

# Enhanced Electrokinetic Remediation of Heavy Metals in Glacial Till Soils Using Different Electrolyte Solutions

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**Abstract:** Previous electrokinetic remediation studies involving the geochemical characterization of heavy metals in high acid buffering soils, such as glacial till soil, revealed significant hexavalent chromium migration towards the anode. The migration of cationic contaminants, such as nickel and cadmium, towards the cathode was insignificant due to their precipitation under the high pH conditions that result when the soil has a high acid buffering capacity. Therefore the present laboratory study was undertaken to investigate the performance of different electrolyte (or purging) solutions, which were introduced to either dissolve the metal precipitates and/or form soluble metal complexes. Tests were conducted on a glacial till soil that was spiked with Cr(VI), Ni(II), and Cd(II) in concentrations of 1,000, 500, and 250 mg/kg, respectively, under the application of a 1.0 VDC/cm voltage gradient. The electrolyte solutions tested were 0.1M EDTA (ethylenediaminetetraacetic acid), 1.0M acetic acid, 1.0M citric acid, 0.1M NaCl/0.1M EDTA, and 0.05M sulfuric acid/0.5M sulfuric acid. The results showed that 46–82% of the Cr(VI) was removed from the soil, depending on the purging solution used. The highest removal of Ni(II) and Cd(II) was 48 and 26%, respectively, and this removal was achieved using 1.0M acetic acid. Although cationic contaminant removal was low, the use of 0.1M NaCl as an anode purging solution and 0.1M EDTA as a cathode purging solution resulted in significant contaminant migration towards the soil regions adjacent to the electrodes. Compared to low buffering capacity soils, such as kaolin, the removal of heavy metals from the glacial till soil was low, and this was attributed to the more complex composition of glacial till. Overall, this study showed that the selection of the purging solutions for the enhanced removal of heavy metals from soils should be primarily based upon the contaminant characteristics and the soil composition.

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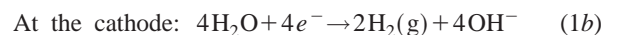
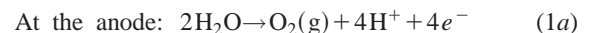
**CE Database subject headings:** Electrokinetics; Soil pollution; Clays; Heavy metals; Soil treatment.

## 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). Innovative methods are needed to treat these sites, and electrokinetics is a process that has shown a great potential for remediating heavy metal-contaminated soils, including low permeable clays and/or heterogeneous soils. Briefly, electrokinetics first involves installing trenches or wells that encompass the contaminated soil zone. Electrodes are then inserted into these trenches or wells, and a low DC voltage gradient or current is applied across the electrodes. The electrodes are strategically located as either cathodes (negatively charged) or anodes (positively charged). Under the induced electric potential, electrokinetic transport mechanisms occur, such as electromigration, electroosmosis, and electrophoresis, which cause the contaminant species to migrate through the soil towards either the cathodes or the anodes (Pamukcu and

Wittle 1992; Probst and Hicks 1993; Acar and Alshwabkeh 1993; Eykholt and Daniel 1994; Segall and Bruell 1995). During the electrokinetic process, or after the process has been completed, the contaminant-laden solution is collected from the electrode compartments/reservoirs. The contaminants can then be extracted from the solution using conventional wastewater treatment techniques.

Although a comprehensive review of the physicochemical processes that are involved in electrokinetics is beyond the scope of this paper, an overview of the processes is presented herein to facilitate an understanding of electrokinetic treatment. Initially, it should be recognized that under an electric potential, the electrolysis of water occurs at the electrodes according to the following reactions:



Thus the electrolysis reactions cause an acidic solution to be generated at the anode and an alkaline solution to be generated at the cathode. Electromigration describes the transport of ionic species, including the metal ions, present in the pore fluid. This process is largely responsible for generating the electrical current, and it includes the migration of  $\text{H}^+$  and  $\text{OH}^-$  ions towards the oppositely charged electrode. Moreover, under an electric potential, electroosmotic flow is produced because the locally existing excess ions migrate in a plane parallel to the particle surface towards the oppositely charged electrode, and, as they migrate, they transfer momentum to the surrounding fluid molecules via viscous forces (Eykholt 1992). Electroosmosis depends on the net amount of ionic migration towards an electrode location, and, in

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low permeability, clayey soils, the net ion migration may be high and it could significantly affect the decontamination process. The following Helmholtz–Smoluchowski (HS) equation is often used to estimate the average electroosmotic flow velocity ( $v_{eo}$ ) (Eykholt and Daniel 1994):

$$v_{eo} = - \frac{D\epsilon_0\zeta}{\eta} E_x \quad (2)$$

According to this equation, the flow velocity is proportional to the electrical gradient ( $E_x$ ), zeta potential ( $\zeta$ ), and dielectric constant ( $D$ ), and it is inversely proportional to the viscosity ( $\eta$ ). The ( $\epsilon_0$ ) term represents the permittivity of vacuum ( $8.854 \times 10^{-12}$  C/V m), and the dielectric constant and viscosity are properties of the pore fluid. The point of zero charge (PZC) refers to the pH at which the net charge on the particle surface is zero. Generally, when the pH is below its PZC, a soil has a positive zeta potential and the electroosmotic flow occurs towards the anode. Conversely, when the pH is above the PZC, the soil has a negative zeta potential and the electroosmotic flow occurs towards the cathode. Alternatively, the electroosmotic flow velocity is given by

$$v_{eo} = K_e E_x \quad (3)$$

where  $K_e$  is referred to as the electroosmotic conductivity. Finally, electrophoresis is the migration of charged colloids, but, in a compact soil system, electrophoresis is less important since colloid-sized particles are generally restrained from movement.

The electrolysis reactions greatly affect the remediation process because the ionic products ( $H^+$  and  $OH^-$ ) may electromigrate and/or be transported by electroosmotic advection towards the oppositely charged electrode location. Thus an acidic ( $H^+$ ) front of solution may move from the anode towards the cathode, and/or an alkaline ( $OH^-$ ) front of solution may move from the cathode towards the anode. The rate of electromigration may also be affected by ionic mobility, and, since hydrogen ions are smaller and have a greater mobility than hydroxyl ions, the acidic front generally moves faster through the soil (Acar and Alshawabkeh 1993). The reaction kinetics, or the rate of the electrolysis reactions at the electrodes, may also affect the generation and movement of the hydrogen and/or hydroxyl ions.

By observing the HS equation, it can be seen that changes in the surface charge of the soil particles (zeta potential) and changes in the pore fluid properties (such as dielectric constant and viscosity) influence the electroosmotic flow. In addition, the electrical gradient may not be uniform through the soil, so the electroosmotic flow is generally not uniform spatially or temporally (Eykholt and Daniel 1994). Therefore the average electroosmotic conductivity ( $K_e$ ) through the soil commonly varies with time, and, as a result of these physicochemical changes, the electroosmotic flow may cease or even reverse in direction.

Several studies have investigated the applicability of electrokinetics for the remediation of soils contaminated with one or more heavy metals (Hamed et al. 1991; Pamucku and Wittle 1992; Reed et al. 1995; Acar et al. 1995; Acar and Alshawabkeh 1996; Yeung et al. 1996; Coletta et al. 1997; Wong et al. 1997; Yang and Lin 1998). Most of these studies used a kaolin clay soil. Kaolin has a low organic content, low acid buffering capacity, consistent mineralogy, it is fairly nonreactive, and it has a low cation exchange capacity (Eykholt 1992). Thus kaolin is a good control soil for laboratory electrokinetic testing because the amount of experimental variation resulting from soil heterogeneity is minimized. In contrast, glacial till is a highly variable clay soil with a relatively high organic content, diverse mineralogy,

and a wider range of particle sizes. Field soils are usually quite heterogeneous, so glacial till is often more representative than kaolin of the soil conditions that are commonly found at contaminated sites. In other words, although testing with kaolin soil is beneficial for analyzing electrokinetic variables, such as the effects produced by the electrolyte solution or voltage gradient, it is inadequate for assessing the effects caused by soil heterogeneities, such as the presence of different minerals and organic matter. In addition, most of the previous electrokinetic investigations only involved a single metal contaminant, often lead, that was artificially contaminated (spiked) into a kaolin soil. At actual contaminated sites, however, several heavy metals often coexist in the soils. Chromium, nickel, and cadmium are the most commonly encountered heavy metals, and they have been found to be present at numerous contaminated sites where glacial soils were predominant (Reddy and Shirani 1997; Reddy et al. 1997).

A few studies have been performed on the geochemical characterization of heavy metals in high acid buffering glacial till soils, and these studies revealed that a significant amount of hexavalent chromium migration occurred towards the anode under the application of an electric potential (Reddy and Parupudi 1997; Chinthamreddy 1999; Chinthamreddy and Reddy 1999; Reddy and Chinthamreddy 1999). The migration of the cationic contaminants, such as nickel and cadmium, however, was limited in the glacial till soil. Since glacial till has a high acid buffering capacity, it neutralizes the acid generated by the electrolysis reaction at the anode. Consequently, during the electrokinetic process, the glacial till soil-solution maintains a high pH and, typically, the cationic contaminants often adsorb to the soil particles or precipitate at these high pH values. It should be recognized that the success of the electrokinetic remediation process is highly dependent upon the ability of the contaminants to migrate, and, for substantial heavy metal transport to occur, it is essential that the contaminant species are desorbed from the soil and they are converted to a soluble or dissolved form.

To enhance the migration of heavy metals in soils, appropriate purging solutions can be introduced, and these solutions act by either dissolving the metal precipitates or by forming soluble complexes with the metals. Since the electrokinetic process is usually performed in situ and may require a significant quantity of solution, the purging solutions should be nontoxic, effective, and economical. Reddy and Chinthamreddy (2003) evaluated different purging solutions for kaolin and found that heavy metal removal can be increased significantly by using appropriate cathode and anode solutions. This paper presents the results of a complementary experimental study that was performed to assess different purging solutions for the removal of Cr(VI), Ni(II), and Cd(II) from glacial till.

