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A Laboratory-Scale Study of Applied Voltage on the Electrokinetic Separation of Lead from Soils

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ABSTRACT

The application of electrokinetic (EK) soil-flushing technology to the separation of lead from a nonsynthetic, fine-grained, low permeability soil was examined. In these laboratory-scale experiments the effects of applied voltage (30 and 60 V DC) on cumulative electroosmotic (EO) flow, charge-input, and lead removal were investigated. To develop a more generalized cause–effect relationship, these parameters were studied using three anode/cathode reservoir conditioning schemes: $NaNO_3$/$NaNO_3$, $NaNO_3$/HAc (acetic acid), and HCl/HAc. Charge-input and cumulative EO flow generally increased when the applied voltage was raised. When reservoir pH controls were used, results were more consistent with theoretically predicted outcomes. Increasing the applied voltage increased the electrolysis of water, which increased the fluid conductivity and charge-input. Although cumulative EO flow increased in proportion to the voltage, the advantage of operating at a higher applied voltage diminished as the amount of lead remaining in the soil decreased. The highest lead removal rates for both the 30 and 60 V tests were achieved using the 0.1 M HCl/1.0 M HAc reservoir conditioning scheme. The addition of HCl to the anode reservoir solution enhanced the impact of the acid front, especially during the initial pore volumes of flow which occurred before the oxidation of water could produce significant amounts of H^+ at the anode. Additionally, HAc in the cathode reservoir prevented the formation of a base front and the subsequent Pb readsorption/precipitation onto soil. The greater cumulative EO flow and charge-input in the experiments conducted with the HCl/HAc reservoir conditioning scheme resulted in faster Pb removal via advection and electrolytic migration. In contrast, the lowest

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remediation and removal values were obtained with the $NaNO_3/NaNO_3$ reservoir treatment scheme, which had a low cumulative EO flow, relative to the other tests, and lacked reservoir fluid pH control. To demonstrate the impact of soil pH on Pb removal, soil-bound Pb concentrations as a function of soil pH were also examined. The "critical pH" range necessary to ensure effective Pb removal was between 4 and 4.5.

INTRODUCTION

Currently, there is a great need to develop cost-effective in-situ remediation techniques to separate contaminants from soils when traditional pump-and-treat and/or ex-situ methods cannot be used. Conventional in-situ technologies have primarily been successful in treating highly permeable, sandy soils. However, electrokinetic (EK) soil flushing has been shown to be a particularly effective remediation technique for the treatment of fine-grained, low permeability soils. These soils are efficient at sequestering contaminants but are resistant to conventional in-situ technologies, primarily due to the difficulty in hydraulically moving groundwater.

Although several investigators have made significant developments in the application of EK technology to the remediation of inorganic- and organic-contaminated soil, there is still a great need for additional research to improve process efficiency and reduce the costs associated with its field deployment. To achieve this end, the application of EK soil-flushing techniques for Pb removal from nonsynthetic low permeability clay soils was investigated. Pb was examined because it is commonly found at industrial sites ranging from battery recycling and disposal plants to oil refineries. Additionally, Pb is the most commonly found inorganic contaminant at Superfund sites (1).

In this research, the effects of applied voltage on electroosmotic (EO) flow, current (expressed as charge-input), and Pb removal were examined. Two voltages (30 and 60 V) with three different anode/cathode reservoir treatment schemes were studied to provide more general conclusions regarding the effects of applied voltage than could be illustrated by using only one reservoir condition.

BACKGROUND

In the context of these remediation experiments, electrokinetics refers to all physical and chemical soil/water phenomena that occur when a direct current (DC) voltage is applied to a soil system. Three mass transport phenomena occur when an electric field is applied to a system of charged particles: electrophoresis, electroosmosis, and electrolytic migration. In a compacted system, such as the soil specimens in this study, the primary electrically induced contaminant transport mechanisms are electroosmotic flow (2) and

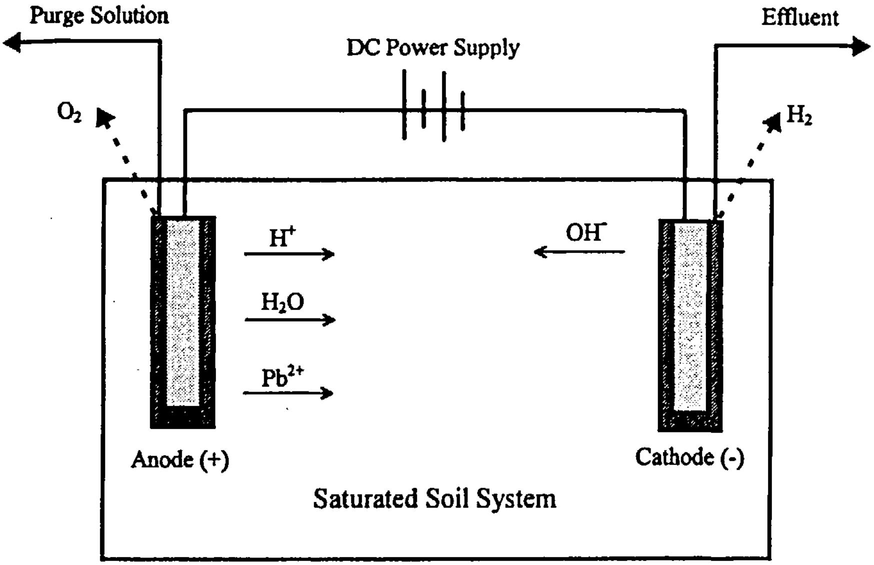


FIG. 1 Schematic of EK soil-flushing process.

electrolytic migration (3). Electrophoresis, the movement of charged colloids under an applied electric field, is neglected in a compacted soil specimen because the solid phase is stationary (4). A schematic of the EK soil-flushing process for a negatively charged soil is presented in Fig. 1.

Electroosmosis is the transport of a liquid under an applied electric field. Transport is facilitated by the presence of a soil surface charge. Since electroneutrality must exist in the bulk fluid, counterions concentrate near the surface of the soil particle and extend through the solution to form an electric double layer (EDL). In a negatively charged soil surface, such as a clay, the counterions in the surface layer (i.e., the Stern layer) will be cations. While some anions exist in the diffuse layer, cations outnumber anions in this region. Under the influence of an applied voltage, cations and anions flow toward the oppositely charged electrode, and the frictional forces which arise from the movement of ions drag water molecules along (5). Since there are more cations in the diffuse layer, the net flow of water is toward the cathode. If the surface had a positive charge, the net movement of particles would be toward the anode. In the bulk solution (i.e., outside the EDL), cation and anion charges are equal and a zero net flow results. A simplified relationship that describes electroosmotic flow is given in

$$q_e = k_e i_e A = k_i I \tag{1}$$

where q_e = electroosmotic flow rate (cm^3/s), k_e = coefficient of electroosmotic permeability ($cm^2/V{\cdot}s$), i_e = potential gradient (V/cm), A = total cross-sectional area (cm^2), k_i = coefficient of water transport efficiency ($cm^3/A{\cdot}s$), and I = electric current (A). Many fine-grained soils have an EO permeability (for a unit potential gradient) which is two or more orders of magnitude greater than the hydraulic conductivity. This makes EO transport of water a possibility in soils which are nearly impermeable from a hydraulic perspective.

Since the main focus of this study is the effects of voltage on EK system parameters, it is important to revisit Ohm's law. In an ideal electric circuit, voltage (V), electric current (I), and resistance (R) are related according to (7)

$$V = IR \tag{2}$$

However, in EK remediation systems, specimen resistance changes with time as well as position. The proportionality relationships between cumulative EO flow and voltage are demonstrated when Eqs. (1) and (2) are combined as follows:

$$q_e = k_i(V/R) \tag{3}$$

As a result, one would theoretically predict the cumulative EO flow rate to double when the voltage is doubled in an ideal system. However, unlike an ideal circuit, the resistance of the soil matrix in an electrokinetic system varies with respect to time.

