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## Effects of initial form of chromium on electrokinetic remediation in clays

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### Abstract

This paper presents the results of a laboratory investigation performed to evaluate the effects of the initial form of chromium on the electrokinetic remedial efficiency for contaminated clays. Electrokinetic experiments were conducted by contaminating clays with chromium in three different forms: Cr(III) alone, Cr(VI) alone, and a combination of Cr(III) and Cr(VI). The same total chromium concentration of 1000 mg/kg was maintained in all cases. Ni(II) and Cd(II) in concentrations of 500 mg/kg and 250 mg/kg, respectively, were also introduced into the clays as co-contaminants to simulate typical electroplating waste constituents. Two different clays, kaolin, a typical low buffering clay and glacial till, a typical high buffering clay, were tested. All tests were conducted with a constant voltage gradient of 1.0 VDC/cm. The test results showed that chromium migration was highest when it was present in kaolin in the Cr(III) form and in glacial till in the Cr(VI) form. When chromium was present in Cr(III) form, migration occurred towards the cathode due to the existence of Cr(III) as cation and cationic hydroxide complexes. Cr(III) migration was not observed in glacial till because of precipitation that resulted from high pH conditions that existed throughout the glacial till. However, when chromium was present in Cr(VI) form, the migration occurred towards the anode, due to the existence of Cr(VI) as soluble oxyanions. The migration of Cr(VI) was higher in glacial till as compared to kaolin due to alkaline conditions that existed in the glacial till, resulting in negligible Cr(VI) adsorption to soil solids. When chromium was present as a combination of Cr(VI) and Cr(III), Cr(VI) migrated towards the anode, while Cr(III) migrated towards the cathode. For these cases, the total chromium migration was lower than the migration observed when only Cr(III) was present in kaolin or when only Cr(VI) was present in glacial till. No migration was observed for the co-contaminants, Ni(II) and Cd(II), in glacial till due to precipitation as a result of alkaline conditions. In kaolin, however, Ni(II) and Cd(II) migrated towards the cathode. Overall, the test results show that significant removal of contaminants from the soils was not achieved for the processing periods utilized. This study clearly demonstrated that the efficiency of the electrokinetic removal of chromium, nickel and cadmium from the contaminated clays depends on the initial form of chromium as well as the soil chemistry. Enhancement strategies should be investigated in order to enhance contaminant migration and to achieve high removal efficiencies. © 2002 Elsevier Science Ltd. All rights reserved.

**Keywords:** Clays; Clean-up; Electroplating waste; Electrokinetic remediation; Electrokinetics; Heavy metals; Pollution; Soils; Subsurface; Remediation

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## 1. Introduction

In-situ remediation of contaminated clays using conventional methods such as soil flushing and bioremediation has proven to be ineffective and costly due to low hydraulic conductivity of these soils. In-situ electrokinetic remediation, also known as electrokinetics, has been shown to be particularly suited for the remediation of clays contaminated with toxic metals such as lead and copper (Hamed et al., 1991; Pamukcu and Wittle, 1992; Eykholt and Daniel, 1994; Hicks and Tondorf, 1994; Acar et al., 1995; Acar and Alshawabkeh, 1996), organic compounds such as phenol and gasoline compounds (Acar et al., 1992; Bruell et al., 1992; Probststein and Hicks, 1993) and radionuclides such as thorium and radium (Ugaz et al., 1994).

In-situ electrokinetic remediation essentially involves installing trenches and/or wells to encompass the contaminated soil zone, inserting electrodes into these trenches or wells and applying a low DC voltage gradient or DC current across the electrodes that are strategically determined as either cathodes or anodes. As a result of the induced electric potential, the contaminants are transported towards either the cathodes or the anodes depending on their charge, cationic or anionic, and the direction of the pore water flow. Contaminants collected at the electrodes are then extracted and subsequently treated above ground. Migration of the contaminants towards either cathodes or anodes is mainly attributed to two major transport mechanisms: electromigration and electro-osmosis (Acar and Alshawabkeh, 1993). The ultimate, overall contaminant removal from the soil using this method depends on: (1) pH gradients developed between the electrodes due to the electromigration of  $H^+$  and  $OH^-$  that are generated at the electrodes due to electrolysis of water, and (2) various geochemical processes such as redox reactions, adsorption–desorption, and precipitation–dissolution that occur throughout the soil.

The migration of chromium in clays during electrokinetics can be quite complex. The complexity of chromium arises due to its existence in two different forms within the subsurface, namely, hexavalent chromium (Cr(VI)) and trivalent chromium (Cr(III)). Cr(VI) exists as oxyanions, specifically hydrochromate ( $HCrO_4^-$ ), dichromate ( $Cr_2O_7^{2-}$ ) and chromate ( $CrO_4^{2-}$ ), depending on the pH and redox conditions. These oxyanions are soluble and remain in solution over a wide pH range (Rai et al., 1989). During electrokinetic remediation, these oxyanions migrate towards the anode (Lindgren et al., 1994). On the other hand, Cr(III) generally occurs in the form of hydroxo complexes, namely,  $Cr(OH)^{2+}$ ,  $Cr(OH)_2^+$ ,  $Cr(OH)_3^0$ ,  $Cr(OH)_4^-$ , and  $Cr(OH)_5^{2-}$ . The cationic Cr(III) species exist over a wide pH range and may migrate towards

the cathode during electrokinetic remediation (Acar et al., 1995). Because of the contrasting migration behavior of Cr(VI) or Cr(III), it is essential to know both the total chromium concentration and its distribution in the form of either Cr(VI) and Cr(III) in contaminated soils, prior to the consideration of electrokinetic remediation.

Nickel (Ni(II)) and cadmium (Cd(II)) commonly co-exist with chromium at many contaminated sites, especially at electroplating waste sites. The Ni(II) and Cd(II) may exist as cationic species and migrate towards the cathode during electrokinetic remediation.

