verify that it had a low (<2.00 μS/cm) electrical conductivity.



Phenanthrene was used as an external standard for calibration, and the standards for the HPLC analyses were prepared in two different concentration ranges, where 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, and the average regression coefficient (R^2) was 0.996. 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 eliminate cross-contamination.

After the electrokinetic tests were completed, a mass balance was conducted for the phenanthrene in the system and compared to the phenanthrene spike. For this investigation, three of the four tests had a final mass that was computed to be within 6% of the initial mass, and one experiment had a final mass computed to be within 21% of the initial mass. 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 Plexiglas chambers, the electrodes, porous stones, tubing, and/or sample bottles. Volatilization of phenanthrene along with the solvents during the extraction procedures may also caused mass balance differences.

RESULTS AND ANALYSIS

The test results included the current, electroosmotic flow, and phenanthrene mass removal measured during the test operation, as well as the pH and phenanthrene concentration profiles in the soil after the tests were completed. By observing Table 2, it can be seen that a comparison of the results from Tests A and B indicate the effects of periodic voltage under a high buffering (0.1 M NaOH) and low voltage gradient (1.0 VDC/cm) conditions on removal efficiency. Whereas, a comparison of the results from Tests C and D indicate the effects of periodic voltage under low buffering (0.01 M NaOH) and high voltage gradient (2.0 VDC/cm) conditions on removal efficiency. It should be noted that “low” and “high” are used as relative terms to differentiate the tests.

Current

Figure 2 shows the changes in the electrical current that occurred during the electrokinetic remediation experiments. Figures 2a, b show a comparison between Tests A and B and Tests C and D, respectively. As seen in this figure, the tests commonly begin with relatively high current values, but then the current reduces rather quickly within the first 10 to 20 days of operation. The high current seen at the start of the voltage application is most likely due to the high conductivity of the initial pore solution as a result of the dissolution of salt precipitates that were associated with the negatively charged clay particles.^[3] Typically though, the current values decrease over time as the ions in the pore solution electromigrate towards the



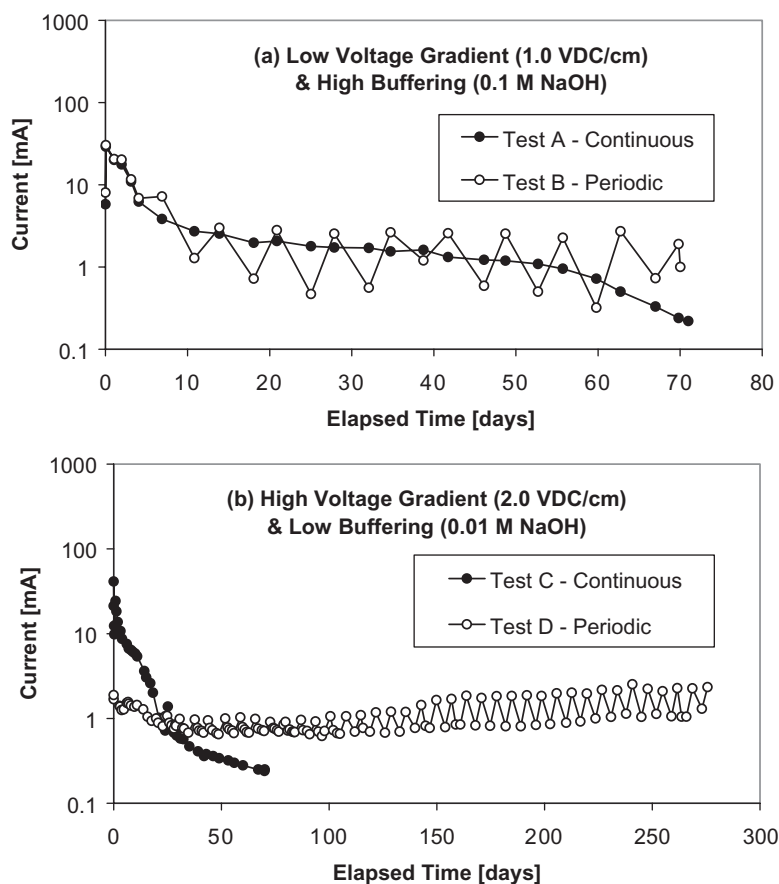


Figure 2. Current measured during electrokinetic remediation.

electrodes and diminish within the soil sample.^[4,39,40] Although the initial number of ions present in the pore solution may diminish, ions are also generated by the electrolysis reactions at the electrodes, and H⁺ ions, which are generated at the anode, are mobilized into the pore solution towards the cathode by the electrokinetic transport mechanisms of electromigration and electroosmosis.^[41] This acidic front of solution moving towards the cathode reduces the pH of the soil, thereby possibly causing additional mineral dissolution and more ion electromigration. As discussed earlier, the acidic solution also causes the charge on the mineral surface to become more positive, and this may reduce electroosmotic flow and/or the number of ions in solution.