Electrolysis, the decomposition of water by an imposed electrical current, occurs at the electrodes during the EK process. The oxidation–reduction reactions of water are presented in Eqs. (4) and (5) (6):

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \text{ (anode)} \tag{4}$$

$$4H_2O + 4e^- \rightarrow 2H_2 + 4OH^- \text{ (cathode)} \tag{5}$$

Water electrolysis results in a pH drop at the anode due to the production of H^+, and a pH increase at the cathode resulting from the production of OH^- ions. These pH extremes at the electrodes influence the pH of the soil between the cathode and the anode. Transport of H^+ toward the cathode via advection, electrolytic migration, and diffusion results in the formation of an acidic front. Similarly, the movement of OH^- toward the anode by electrolytic migration and diffusion creates a basic front. The acidic front steadily sweeps across the sample toward the cathode, lowering the pH of the entire soil specimen, while the formation of a basic front yields a high pH zone in the soil surrounding the cathode. These pH gradients greatly affect the mobility of heavy metals in a soil system and the efficiency of EO flow. Several researchers have altered the chemistry of the system by altering the reservoir solution(s) to enhance EK remediation in synthetic soils (7, 8) and in field soil samples (9).

Electrolytic migration is the movement of ions toward the electrode of opposite charge under an applied electric field. Cationic heavy metals, such as lead, are most soluble at a low pH. As the H^+ produced at the anode moves across the soil sample, the cationic metals which were sorbed to the soil particles or precipitated as solids can be solubilized and undergo transport by diffusion as well as transport via EK processes, such as advection by EO flow and electrolytic migration. Diffusion and electrolytic migration of OH^- ions, produced at the cathode, increase the pH of the system in the vicinity of the cathode and may precipitate desorbed ions. Thus, a decrease in the number of ions available for EO flow and electrolytic migration results. Additionally, H^+ and OH^- associate and dissociate relatively easily with water. Large quantities of H^+ and OH^- are produced at the electrodes. The ionic mobility (in an infinite solution) of H^+ is 3625×10^6 cm^2/V·s, the highest for the listed cations. Similarly, the ionic mobility (in an infinite solution) of OH^- is 2058×10^6 cm^2/V·s, the highest for the listed anions (7). Thus, H^+ and OH^- have a relatively high degree of mobility in water. Since ionic mobility under an electrical gradient has been shown to be approximately 40 times greater than diffusion (locally, under specific concentration gradients), electrolytic migration can contribute a significant component to total mass transport (7).

MATERIALS AND METHODS

Test Soil Selection

The soil sample used in this study was obtained from Erie County, New York, and was characterized by the Soil Conservation Service as a "Galen" fine sandy loam (10). Unlike earlier experiments in which pure clay samples were used, the soil specimen examined in this study was specifically chosen to resemble actual material conditions encountered in the field. The soil was previously characterized in West Virginia University's Civil and Environmental Engineering Laboratories and the results are presented in Table 1 (9, 11–14). Of particular interest is the low consolidated hydraulic conductivity of 4.5×10^{-7} cm/s (void ratio = 0.70) which would preclude hydraulically induced soil-flushing as a treatment option.

Soil Contamination and Consolidation

Sample contamination was carried out in two steps. First, a predetermined soil Pb concentration was obtained by mixing pulverized soil with appropriate

TABLE 1
Select Soil Parameters

Parameter	Method (and Reference)	Value
Soil pH (1:5, soil:water)	1:5 slurry	5.4 ± 0.2
Indigenous Pb content, mg/kg	Nitric extraction, USEPA Method 7420 (11)	21 ± 0.50
CEC, meq/100 g soil	USEPA Method 9081 (11)	25.6 ± 0.60
Total Fe content, mg/kg	Nitric extraction, USEPA Method 7420 (11)	15,500 ± 120
Total Al content, mg/kg	Nitric extraction, USEPA Method 7420 (11)	10,200 ± 325
Total Mn content, mg/kg	Nitric extraction, USEPA Method 7420 (11)	800 ± 20
Free iron oxide, mg/kg	Na dithionite extraction (12)	3,700 ± 120
Amorphous iron oxide, mg/kg	AAO extraction (13)	2,600 ± 70
Amorphous aluminum oxide, mg/kg	Na dithionite extraction (12)	850 ± 90
Amorphous manganese oxide, mg/kg	AAO extraction (13)	18 ± 5
Hydraulic conductivity (consolidated), cm/s	ASTM D 5084 (14)	4.5×10^{-7}
Hydraulic conductivity (unconsolidated), cm/s	ASTM D 2434 (14)	2.3×10^{-4}

amounts of a stock lead solution [1700 mg/L as $Pb(NO_3)_2$ adjusted to pH of 4.7]. The expected soil-Pb concentration was approximately 1000 mg/kg [far below the maximum concentration of 26,500 mg/kg based on the soil's cation-exchange capacity (CEC)]. The slurry was thoroughly mixed to ensure sample homogeneity. The soil-lead slurry was then transferred to a pneumatic consolidator. Pressure was applied for 28 hours as follows: 5 psi for 2 hours, 10 psi for 2 hours, 15 psi for 10 hours, 20 psi for 10 hours, 25 psi for 2 hours, and 30 psi for 2 hours. It should be noted that the contamination process used in this study does not exactly replicate conditions found at an actual waste site because the effects of aging and secondary contaminant(s) were not taken into account (9).

EK Reactor Design

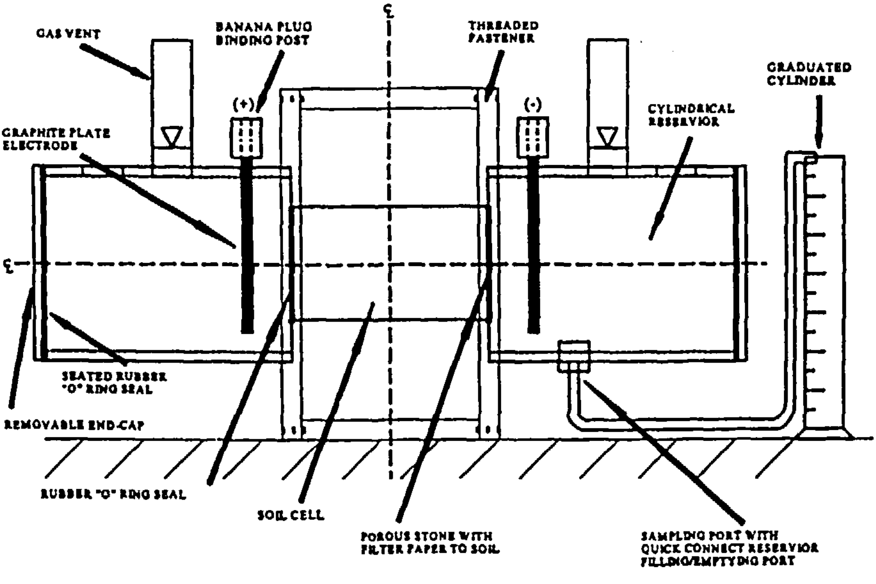
A diagram of the EK soil-flushing reactor, based on earlier models developed at Lehigh University (15), is presented in Fig. 2. This convenient design allowed the acrylic sleeve containing the consolidated soil specimen (7.5 cm in length, 3.5 cm in diameter) to be easily incorporated into the reactor. An open flow apparatus was used to measure the flow volume and to vent gases produced during electrolysis (7). Flow was determined by measuring the effluent from the cathode reservoir using a graduated cylinder. Influent to the anode reservoir was provided by a Mariotte bottle. The effluent port and the

Mariotte bottle were maintained at approximately the same level to minimize the hydraulic gradient across the reactor system, ruling out hydraulically-driven water movement.

The interface at each end of the soil sample contained porous stones and 8 μm filter paper. The electrode reservoirs were filled with an appropriate conditioning fluid. A 30 or 60 V DC potential was then applied. The effluent was collected in graduated cylinders, preserved if necessary, and stored for analysis.