The use of electrokinetics for remediating clays, contaminated with electroplating wastes consisting mainly of chromium, cadmium and nickel has been investigated in bench-scale experiments (Reddy et al., 1997; Reddy and Parupudi, 1997). In these studies, chromium was in hexavalent form. Reddy et al. (1997) focussed on the electrokinetic removal of only Cr(VI) from three different types of clays; kaolin, Na-Montmorillonite, and glacial till, both with and without the presence of iron oxides. This research showed that the Cr(VI) migration towards the anode depends on the soil mineralogy and naturally occurring iron oxides in the soil. In another study, Reddy and Parupudi (1997) determined the synergistic effects of co-existing Ni(II) and Cd(II) on Cr(VI) removal in both kaolin and glacial till, and found that these effects are also dependent on the soil type. Although these previous studies determined the influence of soil composition on Cr(VI) migration under an induced electric potential, the effects of the initial form of chromium on the electrokinetic remedial efficiency for contaminated clays was not studied.

This paper presents the results of a laboratory investigation performed to systematically evaluate the effects of the initial form of chromium on electrokinetic remediation efficiency. Laboratory electrokinetic experiments were performed using two different clays, kaolin and glacial till, which had been contaminated with Ni(II) and Cd(II) as co-contaminants and chromium in different initial forms, either Cr(VI), Cr(III), or a combination of Cr(VI) and Cr(III). These contaminants were selected to simulate typical electroplating waste constituents. The experimental results were used to assess the migration of chromium in different forms as well as Ni(II) and Cd(II) in the selected soils.

## 2. Materials and methods

### 2.1. Test variables

Two different clays were selected for this study: kaolin, which is a low buffering soil, and a glacial till, a high buffering soil. These soils have been characterized in detail and have been used in related investiga-

Table 1  
Composition and properties of soils tested

Soil type	Glacial till	Kaolin
Source	DuPage County, Illinois Obtained by the authors	KGa-1a: Washington County, Georgia Obtained from Clay Minerals Society, MO
Mineralogy	Quartz: ~31% Feldspar: ~13% Carbonate: ~35% Illite: ~15% Chlorite: ~4–6% Vermiculite: ~0.5% Smectite: trace	Kaolonite: ~100%
Cation Exchange Capacity, meq/100 g (ASTM D9081)	13.0–18.0	1.6
Initial pH (ASTM D4972)	7.7–8.3	5.0
% Finer than 0.075 mm (ASTM D422)	84	100
Atterberg Limits: LL (%) PL (%) (ASTM D2487)	29–31 16–17	44 29
Hydraulic Conductivity, cm/s (ASTM D2434)	$1.0 \times 10^{-8}$	$8.8 \times 10^{-8}$

tions (Reddy and Shirani, 1997; Reddy et al., 1997; Reddy and Parupudi, 1997). Table 1 summarizes the composition and properties of these soils. These soils were contaminated using chromium in three different forms: (1) Cr(III) in a concentration of 1000 mg/kg, (2) Cr(VI) in a concentration of 1000 mg/kg, and (3) Cr(III) and Cr(VI), each in concentrations of 500 mg/

kg. In addition to chromium, Ni(II) and Cd(II) were also added to the soils in concentrations of 500 mg/kg and 250 mg/kg, respectively, for all experiments, to simulate typical electroplating waste contamination. A total of six electrokinetic experiments were conducted with the initial conditions shown in Table 2. A constant voltage gradient of 1 VDC/cm was applied for all tests.

Table 2  
Initial conditions for electrokinetic experiments

Test	Soil	Water content (%)	Dry density ( $\text{g}/\text{cm}^3$ )	Initial Contaminant Concentration (mg/kg)					Soil pH
				Cr(III)	Cr(VI)	Total Cr	Ni(II)	Cd(II)	
EKK-1	Kaolin	32.9	1.44	1000	0	1000	500	250	3.83
EKK-2	Kaolin	40.6	1.32	0	1000	1000	500	250	5.36
EKK-3	Kaolin	35.7	1.28	500	500	1000	500	250	4.06
EKGT-1	Glacial till	25.1	1.62	1000	0	1000	500	250	6.74
EKGT-2	Glacial Till	26.6	1.64	0	1000	1000	500	250	7.36
EKGT-3	Glacial till	24.8	1.62	500	500	1000	500	250	7.04

## 2.2. Electrokinetic reactor

Fig. 1 shows the schematic of the electrokinetic reactor used for this study. The detailed description of this reactor has been given by Reddy et al. (1997). The reactor consists of an electrokinetic cell, two electrode compartments, two electrode reservoirs, a power source and a multimeter. The plexiglass 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 (made with aluminum oxide bonded with glass). The electrode compartments are connected to either end of the cell using screws. Electrode reservoirs were made of 3.8-cm inner diameter plexiglass tubes and were connected to the electrode compartments using Tygon tubing. Exit ports were created in the electrode compartments and thin tubes were then inserted into these ports to allow 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 voltage and measure the current flow through the soil sample during the testing.

## 2.3. Testing procedure

Approximately 1100 g of dry soil was used for each test. Chromic chloride, potassium chromate, nickel chloride and cadmium chloride were used as sources of Cr(III), Cr(VI), Ni(II), and Cd(II), respectively. The required amounts of these chemicals that would yield the desired 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 HDPE container. A total of 375 ml of deionized water (35% moisture content) was used for kaolin, while 285 ml of deionized water (25% moisture content) was used for the glacial till. These moisture contents represent typical field moisture conditions in these soils. 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 initial water content and dry density of soil samples after compaction for each test are summarized in Table 2. 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

