



Project Summary

Theoretical and Experimental Modeling of Multi-Species Transport in Soils Under Electric Fields

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This project investigated an innovative approach for transport of inorganic species under the influence of electric fields. This process, commonly known as electrokinetics uses low-level direct current (dc) electrical potential difference across a soil mass applied through inert electrodes placed in an open flow arrangement. The application of low-level dc current across electrodes placed in the soil mass causes physiochemical and hydrological changes in the soil-water-electrolyte medium leading to contaminant transport and removal.

The feasibility and efficiency of transporting lead under electric fields was investigated in this study at pilotscale in three one-ton Georgia kaolinite specimens spiked with lead nitrate solution. Electrode spacing was set at 72.4 centimeters (cm). Tests were conducted on specimens with a lead nitrate concentration of 856 milligrams per kilogram (mg/kg) to 5,322 mg/kg. Pore pressures and temperatures developed across the soil mass, electric potential distributions, pH distributions, and lead transport were investigated.

The results demonstrate that heavy metals and species that are solubilized in the anodic acid front can be efficiently transported by electromigration under an electric field applied across electrodes placed in soils. After 2,950 hours of processing and an energy expenditure of 700 kWh/m³, 55% of the lead removed across the soil was found precipitated within the last two cm close to the cathode, 15% was left in the soil

before the 2 cm zone, 20% was found precipitated on the fabric separating the soil from the cathode compartment, and 10% was unaccounted for. Overall, The project adequately demonstrated the potential applicability of the process, and it appears that the process is appropriate for testing on a larger scale.

A theoretical model was also developed for multi-component species transport under coupled hydraulic, electric, and chemical potential differences. A mass balance of species and pore fluid coupled with a charge balance across the medium resulted in a set of differential equations. Sorption, aqueous phase and precipitation reactions were modeled by a set of algebraic equations. Instantaneous chemical equilibrium conditions were assumed. Transport of H⁺, OH⁻, and Pb²⁺ ions, the associated chemical reactions, electric potential, and pore pressure distribution across the electrodes in electrokinetic remediation were modeled. Model predictions of acid transport, lead transport, and pore pressure distribution displayed agreement with the pilotscale results validating the formalisms offered for multi-component transport of reactive species under an electric field. The model also bridges the gap between the electrochemistry and mechanics in electroosmotic consolidation of soils.

This project summary was developed by the National Risk Management Laboratory's Land Remediation and Pollution Control Division to announce

key findings of the research project that is fully documented in a separate report of the same title (see project report ordering information at back).

Introduction

Electrokinetic remediation technology using low level dc electrical potential difference is shown in Figure 1. The applied electrical current or electric potential difference leads to electrolysis reactions at the electrodes generating an acidic medium at the anodes and an alkaline medium at the cathodes. The acids generated at the anode advances through the soil toward the cathode by transport mechanisms including ion migration due to electrical gradients, pore fluid advection due to prevailing electroosmotic flow, pore fluid flow due to any externally applied or internally generated hydraulic potential difference, and diffusion due to generated chemical gradients. The alkaline medium developed at the cathode will first advance toward the anode by ionic migra-

tion and diffusion. However, the mass transport of the H^+ ions will neutralize this base front preventing its transport toward the anode. Free chemical species present in the pore fluid and/or desorbed from the soil surface will be transported toward the electrodes depending on their charge. The primary driving mechanisms of species transport are the same as the acid or base transport mechanisms. As a result of the transport of chemical species in the soil pore fluid, cations will collect at the cathode and anions at the anode. Heavy metals and other cationic species will be removed from the soil with the effluent, or they will be deposited at the cathode.

Species transport mechanisms under electric fields are envisioned to be employed in remediating soils from organic and inorganic species (electrokinetic remediation), injections of microorganisms and nutrients in bioremediation, injections of grouts in soil stabilization and waste containment, soil and pore fluid characterization and species extraction using pen-

etrating probes, diversion systems for contaminant plumes, and leak detection systems in containment barriers.

Methodology

The primary objective of the pilotscale testing was to demonstrate removal of lead in the soil samples. Three pilotscale tests (PST) were conducted using lead-spiked Georgia kaolinite. This mineral was selected for this study because of its low activity and high electroosmotic water transport efficiency relative to other clay minerals. Lead nitrate $[Pb(NO_3)_2]$ salt was used as the source of lead because of its high solubility in water and its ability to provide the necessary ionic forms of lead and nitrate.