Generally, the current measurements show that when the voltage is applied periodically, the current values follow an up and down pattern. The current decreases fairly rapidly over the five days when the voltage is applied continuously due to the movement of ions towards the electrodes, however, when the voltage is not applied during the “down time,” it is evident that additional ions move into the



solution. This is evident because when the voltage is re-applied, a noticeably higher current exists. Apparently, the “down time” facilitates reactions that increase soil–solution interaction and results in additional ion dissolution and/or the micellar solubilization of ions.

Figure 2 shows that compared to the continuously applied voltage tests, the tests using the periodic voltage application appeared to sustain a relatively high average current value for a longer duration. This is seen most clearly in Fig. 2b where Test D, which used a periodic mode of voltage application, resulted in a high sustained average current level for over 250 days, while Test C, which used the same test variables except with a continuous mode of voltage application, resulted in a rapidly decreasing current level that fell below 1 mA after 25 days and kept decreasing. Both of the tests using the continuous mode of voltage application had current values that kept decreasing over time, which was most likely caused by the depletion of the ions in the solution by electromigration towards the electrodes and/or by changes occurring to the charge on the mineral surface as a result of the electrolysis reactions.

A comparison of Figs. 2a, b shows that for the two tests using the continuously applied voltage, the test using the low buffering concentration and high voltage, Test C, resulted in a decline of current that was more rapid than the decline measured in the test using the higher buffering concentration and low voltage, Test A. Thus, it is evident that the higher power provided by the high voltage gradient increases the rate of electromigration, and the high voltage combined with the lower buffering concentration may have allowed greater H^+ ion generation as a result of an increase in the electrolysis reaction at the anode. The H^+ ions could increase the positive charge on the mineral surface, and, by H–S theory, thereby reduce the electroosmotic flow towards the cathode.

Figure 2b shows that compared to Test C, Test D had a lower initial current value, and this is most likely due to minor differences or impurities in the soil. Even with laboratory grade kaolin, soil chemistry may vary between samples,^[4] and it appears that there were not as many mobile ions initially present in the soil sample of Test D at the start of testing. It is also of interest to note that Test D shows that the current may slightly increase over time during a periodic voltage test, and this could be the result of additional mineral dissolution occurring during the “down time” interval, or the effects of improved flushing action as a result of pulsing the electric potential.

As mentioned earlier, kaolinite dissolution may result from the migration of low pH solution generated by electrolysis at the anode. Carrol-Webb and Walther^[10] found that long-term kaolinite dissolution occurred at low pH values to pH = 4, was constant from pH = 4–8, and then increased with pH when the pH was greater than 10. The short-term dissolution rate was higher, and Eykholt^[4] explains that when kaolinite is placed in an acid environment, the exposed aluminum surface groups readily dissolve, and, after roughly 100 h, the rates become steady because of the reduction in aluminum group exposure. Thus, the dissolution of kaolinite in the periodic test may have increased the amount of dissolved species, such as aluminum ions, and this could have caused a minor increase in current or electroosmotic flow, or it could have affected the charge on the mineral surface. In the periodic test, greater mixing of the stagnant layer of solution near the particle surface with the



more turbulent bulk liquid may have also contributed to the slight increase of current (as will be discussed in a later section).