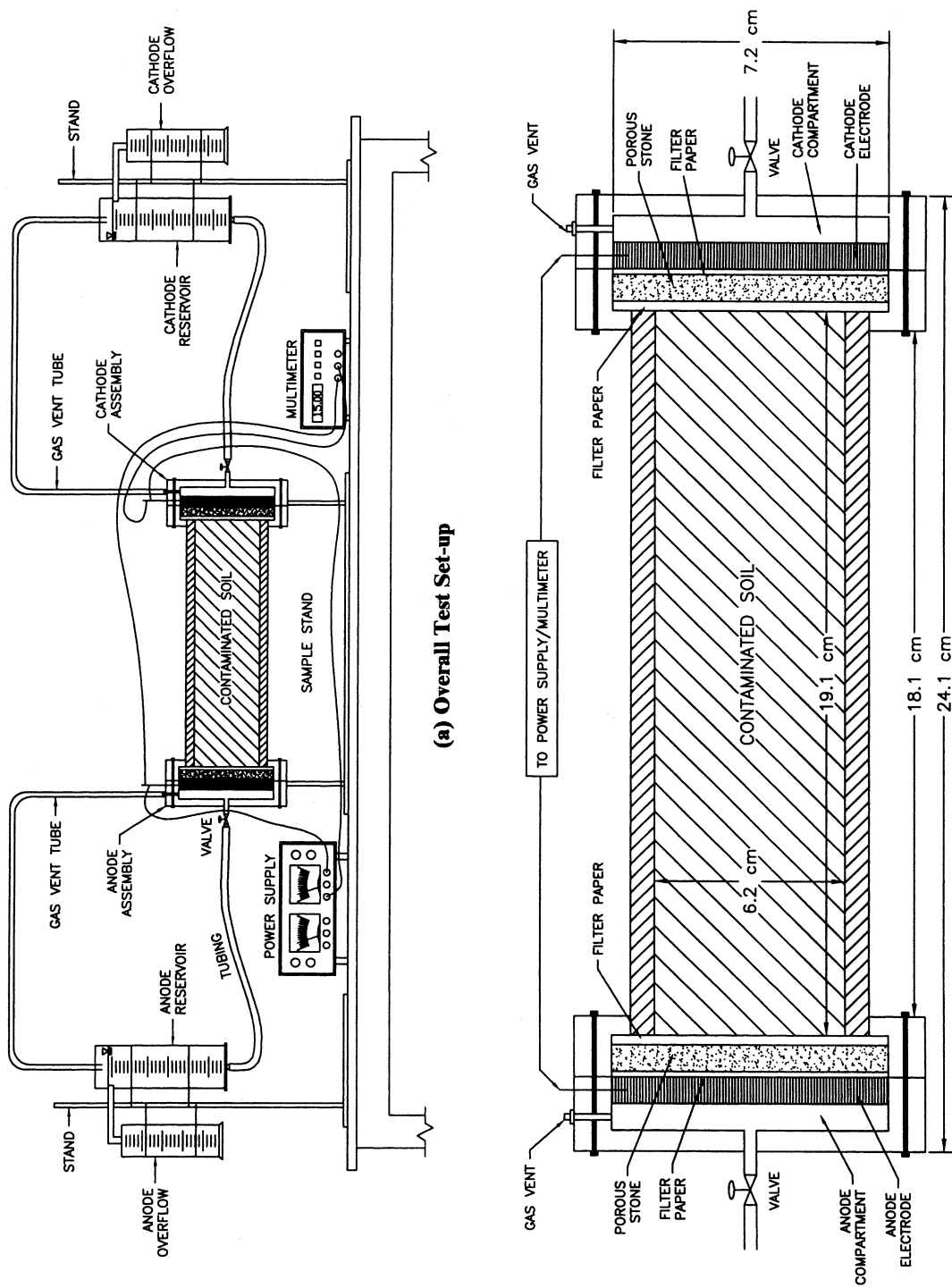
electrode and the porous stone as well as between the porous stone and the soil.

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; 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 and 60 mg/l CaCO<sub>3</sub>, respectively. The electrokinetic cell was then connected to the power supply and a constant voltage gradient of 1 VDC/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 or when no significant change in the water flow (electro-osmotic flow) was observed or when no change in the electrical conductivity of the electrode reservoir solutions was observed. The maximum test duration was 250 h for kaolin and 170 h for glacial till.

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. 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 glass bottles. 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 and the solids were allowed to settle. The pH, redox potential and the electrical conductivity of the soil as well as that of the aqueous solutions from the electrodes were measured. The moisture content of each soil section was also determined.

## 2.4. Chemical analysis

Contaminants in different soil sections were extracted by performing acid digestion in accordance with USEPA 3050 procedure (USEPA, 1986). Total concentrations of chromium, nickel and cadmium were determined using this extraction procedure. Approximately 1 to 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 (HNO<sub>3</sub>). The mixture was stirred thoroughly, the beaker was covered with a watch



**(b) Cell Details**

Fig. 1. Schematic of electrokinetic reactor.

glass and heated to 95 °C, and refluxed for 15 min. The sample was then cooled. Five milliliters of concentrated HNO<sub>3</sub> was added and again refluxed 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 deionized water and 3 ml of 30% hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) 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 H<sub>2</sub>O<sub>2</sub> was continued until the effervescence was at a minimum. The maximum amount of H<sub>2</sub>O<sub>2</sub> added was less than 10 ml. The sample was cooled and 5 ml of concentrated HNO<sub>3</sub> and 10 ml of deionized water were added and the 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 soil sections in accordance with USEPA 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 °C for 60 min with continuous stirring. The sample was then cooled and the pH was adjusted to between 7 and 8, using HNO<sub>3</sub>. The sample was then diluted to 100 ml and the supernatant was obtained through centrifugation. The supernatant was analyzed using AAS to determine Cr(VI) concentrations. Cr(III) concentrations were calculated by subtracting Cr(VI) concentrations from the total chromium concentrations determined, based on the acid digestion procedure.

### 2.5. Quality assurance

The reproducibility of testing procedure and 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 compartments were soaked in a dilute acid solution for 24 h 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 duplicates; (4) the AAS calibration was checked after testing every five samples; and (5) a mass balance analysis was performed for each test. Table 3 summa-

rizes the detailed mass balance analyses for all of the tests. From Table 3, it can be seen that the mass balance differences are less than 10%. These differences were mainly attributed to the non-uniform contaminant distribution within the selected soil sample for chemical analysis and to the adsorption of contaminants onto the electrodes and porous stones.

## 3. Results and discussion

### 3.1. Electric current

The current densities, calculated by dividing the measured current by the cross-sectional area of the soil specimen, for both kaolin and glacial till are shown in Fig. 2a,b, respectively, for tests with different initial forms of chromium. For both soils, the current initially increased rapidly, reached a peak value, then decreased and finally stabilized. The current stabilized at 0.02–0.26 mA/cm<sup>2</sup> in both soils within approximately 100 h. For kaolin with Cr(III), the electric current increased to 1.72 mA/cm<sup>2</sup> within 25 h and then decreased. When Cr(VI) was present, the current gradually increased to 0.69 mA/cm<sup>2</sup> within 10 h and then decreased gradually. When both Cr(III) and Cr(VI) were present, the current increased to 1.16 mA/cm<sup>2</sup> and then decreased to 0.66 mA/cm<sup>2</sup> within the first 5 h of testing, followed by a gradual decrease. On the other hand, in glacial till when Cr(III) was present, the electric current increased to 0.46 mA/cm<sup>2</sup> within 20 h and then gradually decreased. When Cr(VI) was present or when a combination of Cr(III) and Cr(VI) was present, the current increased to 2.52 mA/cm<sup>2</sup> within 5 h and then rapidly decreased to less than 0.03 mA/cm<sup>2</sup> after 70 h.