EK Flushing and Specimen Analyses

Individual tests were conducted at 30 and 60 V DC for three different reservoir conditioning schemes at 1, 5, 10, 21, 30, and 40-day periods. A summary of voltage and reservoir conditions for each of the six EK soil-flushing experiments is presented in Table 2. One exception to the temporal plan was the 40-day test in Test 5D. This experiment was ended at 21 days because of flow cessation and subsequent concern over high electrode reservoir temperatures. It should be noted that remediation can occur without flow



NOTE: DRAWING IS NOT TO SCALE.

FIG. 2 Diagram of the EK soil-flushing reactor, based on earlier models developed at Lehigh University (15).

due to ionic migration. The 500 μS/cm conditioning fluid was used as a laboratory control procedure to establish a baseline behavior. For Tests 1D through 4D, $NaNO_3$ was added as a salt until the conductivity was 500 μS/cm.

Upon completion of each individual EK flushing experiment, the soil specimen was removed and analyzed to determine the extent of Pb removal from the soil as well as soil pH and conductivity as a function of distance from the electrodes. The sample was divided into eight equal segments, weighed, and dried to determine water content. Conductivity and pH measurements of each section were made after diluting a 5-g portion of each segment in 25 mL of deionized water. Each segment was then digested with 13 mL of 15.8 M HNO_3, shaken for 48 hours, and filtered through a 0.45-μm filter. The filtrate was analyzed for Pb using a Perkin-Elmer Model 3100 Atomic Absorption (A.A.) spectrophotometer. The initial conditions of the soil specimen were considered to be identical to those of the trimmed soil sections, based on the results of contamination/consolidation trials performed by Reed et al. (16).

Quality Assurance and Quality Control

Recognizing the critical need for quality assurance and quality control procedures to provide legitimacy to one's analytical and experimental efforts, care was taken to perform duplicate analyses and to follow consistent laboratory practices. All measurements were made using calibrated instruments, and all dilutions and standards were prepared using calibrated pipettes. Percent recoveries were calculated on 11% of the digested Pb samples. All percent recoveries were within 10%, indicating the absence of significant matrix interferences.

A mass balance on Pb was performed after completion of each experiment. The average error in closure of the lead mass balance, CE, for each experiment

TABLE 2
Summary of Voltage and Reservoir Conditions for Each of the Six EK Soil-Flushing Experiments

Test	Anode reservoir	Cathode reservoir	Voltage (V)
1D	500 μS/cm[a]	500 μs/cm[a]	60
2D	500 μS/cm[a]	500 μs/cm[a]	30
3D	500 μS/cm[a]	1.0 M HAc[b]	60
4D	500 μS/cm[a]	1.0 M HAc	30
5D	0.1 M HCl	1.0 M HAc	60
6D	0.1 M HCl	1.0 M HAc	30

[a] Added as $NaNO_3$.
[b] Acetic acid.

TABLE 3
Closure of Pb Mass Balance

Test	Average closure error (%) ± standard deviation	High value	Low value
1D	6.41 ± 2.19	10.31	4.04
2D	9.43 ± 2.98	13.30	5.82
3D	7.67 ± 3.61	12.25	3.88
4D	7.54 ± 6.03	16.34	1.20
5D	7.16 ± 2.62	11.01	4.74
6D	7.69 ± 1.97	11.05	5.98

is presented in Table 3. The error in closure of the mass balance was calculated according to Eq. (6). An error in closure of 0% indicates that all of the initial soil-bound lead has been accounted for.

$$\mathrm{CE}\,(\%) = 100 \times \{[\mathrm{Pb}_0 - (\mathrm{Pb}_f + \mathrm{Pb}_{elec} + \mathrm{Pb}_{eff} + \mathrm{Pb}_{pre} + \mathrm{Pb}_{res})]/\mathrm{Pb}_0\} \tag{6}$$

where Pb_0 = initial mass of soil-bound lead (mg)
Pb_f = mass of soil-bound lead remaining after treatment (mg)
Pb_{elec} = mass of lead electroplated on cathode electrode (mg)
Pb_{eff} = mass of lead in effluent (mg)
Pb_{pre} = mass of precipitated lead in reservoir liquid (mg)
Pb_{res} = mass of solubilized lead in anode and cathode reservoirs (mg)

The amount of lead present in the reservoir was measured directly. Each cathode electrode was refluxed for 2 hours in two serial digestions of 200 mL 8.0 M nitric acid (HNO_3) at 180°F. The digestate was then diluted with deionized water to 250 mL and analyzed. The majority of lead removed from the soil was found electroplated on the cathode and in the reservoir sludge formed by chemical precipitation. As expected, the amount of Pb plated on the cathode increased with treatment time. For example, in Test 1D, the amounts of Pb plated on the cathode for the 1, 5, 10, 21, 30, and 40-day experiments were 19, 29, 33, 47, 55, and 57 mg, respectively. A sectional analysis of the specimen was performed to determine the amount of lead remaining on the soil. No significant amounts of lead were observed in the effluent reservoir liquids.

RESULTS AND DISCUSSION

The effects of applied voltage on electroosmotic (EO) flow, current (expressed as charge-input), and Pb removal were examined. Two voltages (30 and 60 V) with three different anode/cathode reservoir treatment schemes were studied to provide general conclusions regarding the effects of applied voltage than could be illustrated with only one reservoir condition. Results for each reservoir conditioning scheme at both 30 and 60 V are presented individually. The effect of final soil pH on Pb concentration is discussed, and Pb removal as a function of reservoir conditioning scheme and applied voltage is examined.

Tests 1D and 2D

The charge-input and cumulative EO flow data versus time for Tests 1D (60 V) and 2D (30 V) are presented in Fig. 3. The length of the soil specimen

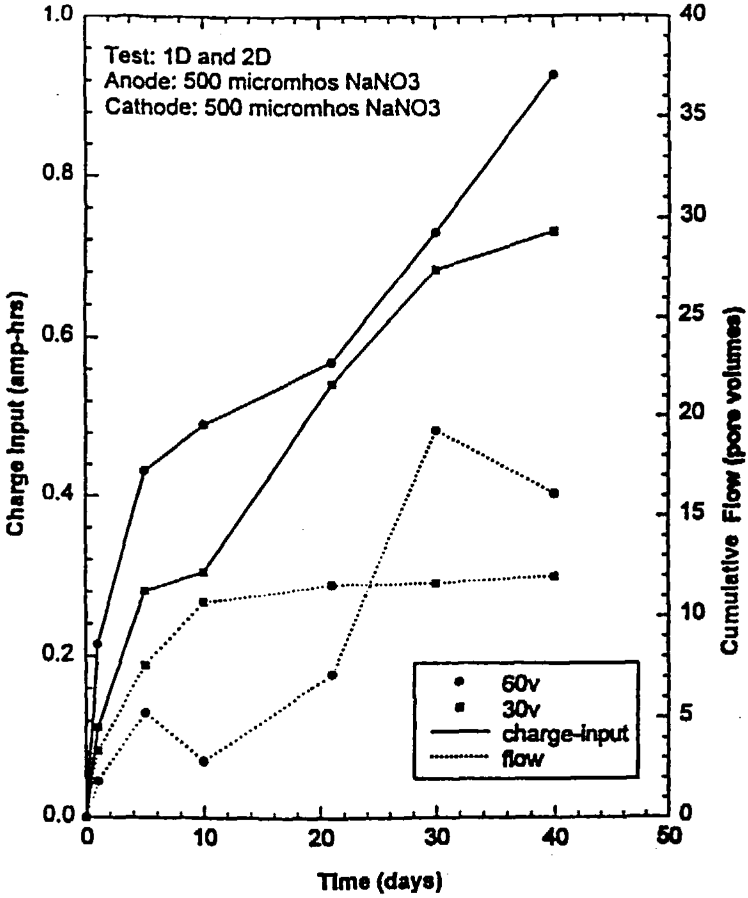


FIG. 3 Charge-input and cumulative EO flow versus time, Tests 1D and 2D.