Electroosmotic Flow

Figures 3a, b show the cumulative electroosmotic flow measurements in the electrokinetic remediation experiments. Figure 3a shows that after around 10 days, roughly corresponding to the time when the reduction in current occurred, the electroosmotic flow reduced in both Tests A and B. It is apparent from Fig. 3a that

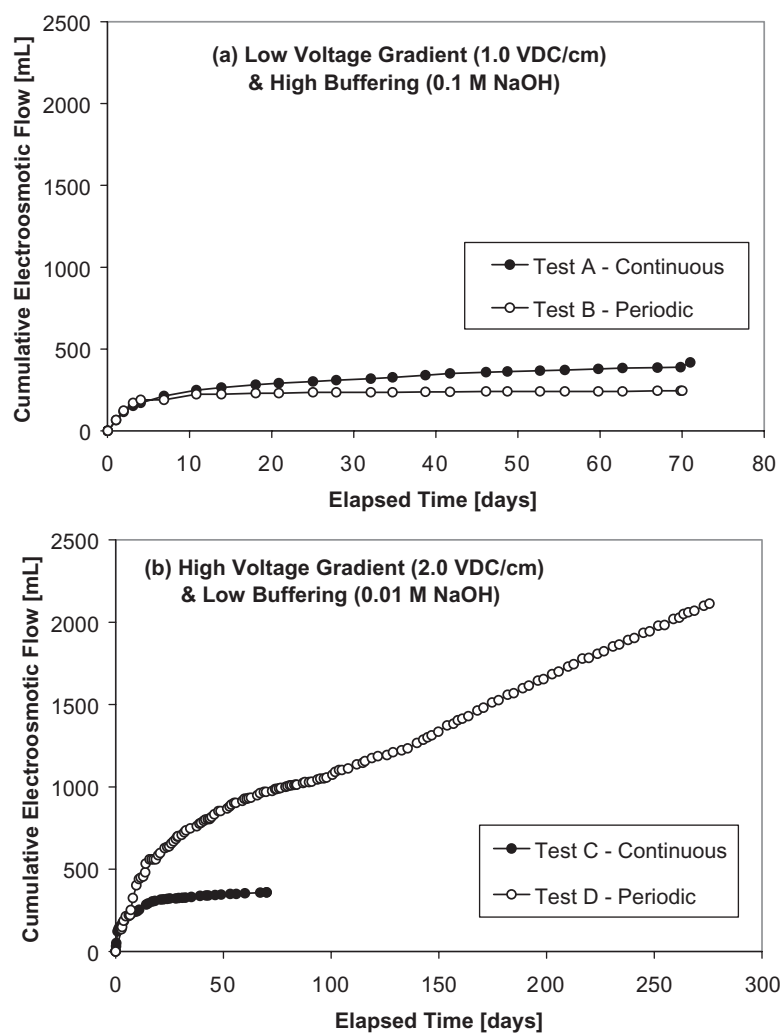


Figure 3. Electroosmotic flow measured during electrokinetic remediation.



over the duration of these experiments the flow reduction was greater in Test B, which used the periodic voltage application, and the test using continuous voltage, Test A, had slightly more cumulative electroosmotic flow. This result was somewhat expected based on the current measurements, because for the first 40 days or so, when the majority of the flow occurred, the average current was higher in Test A than in Test B. Although high current does not necessarily indicate a higher electroosmotic flow, it correlates to ion movement, and that is basically the way in which electroosmotic flow is generated. It is possible that the pulsing effect produced by the periodic voltage application caused the pore spaces to become clogged in Test B, and this inhibited the electroosmotic flow, which practically ceased after about the first 20 days. Test A, using the continuous voltage, had an average flow that was over 20 mL/day during the first 10 days, but, from about day 10 to day 70, the average flow reduced to around a tenth of the initial flow, or to about 2 mL/day. The electroosmotic flow reduction in Test A was probably a result of the gradual depletion of ions in the pore solution and/or due to changes to the charge on the mineral surface caused by the electrolysis reaction at the anode.

Figure 3b compares the results of the cumulative electroosmotic flow during Tests C and D. Test D, which used a periodically applied voltage, resulted in a much more sustained flow rate that continued for over 250 days, while Test C, which used a continuously applied voltage, had diminished flow after less than 25 days. Test D was operated for about 275 days and resulted in a cumulative electroosmotic flow of approximately 2100 mL, which is an average flow rate of over 7 mL/day. Conversely, Test C had high initial average flow rate of roughly 13 mL/day during the first 25 days, but then the average flow rate reduced to less than 1 mL/day. The cumulative volume for Test C was comparatively low at around 360 mL after 70 days. The flow rates for these tests correlate well to the current values, which, as seen earlier in Fig. 2b, were fairly high and consistent for Test D but rapidly decreased to below 1 mA after about 25 days for Test C. From these results, it is evident that the periodic mode of voltage application can significantly improve and sustain the electroosmotic flow.