The measured electric current is proportional to the dissolved species present in the solution (Acar and Alshawabkeh, 1993). The presence of Cr(III) in dissolved form in kaolin and the presence of Cr(VI) in dissolved form in glacial till have resulted in higher electric currents. During the process, the electrical conductance decreases perhaps as a result of decreased dissolved species due to precipitation. The precipitation was the result of high pH near the cathode in kaolin and throughout the glacial till; consequently, electric current decreases. The measured currents demonstrate that energy expenditures during electrokinetic remediation of chromium contaminated soils will depend on the form of chromium present and the type of soil.

### 3.2. Conditions at electrodes

Water flow, pH, redox potential and electrical conductivity (EC) were measured in both the anode and cathode reservoirs at different time periods during the application of the voltage gradient (Chinthamreddy, 1999). Electro-osmotic flow was towards the cathode

Table 3  
Mass balance analysis

Test	Soil type	Contaminant	Initial contaminant mass in soil (mg) <sup>a</sup>	Contaminant mass after electrokinetic treatment			Mass balance (%)
				Remaining in soil (mg)	Anode reservoir (mg)	Cathode reservoir (mg)	
EKK-1	Kaolin	Cr(Total)	843.12	764.70	1.40	ND <sup>b</sup>	91
		Ni(II)	332.84	310.44	0.68	0.01	93
		Cd(II)	133.94	141.79	0.01	0.01	106
EKK-2	Kaolin	Cr(Total)	713.47	626.47	28.39	0.09	92
		Ni(II)	290.28	334.32	0.63	0.07	115(?)
		Cd(II)	160.65	149.30	ND	ND	93
EKK-3	Kaolin	Cr(Total)	619.87	602.73	17.74	0.07	100
		Ni(II)	263.75	264.07	2.64	0.05	101
		Cd(II)	145.09	145.98	1.55	0.01	102
EKG1-1	Glacial till	Cr(Total)	1002.86	981.55	12.38	0.07	99
		Ni(II)	440.31	405.72	4.21	0.02	93
		Cd(II)	229.57	213.57	ND	0.21	93
EKG1-2	Glacial till	Cr(Total)	944.00	781.94	108.54	0.05	94
		Ni(II)	420.67	379.99	30.73	0.02	98
		Cd(II)	204.85	205.55	0.38	ND	100
EKG1-3	Glacial till	Cr(Total)	993.72	865.38	29.22	0.06	90
		Ni(II)	397.64	378.52	5.82	0.03	97
		Cd(II)	217.46	210.55	0.70	ND	97

<sup>a</sup> Based on the actual mass of the soil used in electrokinetic cell and the concentrations measured in the contaminated soil prior to electrokinetic testing.

<sup>b</sup> ND = not detected.

in both soils. Initially, flow occurred very slowly, an increase in flow was then detected, followed by a very low flow. The average electro-osmotic flow velocity varied from 0.008 to 0.036 cm/h in kaolin, and from 0.003 to 0.02 cm/h in glacial till. The highest flow in kaolin was observed when Cr(III) was present, whereas the highest flow in glacial till was observed when Cr(VI) was present. Electro-osmotic tests were also conducted on clean kaolin and glacial till, to assess the effects of the presence of heavy metals on the electro-osmotic flow (Chinthamreddy, 1999). These tests were also conducted under a voltage gradient of 1 VDC/cm and exhibited an average electro-osmotic flow velocity of 0.013 cm/h for kaolin and 0.03 cm/h for glacial till. Thus, the electro-osmotic flow is slightly influenced by the soil type and the presence of the contaminants, including the form of chromium. The ionic species present in kaolin were relatively higher than those present in the glacial till because of precipitation of cationic metal species [Cr(III), Ni(II) and Cd(II)], due to the high pH conditions prevalent in the glacial till. As a result of this, the electro-osmotic flow in contaminated kaolin is higher than that observed in the contaminated glacial till.

The potable water initially introduced into the anode and cathode reservoirs had a pH value ranging from 7.6 to 7.8. Due to the applied electric potential, electrolysis of water produces H<sup>+</sup> at the anode and OH<sup>-</sup> at the cathode. Consequently, pH of anolyte (anode solution) was reduced, while the pH of catholyte (cathode solution) was increased. For both kaolin and glacial till, pH of anolyte reduced to 2.5–3.0 and pH of catholyte increased to 10–12. These results show that electrolysis reactions occurred at electrodes in all of the tests and the measured pH values are consistent with the values reported in the literature (Acar and Alshwabkeh, 1993).

The initial redox potential of potable water used in both anode and cathode reservoirs ranged from 125 to 175 mV. Under the induced electric potential, the redox potential of anolyte was increased, while the redox potential of catholyte was decreased for both kaolin and glacial till. The redox potential of anolyte ranged from 250 to 450 mV for kaolin and from 450 to 500 mV for glacial till. The redox potential of catholyte ranged from -100 to 5 mV in kaolin and -100 to 40 mV in glacial till. These changes in redox potentials in the electrode solutions reflect the oxidizing conditions at the anode and reducing conditions at the cathode.