Two pilotscale tests were conducted on kaolinite spiked with lead at concentrations of about 856 micrograms per gram ($\mu g/g$) and 1533 $\mu g/g$. A third pilotscale test was conducted on a kaolinite/sand mixture spiked with lead at a concentration of 5322 $\mu g/g$. Three rows of elec-

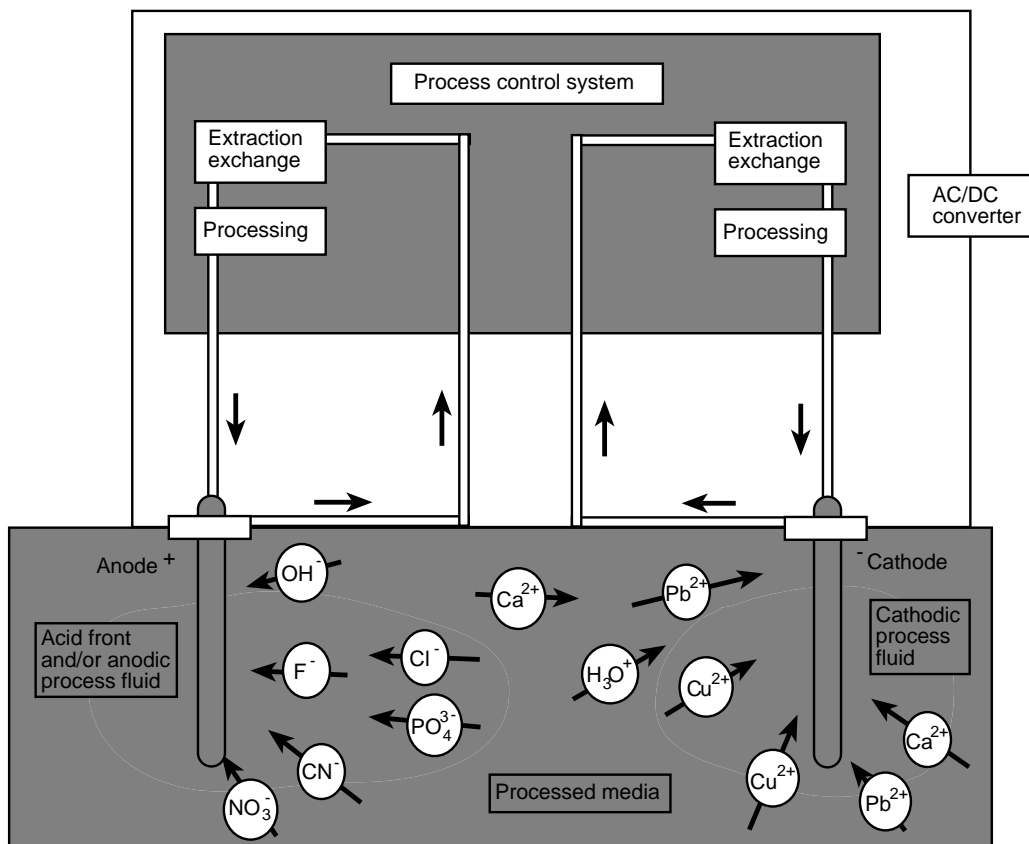


Figure 1. Schematic of electrokinetic soil processing showing migration of ionic species, transport of acid front and/or processing fluid across the process medium (Acar and Alshawabkeh)

trodes were placed in compartments in the soil. A polyacrylate frame was placed in each compartment to hold the electrodes. Each cathode and anode series consisted of a row of five equally spaced electrodes with a center-to-center spacing of 18.3 cm. The central row of electrodes was designated as anode while the two outer rows were designated as cathodes. Electrode row spacing was set at 72.4 cm. The schematic diagram of the container with electrode configuration is shown in Figure 2.

Since the electroosmotic flow was expected to occur from the anode toward both cathodes, a water tank was connected to the anode reservoir to supply the required amount of fluid flow. Water was collected from both cathode compartments in separate containers. In order to avoid introduction of advection due to external hydraulic potential differences, the hydraulic head was kept constant at zero head difference at the cathode and anode compartments during experiment. This provision permitted evaluation of the singular effect of the electrical potential gradients

on water flow within the system. The pilotscale sample in each test was composed of two identical halves or cells. An electrical current of 1.7 amperes (A) was supplied to the sample at the anode. This current was divided to supply the two cells with .85A each. The cross sectional area of the soil treated was 6,398 cm² (91.4 cm width x 70.0 cm height) and the applied current density was 0.14 milliamperes per centimeter (mA/cm). Voltage probes, tensiometers, and thermocouples were used to monitor changes in voltage distribution, suction, and temperature across one cell, while the second cell was used to assess the concentration changes with time. Experiment related parameters are summarized in Table 1.