By observing Figs. 2a and 3a, it appears that the low voltage gradient was inadequate for use with the periodic mode of voltage application, because, after 20 days, the electrical current in Test B was sufficiently high but there was a low amount of electroosmotic flow. It is possible that nonuniform electroosmotic flow and variable pore pressures caused soil consolidation,^[12] and/or the flow reduced due to changes to the charge on the mineral surface as a result of the electrolysis reaction at the anode. Since the average current in Test B was similar to Test D, it is unlikely that the reduction in electroosmotic flow was a result of insufficient ion electromigration or ion depletion.

Relative to the other tests, Test D produced a higher and more sustained flow and this was apparently due to both the higher voltage gradient and periodic voltage application. Shang et al.^[42] have hypothesized that under an electric potential, the diffuse double layer becomes polarized, and the charges are distorted in the direction of the electric field. The polarization of electrical charge at the clay particle surface could reduce the intensity of the electric field and diminish the electroosmotic flow. When the voltage was not applied during the “down time,” depolarization of the double layer probably occurred, since the applied electric field was absent.



Consequently, after the “down time,” when the voltage was re-applied, the electric field intensity was greater than before the “down time,” and this resulted in a higher electroosmotic flow.

Cumulative Mass in Solution

Figure 4 shows the cumulative mass and percentage of mass of phenanthrene that was removed during the electrokinetic tests. It can be seen in Fig. 4a that Test A, using the continuously applied voltage, had a slightly greater cumulative mass

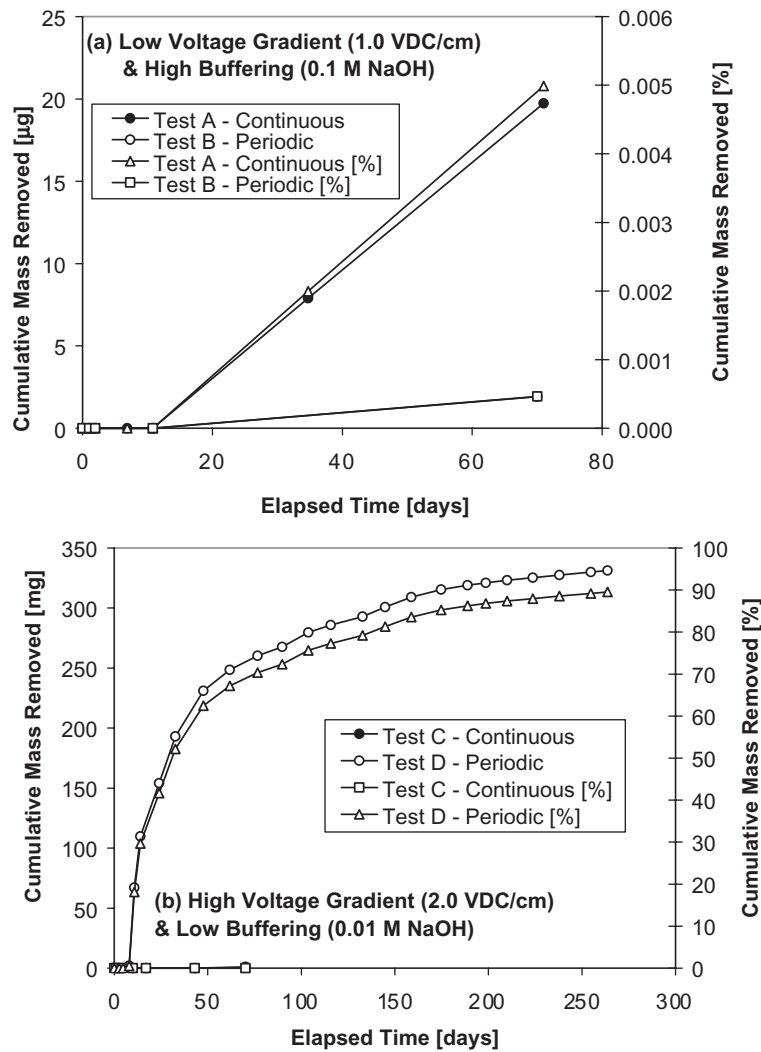


Figure 4. Phenanthrene mass removal during electrokinetic remediation.



removal than that of Test B with periodic voltage application. This may have been a result of the somewhat higher electroosmotic flow in Test A, seen earlier in Fig. 3a. Although Test A had a bit higher mass removal, it should be recognized that both Tests A and B had poor mass removal overall compared to the initial contaminant mass spiked into the soil, which was approximately 400 mg. The contaminant removal for Tests A and B was much less than what was expected based on the batch tests reported by Saichek^[30] that employed the same type of soil and flushing solution, so it is evident that the mass transfer mechanisms that function during electrokinetic remediation differ from those that function during batch tests. It is important to note that compared to Test D, which employed the high periodic voltage gradient (2.0 VDC/cm), the small amount of mass removal in Test B indicates that the low periodic voltage gradient (1.0 VDC/cm) was not effective for contaminant removal.