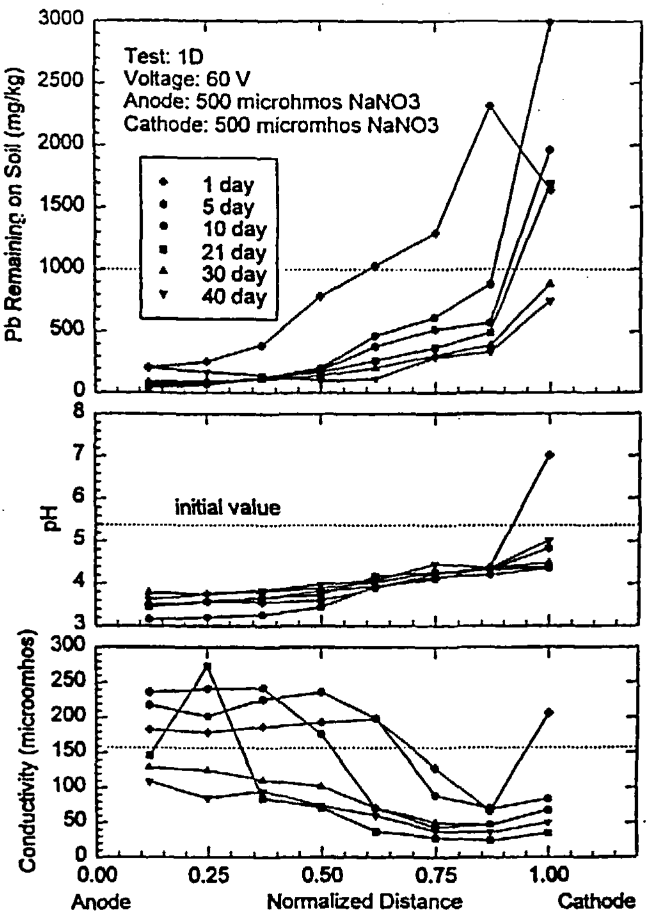


FIG. 4 Soil-Pb, pH, and conductivity distributions for Test 1D.

was 7.5 cm. Current density decreased from a maximum initial value of 1.5 mA/cm^2 to a final value of ~0.1 mA/cm^2 in the experiments conducted in Test 1D. The data points in the cumulative EO flow versus time plots are the results of six individual experiments taken off at a specified day and not results for one specimen examined at six different times. The decrease in cumulative flow from ~19 pore volumes at Day 30 to ~16 pore volumes at Day 40 in Test 1D was due to experimental variation.

Plots of Pb remaining on the soil, pH, and conductivity versus normalized distance are presented in Figs. 4 and 5 for Tests 1D and 2D, respectively. In these tests, both the anode and cathode reservoirs contained 500 μS/cm

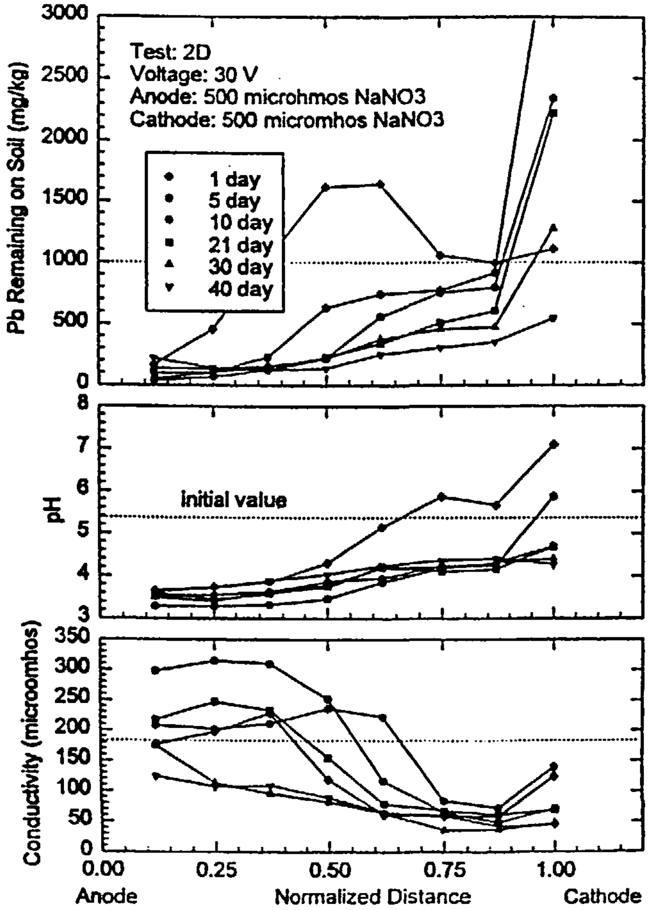


FIG. 5 Soil-Pb, pH, and conductivity distributions for Test 2D.

$NaNO_3$ which served as a laboratory control to establish baseline behavior to judge the effects of both increased voltage and reservoir conditioning agents. As mentioned earlier, doubling the voltage in an ideal circuit should theoretically double the current and, as a result, the charge-input in an ideal system. However, the charge-input did not double when the voltage was increased from 30 to 60 V. Current density decreased from a maximum initial value of 0.7 mA/cm^2 to a stable value of ~0.1 mA/cm^2 from 100 hours through the end of testing in the experiments conducted in Test 2D. The average charge-input was 0.026 A·h/d in the 30-V test and 0.032 A·h/d in the 60-V test, which corresponded to an average charge-input increase of 23% between the 30 and 60-V tests. In addition, the resistance of the soil specimen varied with time in these experiments, unlike a resistor in an ideal circuit. The soil resistance of the 60-V test averaged 63% higher than the 30-V test. This higher resistance related to the lower average soil conductivity in the 60-V tests and accounted for the lower than anticipated increase in charge-input.

Based on Eq. (3), the flow volume, q_e, is directly proportional to the applied voltage, V. The average cumulative EO flow was 0.512 pore volumes per day (PV/day) in the 60-V test and was 0.526 PV/day in the 30-V test. Additionally, the electroosmotic permeability, k_e, varied over the test period, where the daily average of the 30-V test was determined to be 105% higher than the 60-V average. This corresponded to the nearly equal average daily flows of these two tests. Flow cessation occurred for the 30-V test at 21 days (Fig. 3), and this experiment was stopped due to concerns about high temperatures in the electrode reservoirs. It should be noted that remediation can still occur via ionic migration in the absence of EO flow. Soil-Pb, pH, and conductivity distributions for Tests 1D and 2D are presented in Figs. 4 and 5, respectively. In Fig. 5 the low conductivity near the cathode and the increased pH accounted for the flow cessation. At a pH above 4.0 to 4.5, Pb was either adsorbed onto the soil (as will be demonstrated later) and/or precipitated as $Pb(OH)_2(s)$, which reduced the soil's conductivity by removing cations from the liquid. The decrease in flow observed can be attributed to a decrease in conductivity (17). The pH increased gradually and the conductivity decreased near the cathode. These trends were also observed in the 30-V test. However, the decrease in conductivity near the cathode was not as pronounced in the 60-V test because the additional charge-input supplied in this test enhanced the propagation of the acid front (through the production of H^+ at the anode) across the soil specimen.

A pronounced peak was observed in the middle of the soil sample for the 1-day test as shown in Fig. 5. In the 1-day test, Pb did not have sufficient time to be transported completely through the sample and into the anode reservoir. Pb was desorbed near the anode reservoir and readsorbed and/or precipitated in a section closer to the cathode reservoir. A similar trend was observed in the 60-V test as presented in Fig. 4. However, the Pb peak occurred much closer to the cathode reservoir in the 60-V test because the added charge-input supplied by doubling the voltage enhanced the transport of Pb via electrolytic migration by increasing the migration velocity. Additionally, the greater cumulative EO flow observed in the 60-V test increased Pb transport via advection, moving the Pb further through the sample than in the 30-V test.

In both the 30 and 60-V tests, the lowest point on the conductivity curve coincided with the maximum Pb remaining on the soil and the highest pH as presented in Figs. 4 and 5. This was likely due to the increased adsorption/precipitation of Pb (i.e., Pb^{2+} and OH^- were no longer associated with the aqueous phase).