## Experimental Methodology

### Electrokinetic Test Setup

Fig. 1 shows the schematic of the electrokinetic test setup used for this study. The setup consists of an electrokinetic cell, two electrode compartments, two electrode reservoirs, a power source, and a multimeter. Each electrode compartment contains a valve to control the flow into the cell, a slotted graphite electrode, and a porous stone. The electrode compartments were connected to the ends of the cell using screws. The electrode reservoirs were made of 3.8 cm i.d. Plexiglas tubes and were connected to the electrode compartments using Tygon (rubber) tubing. The electrode reservoirs were graduated to measure inflow and outflow. Exit ports

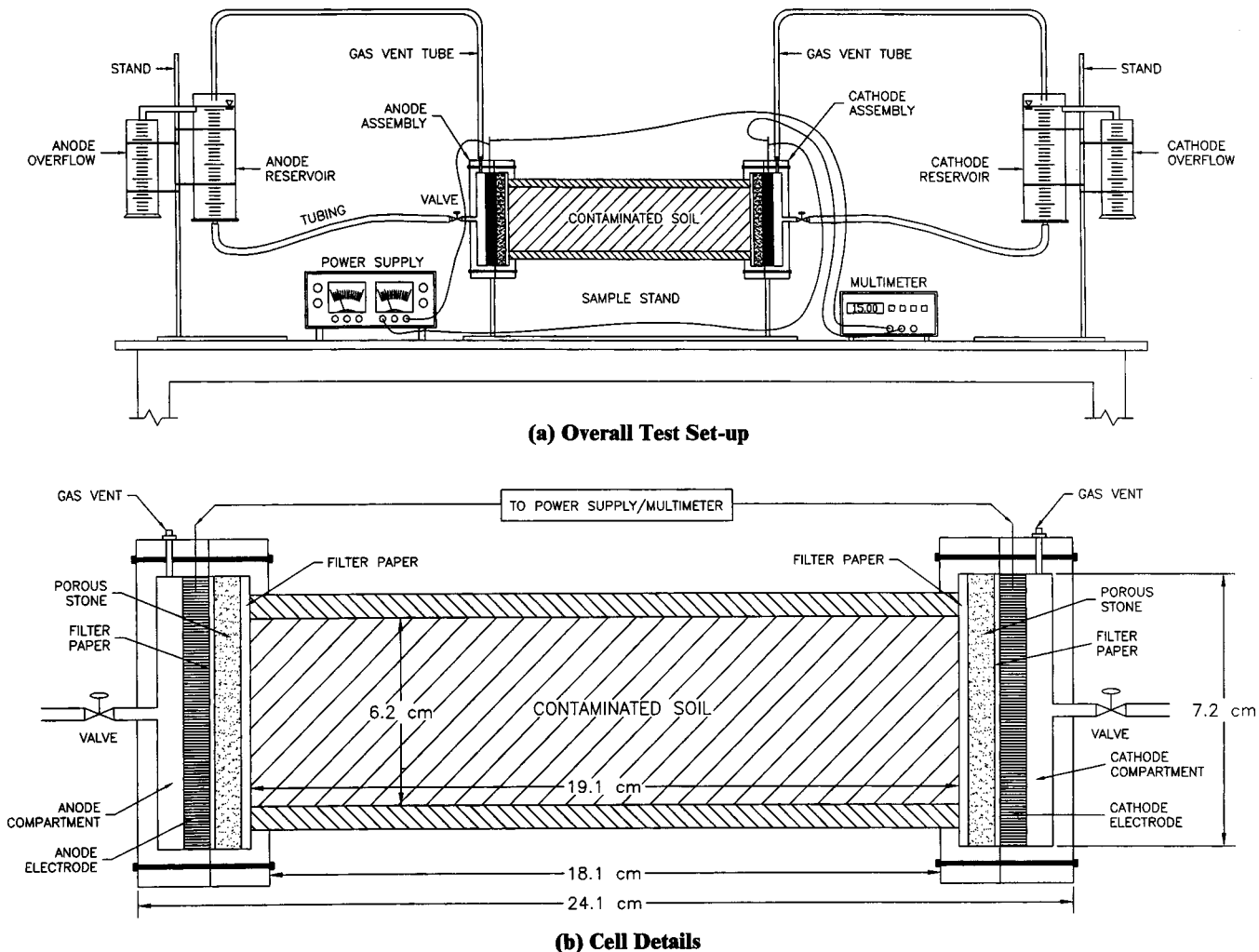


Fig. 1. Bench-scale electrokinetic test setup

were created in the electrode compartments and thin tubes were then inserted into these ports to allow the gases that are generated from the electrolysis of water to escape. The other end of these gas tubes was connected into the reservoirs to collect any liquid that was removed along 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 testing. For additional information, refer to Reddy et al. (1997), which provides a detailed description of this same setup.

### Test Variables

Glacial till 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 glacial till soil was spiked with Cr(VI), Ni(II), and Cd(II) in concentrations of 1,000, 500, and 250 mg/kg, respectively, for all of the experiments to simulate typical electroplating waste contamination. A total of six different tests were performed to investigate the effect of different electrode purging solutions on electrokinetic remedial efficiency, as summarized in Table 2. The description, and rationale, of these different purging solutions is as follows. For the EKG-Untreated test, tap water was employed in both the cathode and anode reservoirs, and this test was

conducted to serve as a baseline test for comparison purposes. For the EKG-EDTA test, EDTA (ethylenediaminetetraacetic acid) was used at a 0.1M concentration in the cathode reservoir while tap water was used in the anode reservoir. EDTA was used in this test to solubilize the contaminants by forming EDTA-metal complexes. The EDTA-metal complexes are anionic, so the EDTA was used in the cathode reservoir because the molecules and complexes were expected to migrate through the soil towards the anode. For the EKG-Hac test, acetic acid ( $\text{CH}_3\text{COOH}$ ,  $\text{pK}_{a1} = 4.76$ ) was used at a 1.0M concentration in the cathode reservoir while tap water was used in the anode reservoir. Acetic acid was used to neutralize the electrolysis reaction at the cathode, so the pH would remain low in the cathode region and the adsorption/precipitation of cationic species would be prevented. For the EKG-Citric Acid test, citric acid [ $\text{C}_3\text{H}_4\text{OH}(\text{COOH})_3$ ,  $\text{pK}_{a1} = 3.13$ ,  $\text{pK}_{a2} = 4.72$ ,  $\text{pK}_{a3} = 6.33$ ] was used at a 1.0M concentration in the cathode reservoir while tap water was used in the anode reservoir. Since citric acid is a multiprotic acid, it was hypothesized that it may be more effective at neutralizing the electrolysis reaction at the cathode, and/or it may complex with heavy metals. In an aqueous solution, the citric acid molecule dissociates into three hydrogen ions and a citrate ligand. Citrate is a tridentate ligand ( $\text{Cit}^{3-}$ ), which means that it can complex with a metal ion at three different locations. For the EKG-EDTA-

**Table 1.** Composition and Properties of Glacial Till Soil (Reddy et al. 1997; Reddy and Parupudi 1997; Chinthamreddy 1999)

Property	Value
Mineralogy	Quartz: 31%
	Feldspar: 13%
	Carbonate: 35%
	Illite: 15%
	Chlorite: 4–6%
	Vermiculite: 0.5%
	Smectite: trace
Particle size distribution (ASTM D 422)	
Gravel	0 %
Sand	20 %
Silt	44 %
Clay	36 %
Atterberg limits (ASTM D 2487)	
Liquid limit	21.7 %
Plastic limit	11.7 %
Plasticity index	10.0 %
Specific gravity (ASTM D 854)	2.71
Moisture-unit weight relationships (Harvard Miniature Compaction Test)	
Maximum dry unit weight	18.5 kN/m <sup>3</sup>
Optimum moisture content	14.5 %
Hydraulic conductivity	$4.1 \times 10^{-8}$ cm/s
Cation exchange capacity (ASTM D 9081)	13–18 meq/100 g
pH (ASTM D 4972)	8.2
Organic content (ASTM D 2974)	2.8 %
USCS classification (ASTM D 2487)	CL

NaCl test, the test conditions were similar to the earlier test that employed 0.1M EDTA in the cathode reservoir, but, for this test, NaCl was used at a 0.1M concentration in the anode reservoir. In this test, it was theorized that the presence of NaCl would help to increase the electrical conductivity of the pore solution and generate a more sustained electrical current. Lastly, for the EKG<sub>T</sub>-H<sub>2</sub>SO<sub>4</sub> test, tap water was used in both electrode reservoirs for 800 h and then sulfuric acid (H<sub>2</sub>SO<sub>4</sub>, pK<sub>a1</sub> < 0, pK<sub>a2</sub> = 1.99) was used at a 0.5M concentration in the cathode reservoir and at a 0.05M concentration in the anode reservoir. This test was conducted for an 800 h time interval to allow the removal of Cr(VI), then the sulfuric acid was used in both the anode and cathode reservoirs to dissolve the cationic contaminants (Ni and Cd).

## Testing Procedure

Approximately 1,100 g of dry glacial till soil was used for each test. Potassium chromate, nickel chloride, and cadmium chloride were used as sources of the heavy metals, Cr(VI), Ni(II), and Cd(II), respectively, and these chemical compounds are all highly soluble in water. The required amount of these chemicals that would yield the desired concentration was weighed, and each chemical was dissolved individually in deionized water. A total of 285 mL of deionized water (for 25% soil moisture content) was used to represent typical field moisture conditions. The soil was then placed in a high-density polyethylene (HDPE) container and the individual contaminant solutions were added and mixed thoroughly with the soil using a stainless steel spatula. The spiked soil was then placed in the electrokinetic cell in layers and compacted uniformly using a hand compactor. The soil-contaminant mixture was then equilibrated for 24 h. The pH, redox potential, and electrical conductivity (EC) were measured for the soil remaining in the HDPE container, before and after the equilibration period. The initial and final weights of the HDPE container, before and after packing the cell, were used to determine the exact amount of contaminated soil that was present in the electrokinetic cell.

