

# Sequentially Enhanced Electrokinetic Remediation of Heavy Metals in Low Buffering Clayey Soils

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**Abstract:** This paper presents the results of an experimental investigation undertaken to evaluate different purging solutions to enhance the removal of multiple heavy metals, particularly chromium, nickel, and cadmium, from a low buffering clay, specifically kaolin, during electrokinetic remediation. Experiments were conducted on kaolin spiked with Cr(VI), Ni(II), and Cd(II) in concentrations of 1,000, 500, and 250 mg/kg, respectively, which simulate typical electroplating waste contamination. A total of five different tests were performed to investigate the effect of different electrode purging solutions on the electrokinetic remedial efficiency. A constant DC voltage gradient of 1 V/cm was applied for all the tests. The removal of heavy metals from the soil using tap water as the purging solution was very low. When 1 M acetic acid was used as the purging solution in the cathode, the removal of chromium, nickel, and cadmium was increased to 20, 19, and 13%, respectively. Using 0.1 M ethylene diamine tetraacetic acid as the purging solution in the cathode, 83% of the initial Cr was removed; however, the nickel and cadmium removal was very low. A sequentially enhanced electrokinetic remediation approach involving the use of water as a purging solution at both the anode and cathode initially, followed by the use of acetic acid as the cathode purging solution and a NaOH alkaline solution as the anode purging solution was tested. This sequential approach resulted in a maximum removal of chromium, nickel, and cadmium of 68–71, 71–73, and 87–94%, respectively. This study shows that the sequential use of appropriate electrode purging solutions, rather than a single electrode purging solution, is necessary to remediate multiple heavy metals in soils using electrokinetics.

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## Introduction

Heavy metals, particularly lead, chromium, nickel, cadmium, mercury, arsenic, and zinc, are a major public health concern at many contaminated sites (U.S. EPA 1995). Electrokinetic remediation has a great potential to remediate heavy-metal-contaminated soils, including the low permeable clays and/or heterogeneous soils at these sites. It essentially involves installing trenches and/or wells that encompass the contaminated soil zone. Electrodes are then inserted into these trenches or wells, and a low DC voltage gradient or DC current is applied across the electrodes, which are strategically determined as either cathodes or anodes. As a result of the induced electric potential, the contaminants are transported toward either the cathodes or the anodes depending on their charge, cationic or anionic, and the direction of the pore water flow (Pamucku and Wittle 1992; Segall and Bruell 1992; Acar and Alshawabkeh 1993; Probststein and Hicks

1993; Eykholt and Daniel 1994). Contaminants collected at the electrodes are then extracted and subsequently treated.

Several studies have been reported that investigated the applicability of electrokinetics to remediation of soils contaminated with a single heavy metal, most often lead (Hamed et al. 1991; Pamucku and Wittle 1992; Acar et al. 1995; Reed et al. 1995; Acar and Alshawabkeh 1996; Yeung et al. 1996; Coletta et al. 1997; Wong et al. 1997; Yang and Lin 1998). However, at many contaminated sites, different heavy metals often coexist together in the soils. Chromium, nickel, and cadmium are the heavy metals that are most commonly encountered, and they have been found at numerous contaminated sites, especially at electroplating, leather tanning, metal finishing, and pigment industry sites (Ottosen et al. 1997; Reddy and Parupudi 1997).

The electrokinetic remedial efficiency largely depends on the types of heavy metals that are present and the composition of the soil (Reddy and Shirani 1997; Reddy et al. 1997; Chinthamreddy 1999; Chinthamreddy and Reddy 1999; Reddy and Chinthamreddy 1999). For example, chromium can exist in two forms, hexavalent chromium [Cr(VI)] and trivalent chromium [Cr(III)]. Cr(VI) exists as anionic complexes, while Cr(III) exists as cation and/or cationic hydroxo complexes. During electrokinetic remediation, Cr(VI) migrates toward the anode whereas Cr(III) migrates toward the cathode. The geochemistry of Cr(VI) and Cr(III) is quite different; for instance, the adsorption of Cr(VI) in soil is negligible at high pH; however, the adsorption/precipitation of Cr(III) in soil is significant at high pH. The toxicity of Cr(VI) and Cr(III) is also quite different. Cr(VI) is known to be toxic, while the toxicity of Cr(III) has not been established. Currently, the remediation of Cr(VI) in soils is being given the utmost priority (Mattson and Lindgren 1993; Haran et al. 1996).

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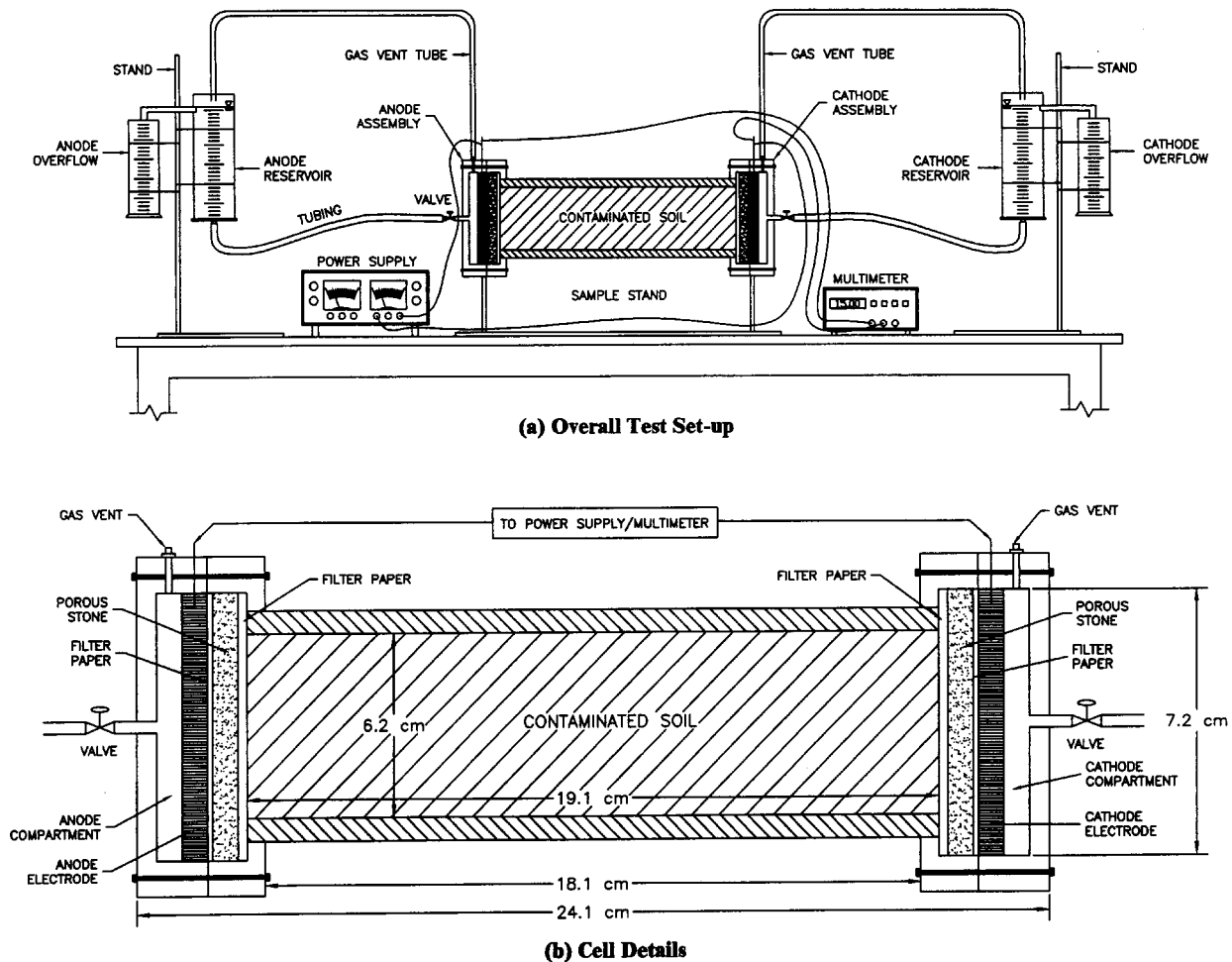


Fig. 1. Bench scale electrokinetic test setup

Other toxic heavy metals, such as Ni and Cd, commonly exist as cations and cationic complexes, and they migrate toward the cathode during electrokinetic treatment. When Cr(VI), Ni, and Cd coexist, the synergistic effects of these multiple contaminants on electrokinetic remediation need to be addressed.

In low buffering soils, such as kaolin, the pH of the soil decreases to 2–3 near the anode and increases to 8–12 near the cathode due to the electrolysis of water at the electrodes. Cr(VI) attempts to migrate toward the anode; however, it is adsorbed to the soil in the low pH regions, thus hindering complete removal from the soil. Ni(II) and Cd(II) attempt to migrate toward the cathode; however, they are adsorbed/precipitated in the high pH regions, thereby hindering their complete removal from the soil at the cathode reservoir. Although significant migration of heavy metals occurs toward the electrodes, the actual removal of the contaminants from the soil is usually insignificant (Reddy et al. 1997; Reddy and Parupudi 1997; Chinthamreddy 1999).

In order to remove the heavy metals from soils, different liquids, other than water, must be used in the electrode reservoirs. The selected liquids, also known as purging solutions, should induce favorable pH conditions in the soil, and/or interact with the heavy metals, so that the heavy metals are removed from the soil (Pamucku and Wittle 1992; Eykholt and Daniel 1994; Acar et al. 1995; Coletta et al. 1997; Puppala et al. 1997).