Pilotscale test specimens were sampled before, during and after the test runs. For the first pilotscale test (PST1), the soil was divided into three horizontal layers, top layer (layer1), middle layer (layer2) and bottom layer (layer3). Each layer was divided into 10 longitudinal sections of 7.0 cm length and six lateral sections of equal size. A total of 180 soil samples were

taken from the first pilot scale test. Each sample represented a soil volume of 2703 cm³. The same sample collection procedure was used for the second (PST2) and third (PST3) pilotscale tests, but with different soil volumes per sample. A total of 400 soil samples were collected from the second pilot scale test, and 80 samples were collected from the third pilotscale test.

Results and Discussion

Lead Transport

Three layers at different elevations were analyzed for lead distribution in PST1. Figure 3 shows a three-dimensional contour diagram of the mean and standard deviation of the final lead distribution across the middle layer in this test. Most of the lead was found precipitated in the last section close to the cathode, which contained about 54% of the initial lead. The soil across the electrodes (excluding the last section) contained about 40% of the initial lead concentration, most of which was found in permeivity of the cracks that

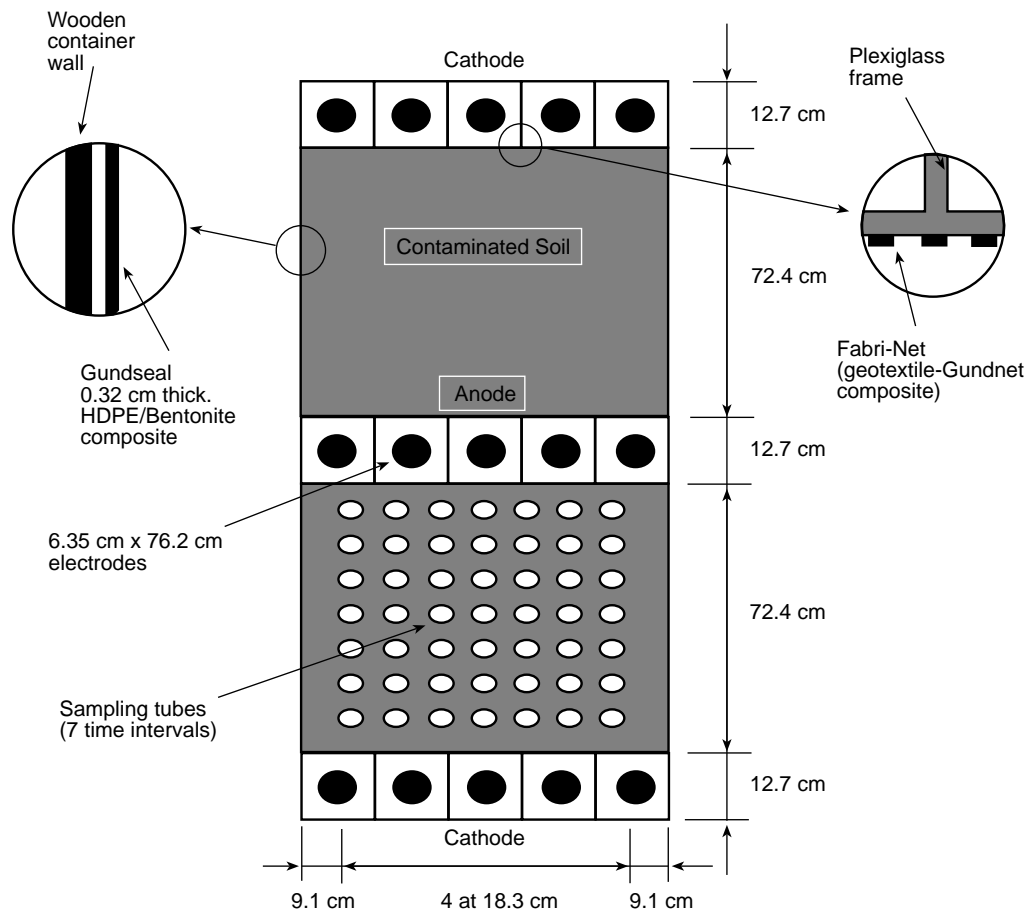


Figure 2. Schematic diagram of pilotscale test container and electrode configuration