Figure 4b shows the cumulative mass of phenanthrene that was removed from Tests C and D, which were performed under high voltage gradient and low buffering conditions. Test C used a continuously applied voltage, whereas Test D used a periodically applied voltage, and there was a significant difference between these two tests. The cumulative phenanthrene mass removed during Test D was over 338 mg (nearly 90% of the initial mass), while virtually no contaminant mass was detected in the effluent from Test C. Evidently, the use of a periodic mode of voltage application and a high voltage gradient were the critical factors responsible for increasing the amount phenanthrene removal. Since the only difference between Tests C and D was the mode of voltage application, this high removal is largely attributed to the kinetic desorption and solubilization reactions and/or the pulsing mechanisms that were caused by the use of the periodic mode of voltage application. As seen earlier in Fig. 3b, the periodic high voltage application was also responsible for maintaining a consistent flow rate that allowed sustained soil–solution–contaminant interaction, and, clearly, this steady flow rate contributed to the high amount of phenanthrene removal.

Comparison of pH

Figure 5 shows the pH that was measured in the different soil sections after they were extruded from the electrokinetic cell at the conclusion of the electrokinetic experiments. Due to the electrolysis reactions, it is generally expected that low pH regions will exist near the anode and high pH regions will occur near the cathode. However, as discussed previously, during the course of testing the acidic solution generated at the anode gradually moves by electromigration and electroosmosis through the soil towards the cathode, thereby lowering the pH of the soil throughout the sample.^[41] As seen for all the tests except Test B, there was an acidic pH profile across the length of the sample. The high pH values near the cathode in Test B were most likely caused by the electromigration of OH^- ions towards the anode. In Test B, the OH^- ions, which are generated by the electrolysis reaction at the cathode, had a greater opportunity to electromigrate into the sample towards the anode because of the low electroosmotic flow. As shown earlier, the electroosmotic flow in Test B greatly reduced after about 20 to 25 days. Normally, when using solutions with a pH