After the cell was packed with soil, the electrode compartments were attached using screws, and then they were connected to the anode and cathode reservoirs using the Tygon tubing. The reservoirs were filled with potable water or the chosen electrolyte solution. Potable water was selected because it is the most probable source of replenishing fluid at field-contaminated sites. The elevations of the electrolyte solutions in both reservoirs were kept the same to prevent a hydraulic gradient from forming across the specimen. Since electrolyte solutions were relatively dilute solutions and had similar densities, thus the density of electrolyte solutions would not significantly affect the hydraulic gradient so as to impact the contaminant transport. The initial pH, redox potential, and electrical conductivity of the potable water was  $7.7 \pm 0.1$ ,  $150 \pm 25$  mV, and  $280 \pm 20$   $\mu$ S/cm, respectively. The total dissolved solids and hardness of the potable water were approximately 200 and 60 mg/L as CaCO<sub>3</sub>, respectively. A constant voltage gradient of 1.0 VDC/cm was applied to the soil sample. The electric current across the soil sample as well as the electroosmotic 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 tests were terminated based on the analysis of several factors, including the current, electroosmotic flow, electrical conductivity, and cumulative mass removal. Generally, the test was stopped when the current stabilized, no significant change in the electroosmotic

**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> )	Redox (mV)	
1	EKGT-Unenhanced	H <sub>2</sub> O	H <sub>2</sub> O	160	24.9	1.6	6.97	199
2	EKGT-EDTA	H <sub>2</sub> O	0.1M EDTA	975	25.0	1.6	7.08	213
3	EKGT-Hac	H <sub>2</sub> O	1.0M Acetic acid	690	24.3	1.6	7.07	213
4	EKGT-Citric Acid	H <sub>2</sub> O	1.0M Citric acid	600	24.8	1.6	7.11	161
5	EKGT-EDTA-NaCl	0.1M NaCl	0.1M EDTA	2,300	24.1	1.6	7.26	113
6	EKGT-H <sub>2</sub> SO <sub>4</sub>	$t=0-800$ h: H <sub>2</sub> O $t=800-1,900$ h: 0.05M H <sub>2</sub> SO <sub>4</sub>	$t=0-800$ h: H <sub>2</sub> O $t=800-1,900$ h: 0.5M H <sub>2</sub> SO <sub>4</sub>	1,900	23.4	1.7	7.04	196

flow was observed, no change in the electrical conductivity of the electrode reservoir solutions was observed, and/or no additional contaminant concentrations were measured in the effluent. The maximum test duration was around 2,300 h.

At the end of each test, aqueous solutions from the anode and cathode reservoirs and the electrode assemblies were collected and final volume measurements were made. The reservoirs and the electrode compartments 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, a 10 g moist soil sample was taken and mixed with 10 mL of deionized water in a glass vial. The mixture was shaken thoroughly by hand for a few minutes and then the solids were allowed to settle. The pH, redox potential, and the electrical conductivity were measured for each soil sample as well as for the aqueous solution in each electrode reservoir. The moisture contents of each soil section were also determined.

### Chemical Analysis and Quality Assurance

The different soil sections were acid digested in accordance with the U.S. EPA 3050 procedure and analyzed using an atomic absorption spectrophotometer (AAS) to determine the concentrations of total chromium, nickel, and cadmium (U.S. EPA 1986; Reddy and Chinthamreddy 2003). The AAS analyses were done in accordance to U.S. EPA method 7190 for chromium, 7520 for nickel, and 7310 for cadmium (U.S. EPA 1986). Aqueous samples from the electrode reservoirs were directly tested using the AAS to determine the contaminant concentrations. Alkaline digestion was performed on soil sections in accordance with the U.S. EPA 3060A procedure, which extracts only Cr(VI) into the solution (U.S. EPA 1986; Reddy and Chinthamreddy 2003). The solution was analyzed using AAS to determine the concentration of Cr(VI). The Cr(III) concentrations were calculated by subtracting Cr(VI) concentrations from the total chromium concentrations determined based on the acid digestion procedure.

The reproducibility of the testing procedures and the results were 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 electrode compartments were soaked in a dilute acid solution for 24 h. These components were rinsed first with tap water and then with deionized water to avoid any cross-contamination between the experiments. (3) Chemical analyses were performed in duplicates. (4) The AAS calibration was checked after testing every five samples. (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 and to the possible adsorption of contaminants onto the electrodes and porous stones.

### Results and Discussion

The test duration, as well as the results of the initial water content, dry density, pH, and redox potential measurements performed on the soil prior to the application of the electric field are presented in Table 2 for each test condition. From this table, it can be seen that the initial soil conditions were similar for all the tests.

The water content was approximately  $24 \pm 1\%$ ; the dry density was approximately  $1.6 \pm 0.5 \text{ g/cm}^3$ ; the pH was in the neutral range of approximately  $7.1 \pm 0.15$ ; and the redox potential was slightly oxidizing.

The coefficient of electroosmotic conductivity ( $K_e$ ) was calculated for each test as follows:

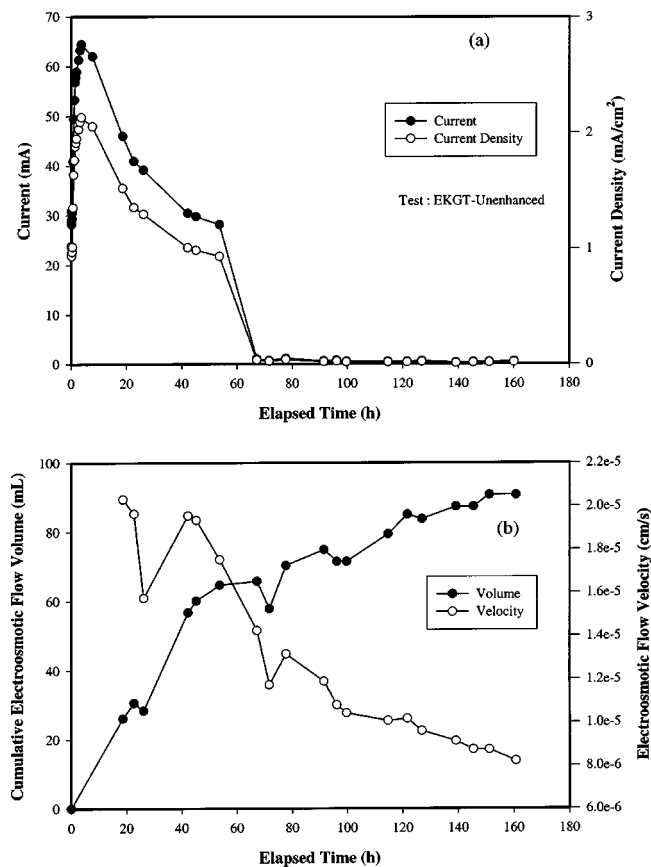
$$K_e = \left( \frac{Q}{t} \right) \left( \frac{1}{A} \right) \left( \frac{L}{\Delta E} \right) \quad (4)$$

where  $Q$  = volume of flow;  $t$  = time period;  $A$  = cross-sectional area of the sample;  $L$  = length of the sample; and  $\Delta E$  = average electric potential difference applied across length of the soil specimen. For all the experiments in this study, a 1.0 VDC/cm voltage gradient ( $E_x = \Delta E/L$ ) was applied, so the magnitude of the electroosmotic conductivity ( $K_e$ ) was the same as the magnitude of the electroosmotic velocity ( $v_{eo} = K_e E_x$ ). The average electroosmotic conductivity for the tests that used different electrode purging solutions varied between  $6.0 \times 10^{-6}$  and  $1.25 \times 10^{-5} \text{ cm}^2/\text{s V}$ . Under the experimental conditions, the hydraulic gradient was prevented from developing across the soil sample; therefore, hydraulic or Darcy's flow was not expected to occur. The hydraulic conductivity of the glacial till used in this study was approximately  $4.1 \times 10^{-8} \text{ cm/s}$ , and even if the hydraulic gradient were as large as 1 cm/cm, the electroosmotic flow in the tests was two to three orders of magnitude greater than the Darcy's flow.

For each of the six tests, the current, current density, electroosmotic flow volume, and electroosmotic flow velocity were plotted versus the elapsed time. Then, after the tests were terminated, the extruded soil was analyzed, and the percentage of the contaminant mass that existed in the soil was plotted versus the distance from the anode electrode. These plots also include the percentage of contaminant mass that was removed into each of the electrode reservoirs as well as the pH that existed in the soil and in the reservoirs at the conclusion of testing. The following discussion presents a brief description and analysis of these results for each of the electrokinetic tests.

### Unenhanced Condition

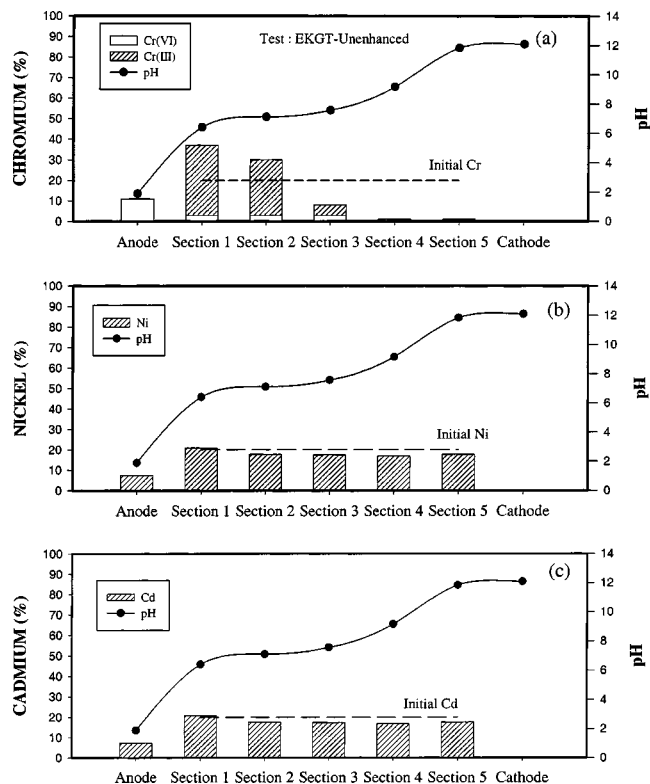
Unenhanced condition refers to the test conducted using tap water as the purging solution in both the anode and cathode reservoirs. As seen in Fig. 2(a), the current increased to its peak value within a few hours, and then it gradually decreased to a low value after approximately 70 h. The highest current density was less than  $2.2 \text{ mA/cm}^2$ . The current or current density is an indication of the amount of ion electromigration that is occurring. Initially, there is a high ionic strength due to the dissolution of salts or contaminants that were associated with the dry soil particles (Mitchell 1993), but, as time passes, these mobile ionic species are depleted as they electromigrate towards the oppositely charged electrode. This same basic trend of a peak current value within a few hours followed by a gradual reduction in current over a much longer duration was seen in all the electrokinetic tests. In the electrode regions, the ionic species may be adsorbed to the soil surface or to the electrode and/or they may react or become neutralized by oppositely charged chemical species. Although the electrolysis of water generates additional ions ( $\text{H}^+$  at the anode and  $\text{OH}^-$  at the cathode) that subsequently electromigrate towards the oppositely charged electrode, this usually does not significantly increase the current. Therefore it is common for the current to reduce with time unless amendments, such as ionic purging solutions, are applied to replenish ions to the soil-solution system.