Tests 3D and 4D

Tests 3D and 4D were conducted with 500 µS/cm, $NaNO_3$ in the anode reservoir, and 1.0 M acetic acid (HAc) in the cathode reservoir. Charge-input and cumulative EO flow versus time for Tests 3D (60 V) and 4D (30 V) are presented in Fig. 6. Current density decreased from a maximum initial value

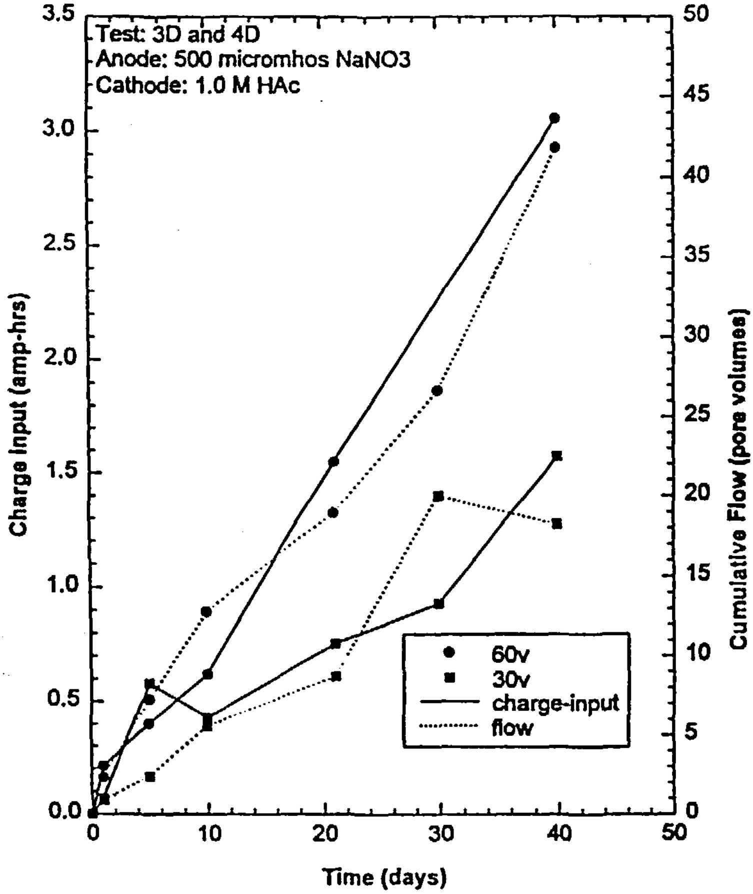


FIG. 6 Charge-input and cumulative EO flow versus time, Tests 3D and 4D.

of 1.6 mA/cm^2 to a stable value of 0.2 mA/cm^2 from 200 hours through the end of testing in the experiments conducted in Test 3D. Current density decreased from a maximum initial value of 0.8 mA/cm^2 to a value of ~0.1 mA/cm^2 from 100 hours through the end of testing in the experiments conducted in Test 4D. The charge-input of the 60-V test was consistently higher than the 30-V test, with one exception to this trend observed in the 5-day experiment. The average charge-input for the 30-V test was 0.04 A·h/d and 0.07 A·h/d for the 60-V test. Over the entire testing period the average charge-input increase that occurred by doubling the voltage was 75%, which approached the anticipated 100% theoretical increase. Through additional experimentation, the soil resistance was found to change with time.

The data points in the cumulative EO flow versus time plots are results of six individual experiments taken off at a specified day and not results for one specimen examined at six different times. The decrease in cumulative flow from ~20 pore volumes at Day 30 to ~18 pore volumes at Day 40 in Test 4D was due to experimental variation. The average cumulative EO flow observed in these experiments was 0.53 PV/day in the 30-V test and 1.06 PV/day in the 60-V test. In this individual case the flow increase due to doubling the voltage was 100%.

Soil-Pb, pH, and conductivity distributions for the 60 and 30-V tests are presented in Figs. 7 and 8, respectively. In both tests the pH remained relatively constant across the soil specimen, with the exception of the 1-day test in which there was not enough time for the pH front to migrate through the entire sample. The addition of HAc to the cathode reservoir served to buffer OH$^-$ production (from electrolysis of water) and prevented the soil pH near the cathode from increasing. Additionally, the HAc in the cathode reservoir prevented reservoir fluid pH from dropping below ~3.5 to 4 as the acid front migrated across the sample.

Conductivity increased with time through the first five soil sections due to the electrolysis reaction at the anode which increased the conductivity of the anode reservoir solution. As anticipated, the Pb remaining on the soil in both the 30 and 60-V experiments decreased with time. Similarly to Tests 1D and 2D, a pronounced peak in the Pb distributions was observed in the 1-day tests. In Fig. 7 the area under the peak (representing the total amount of Pb in these soil segments) is approximately equal to the area under the curve in the vicinity of the anode reservoir. In Fig. 8, Pb had not migrated through the sections closest to the cathode reservoir, since the Pb on the soil remained approximately equal to the initial level of 1000 mg/kg. As discussed earlier, Pb was desorbed from sections near the anode reservoir and readsorbed/precipitated in soil sections close to the cathode reservoir. The Pb peak migrated closer to the cathode reservoir in the 60-V test as a result of transport via advection and electrolytic migration.

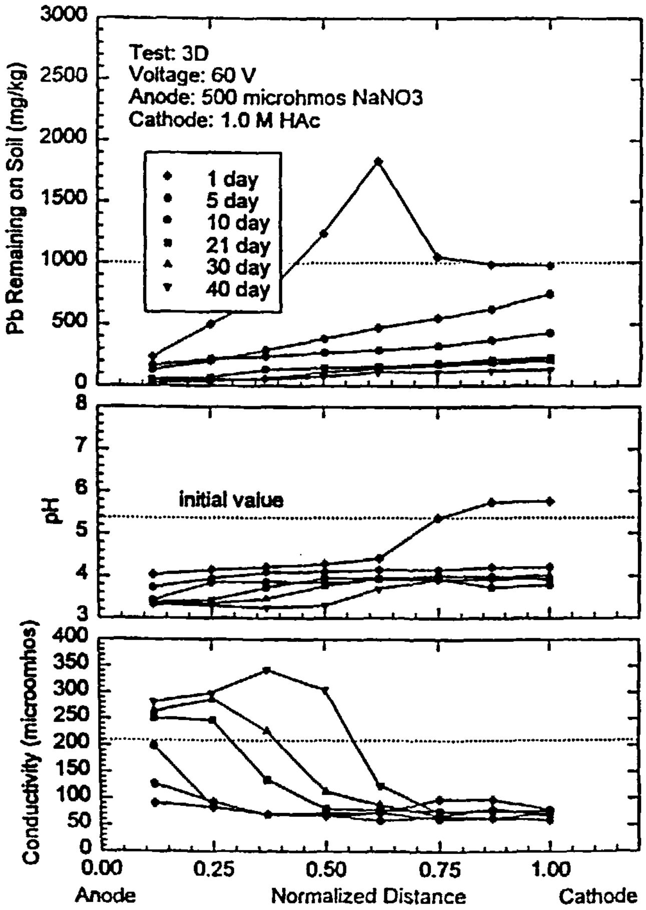


FIG. 7 Soil-Pb, pH, and conductivity distributions for Test 3D.

Tests 5D and 6D

Tests 5D and 6D were conducted with 0.1 M hydrochloric acid (HCl) in the anode reservoir and 1.0 M HAc in the cathode reservoir. The charge-input and cumulative EO flow versus time for Tests 5D and 6D are presented in Fig. 9. The 60-V experiment did not include data for Day 40 because flow cessation had occurred at Day 21. This experiment was stopped due to concerns about high temperatures in the electrode reservoirs. It should be noted that remediation can occur without flow due to ionic migration.