This paper presents results of an experimental investigation that was undertaken to evaluate different purging solutions for the

removal of multiple heavy metals, particularly chromium, nickel, and cadmium, from a low buffering clay, specifically, kaolin. These test results helped to identify the most effective enhancement strategy for the removal of heavy metals from this soil.

## Experimental Methodology

### Electrokinetic Test Setup

Fig. 1 shows the schematic of the electrokinetic test setup used for this study. Reddy et al. (1997) have described this setup in detail. The setup consists of an electrokinetic cell, two electrode compartments, two electrode reservoirs, a power source, and a multimeter. The Plexiglas electrokinetic cell has an inside diameter of 6.2 cm and a total length of 19.1 cm. Each electrode compartment consists of a valve to control the flow into the cell, a slotted graphite electrode, and a porous stone. The electrode compartments are connected to either end of the cell using screws. Electrode reservoirs were made of 3.8 cm inner diameter Plexiglas tubes and were connected to the electrode compartments using Tygon tubing. Exit ports were created in the electrode compartments, and then thin tubes were inserted into these ports to allow the gases generated from the electrolysis of water to escape. The other end of each of these gas tubes was connected into the reservoirs to collect any liquid that was removed along

**Table 1.** Composition and Properties of Kaolin

Property	Value
Mineralogy	Kaolinite: 100% Muscovite: trace Illite: trace
Particle size distribution (ASTM D 422)	
Gravel	0%
Sand	4%
Silt	18%
Clay	78%
Atterberg limits (ASTM D 2487)	
Liquid limit	50.0%
Plastic limit	27.4%
Plasticity index	22.6%
Specific gravity (ASTM D 854)	2.60
Moisture–unit weight relationships (Harvard miniature compaction test)	
Maximum dry unit weight	14.4 kN/m <sup>3</sup>
Optimum moisture content	27%
Hydraulic conductivity	$1.0 \times 10^{-8}$ cm/s
Cation exchange capacity (ASTM D 9081)	1.0–1.6 meq/100 g
pH (ASTM D 4972)	4.9
Organic content (ASTM D 2974)	Near 0%
Unified Soil Classification System (ASTM D 2487)	CL

with the gases. A power source was used to apply a constant voltage to the electrodes, and a multimeter was used to monitor the voltage and measure the current flow through the soil sample during the testing.

### Test Variables

Kaolin, which is a low buffering soil, has been characterized in detail and has been used in related investigations (Reddy et al. 1997; Reddy and Parupudi 1997). Table 1 summarizes the composition and properties of this soil. The soil was spiked with Cr(VI), Ni(II), and Cd(II) in concentrations of 1,000, 500, and 250 mg/kg, respectively, for all the experiments, to simulate typical electroplating waste contamination. A total of five different tests were performed to investigate the effect of different electrode purging solutions on the electrokinetic remedial efficiency

in kaolin. Table 2 illustrates these test conditions. A constant DC voltage gradient of 1 V/cm was applied for all the tests.

For the first test (EKK-Cr6-Ni-Cd), tap water was used in both the anode and cathode reservoirs. This test served as a baseline experiment. For the second test (EKK-HAc), 1 M acetic acid was used in the cathode reservoir and tap water was used in the anode reservoir. Acetic acid was introduced from the cathode reservoir to depolarize the cathode electrolysis reaction and maintain a low pH in cathode. For the third test (EKK-EDTA), a 0.1 M ethylene diamine tetraacetic acid (EDTA) solution was used in the cathode reservoir and tap water was used in the anode reservoir. EDTA was used to investigate the complexation of heavy metals and the transport of heavy metal–EDTA complexes. For the fourth test (SQEEK-1), tap water was initially used in both the anode and cathode reservoirs to allow the transport of heavy metals toward the electrodes. Subsequently, after 310 h, 1 M acetic acid was used in the cathode reservoir to maintain a low pH and 1 M NaOH solution was used in the anode reservoir to maintain a high pH. The solutions and concentrations were selected for counteracting the electrolysis of water at the particular electrode. These solutions were used to enhance the solubility of the heavy metals and prevent their adsorption/precipitation.

For the last test (SQEEK-2), tap water was used initially in both the anode and cathode reservoirs, as in the fourth test (SQEEK-1). Then, after approximately 500 h, 1 M acetic acid was used in the cathode to maintain a low pH and allow the transport of cationic heavy metals toward the cathode. Tap water was continued in the anode reservoir. Subsequently, after about 1,350 h, 1 M NaOH solution was added to the anode reservoir to increase the soil pH and to allow the transport of Cr(VI) into the anode (1 M acetic acid was continued in the cathode reservoir). It should be noted that the tests conducted in this study were aimed at assessing the relative performance of different purging solutions when used at the selected concentrations. For the fourth and fifth tests (SQEEK-1 and SQEEK-2), the rationale for deciding what time to change the purging solutions was based on the heavy metal concentrations and the electrical conductivity of the solution in the electrode reservoirs, as well as the electrical current and electroosmotic flow values.

### Testing Procedure

Approximately 1,100 g of dry soil was used for each test. Potassium chromate, nickel chloride, and cadmium chloride were used as sources of Cr(VI), Ni(II), and Cd(II), respectively. The required amounts of these chemicals that would yield the desired

**Table 2.** Electrokinetic Testing Program

Test	Designation	Anode purging solution	Cathode purging solution	Test duration (h)	Initial Soil Conditions				
					Water content (%)	Dry density (g/cm <sup>3</sup> )	pH	Redox (mV)	EC (mS/cm)
1	EKK-Cr6-Ni-Cd	H <sub>2</sub> O	H <sub>2</sub> O	260	40.6	1.32	5.36	268	1,884
2	EKK-HAC	H <sub>2</sub> O	1 M acetic acid	120	32.9	1.4	5.63	268	1,884
3	EKK-EDTA	H <sub>2</sub> O	0.1 M EDTA	340	36.5	1.3	4.51	333	1,371
4	SQEEK-1	$t=0-310$ h: H <sub>2</sub> O $t=310-710$ h: 1 M NaOH	$t=0-310$ h: H <sub>2</sub> O $t=310-710$ h: 1 M acetic acid	710	32.6	1.4	4.56	330	1,638
5	SQEEK-2	$t=0-500$ h: H <sub>2</sub> O $t=500-1,350$ h: H <sub>2</sub> O $t=1,350-2,250$ h: 1 M NaOH	$t=0-500$ h: H <sub>2</sub> O $t=500-1,350$ h: 1 M acetic acid $t=1,350-2,250$ h: 1 M acetic acid	2,250	33.3	1.4	6.73	205	2,200

Notes: Soil, kaolin; Contaminants, Cr(VI)=1,000 mg/kg, Ni(II)=500 mg/kg, Cd(II)=250 mg/kg; DC voltage gradient, 1 V/cm.

concentrations were weighed and then dissolved individually in deionized water. These contaminant solutions were then added to the soil and mixed thoroughly with a stainless steel spatula in a high density polyethylene (HDPE) container. A total of 375 mL of deionized water (35% moisture content) was used to represent typical field moisture conditions. The contaminated soil was then placed in the electrokinetic cell in layers and compacted uniformly using a hand compactor. The exact weight of the soil used in the cell was determined and the soil was equilibrated for 24 h. The pH, redox potential, and electrical conductivity (EC) of the remaining contaminated soil in the HDPE container were measured both before and after equilibration. The electrode compartments were then connected to the electrokinetic cell. In each electrode compartment, filter papers were inserted between the electrode and the porous stone as well as between the porous stone and the soil.

The electrode compartments were connected to the anode and cathode reservoirs using Tygon tubing. The reservoirs were then filled with potable water. Potable water was selected because it is the most likely source of replenishing fluid at most field contaminated sites. The elevation of water in both reservoirs was kept the same to prevent a hydraulic gradient from forming across the specimen. The pH, redox potential, and electrical conductivity of the potable water used for the tests were measured, and these values were  $7.7 \pm 0.1$ ,  $150 \pm 25$  mV, and  $280 \pm 20$   $\mu$ S/cm, respectively. The total dissolved solids and hardness of the potable water were approximately 200 mg/L and 60 mg/L  $\text{CaCO}_3$ , respectively. The electrokinetic cell was then connected to the power supply and a constant DC voltage gradient of 1 V/cm was applied to the soil sample. The electric current across the soil sample as well as the water flow, pH, redox potential, and electrical conductivity in both the anode and cathode reservoirs were measured at different time periods throughout the duration of the experiment. The test was terminated when the current stabilized, when no significant change in the water flow (electroosmotic flow) was observed, and/or when no changes in the electrical conductivity or the contaminant concentrations of the electrode reservoir solutions were measured. These parameters were indicative of the changes taking place within the soil, and the absence of these changes would signify that near equilibrium conditions were achieved and the trend for contaminant fate and transport would be evident.

At the end of each test, aqueous solutions from the anode and cathode reservoirs and the electrode assemblies were collected and volume measurements were made. Then, the reservoirs and the electrode assemblies were disconnected, and the soil specimen was extruded from the cell using a mechanical extruder. The soil specimen was sectioned into five parts and each part was weighed and subsequently preserved in a glass bottle. From each soil section, 10 g of soil was taken and mixed with 10 mL of deionized water in a glass vial. The mixture was shaken thoroughly by hand for several minutes and the solids were then allowed to settle. The pH, redox potential, and the electrical conductivity of the soil as well as of the aqueous solutions from the electrodes were measured. The moisture content of each soil section was also determined.