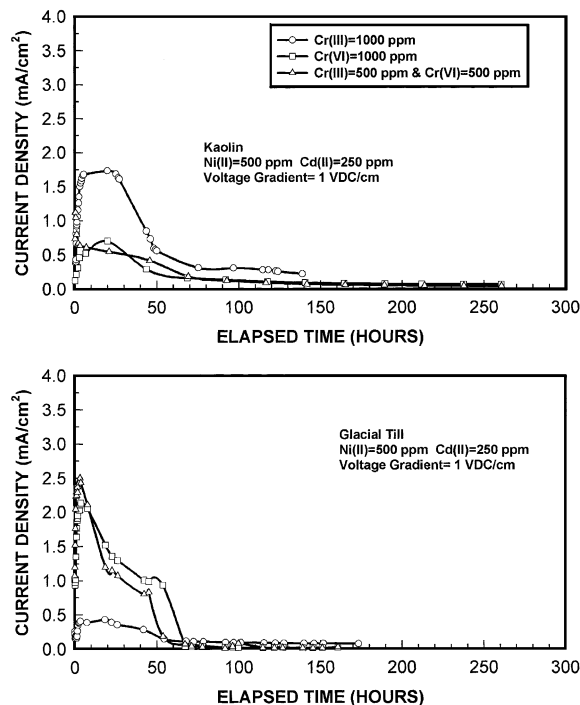


Fig. 2. Current variations.

The initial electrical conductivity (EC) value of the potable water used in both the anode and cathode reservoirs ranged from 260 to 300  $\mu\text{S}/\text{cm}$ . For kaolin, the EC values of anolyte increased to 2700  $\mu\text{S}/\text{cm}$  when Cr(III) was present, while EC values ranged from 450 to 600  $\mu\text{S}/\text{cm}$  when Cr(VI) and a combination of Cr(III) and Cr(VI) were present. However, the EC values of catholyte increased to 23 000, 9000 or 1500  $\mu\text{S}/\text{cm}$  when Cr(III), Cr(VI), or a combination of Cr(III) and Cr(VI) were present, respectively. For glacial till, the EC values of anolyte gradually increased to 1500, 9500, and 5000  $\mu\text{S}/\text{cm}$  when Cr(III), Cr(VI), and a combination of Cr(III) and Cr(VI) were present, respectively. The EC values of catholyte were unchanged when Cr(III) was present; however, EC values increased to 3000–3500  $\mu\text{S}/\text{cm}$  when Cr(VI) and a combination of Cr(III) and Cr(VI) were present. The EC values are proportional to the concentration of ionic species. Relatively high EC values at the anolyte and catholyte in kaolin when Cr(III) was present indicate higher ionic concentration in both electrode solutions, but an increase of two orders of magnitude in the catholyte suggests a significant ionic concentration in the catholyte. In glacial till, the high EC values of anolyte and catholyte when Cr(VI) and a combination of Cr(III) and Cr(VI) were present, indicate a significant increase in ionic concentration. There was no change in EC when Cr(III) was present, which indicates

a negligible change in ionic concentration in both the anode and cathode solutions.

### 3.3. pH profiles

Fig. 3a,b show the pH profiles in kaolin and glacial till, respectively, after the electrokinetic testing. The initial pH of kaolin ranged from 3.83 to 5.36 (Table 2). It can be clearly seen from Fig. 3a that for all forms of chromium, the soil pH decreased to 2.0–2.2 through two-thirds of the specimen near the anode, but the pH increased to 9.0–11.8 near the cathode region. The pH variation in glacial till was quite different from that of kaolin as seen in Fig. 3b. The initial pH of glacial till prior to electrokinetic treatment ranged from 6.74 to 7.36 (Table 2). After the electrokinetic treatment, the soil pH remained approximately the same, ranging from 6.0 to 6.7 throughout the soil except near the cathode where the soil pH increased to 9.8–11.9. These results show that  $\text{H}^+$  ions generated at the anode migrated easily through the kaolin, but they did not migrate into the glacial till. Because of high carbonate content, the glacial till possessed a high acid buffering capacity and neutralized the  $\text{H}^+$  ions near the anode region (Sposito, 1989; Reddy and Parupudi, 1997; Reddy and Shirani, 1997). The  $\text{OH}^-$  ions generated at the cathode migrated into both kaolin and glacial till, but the extent of  $\text{OH}^-$  ions migration is limited due to their low mobility as compared to the  $\text{H}^+$  ions (Acar and Alshawabkeh,

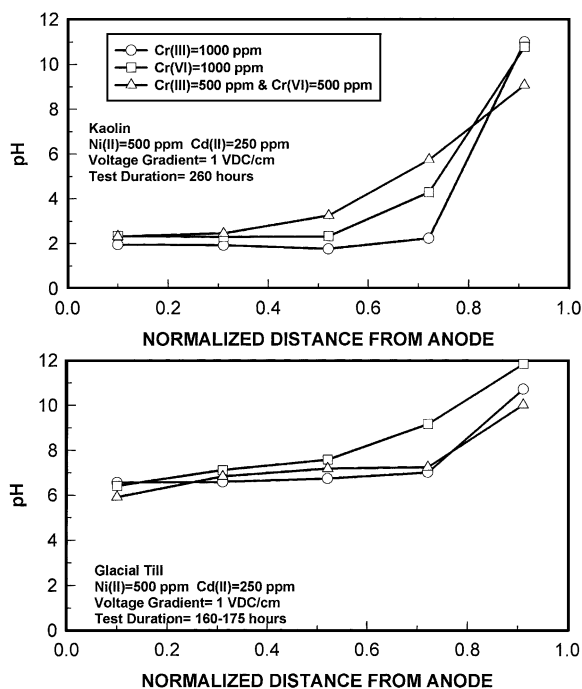


Fig. 3. pH profiles.

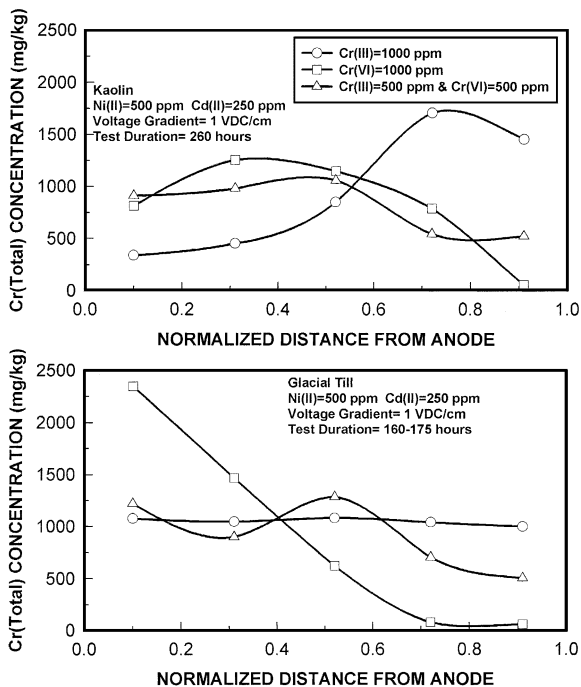


Fig. 4. Total chromium concentration profiles.