Current density decreased from a maximum initial value of 2.0 mA/cm^2 to a minimum value of ~0.7 mA/cm^2 at 80 hours. Current density then increased steadily to a final value of 1.2 mA/cm^2 observed at the end of Test 5D. In Test 6D, current density decreased from a maximum initial value of 0.9 mA/cm^2 to a minimum value of ~0.3 mA/cm^2 at ~200 hours. Current density then increased steadily to a final value of 0.5 mA/cm^2, observed at the end of Test 6D. The average charge-input observed in the 60-V test was 0.237 A·h/d and 0.115 A·h/d in the 30-V test, which corresponded to a 106% charge-input increase when the voltage was doubled. The average cumulative EO flow

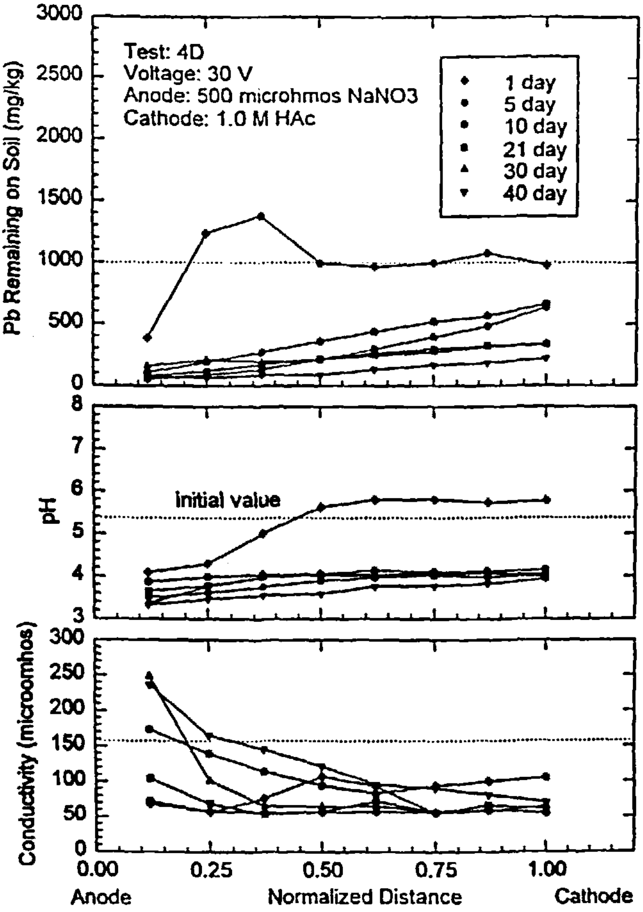


FIG. 8 Soil-Pb, pH, and conductivity distributions for Test 4D.

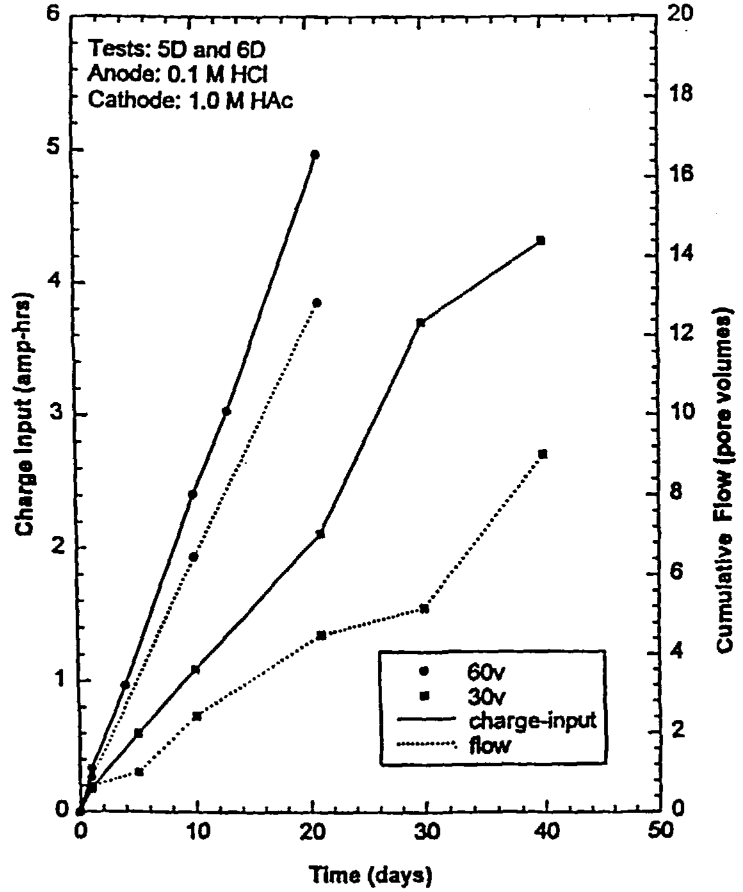


FIG. 9 Charge-input and cumulative EO flow versus time, Tests 5D and 6D.

observed in Test 5D was 0.374 PV/day, and the average cumulative EO flow in Test 6D was 0.231 PV/day. This corresponded to a 62% flow increase when the voltage was doubled. However, the electroosmotic permeability, k_e, of the 60-V tests averaged 14.4% lower than that of the 30-V tests, which correlated to the lower than anticipated flow increase.

Soil-Pb, pH, and conductivity profiles are presented for Tests 5D and 6D in Figs. 10 and 11, respectively. As in other experiments, Pb was desorbed/solubilized, then readsorbed/precipitated closer to the cathode in early experiments. After 5 days the majority of Pb was removed from the soil. The addition of HCl to the anode reservoir in both the 30 and 60-V tests quickly lowered the soil pH near the anode. The HAc in the cathode reservoir buffered base production and kept the pH from rising near the cathode. The migration of the high conductivity HCl solution caused a large increase in soil conductivity. In Fig. 10, only a fraction of the Pb remained on the soil near the cathode reservoir in the 1-day test. The near total removal of Pb from the soil sample in this test was due to a combination of higher charge-input and slightly higher EO flow obtained in the case of the 0.1 M HCl/1.0 M HAc reservoir conditioning scheme. Also, a large H^+ concentration caused

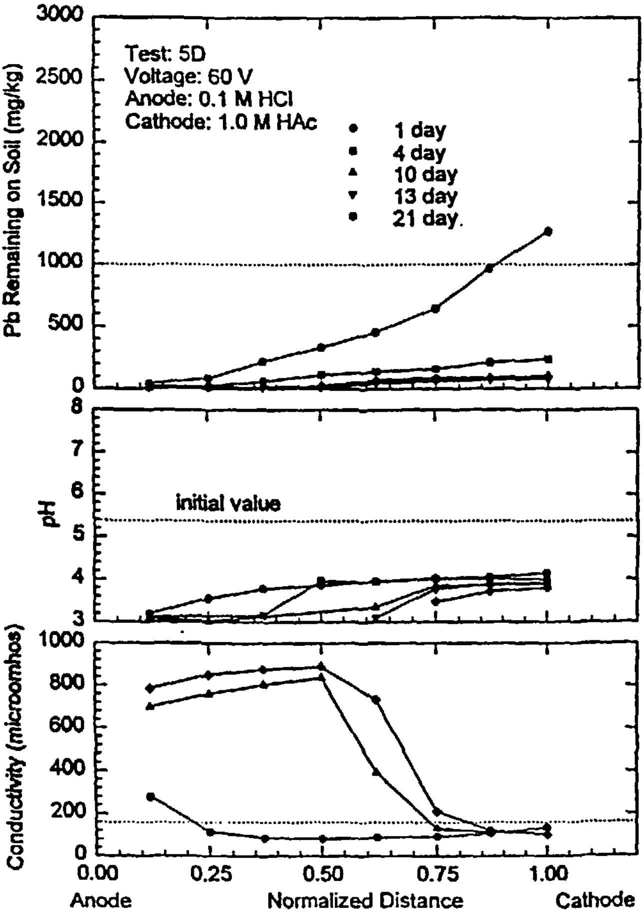


FIG. 10 Soil-Pb, pH, and conductivity distributions for Test 5D.