### **Chemical Analysis**

Contaminants in different soil sections were extracted by performing acid digestion in accordance with the U.S. EPA 3050 procedure (U.S. EPA 1986). Total concentrations of chromium, nickel, and cadmium were determined using this extraction pro-

cedure. For this procedure, approximately 1–2 g of a representative sample from each section was weighed accurately in a conical beaker and then mixed with 10 mL of 1:1 nitric acid ( $\text{HNO}_3$ ). The mixture was then stirred thoroughly. After stirring, the beaker was covered with a watch glass and heated to  $95^\circ\text{C}$ , whereby it was refluxed for 15 min. The sample was then cooled, 5 mL of concentrated  $\text{HNO}_3$  were added, and it was refluxed again for 30 min. This last step was then repeated once. The conical beaker was then covered with a ribbed watch glass, and the sample was allowed to evaporate to 5 mL. The sample was cooled, and 2 mL of deionized water and 3 mL of 30% hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) were added. The mixture was warmed to observe the peroxide reaction and heated until the effervescence subsided. The sample was then cooled, and the addition of 1 mL  $\text{H}_2\text{O}_2$  was continued until the effervescence was at a minimum. The maximum amount of  $\text{H}_2\text{O}_2$  added was less than 10 mL. The sample was cooled, and 5 mL of concentrated  $\text{HNO}_3$  and 10 mL of deionized water were added. This mixture was refluxed for 15 min. The sample was diluted to 100 mL and centrifuged to separate the supernatant. The supernatant was analyzed using an atomic absorption spectrophotometer (AAS) to determine the concentrations of total chromium, nickel, and cadmium. Aqueous samples from the electrode reservoirs were directly tested using AAS for the contaminant concentrations.

Alkaline digestion was performed on the soil sections in accordance with the U.S. EPA 3060A procedure, which extracts only Cr(VI) into the solution. For this extraction, approximately 2.5 g of soil sample was weighed accurately and 50 mL of extractant solution was added. The extractant solution was prepared by dissolving 35.09 g of sodium bicarbonate (0.28 M) and 20 g of sodium hydroxide (0.5 M) in deionized water to make 1 L of solution. The soil-extractant mixture was then heated to  $95^\circ\text{C}$  for 60 min with continuous stirring. The sample was then cooled and the pH was adjusted to between 7 and 8 using  $\text{HNO}_3$ . The sample was then diluted to 100 mL and the supernatant was obtained by centrifugation. The supernatant was analyzed using AAS to determine the Cr(VI) concentration. Cr(III) concentrations were then calculated by subtracting Cr(VI) concentrations from the total chromium concentrations determined based on the acid digestion procedure.

### **Quality Assurance**

The reproducibility of the testing procedure and results was verified by performing selected replicate tests (Chinthamreddy 1999). To ensure the accuracy of the test results, the following precautions were taken: (1) new electrodes, porous stones, and tubing were used for each experiment; (2) the electrokinetic cell and compartments were soaked in a dilute acid solution for 24 hours and then rinsed first with tap water and finally with deionized water to avoid cross contamination between the experiments; (3) chemical analyses were performed in duplicate; (4) the AAS calibration was checked after testing every five samples; and (5) a mass balance analysis was performed for each test. The contaminant mass that was accounted for after the electrokinetic testing was within  $\pm 10\%$  of the mass of the heavy metal that was initially added to the soil. These differences were mainly attributed to the nonuniform contaminant distribution within the selected soil sample for chemical analysis and to the adsorption of contaminants onto the electrodes and porous stones.

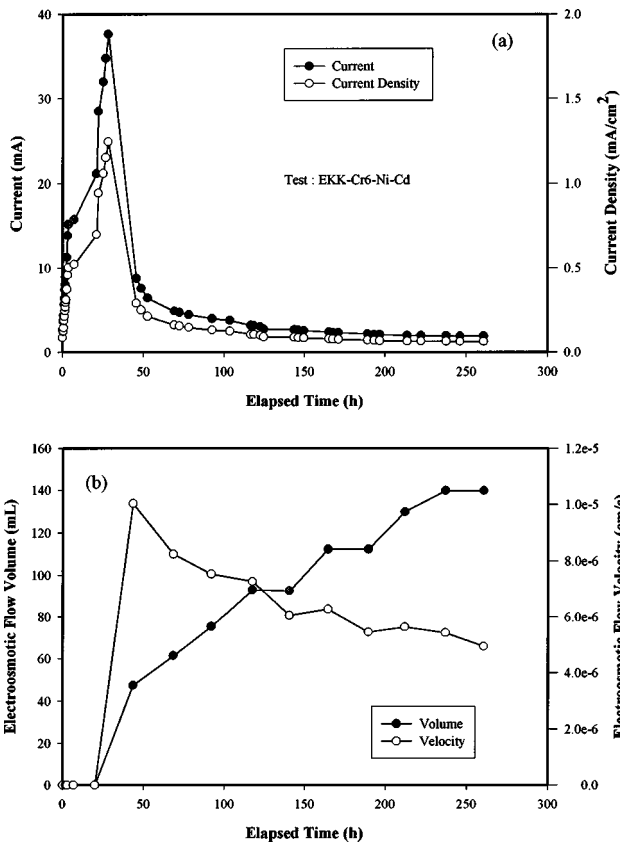


Fig. 2. Current and electroosmotic flow variations: unenhanced conditions

## Results

### Unenhanced Condition

Fig. 2 shows the current, current density, electroosmotic flow, and electroosmotic velocity variations for the test that was performed under unenhanced conditions, i.e., using water in both the anode and cathode reservoirs. In this test, the current increased from an initial value of 3 mA to a peak value of 38 mA in approximately 30 h, and then it started decreasing. The current then decreased to a low value and stabilized at approximately 2 mA. The maximum current density for this test was 1.25 mA/cm<sup>2</sup>. The current density value stabilized at 0.15 mA/cm<sup>2</sup> toward the end of the testing. The electroosmotic flow was negligible during the first 20 h, and then it started increasing. A maximum of 140 mL of electroosmotic flow was obtained in 260 h of testing. The electroosmotic velocity increased to a high value of 1 × 10<sup>-5</sup> cm/s in the first 40 h, and then it started decreasing. An average electroosmotic velocity of 6.7 × 10<sup>-6</sup> cm/s was observed during the test. The velocity values are consistent with the range of values reported in the literature (Mitchell 1993).

Fig. 3 shows the distribution of Cr, Ni, and Cd in both the soil and the electrode reservoirs for the test conducted under unenhanced conditions. The pH distribution is also shown to further explore the observed heavy metal distribution. Due to the electrolysis of water, the pH of the tap water in the anode decreased to 2 because of the formation of H<sup>+</sup> ions, while the pH of the tap water in the cathode increased to 12 due to the formation of OH<sup>-</sup> ions. The pH of the soil was reduced to 2 throughout two-thirds of the soil beginning at the anode, while the pH of the soil increased

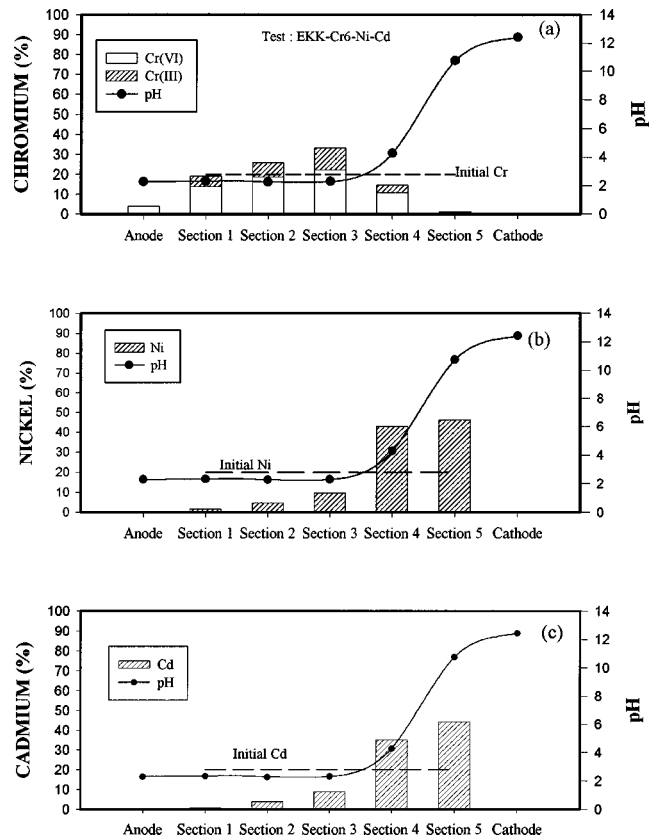


Fig. 3. Contaminant distribution in soil after electrokinetic treatment: unenhanced conditions

to 11 in the vicinity of the cathode. The pH changes that were observed are fairly consistent with other reported electrokinetic studies. Due to the smaller ionic radius, the mobility of an H<sup>+</sup> ion is approximately twice the mobility of an OH<sup>-</sup> ion, and some researchers postulate that this is the reason why H<sup>+</sup> ions migrate farther into the soil as compared to OH<sup>-</sup> ions (Acar and Alshawabkeh 1993). The reaction kinetics and the type and concentration of the ions at the graphite electrodes may also affect the generation rate and migration of the H<sup>+</sup> and OH<sup>-</sup> ions, and the effects of the electrokinetic transport processes, electromigration and electroosmosis, should also be considered. The observed migration of Cr, Ni, and Cd was consistent with the changes in the soil pH.