**Fig. 2.** Variation of (a) current and current density, and (b) electro-osmotic flow volume and velocity: unenhanced condition

Fig. 2(b) shows that the cumulative electroosmotic flow volume rapidly increased at the beginning of the experiment, but, over time, the amount of flow reduced, and it was negligible by the end of testing. This figure also shows that the electroosmotic flow velocity generally decreased throughout the test. It should be noted that for all six electrokinetic experiments, the volume of flow increased at the cathode, so for each test, the predominant migration of excess ions (cations) was towards the cathode. Since electroosmosis is primarily driven by electromigration, the current usually correlates to the electroosmotic flow, or flow velocity, and this behavior is evident in Fig. 2(b). Incidentally, when the ionic concentration is high, the thickness of the diffuse double layer reduces, which may constrict the electroosmotic flow (Mitchell 1993). Consequently, near the end of testing, when the ion concentration has been reduced, the flow may be comparatively high even though the current is low. This is because the thickness of the diffuse double layer has increased, and this may partially explain why the electroosmotic flow was still appreciable even after the current had reduced substantially.

Fig. 3 shows the distribution of chromium, nickel, and cadmium in the soil and also in the electrode reservoirs along with the pH distribution. The chromium distribution profile in Fig. 3(a) shows the speciation of chromium and whether it was present as the Cr(VI) or Cr(III) form. Cr(VI) (the initial form that was spiked into the soil) commonly exists as an anionic species or complex, whereas Cr(III) usually exists as a cationic species or a cation (Chinthamreddy 1999). During electrokinetics, Cr(VI) species migrate towards the anode, but Cr(III) species migrate to-

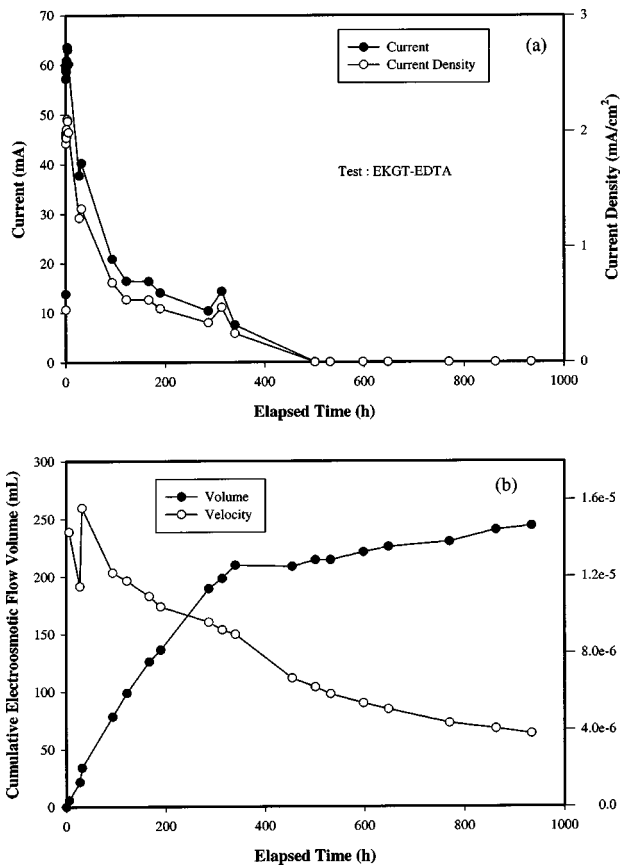


**Fig. 3.** Distribution of (a) chromium, (b) nickel, and (c) cadmium in the soil after electrokinetic treatment: unenhanced condition

wards the cathode. Cr(VI) generally adsorbs to the soil under low pH conditions, however, Cr(III) adsorbs or precipitates under high pH conditions.

As seen in Fig. 3, compared to the initial pH values, which were close to neutral, the pH changed significantly in the soil near the electrodes and, particularly, in the solution reservoirs. As explained earlier, the changes in pH that occur are a result of the electrolysis reactions. The high acid buffering capacity of the soil was attributed to the 35% carbonate content of glacial till, and, as expected, the carbonates buffered the acidic solution generated at the anode. The pH values through most of the soil remained substantially higher than the pH values measured in the anode reservoir or in the soil region adjacent to the anode.

As illustrated by Fig. 3(a), the chromium concentrations in the soil sections near the cathode were negligible, which indicates that Cr(VI) migrated towards the anode. The chromium speciation, however, indicates that most of the chromium that migrated towards the anode was then reduced to Cr(III). Furthermore, since Cr(VI) was reduced to Cr(III), it either adsorbed to the soil or precipitated under the high pH conditions that existed by the anode (due to the high buffering capacity of glacial till). The reasons why Cr(VI) was reduced to Cr(III) need to be explored further, but it may have been due to the organic matter in the glacial till, due to reactions in the soil with electron donating species, and/or due to the electrolysis reaction at the anode. As shown in Figs. 3(b and c), the migration of nickel and cadmium was negligible. These cations or cationic species were adsorbed or precipitated throughout the soil as a result of the high pH conditions that existed. Small amounts of nickel and cadmium, however, were measured in the anode reservoir. Apparently, the low pH solution in the anode reservoir may have allowed some dissolution of these metals in the soil adjacent to the anode, and

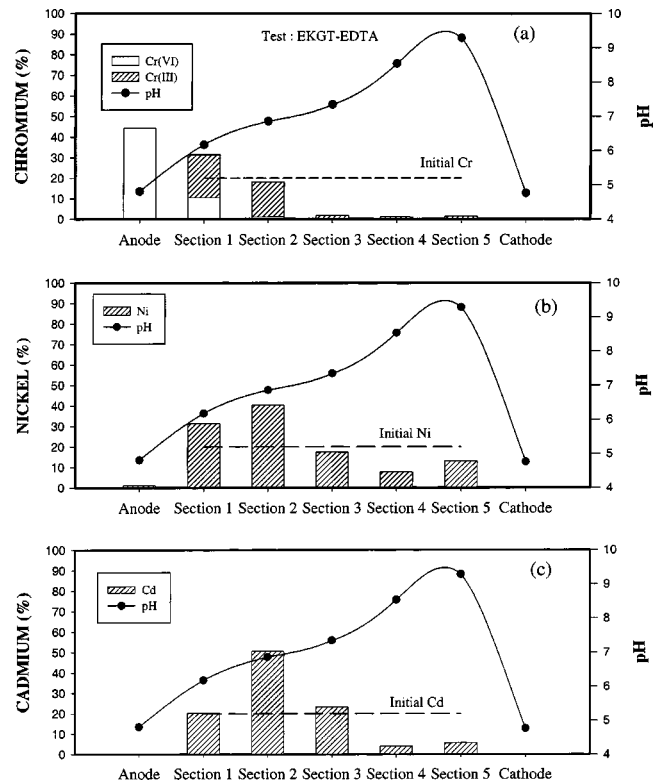


**Fig. 4.** Variation of (a) current and current density, and (b) electro-osmotic flow volume and velocity: ethylenediaminetetraacetic acid (EDTA) enhancement

these cations subsequently diffused into the anode reservoir. This diffusion, however, did not significantly contribute to contaminant removal.

#### Ethylenediaminetetraacetic Acid Enhancement

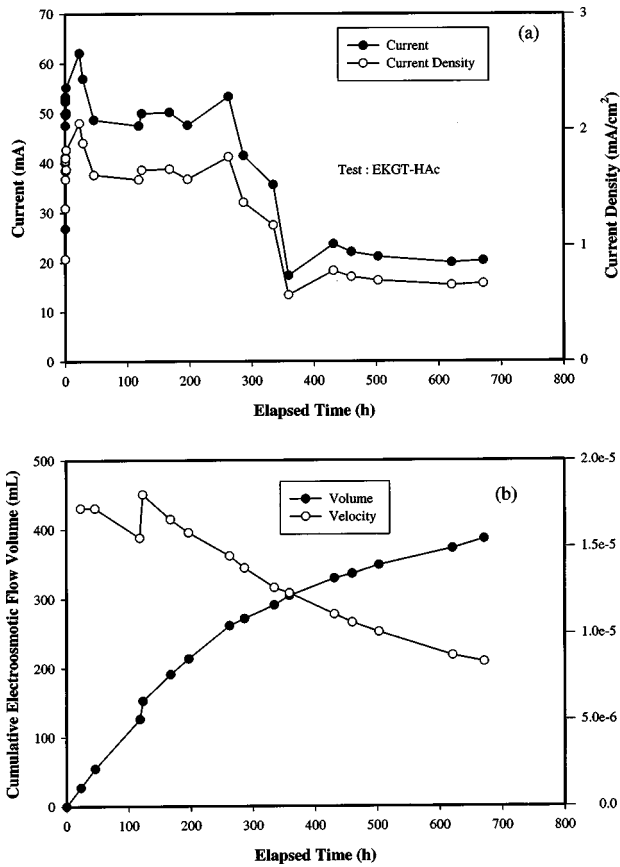
As shown in Fig. 4(a), the electrical current and current density in the test using 0.1M EDTA at the cathode followed the same trend as in the test without enhancement. The current reached a peak value of 65 mA within a few hours after the test was started, and then the current decreased to a negligible value after approximately 500 h. The maximum current density was less than 2.2 mA/cm<sup>2</sup>. Compared to the test without enhancement, the current in the EDTA test was more sustained, and this is attributed to the presence of EDTA, which may have increased the current by introducing EDTA-metal complexes and/or by replenishing the soil-solution system with additional or exchangeable ions. The electroosmotic flow also correlated with the current, and it was initially high but reduced substantially as the current subsided [Fig. 4(b)]. Although the peak current values in the unenhanced and EDTA tests were nearly the same initially, by comparing Figs. 2 and 4, it can be seen that the more sustained current in the EDTA enhancement test generated a prolonged electroosmotic flow that resulted in a higher cumulative volume. The electroosmotic flow in the unenhanced test essentially stopped after only 160 h, producing about 90 mL, whereas in the EDTA enhanced test, the flow was appreciable for nearly 400 h, producing around 210 mL.