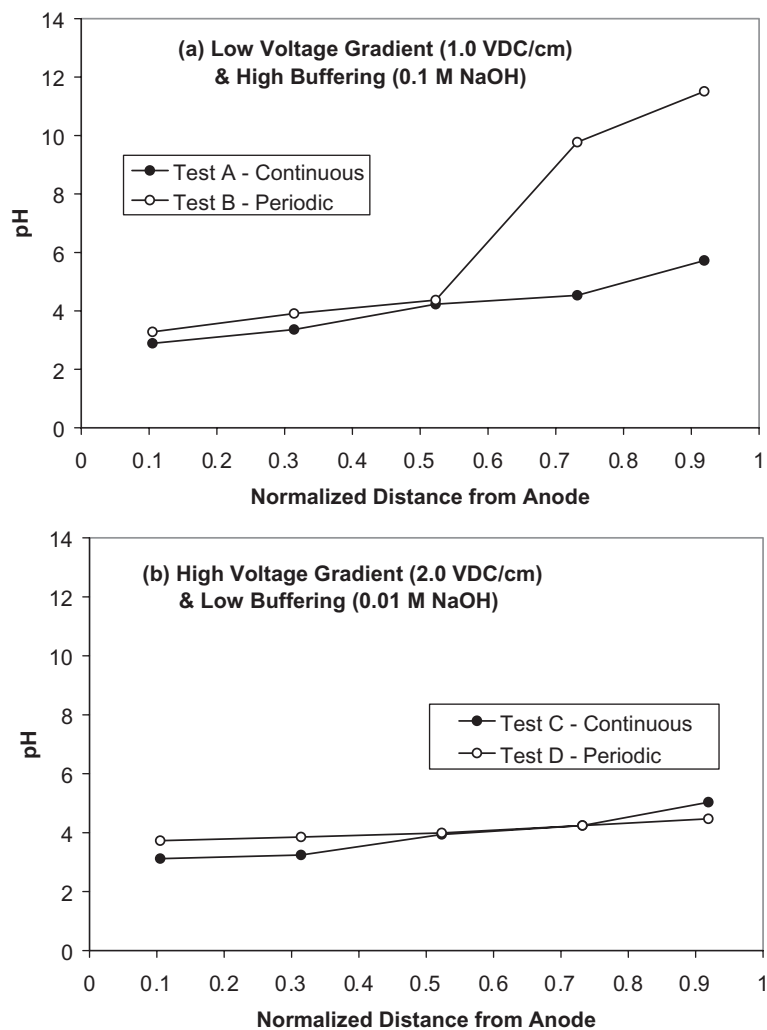


Figure 5. Soil pH after electrokinetic remediation.

greater than the pH_{pzc} , the electroosmotic flow through kaolin is towards the cathode, and under high electroosmotic flow conditions, OH^- electromigration towards the anode is hindered because it opposes the direction of electroosmotic flow. In Test B, the periodically applied low voltage gradient may have generated variable pore pressures that resulted in the clogging of pore spaces, and the low amount of electroosmotic flow could have allowed OH^- ion electromigration from the cathode compartment towards the anode.

The electrokinetic operating conditions may also affect the pH, because, for the tests using the periodic voltage application, the electrolysis reactions should reduce or stop during the interval when the voltage is not applied, and, for the tests that employ a higher voltage gradient, the rate of the electrolysis reactions should



increase. Moreover, it was expected that using a NaOH acid buffer would cause the pH to remain higher near the anode because it should counteract the electrolysis reaction. Based on the results in Fig. 5, however, neither the 0.01 M nor the 0.1 M NaOH buffering concentration appeared to be effective for either mode of voltage application or amount of voltage gradient, and the soil pH profiles for all the tests show that the final pH values in the soil were acidic adjacent to the anode. It seems that with the test variables and operating conditions used in these experiments, the electrolysis reaction always lowered the pH to approximately 3.0 near the anode.

Since, by H-S theory, acidic pH solutions may reduce the electroosmotic flow rate by causing the soil minerals to possess a more positive surface charge and zeta potential, the flow velocity towards the cathode should have decreased over time. It is important to observe that along the soil profiles the pH near the anode in all the tests appears to be lower than the pH_{pzc} of kaolinite, which is estimated to be around 4.5.^[43] As stated earlier though, the zeta potential may be a function of many parameters besides the pH, such as the ionic species that are present and the ionic strength of the pore solution.^[7] In addition, low pH solutions may cause clay flocculation, which produces a more open clay structure with a greater hydraulic conductivity.^[11]

Comparison of Phenanthrene Concentration

Figure 6 shows the residual phenanthrene concentration in the different soil sections after they were extruded from the electrokinetic cell at the conclusion of the electrokinetic experiments. Figures 6a, b show that the residual concentration of phenanthrene was low near the anode for all the experiments, and this was probably caused by the higher rate of inflow, flushing action, and soil–solution–contaminant interaction that may occur near the anode section. As mentioned earlier, the more open structure of the clay near the anode due to the low pH may have caused the particles to flocculate, thereby allowing greater soil–solution–contaminant interaction. Furthermore, since the kaolin used in these experiments has a low organic content, the phenanthrene was probably weakly sorbed or bonded to the mineral surface. It is also important to note that the electroosmotic flow is a function of many variables, including the ionic strength, zeta potential, and electrical gradient, so the flow and pore pressure may vary along the length of the soil sample. Therefore, some soil sections, such as near the inlet, or anode region, may experience high flow and soil–contaminant–solution interaction, while other soil sections, such as those near the middle or cathode end, may be more stagnant due to soil consolidation and pore clogging and tend to accumulate contaminants from the inflow end. Visual evidence of soil consolidation near the cathode was usually apparent after the soil was extruded from the test cell.