Chromium speciation is primarily a result of the pH and Eh (redox potential) in the soil-solution environment, and Chinthamreddy (1999) presents an overview of chromium geochemistry. Basically, Cr(VI) species are generally soluble and mobile, and, in an oxidizing environment, Cr(VI) exists as HCrO<sub>4</sub><sup>-</sup> under very low pH conditions, Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> under low to neutral conditions, and CrO<sub>4</sub><sup>2-</sup> under alkaline conditions. Conversely, Cr(III) species often precipitate and are generally immobile. Cr(III) commonly exists as a soluble Cr<sup>3+</sup> cation under low pH conditions, but precipitates as Cr<sub>2</sub>O<sub>3</sub> or Cr(OH)<sub>3</sub> under neutral to alkaline conditions.

Since chromium was used in the form of Cr(VI) in this test, the chromium migrated toward the anode as shown in Fig. 3(a). Most of the chromium was removed from the cathode region, and a large amount of chromium was found in the middle of the soil specimen. Only a small portion of chromium, less than 5%, migrated into the anode reservoir. The distribution of chromium in

the form of Cr(VI) and Cr(III) is also shown in Fig. 3(a). The majority of the chromium was present in Cr(VI) form, and the partial reduction of Cr(VI) to Cr(III) was observed in the three sections near the anode. The low migration of chromium into the anode reservoir may have been caused by adsorption of Cr(VI) under the low pH conditions. In addition, since some Cr(VI) was reduced to Cr(III) in the sections near the anode, the Cr(III) species may have then migrated toward the cathode.

Figs. 3(b and c) show the nickel and cadmium profiles, respectively, along with the pH profiles throughout the soil. From these results, it can be seen that nickel and cadmium successfully migrated toward the cathode and, consequently, large amounts of nickel and cadmium were found in the soil near the cathode. However, the removal of these metals into the cathode reservoir was negligible, and this low removal may have been due to the precipitation of nickel and cadmium that occurred within the soil in the high pH regions near the cathode.

### Acetic Acid Enhancement

As explained in the previous section, when tap water is used as the purging solution, the removal of both Ni and Cd is severely affected by the precipitation of these metals in the soil near the cathode region. This precipitation is due to development of high pH conditions that result from the electrolysis reactions at the cathode. To counter this fixation mechanism, acetic acid was used in the cathode as a purging solution. Acetic acid is a monoprotic acid that has the chemical formula  $\text{CH}_3\text{COOH}$ . In aqueous solutions, acetic acid dissociates partially into the hydrogen ion  $\text{H}^+$ , and partially into the acetate ion  $\text{CH}_3\text{COO}^-$ . The  $\text{H}^+$  ions thus produced can decrease the solution pH and dissolve metal precipitates, while the acetate ion may complex with the other metal ions that are present in the solution. However, the stability constants of acetate-metal complexes are low, and, therefore, acetate-metal complexation is usually not very significant (Stumm and Morgan 1996).

In this study, acetic acid at a concentration of 1 M was used as the purging solution. This concentration has been determined to be adequate in order to maintain a low pH at the cathode (Ugaz et al. 1994). Acetic acid was also used in previous electrokinetic studies for the removal of lead, copper, and radionuclides from clays (Eykholt and Daniel 1994; Ugaz et al. 1994; Reed et al. 1995). Acetic acid has been used in several studies because it is a weak acid and does not increase the conductivity of the soil; therefore, the energy costs are not increased. Additionally, acetic acid is biodegradable, so it is environmentally safe.

Fig. 4 shows the current and electroosmotic flow through the soil specimen for the acetic acid enhancement test. This test was conducted for a total of 120 h. The current increased to a high value of 65 mA in 30 h, then decreased to a low value of 5 mA in 72 h, and then stabilized at this value. The current density was less than  $2 \text{ mA/cm}^2$  throughout the entire test duration. At such low current densities, the heating effects produced by the electric current do not need to be considered (Reed et al. 1995). As shown in Fig. 4, the flow volume toward the cathode increased to about 60 mL in 70 h, and then it decreased to 55 mL in 120 h. The final flow was about 0.2 pore volumes. The electroosmotic flow velocity increased rapidly to a value of  $6 \times 10^{-6} \text{ cm/s}$  during the first 25 h, and then it decreased to approximately  $2 \times 10^{-6} \text{ cm/s}$  after 55 h. The flow velocity then increased to  $7.5 \times 10^{-6} \text{ cm/s}$  after 72 h, and, eventually, it started decreasing toward the end of the testing period. The average electroosmotic velocity observed over the entire test duration was calculated to be approximately

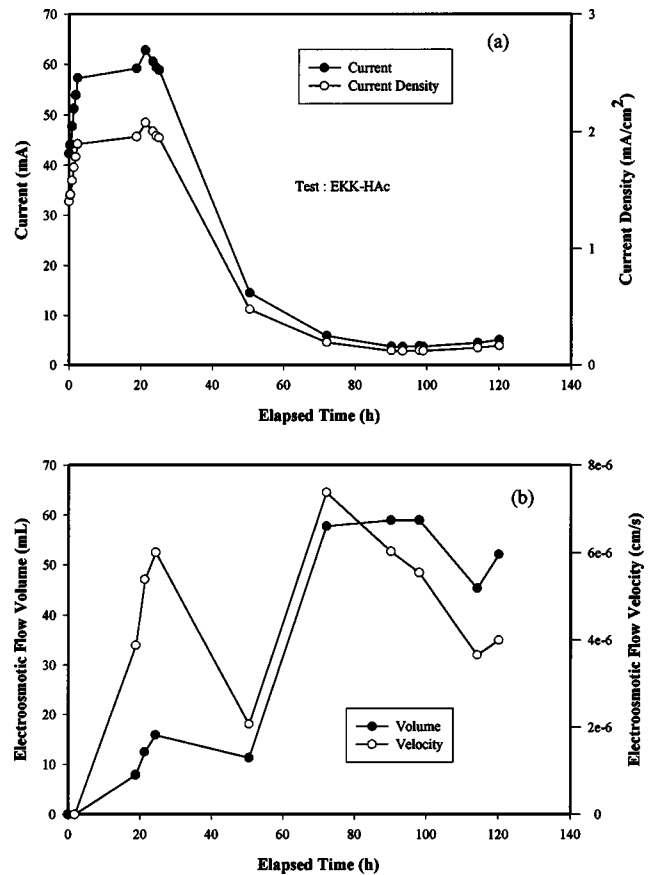


Fig. 4. Current and electroosmotic flow variations: acetic acid enhancement

$4.1 \times 10^{-6} \text{ cm/s}$ . Based on these low electroosmotic flow and flow velocity measurements, it appears that electroosmosis did not significantly induce heavy metal migration, and electromigration was probably the more dominant contaminant transport mechanism.

Fig. 5 illustrates the chromium, nickel, and cadmium distributions along with the pH values after the electrokinetic treatment. The pH profile shows that, although the pH in the cathode reservoir is maintained at approximately 3.5, the pH in the soil near the cathode reached a value of almost 8. These pH values indicate that the cathode reaction may not have been completely depolarized during the experiment. The chromium profile shows that the majority of chromium migrated toward the anode, and all of the chromium was removed from the two soil sections closest to the cathode region. However, as in the unenhanced test, most of the chromium resided in the soil sections that were nearest to the anode region. The low soil pH near the anode may have caused significant adsorption of chromium, thus retarding chromium migration to the anode reservoir. About 20% of the chromium moved into the anode reservoir as compared to about 3% in the unenhanced test. As seen in Fig. 5(a), and as observed earlier in the unenhanced test, some of the total chromium that was initially introduced as Cr(VI) was partially converted to Cr(III). By introducing the acetic acid at the cathode, the pH was lowered at the cathode by introducing  $\text{H}^+$  ions. The acetic acid also introduced acetate ions into the soil, which then migrate toward the anode. However, since chromium-acetate complexes are generally not stable; it seems that the introduction of acetic acid did not greatly affect the migration behavior of the chromium in the soil. Overall,

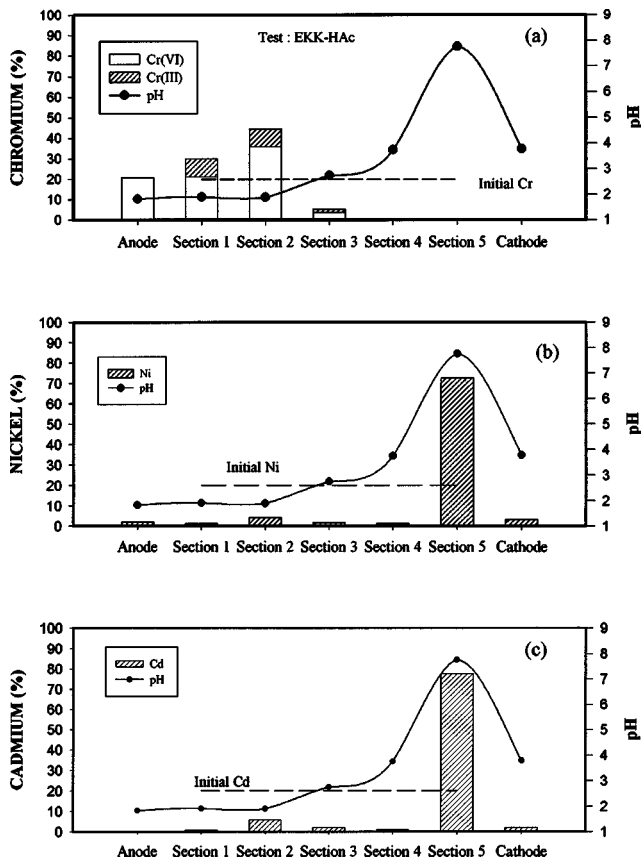


Fig. 5. Contaminant distribution in soil after electrokinetic treatment: acetic acid enhancement

compared to the unenhanced test, these results indicate that the use of acetic acid in the cathode does not significantly affect chromium removal.