**Fig. 5.** Distribution of (a) chromium, (b) nickel, and (c) cadmium in the soil after electrokinetic treatment: ethylenediaminetetraacetic acid (EDTA) enhancement

Fig. 5 illustrates the distribution of chromium, nickel, and cadmium as well as the pH profile at the conclusion of the EDTA electrokinetic test. The pH profile in Fig. 5 was comparable to the pH profile in the unenhanced test seen in Fig. 3, however, the pH in the EDTA test was substantially lower in the soil region adjacent to the cathode and much lower in the cathode reservoir. This indicates that the 0.1M EDTA solution was partially successful at neutralizing the OH<sup>-</sup> ions that were generated by the electrolysis reaction at the cathode. In addition, it appears that the EDTA may have substituted or exchanged sorption sites with anionic Cr(VI) species, and this resulted in greater chromium solubility and migration into the anode reservoir. Fig. 5(a) shows that nearly 45% of the chromium was removed at the anode reservoir, and the chromium concentrations were negligible in the three soil sections nearest to the cathode. The chromium speciation shows that, except for the soil very close to the anode, the chromium remaining in the soil reduced to the Cr(III) form. The chromium in the Cr(III) form may have adsorbed or precipitated in the soil since the pH in this region was higher than 6. Since EDTA forms stable complexes with Cr(III), increasing the processing time may have increased the chromium removal.

As observed in Figs. 5(b and c), some nickel and cadmium migration occurred, which was contrary to the unenhanced test, where these contaminants precipitated without any migration. It seems that the negatively charged EDTA-nickel and EDTA-cadmium complexes moved towards the anode, but as the pH became lower, it was thermodynamically favorable for the EDTA to complex with H<sup>+</sup>. Lindsey (1979) explains that due to the large number of species and equilibria involved, the stability-pH determination for chelates, such as EDTA, in soils can be complex. Under the low pH conditions near the anode, the nickel or



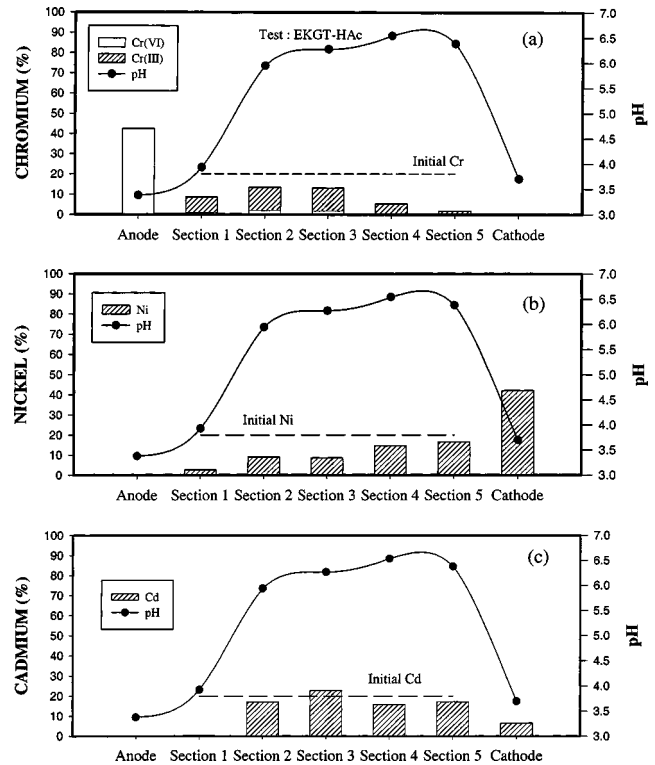
**Fig. 6.** Variation of (a) current and current density, and (b) electro-osmotic flow volume and velocity: acetic acid enhancement

cadmium ions dissociated from the EDTA complex, and it seems that they adsorbed or precipitated without any further migration. Compared to the test without enhancement, however, it is evident that the EDTA solution was somewhat effective at causing nickel and cadmium migration and reducing their concentrations in the soil sections near the cathode. The migration of these nickel/cadmium EDTA complexes may have also been hindered due to their large size and their direction of migration, which opposed the direction of electroosmotic flow.

### Acetic Acid Enhancement

Fig. 6(a) shows that the test using acetic acid enhancement had a high and sustained electrical current and current density compared to the previously discussed tests. In the unenhanced and EDTA tests, the current dropped below 40 mA after about 40 h, but in the acetic acid test, the current remained above or near 40 mA, or current density remained above or near 1.3 mA/cm<sup>2</sup>, for nearly 300 h before decreasing. Compared to the earlier tests, the current and current density remained high and were still at around 20 mA and 0.6 mA/cm<sup>2</sup>, respectively, after almost 700 h. Corresponding to the high and sustained current in the acetic acid test, the electroosmotic flow volume, shown in Fig. 6(b), was substantially higher than the earlier tests, and around 400 mL were produced after 700 h of testing.

Fig. 7 shows that the pH values remained below 7.0 throughout the soil, which was lower than in the unenhanced or EDTA tests. This indicates that, as expected, the 1.0M acetic acid was better than the 0.1M EDTA for partially neutralizing the OH<sup>-</sup>

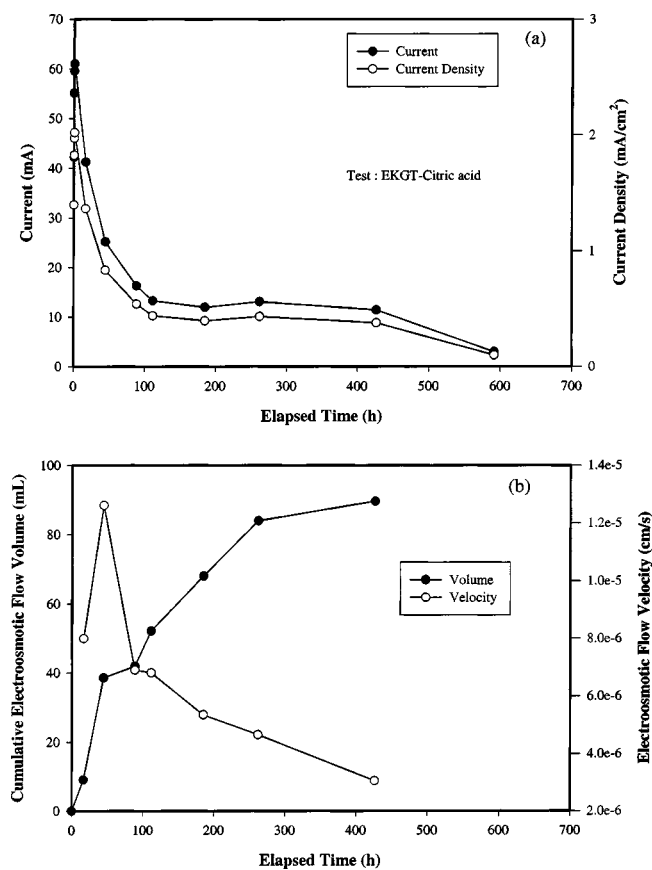


**Fig. 7.** Distribution of (a) chromium, (b) nickel, and (c) cadmium in the soil after electrokinetic treatment: acetic acid enhancement

ions generated by the electrolysis reaction at the cathode. The higher electroosmotic flow volume in the acetic acid test may have contributed to increasing the H<sup>+</sup> concentration. The H<sup>+</sup> ions generated by the electrolysis reaction at the anode electromigrate towards the cathode, and, since the electroosmotic flow was in the same direction, the congruence of the transport mechanisms may have resulted in significantly lower pH values. Moreover, the low pH values through the soil may have increased metal species solubility and/or salt or soil dissolution, which resulted in a higher ionic concentration and an increased electrical current.

As observed in Fig. 7(a), similar to the previous tests, it is evident that the anionic Cr(VI) species migrated towards the anode, and nearly 45% of the total chromium was collected in the anode reservoir. Most of the chromium remaining in the soil, however, was found to be reduced to the Cr(III) form, and soluble Cr(III) species are commonly cationic and migrate towards the cathode. Since the pH value of the soil section adjacent to the anode was less than 4, the Cr(III) in this region probably migrated towards the cathode. Once this Cr(III) reached a location where the soil pH was about 7, it may have adsorbed or precipitated. The conflicting migration characteristics of chromium were probably responsible for the higher concentrations of chromium that were found in the middle portion of the soil specimen.