Table 1. Initial Conditions for Pilotscale Tests

Parameter	Test 1	Test 2	Test 3
Current (mA)	850.0	1700.0	1700.0
Container Dimensions (cm)			
Width	91.4	70.0	70.0
Depth	91.4	70.0	70.0
Length	91.4	70.0	70.0
Test Duration (hr)	1,300	2,950	2,500
Current Density ($\mu\text{A}/\text{cm}^2$)	132.8	132.8	132.8
Initial Soil pH	4.7	4.5	4.2
Initial Pb Concentration ($\mu\text{g}/\text{g}$)	856	1,533	5,322
Initial Water Content (%)	44.1	44.3	24.6
Initial Dry Density (g/cm^3)	1.222	1.22	1.80
Initial Saturation (%)	91	91	90

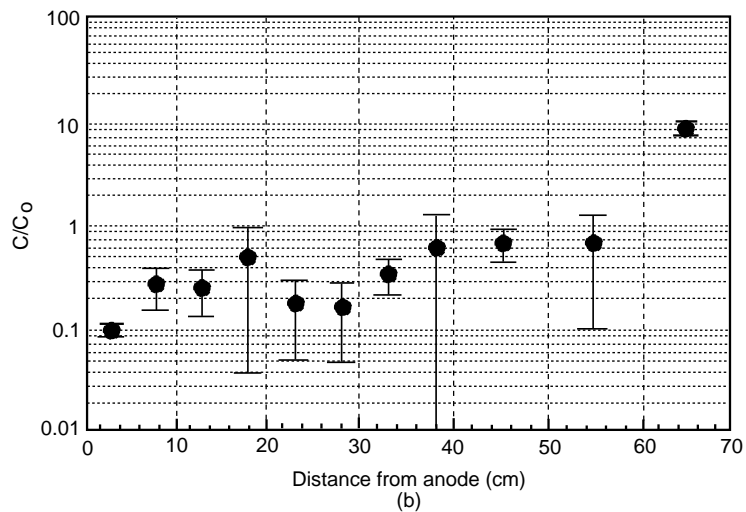
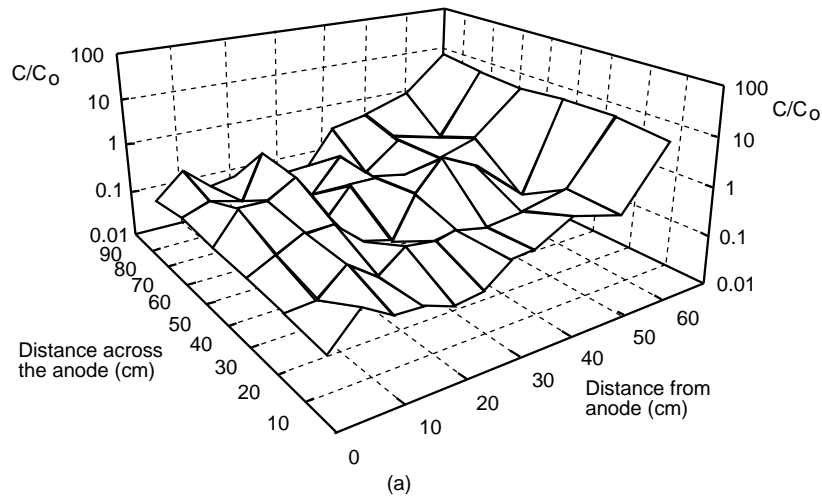


Figure 3. Final lead concentration/initial lead concentration (C/C_0) across the middle layer of PSTI (a) 3-D contour diagram and (b) mean and standard deviation.

formed in the soil due to consolidation. Approximately 1% of the initial lead concentration was electrodeposited and/or precipitated at the electrodes.

In PST2 most of the soil across the top layer (up to the last 7 cm of the cathode zone) displayed more than 90% removal with a final concentration of less than 150 $\mu\text{g/g}$. Most sections of the soil contained a final lead concentration of less than 50 $\mu\text{g/g}$, with removal efficiencies of up to 98% of the initial lead. The bottom and middle layers exhibited similar lead concentration profiles. More than 90% removal (up to 98% in most parts of the layers) was achieved across the specimen. All layers demonstrated that most of the lead was transported to the cathode zone. Figure 4 shows final lead concentrations and the mean and standard deviation of final lead concentrations across the middle layer of PST2. Soil type, pore fluid chemistry,

and pH were the major factors that affected lead sorption and retardation.