The nickel distribution profile is shown in Fig. 5(b). This profile clearly demonstrates the migration of Ni toward the cathode. When the soil pH is below 6, nickel exists in the pore water in ionic form. This may have been the case for the soil sections near the anode where the soil pH was low, thus favoring existence of nickel in the pore water and allowing migration of the nickel

toward the cathode under the induced electric potential. The nickel from most of the low pH soil sections migrated toward the cathode. However, when the nickel encountered the high pH conditions near the cathode, it precipitated as a hydroxide. Although over 70% of the nickel was found in the soil adjacent to the cathode, only about 3% of it actually migrated into the cathode reservoir. By comparing these results to the nickel results from the unenhanced test, it is clearly evident that using acetic acid in the cathode was beneficial and the introduction of acetic acid allowed significantly higher nickel migration toward the cathode.

Fig. 5(c) shows the cadmium profile through the soil specimen after electrokinetic treatment. The migration of cadmium was found to be similar to the migration of nickel. A negligible amount of cadmium was found in all the soil sections except for the section next to the cathode. All of the cadmium that migrated toward the cathode was precipitated as hydroxides in the section closest to the cathode due to high pH conditions. Only about 2% of the total cadmium actually migrated into the cathode reservoir. The use of acetic acid was an improvement over the unenhanced test, where cadmium was found in two sections near the cathode. Thus, using acetic acid in the cathode increased the cadmium migration toward the cathode; however, all of the cadmium accumulated in the last section. In summary, acetic acid was not effective in maintaining the pH below 5 throughout the soil, so it was not successful at removing either nickel or cadmium from the soil.

As mentioned earlier, the addition of acetic acid to the cathode reservoir generates  $H^+$  ions and acetate ions near the cathode. The  $H^+$  ions lowered the pH near the cathode and hindered the transport of the  $OH^-$  ions that were generated by the electrolysis of water into the soil. As a result, the soil pH at the cathode was not expected to increase. Being negatively charged, the acetate ions migrated into the soil due to electromigration. Table 3 gives the stability constants of the nickel-acetate and cadmium-acetate complexes. From Table 3, it can be seen that the stability of nickel and cadmium acetates is very low. Therefore, the formation of such metal complexes is not significant, and hence the migration of nickel and cadmium was not significant. It may be possible for the  $H^+$  ions generated at the cathode to diffuse into the soil and dissolve the metal precipitates that may have formed at the cathode due to high pH conditions. The slow diffusion of  $H^+$  ions into the soil means that longer remediation times for both nickel and

Table 3. Stability Constants of Nickel and Cadmium Complexes

	LIGAND (L)					
	EDTA		Acetate		$OH^-$	
	Complex	Stability constant	Complex	Stability constant	Complex	Stability constant
$H^+$	HL	11.12	HL	4.76	HL	14
	$H_2L$	17.8				
	$H_3L$	21.04				
	$H_4L$	23.76				
	$H_5L$	24.76				
$Ni^{2+}$	NiL	20.4	NiL	1.4	NiL	4.1
	NiHL	24			NiL <sub>2</sub>	9.0
	NiOHL	21.8			NiL <sub>3</sub>	12.0
					NiL <sub>2</sub> (s)	17.2
$Cd^{2+}$	CdL	18.2	CdL	1.9	CdL	3.9
	CdHL	21.5	CdL <sub>2</sub>	3.2	CdL <sub>2</sub>	7.6
					CdL <sub>2</sub> (s)	14.3



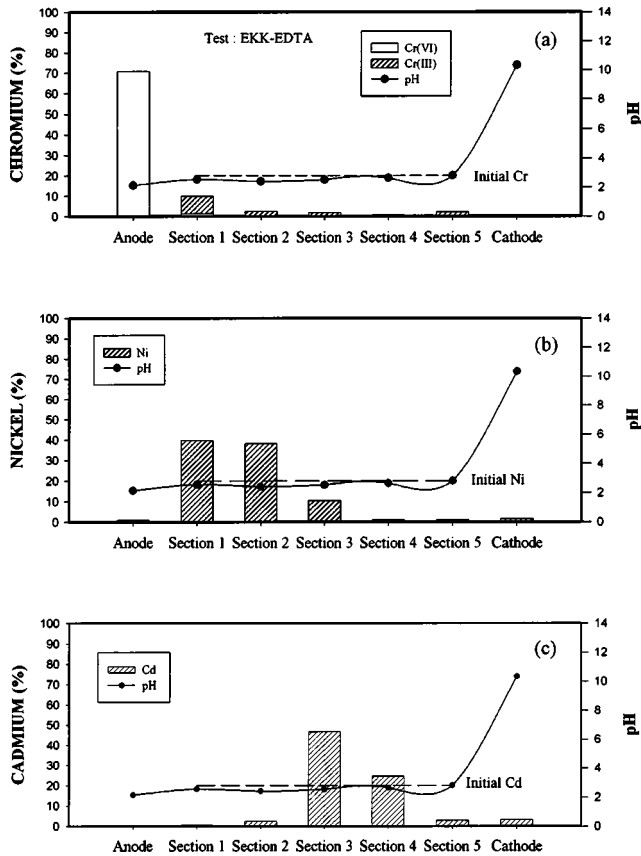


Fig. 7. Contaminant distribution in soil after electrokinetic treatment: EDTA enhancement

Most of the nickel migrated from the soil sections near the cathode and accumulated in the soil sections near the anode. However, only about 1% of the nickel actually migrated into the anode reservoir. The reason for this low migration of nickel into the anode reservoir may be due to the fact that the EDTA formed thermodynamically preferable complexes with  $H^+$  ions. The stability constants of the various EDTA- $H^+$  complexes vary between 11.12 and 24.76. As the nickel-EDTA complex with a stability constant of 20.4 reaches the anode region, EDTA may dissociate from nickel and complex with  $H^+$  instead. Since the dissociated nickel ions are positively charged, they will be repelled from the anode and do not migrate into the anode reservoir. This resulted in a high concentration of nickel near the anode soil sections, and a low amount of nickel removal from the soil.

Fig. 7(c) shows the cadmium profile. Unlike chromium and nickel, most of the cadmium was removed from sections 1 and 2 near the anode as well as section 5 near the cathode. However, the cadmium accumulated in sections 3 and 4. From Table 3, it can be seen that EDTA thermodynamically prefers to form complexes with nickel when both nickel and cadmium are present. Therefore, when EDTA enters the soil from the cathode reservoir, it first forms complexes with nickel. After the nickel has migrated further into the soil toward the anode, the new EDTA molecules entering the soil will then complex with cadmium. Thus, during the initial stages, EDTA-Cd complexation may not be significant, and Cd, existing as the  $Cd^{2+}$  cation, will migrate toward the cathode. However, at later experimental stages, EDTA-Cd complexes may be formed near the cathode, and these complexes will attempt to migrate back toward the anode. Such contradicting directions of cadmium at initial and later stages may have resulted

in cadmium accumulation in the middle of the soil specimen. Overall, cadmium migration into the anode reservoir was negligible, and only approximately 1.7% of the total cadmium was removed into the cathode reservoir. These results suggest that the use of EDTA may be less efficient for cadmium migration as compared to the migration of cadmium in both the unenhanced test and the acetic acid enhanced test.

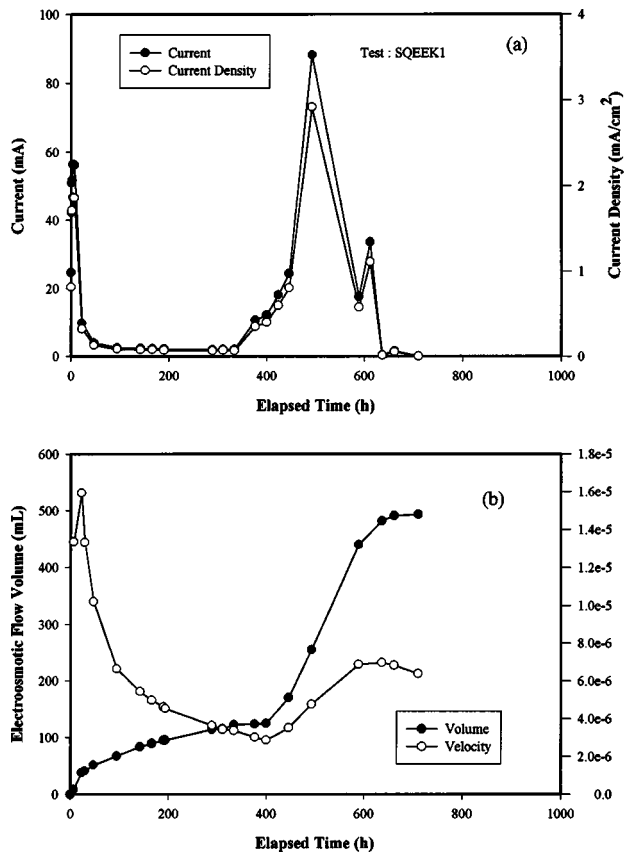
### Sequential Enhancement

As explained in previous sections, the electrokinetic tests performed using 1 M acetic acid or 0.1 M EDTA as purging solutions in the cathode significantly affected the migration of chromium, nickel, and cadmium in the soil. A maximum removal of 70% of the total chromium was achieved with EDTA enhancement; however, only 20% chromium removal was achieved with the acetic acid enhancement. Both nickel and the cadmium removal were low using these two purging solutions. In the acetic acid enhancement test, both the nickel and cadmium migrated and then accumulated very close to the cathode. In the EDTA enhancement test, the migration of Ni and Cd was different from the migration that was observed in the acetic acid enhancement test; however, for both the EDTA and acetic acid enhancement tests, a negligible amount of nickel and cadmium was removed.