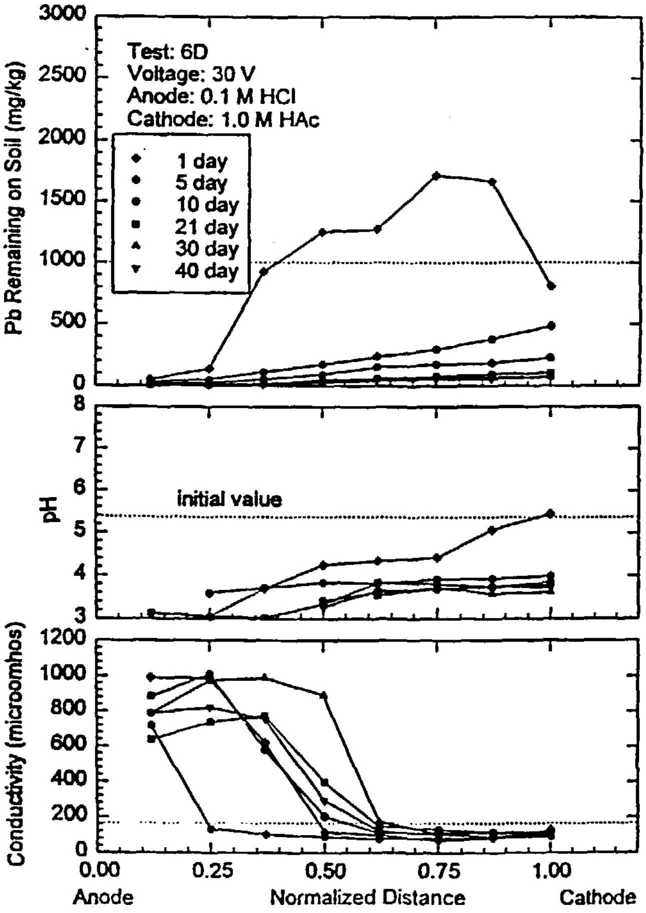


FIG. 11 Soil-Pb, pH, and conductivity distributions for Test 6D.

the desorption of soil-bound Pb. Finally, better behaved conductivity distributions obtained with pH-controlled conditioning treatments were also evident.

Soil Pb Concentration as a Function of Final Soil pH

To demonstrate the effect of pH on soil Pb retention, soil-Pb versus pH is presented in Fig. 12 for all soil segments. As discussed earlier, the concentration of Pb remaining on the soil is directly proportional to the soil pH (i.e., Pb retention decreases with decreasing pH). A gradual rise in soil-Pb concentration was observed as the soil pH was increased from 2.7 to 4.0. However, as the soil pH was increased from 4.0 to 4.5, there was a dramatic increase in Pb retention by the soil. Above this pH range, the amount of Pb remaining on the soil after treatment was greater than or equal to the 1000 mg/kg initial soil Pb concentration (due to the transport of desorbed Pb into a higher pH zone where the transported Pb was readsorbed/precipitated). Thus, the "critical pH" (i.e., the pH value below which the majority of soil-bound Pb will be mobilized) lies in the 4 to 4.5 range.

Pb Removal as a Function of Reservoir Conditioning Scheme and Applied Voltage

Percent remediation versus time plots for each of the three reservoir conditioning schemes are presented in Fig. 13 for the 30-V and the 60-V tests. Percent remediation is defined as the amount of Pb removed from the soil system divided by the initial amount of Pb in the soil system. The slope of the percent remediation curve represents the Pb removal rate.

Several trends were evident when comparing the Pb removal of each reservoir conditioning scheme at the two applied voltages. In Table 4 the maximum

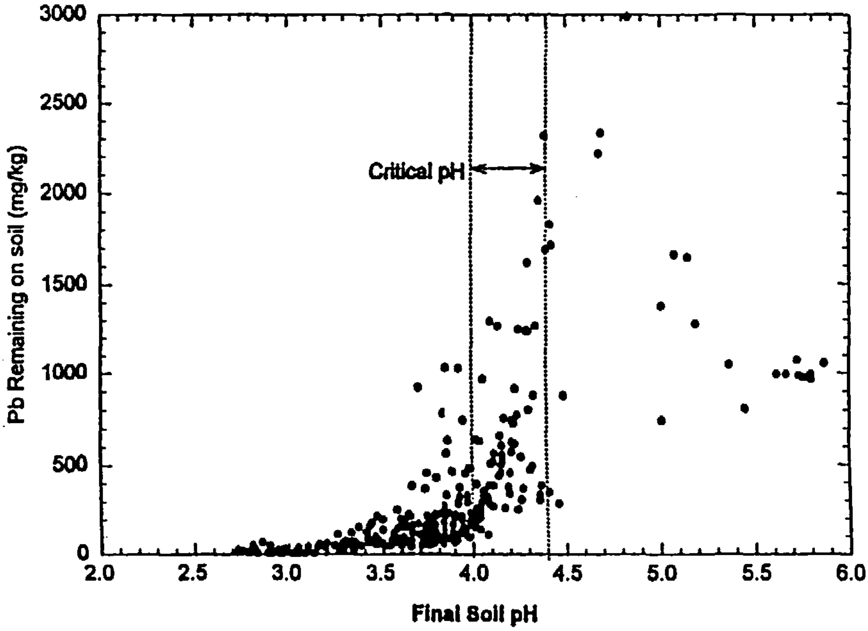


FIG. 12 Pb remaining on soil versus final soil pH for all tests.

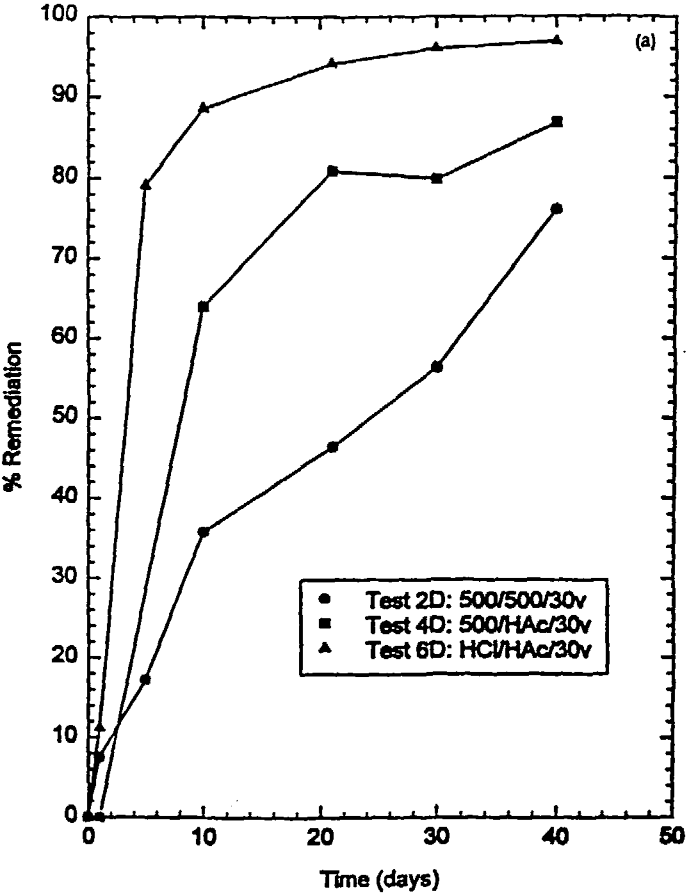


FIG. 13 Percent remediation versus time for each of the three reservoir conditioning schemes for the (a) 30 V and the (b) 60 V tests.