As indicated by Figs. 7(b and c), nickel and cadmium migrated towards the cathode, and about 45% of the total initial nickel mass and 10% of the cadmium mass was collected in the cathode reservoir. Since the pH of the soil remained below 7.0, these cationic species probably existed as ionic forms that could migrate towards the cathode. Nearly all of the nickel and cadmium was removed from the soil section adjacent to the anode where the pH value was near 4.0. Based on the removal and the residual soil concentrations of these cationic species, it is evident that the conditions were thermodynamically favorable for nickel removal



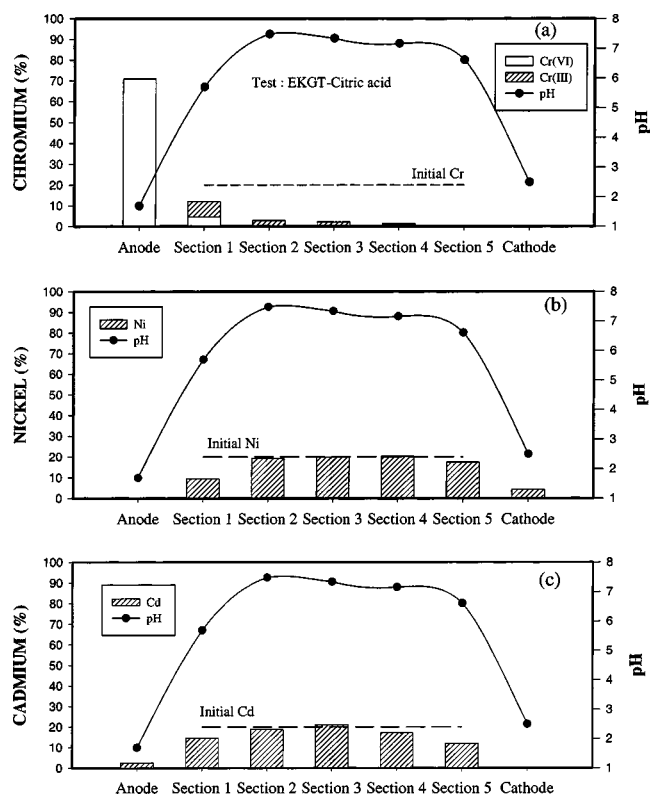
**Fig. 8.** Variation of (a) current and current density, and (b) electro-osmotic flow volume and velocity: citric acid enhancement

rather than cadmium, and other researchers have also determined that there is preferential contaminant removal when coexisting contaminants are present (Acar and Alshawabkeh 1993; Jensen et al. 1994). Due to the soil-solution chemistry, certain contaminants may have a greater tendency to be adsorbed and/or to precipitate. Since the chromium migrated in a direction opposite to the electroosmotic flow, electromigration must have been the primary contaminant transport mechanism for chromium, but electroosmosis may have aided nickel and cadmium transport towards the cathode.

### Citric Acid Enhancement

Fig. 8(a) shows that the electrical current and current density in the citric acid test followed the same trend as the experiments described earlier. The current quickly reached a peak near the beginning of the test, and then the current decreased somewhat rapidly to about 10 mA after 100 h. The current then remained at around 10 mA for close to 300 h before reducing further. The maximum current density was 2 mA/cm<sup>2</sup> in this test. As illustrated in Fig. 8(b), the high initial current and high ionic migration resulted in a considerable electroosmotic flow volume during the first 100 h, but, the effect of the rapid reduction in current was a lower cumulative flow volume (about 90 mL) that was similar to the unenhanced test.

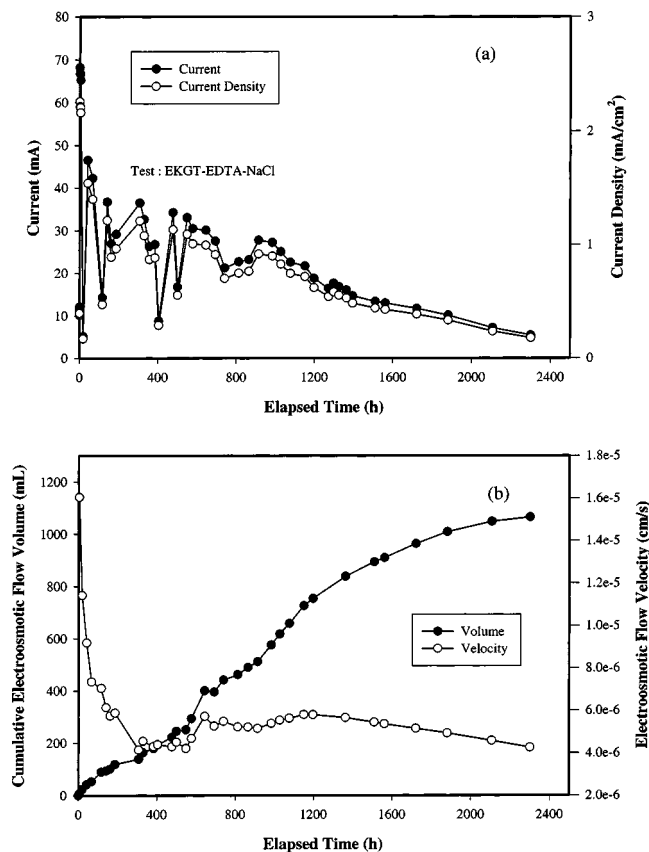
The pH profile, which is depicted in Fig. 9, shows that the pH in both of the electrode reservoirs was below 3.0, but the pH in the soil was much higher due to the buffering capacity and varied from about 5.5 to 7.5. Since the pH did not increase in the soil near the cathode, as observed in the unenhanced test, the citric



**Fig. 9.** Distribution of (a) chromium, (b) nickel, and (c) cadmium in the soil after electrokinetic treatment: citric acid enhancement

acid was effective at neutralizing the OH<sup>-</sup> ions generated by electrolysis at the cathode. Compared to the 1.0M acetic acid test shown in Fig. 7, the 1.0M citric acid test had a lower pH value in the cathode reservoir. Along the length of the soil specimen, however, the acetic acid test had lower pH values. Apparently, the anionic citric acid molecules or the formation of citric acid complexes resulted in more electromigration of species from the cathode towards the anode, and, in contrast to the acetic acid test, this resulted in a lower current and reduced electroosmotic flow. Since there was a lower electroosmotic flow towards the cathode in the citric acid test, the migration of H<sup>+</sup>, produced from the electrolysis reaction at the anode, was lower, so the pH in the soil remained slightly higher. It is crucial to remember that the electroosmotic flow is generated by the net amount of flow in one direction, or, in other words, the flow towards the cathode needs to be greater than the flow towards the anode for appreciable volume to occur at the cathode.

As shown in Fig. 9(a), nearly all of the soil sections, except for the section adjacent to the anode, had low chromium concentrations, and more than 70% of the total initial chromium was collected in the anode reservoir. This reinforces the suggestion purported earlier that citric acid molecules or complexes were migrating towards the anode, and it seems the presence of chromium-citrate complexes or the substitution of citrate for the chromium adsorbed on the soil particles resulted in a high amount of chromium removal. Conversely, Figs. 9(b and c) show that the citric acid was not effective for removing nickel or cadmium. The results indicate that some nickel and cadmium may have been converted to ionic form due to the low pH of the reservoir solutions, and this caused a minor amount of electromigration and/or diffusion within the soil or into the electrode reservoirs. Evi-



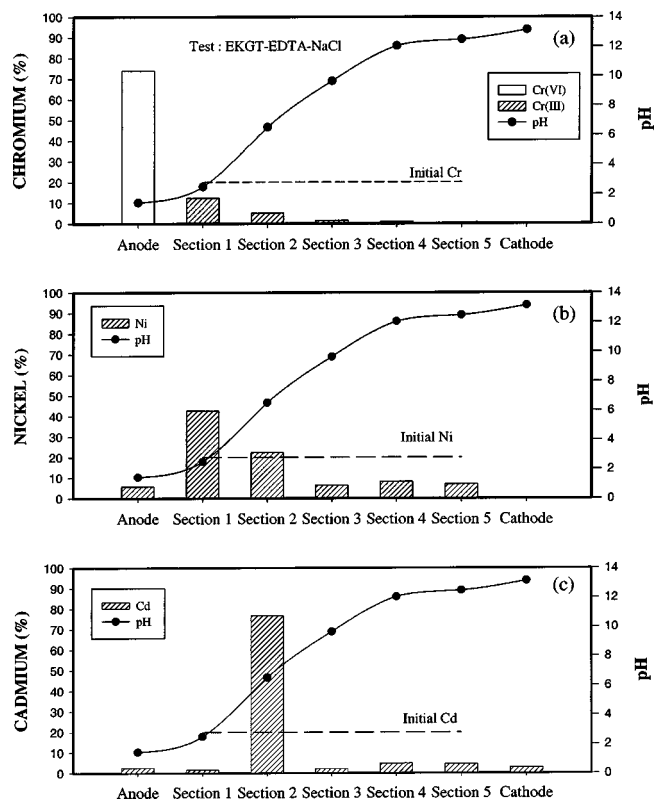
**Fig. 10.** Variation of (a) current and current density, and (b) electro-osmotic flow volume and velocity: ethylenediaminetetraacetic acid-sodium chloride (EDTA-NaCl) enhancement

dently, however, citric acid is not effective for the removal of cationic contaminants, such as nickel and cadmium, under electrokinetics.

### Sodium Chloride and Ethylenediaminetetraacetic Acid Enhancement

As illustrated in Fig. 10(a), similar to the other tests, the current and current density in the NaCl and EDTA enhanced test was high initially, and then decreased over time. The current and current density fluctuated between 10 and 40 mA and 0.3 and 1.3 mA/cm<sup>2</sup>, respectively, before it began gradually decreasing to low values. These fluctuations may have corresponded to the replenishment of the purging solutions in the electrode reservoirs, which supplied additional ions to the soil-solution system. Compared to the test that used EDTA without NaCl in Fig. 4(a), the current was significantly higher and more sustained due to the presence of the NaCl. A comparison of Fig. 4(b) with Fig. 10(b) shows that the NaCl solution was effective at increasing and maintaining the electroosmotic flow, and, after about 2,300 h, over a liter of cumulative volume was collected.