Based on these results, it can be concluded that the effective removal of all of the heavy metals chromium, nickel, and cadmium, may not be possible with only a single enhancement; rather, this removal may require a process called sequential enhancement. In the first stage of sequential enhancement used in this study, the contaminants are allowed to migrate toward the respective electrodes without any enhancement. In this stage only tap water was used in the reservoirs. Then, acetic acid was added from the cathode for the removal of cationic contaminants that have already precipitated in the soil close to the cathode. At the later stage of experimentation, an alkaline solution (NaOH) was added from the anode for the removal of anionic contaminants that have been adsorbed to the soil near anode.

In order to test this sequential enhancement approach, two experiments were performed. These experiments have been designated as SQUEEK-1 and SQUEEK-2 (SQUEEK stands for sequentially enhanced electrokinetics). The first test, SQUEEK-1, was conducted by adding tap water from both the electrode reservoirs at the beginning of the test. After 310 h, 1 M acetic acid was introduced into the cathode reservoir and 1 M sodium hydroxide solution was introduced into the anode reservoir. In the second test, SQUEEK-2, tap water was added from both the electrodes at the beginning of the testing; then, after approximately 500 h, 1 M acetic acid was added from the cathode reservoir. After 1,350 h, 1 M sodium hydroxide solution was added from the anode reservoir. The time durations of each stage of purging were decided based upon the heavy metal concentrations and the electrical conductivity in the reservoirs, as well as the electric current and electroosmotic flow values. These two tests were performed to determine if there would be any difference in the removal of the contaminants with the use of the anode and the cathode purging solutions at the same time versus the use of the anode and cathode purging solutions at different times.

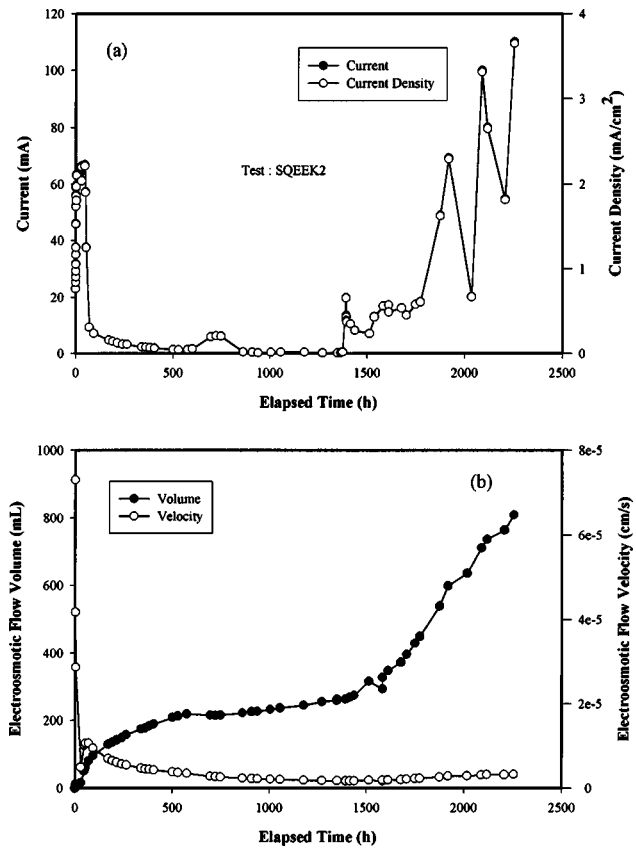
Figs. 8 and 9 show the current, current density, electroosmotic flow, and electroosmotic flow velocity variations with time for SQUEEK-1 and SQUEEK-2, respectively. In both tests, the current reached a high value within a few minutes after the tests began, then it decreased, and finally the current stabilized at a low value within 50 h. The current increased again after the purging solu-



**Fig. 8.** Current and electroosmotic flow variations: sequential enhancement (SQUEEK1)

tions were added at the electrodes. In SQUEEK-1, the current densities increased significantly after the acetic acid and sodium hydroxide were added from cathode and anode reservoirs, respectively. In SQUEEK-2, the highest current densities were observed after the sodium hydroxide was introduced from the cathode reservoir. In both tests, the use of sodium hydroxide increased the conductivity of the soil and was responsible for the high current densities. The electroosmotic flow also increased after the purging solutions were added to both the reservoirs in SQUEEK-1. In SQUEEK-2, the flow rate did not increase after acetic acid was added to the cathode reservoir; however, the flow rate did increase after sodium hydroxide was added to the anode reservoir. Overall, approximately 1.9 of a pore volume of flow was observed in 710 h in SQUEEK-1, and 3.2 pore volumes of flow were observed in 2,250 h in SQUEEK-2. The average electroosmotic velocity was  $6.6 \times 10^{-6}$  cm/s in SQUEEK-1 and  $3.2 \times 10^{-6}$  cm/s in SQUEEK-2.

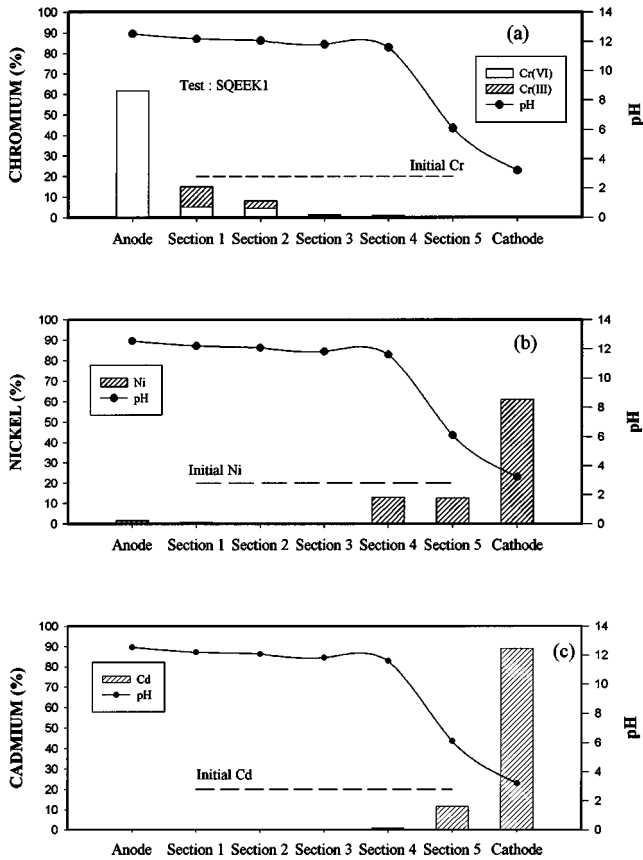
Figs. 10(a) and 11(a) show the chromium profiles along with the pH profiles for both tests SQUEEK-1 and SQUEEK-2, respectively, after the electrokinetic testing. For both tests, the soil pH increased to 12 throughout most of the soil specimen, except in the section closest to the cathode, where the pH was about 6 in SQUEEK-1 and 5 in SQUEEK-2. The high pH through most of the soil was due to the addition of sodium hydroxide, which is a strong base, from the anode reservoir. However, due to the presence of acetic acid, the pH value was low near the cathode. In both tests, about 60% of the chromium migrated into the anode reservoir. In SQUEEK-1, 24% of the chromium was found in the two sections near the anode and a speciation analysis showed that 63% of the total chromium in these two sections existed as



**Fig. 9.** Current and electroosmotic flow variations: sequential enhancement (SQUEEK2)

Cr(III). This Cr(III) may have immediately precipitated as hydroxides due to the high pH as a result of sodium hydroxide usage in the anode reservoir. In SQUEEK-2, the presence of chromium was detected in very small quantities in all of the soil sections. Speciation analysis in this case showed that chromium existed mostly as Cr(III) in all sections of the soil, which was different from the speciation in SQUEEK-1. During the initial stage of both tests, when tap water was used as the purging solution, chromium migration may have been the same. However, in SQUEEK-2, the Cr(III) that was observed near the anode may have existed as a  $\text{Cr}^{3+}$  cation in the pore water due to the low pH. When acetic acid was used in the cathode reservoir and tap water was used in the anode reservoir, the  $\text{Cr}^{3+}$  cations migrated toward the cathode. As soon as the sodium hydroxide was introduced into the anode, the soil pH increased throughout the soil, and that pH increase may have caused Cr(III) to precipitate in all the sections in which Cr(III) was present. This result shows that the actual sequence of using the purging solutions may greatly affect chromium migration and removal. It should be noted that over 70% chromium removal was achieved in the EDTA enhancement test. This high removal may be due to the complexation of EDTA with the Cr(III) that was present near the anode, and the subsequent migration of EDTA-Cr(III) complexes into the anode. The use of EDTA in sequential purging may have a great remediation potential for multiple-metal-contaminated soils; however, this aspect was not investigated in this study.