Pb removal obtained in each test is presented. The Pb removal in the 60-V tests was greater than that of the 30-V tests for each reservoir condition. The 30 and 60-V tests reached approximately the same percent remediation at the end of the test period. The higher removal of the 60-V tests can be seen by qualitatively comparing the curves presented in Fig. 13(a and b). In the 30-V tests, 75% of the Pb was removed in 5 days with the HCl/HAc reservoir treatment scheme compared to 17 days with the $NaNO_3$/HAc reservoir fluids and 39 days with the $NaNO_3$/$NaNO_3$ reservoir fluids. In the 60-V tests, the HCl/HAc reservoir treatment scheme removed 75% of the Pb in 3 days as

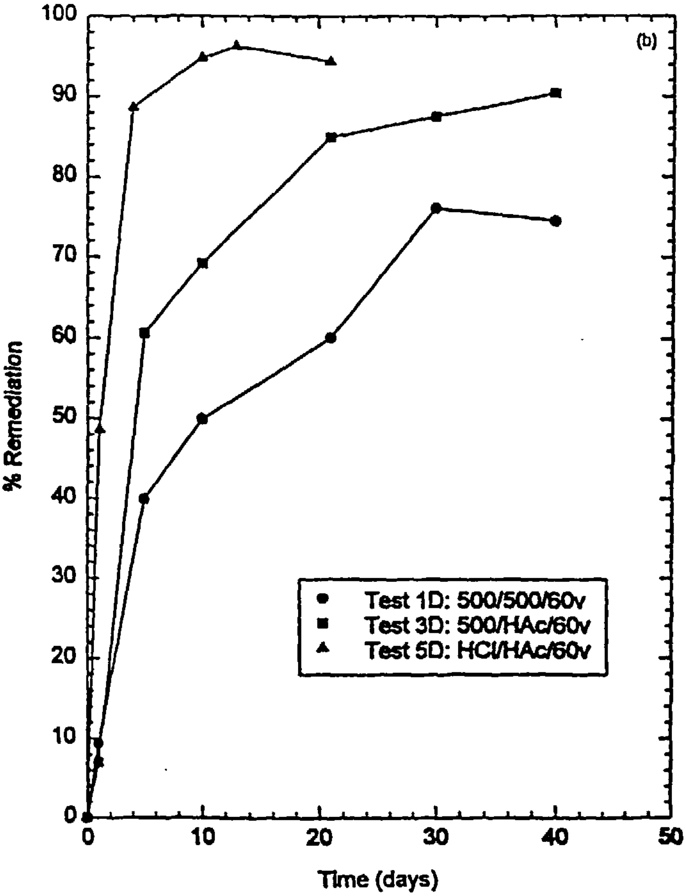


FIG. 13 *Continued.*

compared to 14 days in the $NaNO_3$/HAc tests and 29 days in the $NaNO_3$/$NaNO_3$ tests. Pb removal rates generally decreased with time under both applied voltages because the remaining Pb was more tightly bound. Soils have a range of binding energies. With time, Pb was removed from sites in order of increasing binding energy. Thus, Pb at the end of a given test was bound more tightly to the soil and was more difficult to remove. The effects of increased voltage on Pb removal became less apparent in the HCl/HAc tests, but were quite noticeable in the $NaNO_3$/$NaNO_3$ tests, where the 60-V test showed a clear removal advantage over the 30-V test. As anticipated, the

TABLE 4
Maximum Pb Removal (in %) Obtained in Each Test

Test (voltage)	Anode reservoir	Cathode reservoir	Maximum Pb removal[a]
1D (60)	$NaNO_3$	$NaNO_3$	76
2D (30)	$NaNO_3$	$NaNO_3$	76
3D (60)	$NaNO_3$	HAc	90
4D (30)	$NaNO_3$	HAc	87
5D (60)	HCl	HAc	96
6D (30)	HCl	HAc	97

[a] Greater Pb removal would have been possible if the length of the tests had been extended.

removal rates for the 60-V test with the $NaNO_3$/HAc reservoir treatment was higher than for the 30-V test, though not by the large margin observed in the $NaNO_3$/$NaNO_3$ test.

In Tests 1D and 2D, the $NaNO_3$/$NaNO_3$ reservoir conditioning scheme did not prevent electrolysis effects from gradually changing the pH in the electrode reservoirs. In particular, the pH of the cathode reservoir increased and a base front moved into the soil. This reduced the soil's conductivity by removing ions from solution [through adsorption of Pb onto soil particles and/or precipitation as $Pb(OH)_2(s)$]. As a result, electrolytic migration decreased, which led to a corresponding decrease in Pb removal. The addition of 1.0 M HAc to the cathode reservoir in Tests 3D and 4D prevented the formation of a base front and facilitated Pb transport through the soil specimen without precipitation. The increased cumulative EO flow observed in Tests 3D and 4D also enhanced Pb removal through increased Pb transport by advection. This accounts for the increase in the degree and rate of Pb removal when 1.0 M HAc was added to the cathode reservoir in both the 30 and 60-V tests when compared to the $NaNO_3$/$NaNO_3$ tests. The addition of 0.1 M HCl to the anode reservoir in Tests 5D and 6D decreased the soil pH rapidly, which resulted in a correspondingly rapid desorption of Pb as well as increased EO flow and electrolytic migration. The presence of 1.0 M HAc in the cathode reservoir buffered the production of base and prevented the pH from rising near the cathode, as discussed earlier. The increased cumulative EO flow obtained using the HCl/HAc reservoir conditioning scheme enhanced the transport of Pb through the sample by advection. Similarly to the 3D and 4D tests, the additional charge-input supplied in the 60-V test resulted in an increase in electrolytic migration, which resulted in an increased Pb removal rate.

SUMMARY AND CONCLUSIONS

The application of electrokinetic (EK) soil-flushing technology for the separation of lead from a nonsynthetic, fine-grained, low permeability soil was examined. In these laboratory-scale experiments the effects of applied voltage (30 and 60 V DC) on cumulative electroosmotic (EO) flow, charge-input, and lead removal were investigated, and a generalized cause–effect relationship was studied using three anode/cathode reservoir conditioning schemes: $NaNO_3/NaNO_3$, $NaNO_3$/HAc (acetic acid), and $NaNO_3$/HCl (hydrochloric acid).

Charge-input increased as the applied voltage increased. Experimental values which were more consistent with the theoretically predicted 100% increase in charge-input as the voltage was doubled were observed in tests performed with pH-controlled reservoir conditions (i.e., $NaNO_3$/HAc and HCl/HAc). This was likely due to the increased conductivity of these reservoir conditioning solutions and soil pore water, which decreased the variability of the experimental results. This also produced a lower overall experimental variation. The fact that soil resistance did not remain constant with time also contributed to the lower than expected charge-input values. Cumulative EO flow increased in direct proportion to the voltage increase in Tests 3D and 4D. The discrepancies between the predicted and observed cumulative EO flow increases were due to differences in the soil's electroosmotic permeability, k_e. Flow cessation occurred for several tests and was attributed to a decrease in conductivity due to the readsorption/precipitation of Pb.

The highest Pb remediation and removal rates were achieved in Tests 5D and 6D when the anode contained 0.1 M HCl in the anode reservoir and 1.0 M HAc in the cathode reservoir for experiments conducted at both 30 and 60 V. The addition of HCl to the anode reservoir solution enhanced the impact of the acid front, particularly during the first few pore volumes of flow which occurred before the oxidation of water could produce significant amounts of H^+ at the anode. The rapid pH decrease allowed for quicker Pb desorption and faster Pb removal. Also, HAc in the cathode reservoir prevented the formation of a base front and the subsequent Pb readsorption/precipitation onto soil. In contrast, the lowest remediation and removal values were obtained with the baseline $NaNO_3/NaNO_3$ reservoir treatment scheme, further illustrating the overall importance of soil pH control on EK remediation. The critical soil pH range necessary to ensure effective Pb removal was between 4 and 4.5.

In general, increasing the voltage decreased the time needed to achieve a specific remediation goal. However, the advantage of the higher voltage diminished as the amount of Pb remaining in the soil decreased. The effects of increased voltage on Pb removal became less apparent in the HCl/HAc tests, but were quite noticeable in the baseline $NaNO_3/NaNO_3$ tests, where the 60-V test showed a clear removal advantage over the 30 V test. Additionally, the HCl/HAc conditioning scheme reached specific remediation goals faster than the other conditioning schemes.

Although HCl and HAc were used as a means for comparison in this study, the field deployment of such conditioning agents would pose problems. The storage of acids at a work site will require additional permitting and worker training. Also, the introduction of an acid to the soil presents regulatory and residual management problems. However, the soil will most likely need to be neutralized after EK flushing because the soil pH is lowered through the migration of H^+ into the cathode reservoir, regardless of the reservoir conditioning agents used.

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