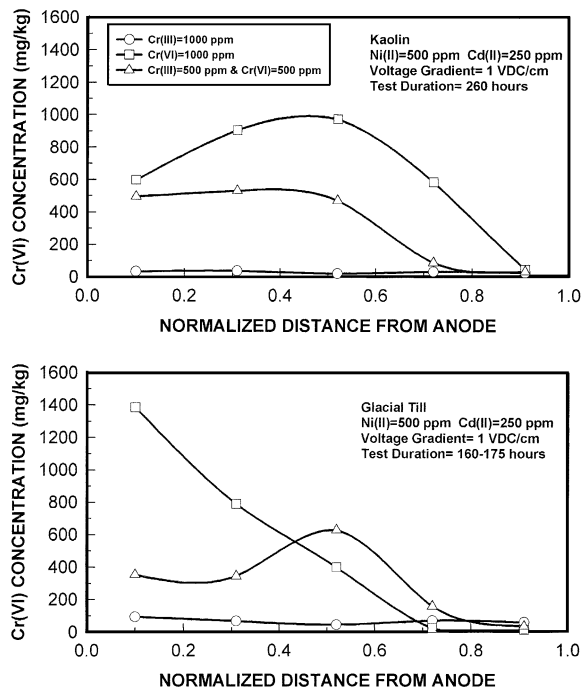


Fig. 5. Cr(VI) concentration profiles.

1993). The significant differences in pH variations in kaolin and glacial till during electrokinetics will have a profound effect on the redox chemistry, adsorption-desorption, and precipitation-dissolution; and consequently, will affect the contaminant migration, and ultimately will control the overall remedial efficiency of the process as discussed in subsequent sections.

### 3.4. Chromium migration

After the experimentation was completed, the total chromium and the Cr(VI) concentrations were measured in each soil section, and the Cr(III) concentrations were then calculated by subtracting the Cr(VI) concentrations from the total chromium concentrations. Figs. 4–6 show the Cr(total), Cr(VI) and Cr(III) concentration profiles in the soil from the anode to the cathode for the three tests performed on both the kaolin and the glacial till. As previously stated, the initial total chromium concentration for all these tests prior to electrokinetic treatment was maintained constant at 1000 mg/kg, but it was distributed as either only Cr(VI) form, only Cr(III) form, or equal concentrations of Cr(VI) and Cr(III).

For kaolin with Cr(III), a significant migration of chromium towards the cathode was observed, as seen in Fig. 4a. Total chromium concentrations varied from 350 mg/kg near the anode to 1700 mg/kg near the cathode. Cr(VI) and Cr(III) profiles shown for this test in Fig. 5a and Fig. 6a clearly demonstrate that the

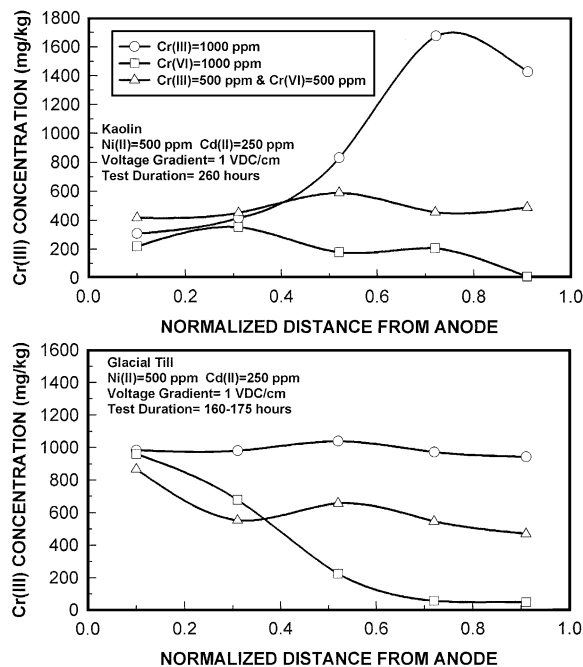


Fig. 6. Cr(III) concentration profiles.

chromium that was introduced as Cr(III) remained as Cr(III) and oxidation of Cr(III) to Cr(VI) did not occur. In the case of glacial till with Cr(III), as seen in Fig. 4b, the total chromium concentration was approximately 1000 mg/kg throughout the specimen, indicating that chromium migration did not occur. It is also evident from the Cr(VI) and Cr(III) concentration profiles shown in Fig. 5b and Fig. 6b that the initially introduced Cr(III) did not oxidize and remained as Cr(III). The low pH conditions in kaolin increased the solubility of Cr(III) and as a result contributed to greater extent of chromium migration; however, high pH near the cathode caused Cr(III) to precipitate (Griffin et al., 1977). The high pH conditions throughout the glacial till caused precipitation of all of the Cr(III), thus hindering any chromium migration.

When the initial form of chromium was Cr(VI), chromium migration towards the anode was observed in both kaolin and glacial till as seen in Fig. 4a and Fig. 4b. For kaolin, the total chromium concentration varied from a negligible amount near the cathode to 1100 mg/kg in the middle of the soil specimen to 800 mg/kg near the anode. A significant amount of chromium was located in the middle of the specimen (Fig. 4a). The Cr(VI) profile for kaolin as shown in Fig. 5a indicates that the majority of the chromium was present in the form of Cr(VI) and this chromium migrated towards the anode. The Cr(III) profile in Fig. 6a shows that small amounts of Cr(VI) were reduced to Cr(III) with concentrations decreasing from 200 mg/kg near the anode to an undetectable level near the cathode.