Figs. 10(b) and 11(b) show the nickel profiles for SQUEEK-1 and SQUEEK-2, respectively. In SQUEEK-1, the nickel migrated toward the cathode and about 60% of the overall nickel migrated into the cathode reservoir. About 10% of the nickel was found in



**Fig. 10.** Contaminant distribution in soil after electrokinetic treatment: sequential enhancement (SQEEK1)

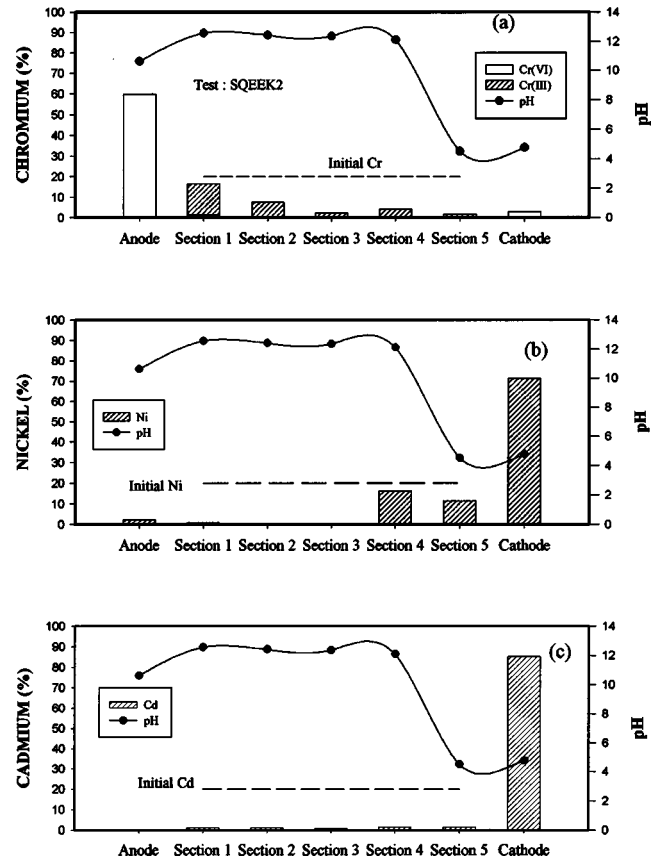
each of the two sections closest to the cathode. The nickel migration in SQEEK-2 was similar to the nickel migration behavior in SQEEK-1. However, in SQEEK-2, a slight increase in the amount of nickel collected in the cathode reservoir was observed as compared to SQEEK-1. In both of the tests, 1–2% of the nickel was found in the anode reservoir, which may be due to the diffusion of nickel in the soil closest to the anode.

Figs. 10(c) and 11(c) show the cadmium profiles for tests SQEEK-1 and SQEEK-2, respectively. Cadmium removal was about 90% in both of these sequentially enhanced tests. In SQEEK-1, the remaining 10% of cadmium was found in the soil section adjacent to the cathode, while all other soil sections were completely free of cadmium. In SQEEK-2, the entire soil specimen contained insignificant amounts of cadmium. Overall, these tests demonstrated that high nickel and cadmium removals could be achieved using sequential enhancement as compared to the other enhancement tests that utilized either acetic acid or EDTA.

## Discussion

### Removal Efficiencies

Figs. 12 and 13 show the overall contaminant removal efficiencies for all of the tests conducted. The removal efficiencies were calculated based on the residual contaminant masses in the soil as well as on the contaminant masses that were obtained in the electrode reservoirs. Based on the residual soil concentrations, Fig. 12 shows that the chromium removal from the soil was 12% in the unenhanced test, 20% using acetic acid enhancement, 83% in the



**Fig. 11.** Contaminant distribution in soil after electrokinetic treatment: sequential enhancement (SQEEK2)

EDTA enhancement test, 71% in SQEEK-1, and 68% in SQEEK-2. Based on the amount of chromium that migrated into the electrode reservoirs, Fig. 13 shows that the chromium removal from the soil was 4% in the unenhanced test, 21% in the acetic acid enhancement test, 71% in the EDTA enhancement test, 62% in SQEEK-1, and 63% in SQEEK-2. The difference in the removal between residual soil concentrations and masses obtained in the electrode reservoirs is attributed to the uncounted contaminant mass that adsorbed to the electrodes.

The test results show that the chromium removal was the highest when EDTA was used in the cathode reservoir as the purging solution. The sequentially enhanced tests yielded chromium removal efficiencies up to 71%, and the remaining chromium in the soil, about 29%, existed in the form of Cr(III). Therefore, using sequential enhancement, all of the chromium in the form of Cr(VI) was removed from the soil, while the remaining chromium existed in the form of Cr(III). Since Cr(III) is less mobile and less toxic than Cr(VI), Cr(III) may not pose a significant environmental risk.

Based on the residual soil concentrations, nickel removal was negligible in the unenhanced test, 19% in the acetic acid enhancement test, 10% in the EDTA enhancement test, 73% in SQEEK-1, and 71% in SQEEK-2. From the amounts of nickel that migrated into the electrode reservoirs, the removal of nickel was negligible in the unenhanced test, 5% in the acetic acid enhancement test, 9% in the EDTA enhancement test, 63% in SQEEK-1, and 73% in SQEEK-2. From Figs. 12 and 13, it can be seen that the nickel removal was the highest using the sequentially enhanced tests as compared to the acetic acid or EDTA enhancement tests. Overall, a maximum amount of 73% of the nickel was removed using the

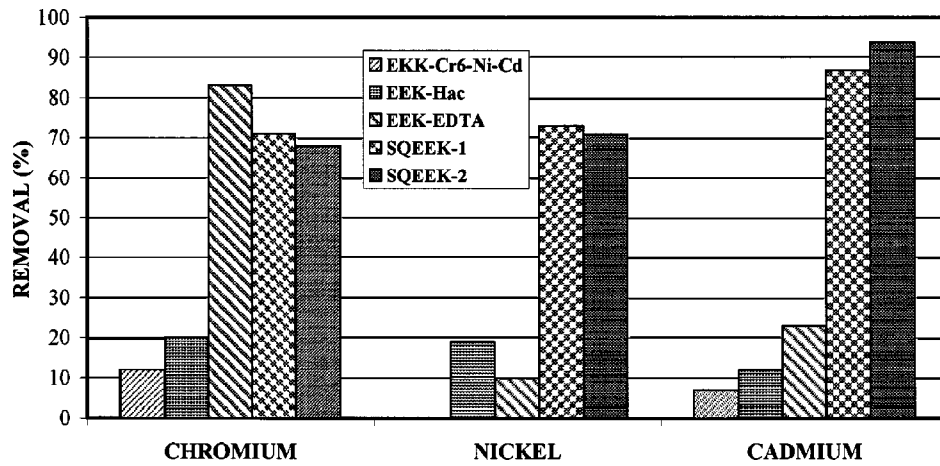


Fig. 12. Removal of heavy metals based on residual soil concentrations

method of sequential enhancement. The remaining nickel existed in the area closest to the cathode, and, consequently, the nickel in this region may be removed by allowing more remediation time for the transport of nickel into the cathode.

Based on the residual soil concentrations, the cadmium removal was 7% in unenhanced test, 12% in the acetic acid enhancement test, 23% in the EDTA enhancement test, 87% in SQEEK-1, and 94% in SQEEK-2. According to the amount of cadmium that migrated into the electrode reservoirs, the cadmium removal was negligible in the unenhanced test, 2% in the acetic acid enhancement test, 2% in the EDTA enhancement test, 80% in SQEEK-1, and 68% in SQEEK-2. The cadmium removal was highest, 87–94%, using sequential enhancement, and in SQEEK-1, the small amount of residual cadmium existed in the soil section adjacent to the cathode. As with nickel, the cadmium removal may also be increased by extending the duration of the electric potential application. Overall, this study demonstrates that sequential enhancement can be effective for the removal of multiple heavy metals from kaolin.

### Energy Expenditure

Fig. 14 shows the energy expenditure in kWh/m<sup>3</sup> of soil processed in all of the experiments that were performed in this study.

The total energy expenditure per unit volume of soil was calculated using the following equation (Hamed et al. 1991):

$$E_u = \frac{1}{V_s} \int VI dt$$

where  $V_s$  = volume of soil processed;  $V$  = voltage difference between the electrodes; and  $I$  = current. From Fig. 14, it can be seen that in all of the tests the energy expenditure increased with time. For the test under unenhanced conditions, the energy expenditure was the lowest of all the tests, approximately 50 kWh/m<sup>3</sup> at the end of 270 h of testing. In the test that used acetic acid in the cathode reservoir, the energy expenditure was approximately 100 kWh/m<sup>3</sup> for the entire duration of 130 h of testing. When EDTA was used in the cathode reservoir, the energy expended was 195 kWh/m<sup>3</sup> for approximately 350 h of testing. The energy expenditure in SQEEK-1 and SQEEK-2 was 400 and 1,300 kWh/m<sup>3</sup>, respectively, for the entire duration of testing.