The initial phenanthrene concentration in the soil was around 400 mg/kg, and, as seen in Fig. 6a, the residual phenanthrene concentrations for Tests A and B were low adjacent to the anode, much higher than the initial concentration near the middle sections, but then close to the initial contaminant concentration in the sections near the cathode. These results suggest that the electroosmotic flushing of surfactant solution mobilized or solubilized the phenanthrene near the anode, but, due to changes in the soil and/or solution chemistry, the contaminant re-adsorbed or



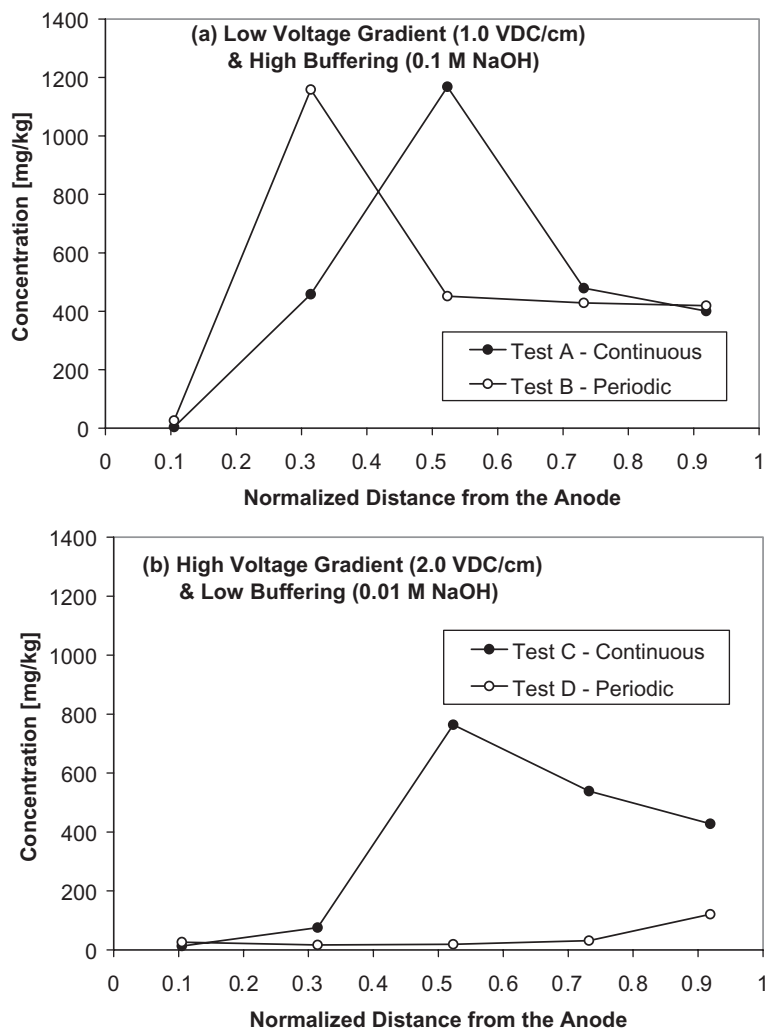


Figure 6. Phenanthrene concentration in the soil after electrokinetic remediation.

deposited onto the kaolin near the middle section of the sample. Evidently, the conditions were insufficient to completely remove the contaminant from the soil and into the cathode reservoir. Compared to Test B, the kaolin in Test A had a high residual phenanthrene concentration located in a soil section that was further towards the cathode, and this may have been caused by the slightly greater cumulative electroosmotic flow.

Figure 6b shows the residual phenanthrene concentration in the soil for Tests C and D, which both employed the high voltage and low buffering conditions, but Test C used a continuous voltage application whereas Test D used a periodic voltage application. From these results, it is apparent that phenanthrene solubilization occurred in both tests, and the phenanthrene migrated towards the cathode in the



direction of electroosmotic flow. In Test C, using the continuous mode of voltage application, it is clear that the surfactant solution produced some phenanthrene mobilization and/or solubilization towards the cathode, because the two soil sections nearest the anode have a very low residual phenanthrene concentration, while the sections further along the soil profile have higher phenanthrene concentrations. As seen previously in Tests A and B, it is apparent that in Test C the phenanthrene sorbed or deposited back onto the soil particles due to changes in the soil and/or solution chemistry. It should also be noted that Test C had a rapid decrease in current and a low amount of cumulative electroosmotic flow, so the low residual phenanthrene concentrations near the anode were most likely the result of the high initial flow that was generated by the continuous and high voltage gradient of 2.0 VDC/cm. In contrast to the other three tests, the chemical analyses of the soil samples taken after Test D was completed showed that very low residual phenanthrene concentrations existed along the length of the sample, which correlates well to the high amount of cumulative mass removed during the operation of Test D. These results suggest that the optimal conditions for contaminant removal consist of using a high, 2.0 VDC/cm, voltage gradient and a periodic mode of voltage application. The benefit of using a higher buffering concentration is difficult to distinguish based upon these test results, but the high amount of phenanthrene removal in Test D indicates that low buffering with 0.01 M NaOH is adequate.