As seen in Fig. 4b for glacial till with Cr(VI), the migration of total chromium from the cathode to the anode was significant as compared to the migration that was observed in kaolin. The total chromium concentration ranged from negligible concentration near the cathode to 2400 mg/kg near the anode. The Cr(VI) concentration profile shown in Fig. 5b shows that chromium migrated predominantly in the form of Cr(VI). The Cr(III) concentration profile in Fig. 6b shows that although chromium was initially introduced as only Cr(VI), high Cr(III) concentrations were observed. The Cr(III) concentrations decreased from 1000 mg/kg near the anode to less than 10 mg/kg near the cathode. This reduction of Cr(VI) to Cr(III) was greater in glacial till as compared to that observed in kaolin. Overall, the migration of chromium in Cr(VI) form was more efficient in glacial till because of the high pH conditions that caused low adsorption of Cr(VI); however, significant adsorption of Cr(VI) in low pH regions near the anode in glacial till as well as through most of kaolin hindered chromium migration (Griffin et al., 1977; Rai et al., 1989; Reddy et al., 1997).

For the combination of Cr(III) and Cr(VI) as the initial chromium form, the migration occurred as shown

in Fig. 4a and Fig. 4b for kaolin and glacial till, respectively. In kaolin, as seen in Fig. 4a, total chromium concentrations varied from 600 mg/kg near the cathode to over 1000 mg/kg at the middle of the specimen and then decreased to approximately 900 mg/kg near the anode region. The Cr(VI) profile shown in Fig. 5a indicates that the portion of chromium that existed in Cr(VI) form migrated away from the cathode regions towards the anode. The remaining chromium in Cr(III) form migrated slightly away from the anode regions towards the cathode, as shown in Fig. 6a. This contrasting migration behavior of Cr(III) and Cr(VI) may be responsible for the overall low migration of chromium towards the electrodes.

For glacial till with Cr(III) and Cr(VI) existing together as the initial chromium form, the total chromium concentrations as shown in Fig. 4b varied from 500 mg/kg near the cathode to 1250 mg/kg in the middle of the specimen. Then, the concentrations decreased towards the anode, but then increased to 1250 mg/kg near the anode. Cr(VI) concentrations, as shown in Fig. 5b, varied from a negligible amount in the cathode region to 600 mg/kg in the middle of the specimen, to 400 mg/kg near the anode. The Cr(III) profile, as shown in Fig. 6b, shows Cr(III) concentration of 500 mg/kg near the cathode to 700 mg/kg in the middle section of the specimen, to 900 mg/kg near the anode. This chromium migration behavior was similar to that behavior observed in kaolin. These results show that chromium that existed as Cr(VI) migrated towards the anode and the portion that existed as Cr(III) may have precipitated.

Table 3 shows that, regardless of the initial chromium form in the soil, chromium migration into the cathode reservoir was negligible for both soils. This result may be due to either the precipitation of Cr(III) in the soil near the cathode or Cr(VI) migration towards the anode. The migration of chromium into the anode reservoir was significant, with the highest amount occurring when only Cr(VI) was present in the soil, followed by the combination of Cr(VI) and Cr(III). The lowest migration into the anode reservoir occurred when Cr(III) alone was present. The highest chromium migration, approximately 11.5% of the initial total chromium in the soil, occurred in the anode reservoir in glacial till containing chromium in Cr(VI) form alone. A slight amount of chromium in the anode compartment was observed even when chromium existed in the soil as only Cr(III). This migration may be attributed to diffusion of Cr(III) as it is likely to exist in dissolved phase because of low pH conditions near the anode.

The electro-osmotic flow occurred from the anode to the cathode in all tests. However, Cr(VI) migration occurred towards the anode, i.e. in the opposite direction of the electro-osmotic flow. This indicates that the predominant contaminant transport process is the elec-

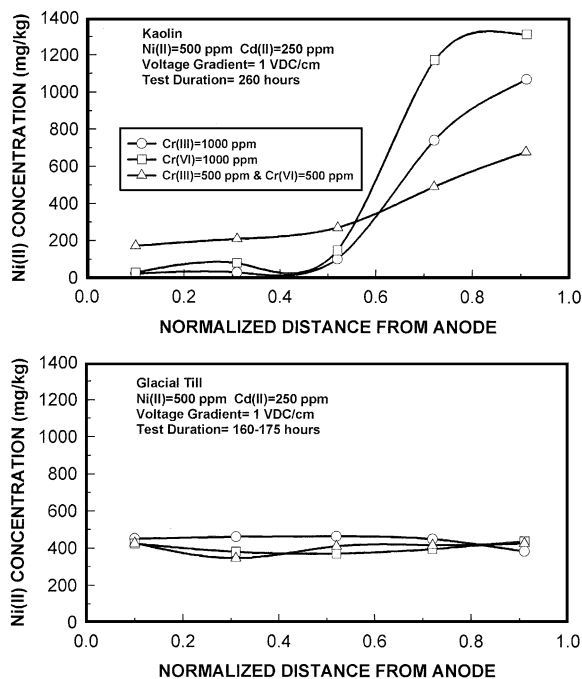


Fig. 7. Ni(II) concentration profiles.

from migration. It has been reported that the electromigration rate is at least 10 times (for some species, it can be as high as 300 times) higher than the advective transport due to electro-osmosis (Acar and Alshawabkeh, 1993). Overall, the experimental results show that significant removal of chromium from the soil into electrode reservoirs was not achieved; therefore investigation of enhancement strategies that induce favorable geochemical conditions in the soil that will allow for enhanced chromium removal is recommended.

### 3.5. Nickel and cadmium migration

In addition to chromium, both nickel Ni(II) and cadmium Cd(II) were introduced into the soils with initial concentrations of 500 and 250 mg/kg, respectively, for all tests, to simulate typical electroplating contamination conditions. Ni(II) and Cd(II) were used to investigate synergistic effects of different forms of chromium on the migration of co-existing Ni(II) and Cd(II) under an induced electric potential.

Fig. 7a,b show the concentration profiles of Ni(II) in kaolin and glacial till, respectively. These results show that Ni(II) migrated towards the cathode in kaolin; however, Ni(II) migration did not occur in the glacial till. A significant amount of Ni(II) migration occurred in kaolin when chromium was present as either Cr(III) only or Cr(VI) only. In these cases, the Ni(II) concentrations varied from non-detectable levels near the anode

to a very high value ranging from 1100 to 1350 mg/kg at the cathode. However, when chromium was present as a combination of Cr(III) and Cr(VI), the Ni(II) migration was moderate, with Ni(II) concentrations 200 mg/kg near the anode to 700 mg/kg near the cathode. The differences in Ni(II) migration rates may be a result of complex adsorption and precipitation behavior, as well as migration rates of Cr(VI) and Cr(III) species when present together in different pH regions within the soil. In glacial till, however, the effects of different forms of chromium on Ni(II) migration are not distinguishable because of all of Ni(II) precipitated under the alkaline conditions that existed throughout the soil.