Energy Expenditure

Energy expenditure is evaluated per unit volume of soil treated in units of kilowatt-hours per cubic meter (kWh/m^3). Energy expenditures in pilotscale tests increased slightly with time within the first 500 hours of processing to about 50 kWh/m^3 , then it increased linearly with time to about 325 kWh/m^3 in PST1 after 1300 hours, 700 kWh/m^3 in PST2 after 2950 hours, and 700 kWh/m^3 in PST3 after 2500 hours of processing. Energy costs ranged from \$16.3 to \$35 per cubic meter of soil with an electric power cost of \$.05/ kWh . The results indicate that steady state conditions were realized within the first 500 hours for PST1 and PST2, and within 700 hours for PST3. Energy expenditure was directly related to the corresponding elec-

tric potentials. Nonlinear changes in energy expenditure early in the tests were associated with the increase in the total voltage applied within the first 1000 hours.

Soil pH

Final pH distributions in PST2 across the middle layer of Cell A are shown in figure 5. One-dimensional pH profiles across the soil specimen were similar and did not display significant changes with depth. The results also indicated that the pH within the anode region decreased to about 2.5 in PST1 and to 1.5 in PST2. In the cathode region the pH remained within the initial value in both tests (4.7 in PST1 and 4.5 in PST2). Slight differences in pH between the two tests at the anode region could be related to the differences in processing time (2950 hours for PST2 and 1300 hours for PST1). After 2950 hours of conducting PST2, the acid front moved to

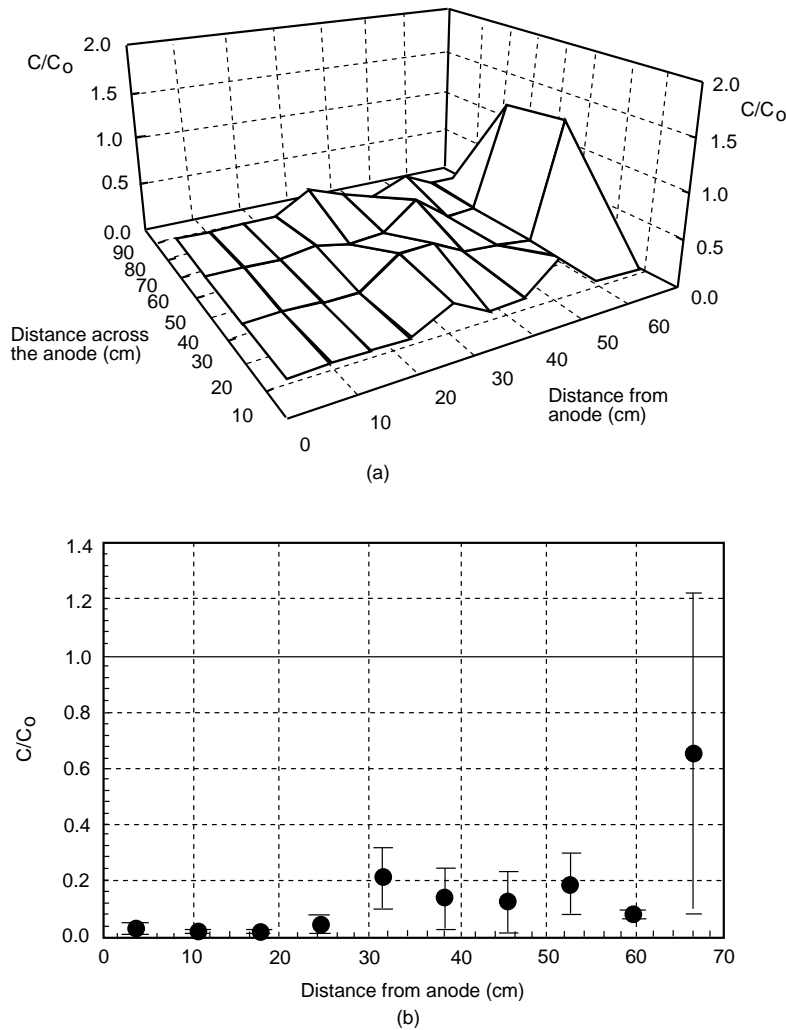


Figure 4. Final lead concentration/initial lead concentration (C/C_0) across cell B in the middle layer of PST2 (a) 3-D contour diagram and (b) mean and standard deviation.