As illustrated in Fig. 11, it appears that the high electroosmotic flow towards the cathode may have diluted the EDTA concentration in the cathode reservoir, because the pH rose to a value of around 13 due to the electrolysis reaction at the cathode. As observed earlier in Fig. 5, in the test with EDTA alone, the pH remained significantly lower at the cathode. The longer duration of the NaCl and EDTA enhancement test was also a factor, because, over time, the products of the electrolysis reactions (H<sup>+</sup>

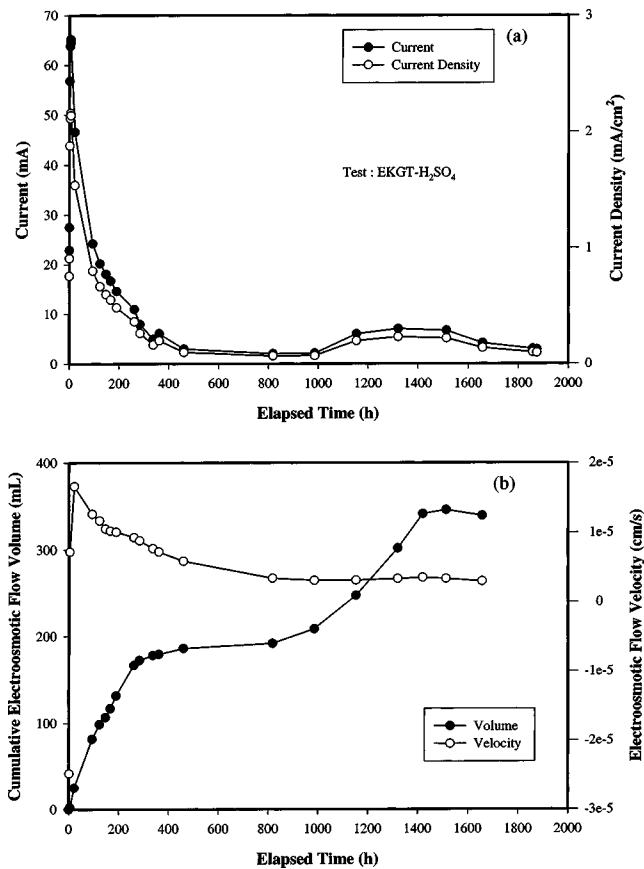


**Fig. 11.** Distribution of (a) chromium, (b) nickel, and (c) cadmium in the soil after electrokinetic treatment: ethylenediaminetetraacetic acid-sodium chloride (EDTA-NaCl) enhancement

and OH<sup>-</sup>) become more concentrated in the respective reservoirs, especially when the flow has reduced. This could be an additional reason why the pH of the cathode solution was higher and the pH of the anode solution was lower compared to Fig. 5.

Fig. 11(a) shows that more than 75% of the chromium was collected into the anode reservoir, and this indicates that the anionic EDTA molecules substituted for adsorbed chromium and/or formed anionic complexes with chromium. This chromium removal was a substantial improvement over the EDTA test without NaCl, and it appears that the presence of NaCl sustained the current and electroosmotic flow, and this was beneficial for chromium removal. Although the current had significantly reduced near the end of testing, it is possible that the residual chromium in the soil in the Cr(III) form could have formed EDTA complexes and migrated to the anode reservoir if the duration of the experiment was increased.

Figs. 11(b and c) both indicate that the EDTA formed complexes with the cationic contaminants, nickel and cadmium, respectively. Nickel and cadmium concentrations were reduced substantially in the three sections closest to the cathode, as these contaminants formed complexes with EDTA and then migrated towards the anode. It was also evident from these results that there was a thermodynamic preference for EDTA to form complexes with H<sup>+</sup> when the pH reduced, because high concentrations of nickel and cadmium were measured in the low pH regions near the anode. These findings support the similar results of the earlier test that used EDTA without NaCl, and suggest that it may be beneficial to increase the pH at the anode when using EDTA. Moreover, the cadmium concentrations were reduced further than the nickel concentrations in the sections near the cathode, so either there may have been a stronger adsorption of nickel

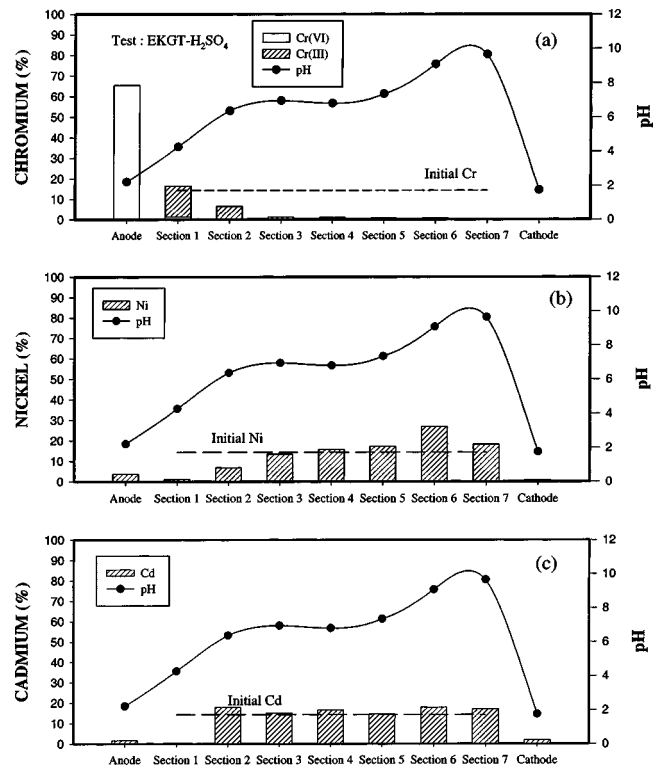


**Fig. 12.** Variation of (a) current and current density, and (b) electro-osmotic flow volume and velocity: sulfuric acid enhancement

to the soil or it may have been thermodynamically favorable for EDTA to complex with cadmium. The low cadmium concentration in the section adjacent to the anode was probably a result of the low pH region caused by electrolysis at the anode. The positively charged cadmium ions were electromigrated towards the cathode until it entered a higher pH region (soil section 2), where it was subsequently adsorbed and/or precipitated.

### Sulfuric Acid Enhancement

As expected, Fig. 12(a) shows that the current and current density in the test using sulfuric acid had a similar behavior to the test without enhancement since the sulfuric acid test was conducted with tap water at the electrodes for the first 800 h. Comparing Fig. 12(a) with Fig. 2(a), however, shows that the test without enhancement had a substantial drop in current after about 65 h, whereas the test with sulfuric acid enhancement had a more sustained current. Since the sulfuric acid test used tap water for the first 800 h, the current should have been similar to the test without enhancement, but glacial till has a variable soil composition and there may have been a greater amount of salt dissolution and ionic electromigration in the test that eventually used sulfuric acid enhancement. After the addition of the 0.05M sulfuric acid to the anode and 0.5M sulfuric acid to the cathode, a slight increase in the current was observed, and this was probably due to the dissolution of salts and minerals and the greater solubility of the cationic contaminants at a lower pH. As illustrated in Fig. 12(b), like the earlier tests, the electroosmotic flow correlated to the current and increased rapidly when the current was high but re-



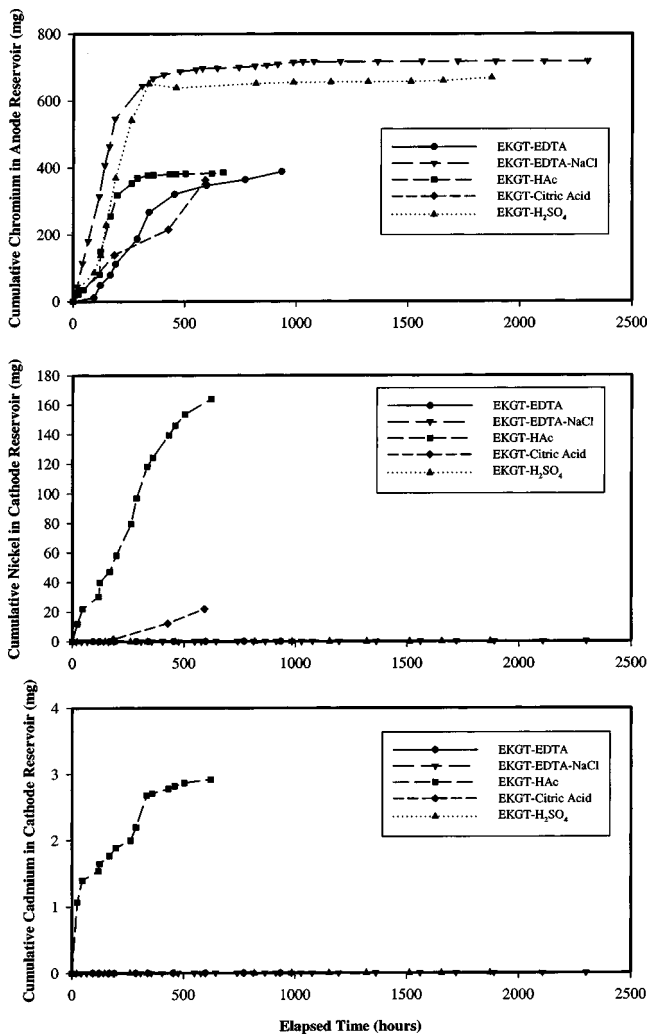
**Fig. 13.** Distribution of (a) chromium, (b) nickel, and (c) cadmium in the soil after electrokinetic treatment: sulfuric acid enhancement

duced when the current subsided. Then, after the sulfuric acid solutions were added, the flow increased again, but after about 1,400 h of testing, even with the sulfuric acid enhancement, the flow was minimal.

Fig. 13 shows that the pH in the cathode reservoir was low due to the sulfuric acid, and it was significantly higher in the soil sections that were nearest to the cathode. During the first 800 h of testing, while using tap water in the electrode reservoirs, the pH in the soil probably increased in the cathode region due to the electrolysis reactions at the cathode and the subsequent migration of  $\text{OH}^-$  into the soil. After the sulfuric acid was added, however, the electroosmotic flow was primarily towards the cathode, so, apparently, the 0.5M sulfuric acid that was introduced to the cathode reservoir did not penetrate into the soil enough to lower the pH near the cathode. Compared to the unenhanced test shown in Fig. 3, it seems that the 0.05M sulfuric acid that was added to the anode was partially successful at lowering the pH in the soil adjacent to the anode, but this result could have also been caused by the longer duration of the sulfuric acid test.