Schwarzenbach et al.^[32] report that there is a stagnant boundary layer of solution that surrounds a saturated soil particle, and the contaminant mass transfer is limited because the contaminant cannot easily diffuse from the stagnant boundary layer to the more turbulent bulk solution. Therefore, by not applying the electric potential, the electroosmotic flow will decrease as will the turbulence of the bulk solution, which should facilitate the diffusion of phenanthrene from the boundary layer to the bulk solution and permit greater movement of surfactant molecules between the bulk solution and the inner boundary layer regions. In addition, the thermodynamics of micelle formation could be sensitive to pressure changes as well as to the turbulence of the solution, and causing the flow to reduce or stop could allow the production of additional micelles and solubilization. Moreover, switching the electric potential on and off could generate a pulse of electroosmotic flow, a pulse of electromigration, and/or a pulse of surfactant molecular movement that results in a flushing action that increases solubilization and/or physically mobilizes the phenanthrene from the inner boundary layer into the bulk solution. Overall, since electrokinetics and the micellar solubilization of a PAH under an electric potential is such a highly complex process, the specific mechanisms controlling the release of the contaminant may be difficult to distinguish, and it is likely that further research will be necessary to ascertain a better understanding of the process.

Energy Expenditure

The energy expenditure (E_u) per unit volume of soil is given by the expression 2^[44]:

$$E_u = \frac{E}{V_s} = \frac{1}{V_s} \int VI dt \quad (2)$$



where E [W-h] is the energy, V_s [m³] is the volume of soil, V [V] is the voltage between the electrodes, I [A] is the current, and t [h] is the time interval. Since Test D had the longest duration (about 275 days) and a 2.0 VDC/cm voltage gradient, it had the greatest energy expenditure of approximately 449 kWh/m³. Tests A, B, and C were conducted for around 70 days, and these tests had much lower energy expenditures of approximately 124, 137, and 233 kWh/m³, respectively. These energy expenditure values may be useful for the estimation of the costs associated with electrokinetically enhanced in-situ flushing. Other costs associated with the acquisition of equipment and materials as well as operating costs will decide the overall treatment cost.

SUMMARY AND CONCLUSIONS

The objective of this laboratory investigation was to assess the effects of employing a periodic voltage application during an electrokinetically enhanced in-situ flushing process for PAH-contaminated clay soils. The periodic voltage effects were evaluated by performing four different bench-scale electrokinetic tests conducted using low voltage and high buffering (1.0 VDC/cm and 0.1 M NaOH) as well as high voltage and low buffering conditions (2.0 VDC/cm and 0.01 M NaOH). Kaolin spiked with 400–500 mg/kg of phenanthrene was used for all the tests. The parameters measured during testing included the electric current, electro-osmotic flow, and cumulative mass removal, and, after each test was completed, the pH and residual phenanthrene concentration in the soil was measured along the length of the soil profile. The conclusions from these experiments are as follows:

- (1) The periodic voltage application generates an electric current that follows an up and down pattern. The current decreases rapidly during the time interval when the voltage is continuously applied, but, during the “down time” when the voltage is not applied, additional ions become solubilized or the diffuse double layer becomes less polarized, so, when the voltage is re-applied, the current is significantly higher than it was before the “down time” started.
- (2) The use of a high voltage gradient (2.0 VDC/cm) along with a periodic voltage application, consisting of a cycle of five days of continuous voltage followed by two days of no voltage application, appear to be the critical factors responsible for significantly increasing contaminant removal. The high removal is attributed to the kinetic desorption and solubilization reactions and/or the pulsing mechanisms that were caused by the use of the periodic mode of voltage application. The electroosmotic flow was also sustained by using the high voltage combined with the periodic mode of application, and this consistent flow largely contributed to the high amount of contaminant removal.
- (3) The results using the electrokinetic test variables and operating conditions in these experiments indicate that neither the 0.01 M nor the 0.1 M NaOH buffering concentration was effective for counteracting the electrolysis reaction at the anode and preventing the pH value from falling below the



pH_{pzc} . Therefore, the advantage of using the higher, 0.1 M, buffering concentration was difficult to discern. However, the high amount of phenanthrene removal accomplished when using the low buffering concentration (0.01 M NaOH) along with the high periodic voltage gradient (2.0 VDC/cm) suggests that the lower buffering concentration is adequate.

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