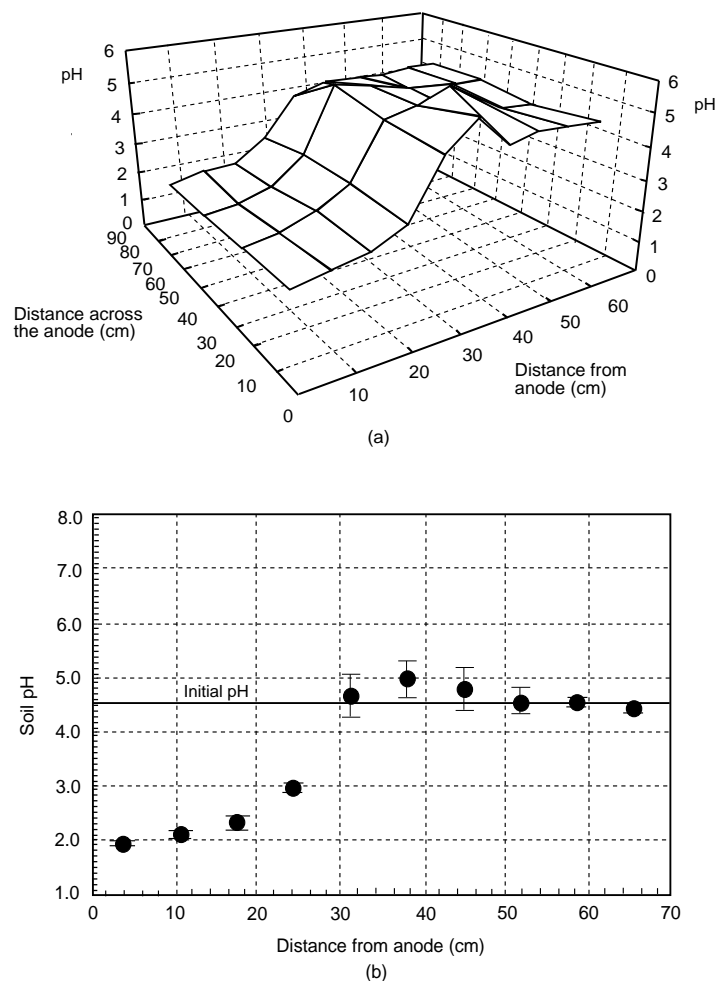


Figure 5. Final pH distributions across cell A in the middle layer of PST2 (a) a 3-D contour diagram and (b) mean and standard deviation.

30-35 cm from the anode. For PST1, the acid front was at a distance of 16 to 18 cm from the anode after 1300 hours of processing.

Temperature Changes

Thermocouples were used to monitor temperature changes across the soil. In PST2, the initial temperature of the sample before processing was 23°C. The temperature increased at different rates across the soil and at the electrode compartments. Soil sections near the cathode experienced the highest increase in temperature (23°C to 42°C) while the anolyte experienced the lowest increase in temperature (23°C to 35°C). The heat flux due to electrical gradients was a function of the electric potential gradient and the heat transfer conductivity of the medium.

The majority of the temperature increase occurred during the first 1000 hours of processing. This temperature increase coincided with an increase in the voltage

across the soil. Temperature changes between the soil and the electrode compartments were related to the voltage distribution. Most of the voltage drop occurred at the cathode region resulting in a higher increase in temperature in that zone.

Transport Modeling

Test results from PST3 were used for comparison with a mathematical model of coupled-reactive multi-component species transport under an electric field in a saturated soil. The modeling of transport parameters result in a system of differential/algebraic equations. The partial differential equations describe fluid flow, charge, and species transport, while algebraic equations describe the chemical reactions in the soil pore fluid.

Figure 6 compares the predicted lead profile after 50 days to the measured profile after 53 days. Both profiles display a significant decrease in lead concentration across the specimen. The predicted pro-

file is lower than the measured profile in the first 40-45 cm from the anode, but display similar qualitative agreement in the cathode region. The model results and their comparisons with pilotscale test results demonstrate that the principles of multi-species transport under an electric field can be formalized.