In SQEEK-1, the energy expenditure during the initial stage of the experiment with tap water in the electrode reservoirs was similar to that in the unenhanced test. However, in this test, the energy expenditure increased rapidly to 400 kWh/m<sup>3</sup> after the electrode purging solutions were introduced into the reservoirs, and then it stabilized after 600 h of processing. In SQEEK-2, the

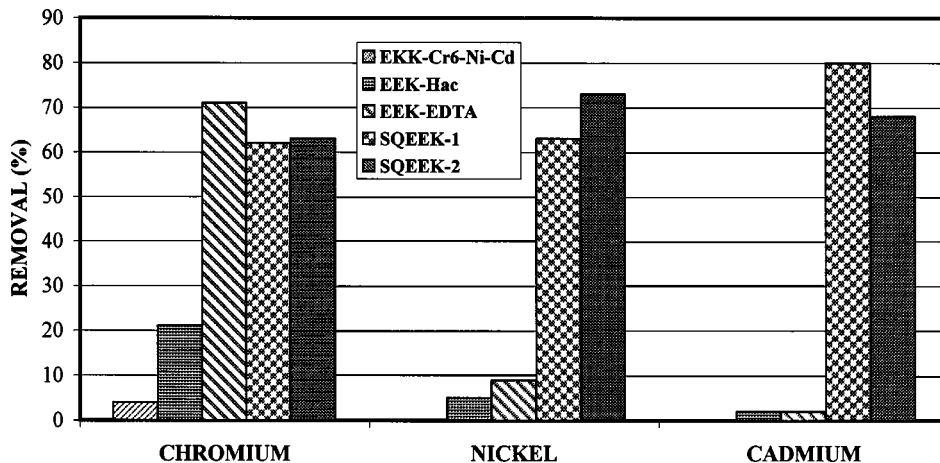


Fig. 13. Removal of heavy metals based on effluent concentrations

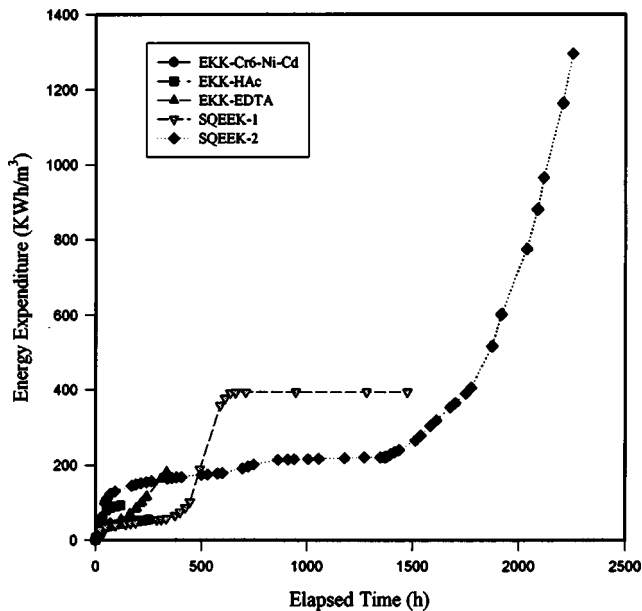


Fig. 14. Energy expenditure for various enhancement tests

energy expenditure increased steadily from the beginning of the experiment, and then it increased rather slowly after acetic acid was introduced into the cathode reservoir. However, the energy expenditure in the SQEEK-2 test increased rapidly after sodium hydroxide was introduced into the system from the anode reservoir.

From the two SQEEK tests, it can be concluded that the introduction of sodium hydroxide may be responsible for a rapid increase in the electric current in the soil due to the increased electrical conductivity of the medium. In the acetic acid enhancement test, the energy expenditure was higher for the duration of the experiment as compared to both the EDTA enhancement test and the SQEEK-1 test. Overall, the energy expended depended on the type of enhancement used and the duration of the experiment. Therefore, when designing an enhanced electrokinetic remediation system, the effect of the purging solution and the effect of test duration on the overall energy expenditure should be thoroughly evaluated in order to minimize the total cost.

### Transport Processes and Geochemistry

In general, the three main contaminant transport processes responsible for contaminant migration toward the electrodes during electrokinetics are electromigration, electroosmosis, and diffusion. The electrical current value reflects the amount of mobile ions in the soil, or the amount of ions that are released from the dissolution of minerals. For this study, the heavy metal contaminants and the use of tap water significantly contributed to the ionic strength of the pore solution. Commonly, within a short period of time, the current reaches a peak value because the mobile ions associated with the soil through the adsorption of ions or ions in the form of salt precipitates are dissolved into the pore solution (Mitchell 1993). As time passes, the current decreases and stabilizes because the initial amount of mobile ions is gradually depleted as they electromigrate toward the respective electrode chamber, where they may concentrate and precipitate or adsorb. The long-term current value is more difficult to understand. Although  $H^+$  and  $OH^-$  ions are generated at the electrodes due to the electrolysis of water, when these ions migrate towards

the opposite electrode, they can meet and react to form water, so they may not significantly contribute to the current (Dzenitis 1997). The  $H^+$  and  $OH^-$  ions may also adsorb to the soil surface and/or cause the dissolution of minerals and/or salt precipitates, and this may lead to a more stable, long-term, supply of charge carriers (Eykholt 1992). Clearly, when purging solutions are used, or even tap water, these solutions supply additional ions for carrying charge. As the ions electromigrate, they transfer momentum to the bulk fluid molecules and generate the electroosmotic flow. As seen from the electroosmotic flow data, however, the electroosmotic advection was low, so, as a contaminant transport mechanism, electroosmosis was probably minor compared to electromigration. The diffusion process also appears to be a slow and minor transport mechanism in all the soil sections, except possibly near the electrodes, where small amounts of heavy metals may have diffused from the soil into the electrode reservoirs. Thus, in these experiments, electromigration was deemed to be the most dominant transport process for contaminant migration into the electrode reservoirs.

In general, the geochemistry of heavy metals is very complex. In addition, the electrolysis reactions that occur due an applied electric field will increase the complexity of the heavy metal geochemistry. Contaminant adsorption, precipitation, and reduction are greatly affected by the type of the soil matrix and by the conditions that develop in the soil due to the electrolysis reactions at the electrodes. Therefore, it should be noted that, due to the complexity of the system, the transient chemistry of heavy metals in the soils cannot be easily delineated.

Under electric fields, extreme pH conditions may develop at the electrodes and in the soils. Under unenhanced conditions, the pH in the low buffering kaolin soil decreased close to the anode and increased near the cathode. Depending on the type of purging solutions and the soil composition, the pH of the soil may change considerably. For example, in the sequentially enhanced tests, when sodium hydroxide was used at the anode reservoir, the pH in the soil increased. On the other hand, the use of acids in the soil may decrease the soil pH. The pH changes in the soil may significantly control the extent of contaminant removal. After electrokinetic treatment, the final soil pH profile that was created should be carefully evaluated, and then the pH may be adjusted to the ultimate desired soil pH using appropriate acidic or alkaline solutions at the particular electrode location.

Based on the results of this study, it would seem feasible that low buffering soils contaminated with multiple heavy metals could be effectively remediated using the sequentially enhanced electrokinetic approach. However, the optimal concentrations for the purging solutions used in the electrode reservoirs have not been determined. Therefore, further research is necessary to develop a cost-effective enhanced electrokinetic system.

### Practical Application

When designing an enhanced electrokinetic system, the electrode solutions should be selected based on the type of soil and the type of contamination in that soil. For multiple heavy metal contaminated soils, sequential electrokinetic remediation is highly recommended based on the results of this study. The selected purging solution should be nontoxic, relatively inexpensive, easily biodegradable, and should not pose any significant environmental risks. The concentration of the electrode purging solutions and the time duration of the remediation process may be the primary concerns for controlling the cost of the process. Therefore, pilot scale tests on soils obtained from the specific contaminated site should be

conducted before applying the sequential method on a full scale basis in order to develop a cost-effective electrokinetic remediation system.

## Conclusions

Based on the experiments conducted in this study, the following conclusions can be drawn:

1. The electrokinetic removal of heavy metals from low buffering soils, such as kaolin, using tap water as the purging solution was very low. The removal of chromium, nickel, and cadmium based on residual soil concentrations was 10, 1.9, and 7%, respectively. The low removal was attributed to Cr(VI) adsorption in the anode region due to low soil pH, and Ni(II) and Cd(II) adsorption/precipitation in the cathode region due to high soil pH.
2. When 1 M acetic acid was used as the purging solution in the cathode, the removal of chromium, nickel, and cadmium was 20, 19, and 13%, respectively. The use of 1 M acetic acid did not significantly affect the migration of chromium in the soil. Depolarization of the cathode electrolysis reaction was only partially achieved by using acetic acid, and thus the acetic acid was ineffective in lowering the soil pH near the cathode. As a result, the nickel and cadmium precipitated near the cathode due to high soil pH conditions, and this precipitation hindered the overall removal of these contaminants. Acetic acid enhancement was not effective in completely removing any of the contaminants used in this study.
3. The chromium removal was the highest using the 0.1 M EDTA purging solution in the cathode. In this case, 70% of the initial chromium was removed into the anode reservoir. The EDTA molecules may have complexed with  $H^+$  ions or they may have adsorbed to the more positively charged soil surface that exists under low pH conditions, and, as a result of this EDTA complexation or adsorption, the previously adsorbed Cr(VI) species were solubilized and migrated into the anode reservoir. Moreover, EDTA may have complexed with the Cr(III) that was present near the anode, and these complexes may have subsequently migrated into the anode reservoir. The nickel and cadmium removal with EDTA was very low due to the preferential complexation of EDTA with  $H^+$  ions in the low pH regions of the anode. Nickel and cadmium dissociated from EDTA, and these dissociated nickel and cadmium ions migrated back toward the cathode.
4. Using the sequentially enhanced electrokinetic remediation approach, the total removal of chromium, nickel, and cadmium was 68–71, 71–73, and 87–94%, respectively. From these results, it can be concluded that for the remediation of multiple heavy metals, sequential conditioning, rather than any single electrode conditioning, is the most effective approach. However, other factors such as the concentration of the purging solutions, total chemical costs associated with the use of the purging solutions, and the energy expenditure of the process need to be optimized by further research.

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