As shown in Table 3, a negligible migration of Ni(II) occurred into the cathode reservoir; however, noticeable amounts of Ni(II) migrated into the anode reservoir for both soils. The amount of Ni(II) that migrated into the anode reservoir ranged from 0.2 to 2.8% of the total initial Ni(II) present in the soil, except for glacial till with Cr(VI) for which 7.3% of Ni(II) migrated into the anode. The lower migration of Ni(II) into the cathode reservoir was attributed to Ni(II) precipitation near the cathode in kaolin and throughout the glacial till due to high pH conditions. The observed migration of Ni(II) into the anode for both soils may be attributed to diffusion, as most Ni(II) exists in the dissolved phase near the anode because of low pH conditions and/or the formation of anionic complexes, which migrated into the anode.

Fig. 8a,b show the concentration profiles of Cd(II) in kaolin and glacial till, respectively. These results are similar to the results for Ni(II) and show that in kaolin, Cd(II) migration was significant when Cr(III) alone or Cr(VI) alone was present, with Cd(II) concentration varying from non-detectable levels near the anode to values ranging from 500 to 550 mg/kg near the cathode. A moderate Cd(II) migration occurred when the combination of Cr(III) and Cr(VI) was present, with Cd(II) concentration ranging from 150 mg/kg near the anode to 300 mg/kg near the cathode. In glacial till, for all forms of chromium, Cd(II) was precipitated without any migration due to the alkaline conditions that existed throughout the soil.

Table 3 shows that Cd(II) migration into the cathode reservoir was either below the detection level or negligible, and very small amounts of Cd(II), ranging from 0.2 to 1.0% of the initial total Cd(II) present in the soil, migrated into the anode reservoir. The Cd(II) migration into the anode reservoir was consistently lower than that of Ni(II) for all of the tests. Similar to Ni(II), Cd(II) migration into the cathode reservoir was hindered by precipitation due to high pH conditions near the cathode, while the migration into the anode reservoir was due to diffusion and/or migration as anionic complexes. These results also clearly demonstrate the need for additional research to investigate proper enhance-

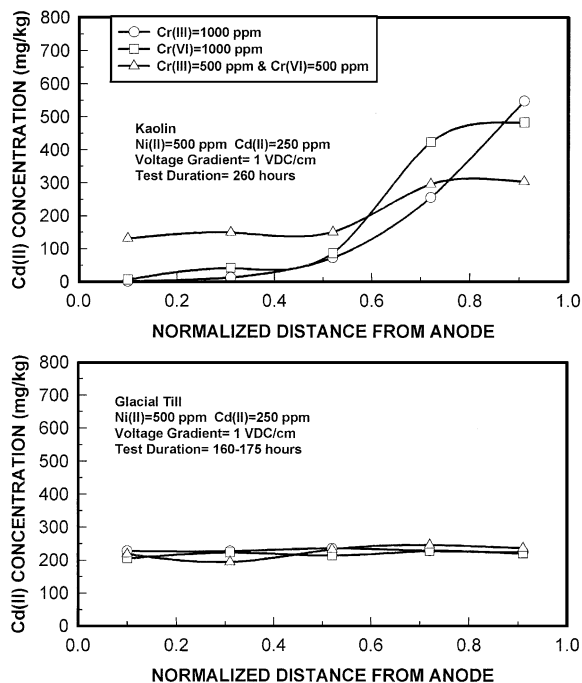


Fig. 8. Cd(II) concentration profiles.

ment strategies to remove both Ni(II) and Cd(II) from the soil and direct them into the reservoirs.

#### 4. Conclusions

This study demonstrated that electrokinetic remedial efficiency during application at typical electroplating waste sites depends on the initial form of chromium, the co-contaminants that exist in the soil and the soil type. The following specific conclusions can be drawn from this study:

1. Chromium in the form of Cr(III) possibly exists as cation and cationic hydroxyl complexes and migrates towards the cathode region. In kaolin, Cr(III) migrated from low pH regions near the anode; however, it precipitated in high pH regions near the cathode. In glacial till, because of the high pH conditions that existed due to its high buffering capacity, Cr(III) precipitated without any migration.
2. Chromium in the form of Cr(VI) exists as oxyanions and migrates towards the anode. In kaolin, moderate migration of Cr(VI) was observed. In glacial till, a significant migration of Cr(VI) towards the anode was observed. A partial reduction of Cr(VI) into Cr(III) was observed near the anode in both soils; however, this reduction was greater in glacial till as compared to kaolin.
3. The migration of chromium in the combined form of Cr(III) and Cr(VI) was complex, with the Cr(III)

species attempting to migrate towards the cathode and the Cr(VI) species attempting to migrate towards the anode. As a result of this contrasting migration behavior of Cr(III) and Cr(VI) species, chromium migration towards the electrodes was inefficient.

4. The migration of co-contaminants, Ni(II) and Cd(II), was affected by the form of chromium as well as the soil type. In kaolin, the migration of Ni(II) and Cd(II) was retarded due to the presence of Cr(III) and Cr(VI) in combination. When chromium existed as either Cr(III) or Cr(VI), the migration of Ni(II) and Cd(II) was significant. Both Ni(II) and Cd(II) were precipitated near the cathode due to high pH conditions. In glacial till, Ni(II) and Cd(II) precipitated throughout the soil due to high pH conditions; therefore, synergistic effects of chromium in different forms on Ni(II) and Cd(II) were not evident in this case.

A significant migration of the contaminants occurred towards the electrodes within the soil; however, migration into the electrode reservoirs was hindered due to adsorption, precipitation and reduction of the contaminants in the soils. It may be possible to enhance contaminant migration and removal from the soil by using enhancement strategies, such as the use of a weak acid rather than water at the cathode to lower soil pH in the cathode regions. Additional research is warranted to determine the most appropriate enhancement strategy that will remove the contaminants from the soil in an efficient, safe and cost-effective manner.

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