Conclusions

Ionic migration is the dominant transport mechanism for heavy metals under an electric field, particularly when the coefficient of electroosmotic permeability is less than 10^{-5} square centimeters per volt-seconds (cm^2/Vs). The contribution of advective transport under electric gradients (electroosmosis) depends on the soil type. However, even when the coefficient of electroosmotic permeability is in the order of $10^{-4} \text{ cm}^2/\text{Vs}$ (e.g. lower activity clays at high water contents), mass flux of H^+ and OH^- ions are at least 10 times greater by ion migration than electroosmosis. At these

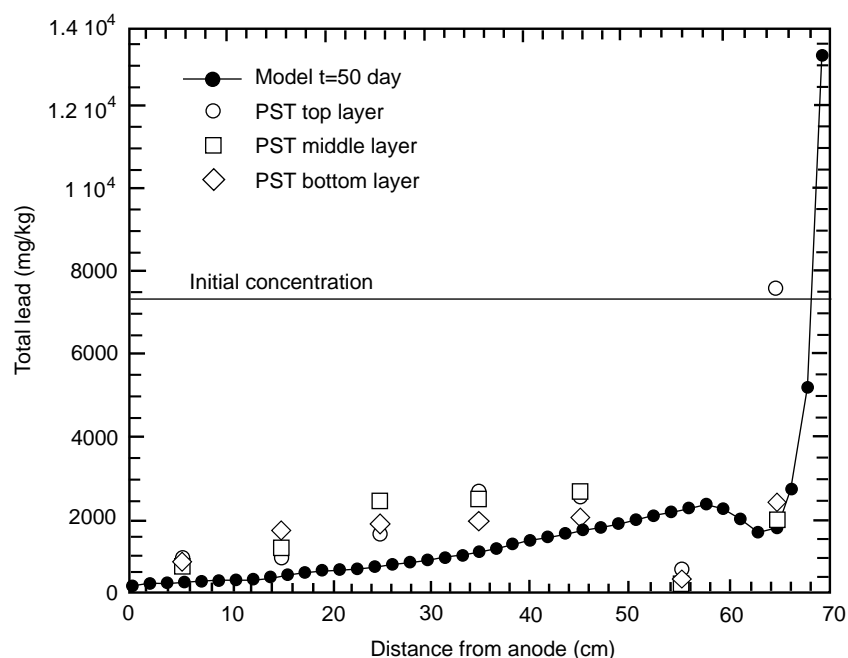


Figure 6. A comparison of the third pilotscale test (PST3) results and modeled total lead concentration after 50 days.

flow rates however, mass flux of other species is of the same order of magnitude. Advection under a hydraulic head difference is significant for soils with hydraulic conductivities greater than 10^{-5} cm/s. Diffusion is significant only at concentration fronts and pH fronts because of the high concentration gradients.

Pilotscale tests conducted at initial lead concentrations of 1533 $\mu\text{g/g}$ and 5322 $\mu\text{g/g}$ resulted in higher removal efficiencies than tests conducted at lower initial concentrations. Tests with higher initial lead concentrations displayed significant lead removal from the soil. More than 90% (up to 98% in most soil regions) removal was achieved across the second pilot scale test except the last 7 cm near the cathode. High concentrations of lead are encountered near the cathode in all tests due to lead hydroxide precipitation in the high pH environment. Almost no lead is found in the effluent or on the electrodes.

The results indicate that the placement of the cathode, whether in direct contact with the soil or at a distance from the soil, greatly influences the amount of lead precipitated or electrodeposited at the cathode.

The results of the pilotscale tests conducted in this study demonstrate the feasibility of electrokinetic soil remediation in full field applications. Precipitation of heavy metals within the cathode region due to the alkaline environment is expected to decrease the efficiency of the process and increase energy expenditure. Enhancement techniques such as controlling the chemistry at the cathode may be necessary to increase the efficiency of removal.

The full report was submitted in fulfillment of Cooperative Agreement No. CR-816828-01-1 by Electrokinetics, Inc., under the sponsorship of the U.S. Environmental Protection Agency.

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Randy A. Parker is the EPA Project Officer (see below).

The complete report, entitled "Theoretical and Experimental Modeling of Multi-Species Transport in Soils under Electric Fields," (Order No. PB97-193056; Cost: \$49.00, subject to change) will be available only from:

National Technical Information Service

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The EPA Project Officer can be contacted at:

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