Fig. 13(a) shows that a large amount of chromium was collected in the anode reservoir and negligible amounts of chromium were found in the soil near the cathode. Clearly, this indicates that chromium migrated towards the anode, and, compared to the test without enhancement, it appears that the introduction of sulfuric acid was beneficial for chromium removal. The sulfuric acid may have contributed to producing Cr(III) dissolution and/or in preventing Cr(VI) reduction or adsorption near the anode.

Figs. 13(b and c) indicate that nickel and cadmium migrated towards the cathode, because both figures show low concentrations in the soil adjacent to the anode and higher concentrations in the soil towards the cathode. Only very small amounts of nickel and cadmium were measured in the cathode reservoir, and the high pH conditions that existed throughout the soil, especially

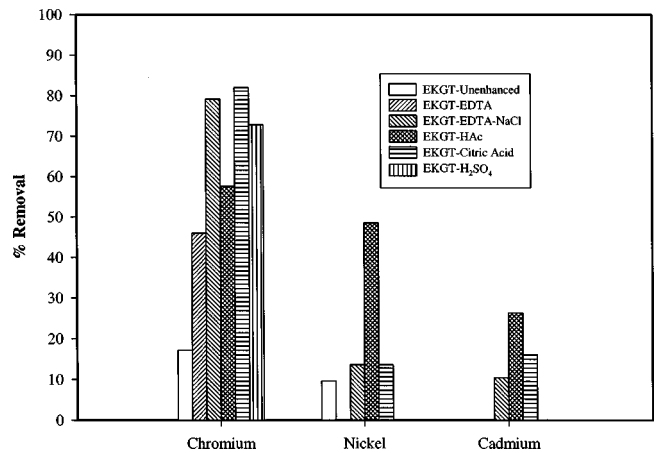


**Fig. 14.** Cumulative mass of chromium, nickel, and cadmium in the electrode reservoirs

near the cathode, caused these cationic contaminants to adsorb/precipitate. Small amounts of nickel and cadmium were also measured in the anode reservoir, and this was attributed to the low pH of the soil adjacent to the anode. Under low pH conditions, it is likely that these contaminants were changed to their ionic form and then there was probably some diffusion into the anode reservoir. Moreover, in their ionic form, some of these cationic contaminants may have also migrated towards the cathode and adsorbed/precipitated when they encountered the high pH conditions.

### Removal Efficiencies and Energy Expenditure

Fig. 14 illustrates the cumulative chromium, nickel, and cadmium concentrations that were measured in the electrode reservoirs during the tests. As seen earlier, chromium mostly accumulated in the anode reservoir whereas nickel and cadmium primarily accumulated in the cathode reservoir. Fig. 14 shows that, during the first 100 h of testing, the chromium migration into the anode reservoir was similar for all of the purging solutions. After 100 h of processing time, however, the rate of chromium migration into the anode reservoir was sustained only in the tests that were conducted with NaCl/EDTA or sulfuric acid. The migration rate was lower or greatly reduced for the other tests that were conducted



**Fig. 15.** Comparison of chromium, nickel, and cadmium removal efficiencies

with EDTA alone, acetic acid, or citric acid. The highest removal of nickel and cadmium occurred in the test using acetic acid enhancement, and, as seen in Fig. 14, nickel removal was significant, but, compared to the initial mass of cadmium, the amount of cadmium removal was low. Although a significant amount of nickel and cadmium migration was evident in the test using NaCl and EDTA enhancement, these contaminants did not collect in either reservoir and the amount of complete removal was negligible.

The percent removal of chromium, nickel, and cadmium calculated based on the residual contamination in the soil is shown in Fig. 15. These results illustrate that when sulfuric acid, NaCl/EDTA, or citric acid enhancement was used, a high amount of chromium removal occurred. Sulfuric acid accomplished a removal efficiency of about 73%, NaCl and EDTA resulted in a removal efficiency of 79%, and the highest chromium removal of 82% occurred when citric acid was used as a purging solution. The purging solution, other than tap water, that produced the lowest chromium removal was EDTA when it was used alone, and this solution achieved a chromium removal efficiency of about 42%. Compared to the amount of chromium removal, the amount of nickel and cadmium removal was limited, and the highest cationic contaminant removal was observed in the test with acetic acid. For the acetic acid test, a removal efficiency of approximately 48% was calculated for nickel and a removal efficiency of around 26% was calculated for cadmium based on the residual soil concentrations. The removal efficiencies of contaminants in each test were also calculated based on the effluent analysis, and these removal efficiencies were approximately the same or slightly lower than those calculated based on the residual soil concentrations (Chinthamreddy 1999). Such differences were attributed to the contaminant mass that was unaccounted for because it was adsorbed onto the graphite electrodes and/or trapped within the porous stones.

Fig. 16 shows the energy expenditure for all the tests performed in this study. As illustrated in this figure, the rate of energy expenditure was similar for all the tests during the first 100 h of testing. As noted earlier, the current generally decreases over time due to the depletion of ions and this reduces the energy expenditure. Thus the tests with the highest energy expenditure were the tests with the highest and most sustained current. Since the test employing EDTA at the cathode and NaCl at the anode had a high current that was maintained for a long duration, it had

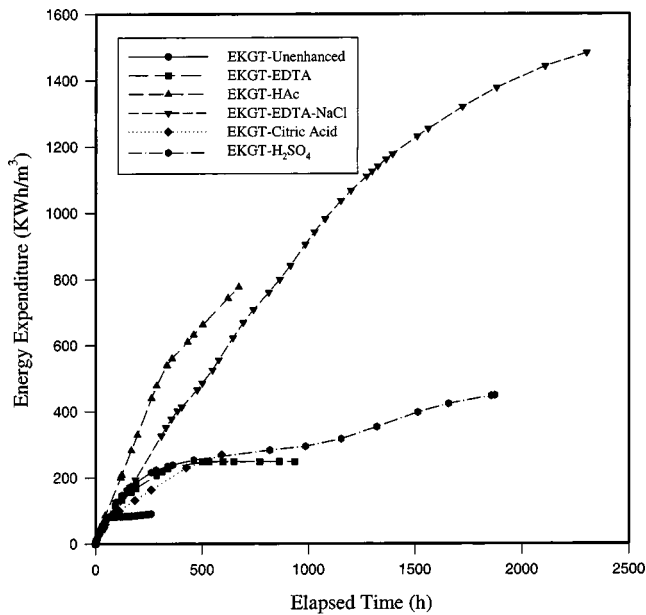


Fig. 16. Energy expenditure for various tests

the highest energy expenditure of about 1,500 kWh/m<sup>3</sup>. The acetic acid test had a sustained current that was also high, and Fig. 16 shows that if the same duration of testing was used, it would have had the highest energy expenditure of around 800 kWh/m<sup>3</sup>. These results show that, over time, the type of purging solution clearly affects the rate of energy expenditure.

## Summary and Conclusions

This study was conducted to investigate the performance of different purging solutions to dissolve metal precipitates and/or form soluble metal complexes and enhance metal contaminant removal during electrokinetics. Bench-scale electrokinetic tests were conducted on a glacial till soil that was spiked with Cr(VI), Ni(II), and Cd(II) in concentrations of 1,000, 500, and 250 mg/kg, respectively, under the application of a 1.0 VDC/cm voltage gradient. The electrolyte solutions tested included 0.1M EDTA, 1.0M acetic acid, 1.0M citric acid, 0.1M NaCl/0.1M EDTA, and 0.05M sulfuric acid/0.5M sulfuric acid, as well as tap water for comparison purposes. Based on the results of these tests, the following main conclusions were drawn:

1. The contaminant removal without enhancement, using tap water in both electrode reservoirs, was very low. The removal of chromium was hindered by the reduction of Cr(VI) to Cr(III) near the anode region and the subsequent precipitation of the Cr(III) due to the high pH conditions. The migration of nickel and cadmium was also severely limited due to the adsorption/precipitation of these contaminants under high pH conditions.
2. In the test using tap water in the anode reservoir and EDTA in the cathode reservoir, the chromium removal from the soil was low compared to the other tests that used special purging solutions. When EDTA was used, it appears that the nickel-EDTA and cadmium-EDTA complexes that formed migrated towards the anode due to the negative charge on these species. In the test using NaCl combined with EDTA, the removal of chromium increased considerably to 79%, and it appears that due to the presence of NaCl, the current and

electroosmotic flow were sustained, and this was beneficial for chromium removal. Nickel and cadmium migrated significantly towards the anode in this test; however, all of the nickel and cadmium eventually accumulated in the soil near the anode. The accumulation of these metals was attributed to the preferential complexation of EDTA with H<sup>+</sup> under low pH conditions.

3. Compared to the NaCl/EDTA, sulfuric acid, or citric acid tests, the test using acetic acid in the cathode reservoir had a low chromium removal efficiency of 57%. The nickel and cadmium removal efficiencies in this test, however, were the highest of any of the tests at approximately 48% and 26%, respectively. Therefore acetic acid was the most effective solution at removing all three of the contaminants simultaneously.
4. The test using citric acid had the highest chromium removal efficiency of around 82%, but the removal of nickel and cadmium was insignificant, so citric acid was determined to be ineffective at complexing and removing cationic contaminants.
5. When tap water was used in the beginning of the experiment followed by the addition of sulfuric acid to the anode and the cathode reservoirs, the chromium removal efficiency was approximately 73%, but the removal of nickel and cadmium was insignificant.

Overall, this study demonstrated that the electrokinetic process is capable of removing multiple heavy metal contaminants from a high acid buffering clay soil. High chromium removal efficiency and partial removal of nickel and cadmium was obtained by applying preselected purging solutions. The NaCl/EDTA combination test achieved the highest migration of all the contaminants towards the regions close to the electrodes, but acetic acid had the greatest removal efficiency for all of the contaminants simultaneously. Clearly, the selection of the purging solutions must be based upon the chemical characteristics of the contaminants and the soil composition. Further research will be required to understand the fundamental contaminant-purging solution interactions and to select the optimal purging solution so that complete removal of multiple heavy metals from soils can be accomplished.

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