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Transient behavior of heavy metals in soils during electrokinetic remediation

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Abstract

This paper presents a systematic bench-scale laboratory study performed to assess the transient behavior of chromium, nickel, and cadmium in different soils during electrokinetic remediation. A series of laboratory electrokinetic experiments was conducted using two different clayey soils, kaolin and glacial till. For each type of soil, four electrokinetic experiments with 1, 2, 4, and 10 d of treatment time were performed. In all tests, the contaminants were Cr(VI), Ni(II), and Cd(II) combined in the soil. A geochemical assessment was performed using the geochemical model MINEQL$^+$ to determine the partitioning of the heavy metals in soils as precipitated, adsorbed, and aqueous forms. Results showed that in kaolin, the extent of Ni(II) and Cd(II) migration towards the cathode increased as the treatment time increased. Unlike kaolin, in glacial till treatment time had no effect on nickel and cadmium migration because of its high buffering capacity. In both kaolin and glacial till, the extent of Cr(VI) migration towards the anode increased as the treatment time increased. However, Cr(VI) migration was higher in glacial till as compared to kaolin because of the high pH conditions that existed in glacial till. In all tests, some Cr(VI) was reduced to Cr(III), and the Cr(VI) reduction rate to Cr(III) as well as the Cr(III) migration were significantly affected by the treatment time. Overall, this study showed that the electroosmotic flow as well as the direction and extent of contaminant migration and removal depend on the polarity of the contaminant, the type of soil, and the treatment duration.

Keywords: Electrokinetic remediation; Soil pollution; Heavy metals; Contaminant speciation; Geochemical model

1. Introduction

The improper disposal and accidental spillage of toxic and hazardous chemicals from domestic, agricultural and industrial activities have led to serious soil contamination, creating an urgent need to find feasible solutions to the problem. Heavy metals, such as lead, chromium, nickel, cadmium and arsenic are major soil contaminants at numerous industrial sites and at many of the Superfund sites throughout the United States (Sharma and Reddy, 2004). Due to the low hydraulic conductivity of fine-grained soils, the remediation of such soils contaminated with heavy metals by conventional methods such as in situ flushing has been found to be very costly and mostly ineffective. Electrokinetic remediation is one of the developing techniques that has significant potential for in situ remediation of the fine-grained soils. Electrokinetic remediation involves applying a low direct current (in order of mA cm^{-2} of the cross-sectional area of the electrodes) or a low potential gradient (in order of V cm^{-1} of the distance between the electrodes) to electrodes that are inserted into the ground. As a result, the contaminants are transported by electroosmosis and electromigration to either the cathode or anode where they are extracted by one or more of the following methods: electroplating, adsorption onto the electrode, precipitation or co-precipitation at the electrode, pumping water near the electrode, or complexing with ion-exchange resins (Lindgren et al., 1992; Acar and Alshawabkeh, 1993).

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The application of a direct electric current to soil results in several changes, such as pH, redox potential and electrolyte concentration, in the soil medium. These changes may impact the nature of the clay surface chemistry and the success of the electrochemical remediation. Understanding the changes in transport processes and geochemical conditions at various stages of electrokinetic remediation process is the fundamental requirement to the success of remediation. A laboratory simulation of electrokinetic process can allow investigation of such fundamental aspects of electrokinetic remediation. Numerous laboratory studies have been performed on electrokinetic remediation of soils contaminated with inorganic, organic, and radionuclides (Bruell et al., 1992; Shapiro and Probstein, 1993; Eykholt and Daniel, 1994; Ugaz et al., 1994; Acar and Alshawabkeh, 1996; Yeung et al., 1996). However, the major drawback of these studies is that they were performed using commercial clays, mostly kaolinite, and they studied only individual contaminants. Studies on field soils with simulated multiple contaminants are relatively few (Rodsand et al., 1995; Reddy and Parupudi, 1997; Reddy et al., 2001). Most of the previous studies were conducted for a specified duration of several days or weeks to remove the contaminant from the soil and few addressed the transient behavior of the contaminant in the soil during electrokinetics. Moreover, some studies showed predicted time-dependant behavior of the contaminant resulted from electrokinetic modeling with validation based on results for a single specific treatment duration (Alshawabkeh and Acar, 1992, 1996; Lindgren et al., 1993; Jacobs et al., 1994; Yeung and Datla, 1995; Yu and Neretnieks, 1996; Haran et al., 1997). In addition, most of these studies were concerned with the residual contaminant distribution in the soil and the overall removal efficiency after the electrokinetic treatment. Many of these studies showed low removal of heavy metals from soils using electrokinetics. Unfortunately, these studies do not investigate a detailed chemical speciation of the contaminants or how the contaminants are held (retained

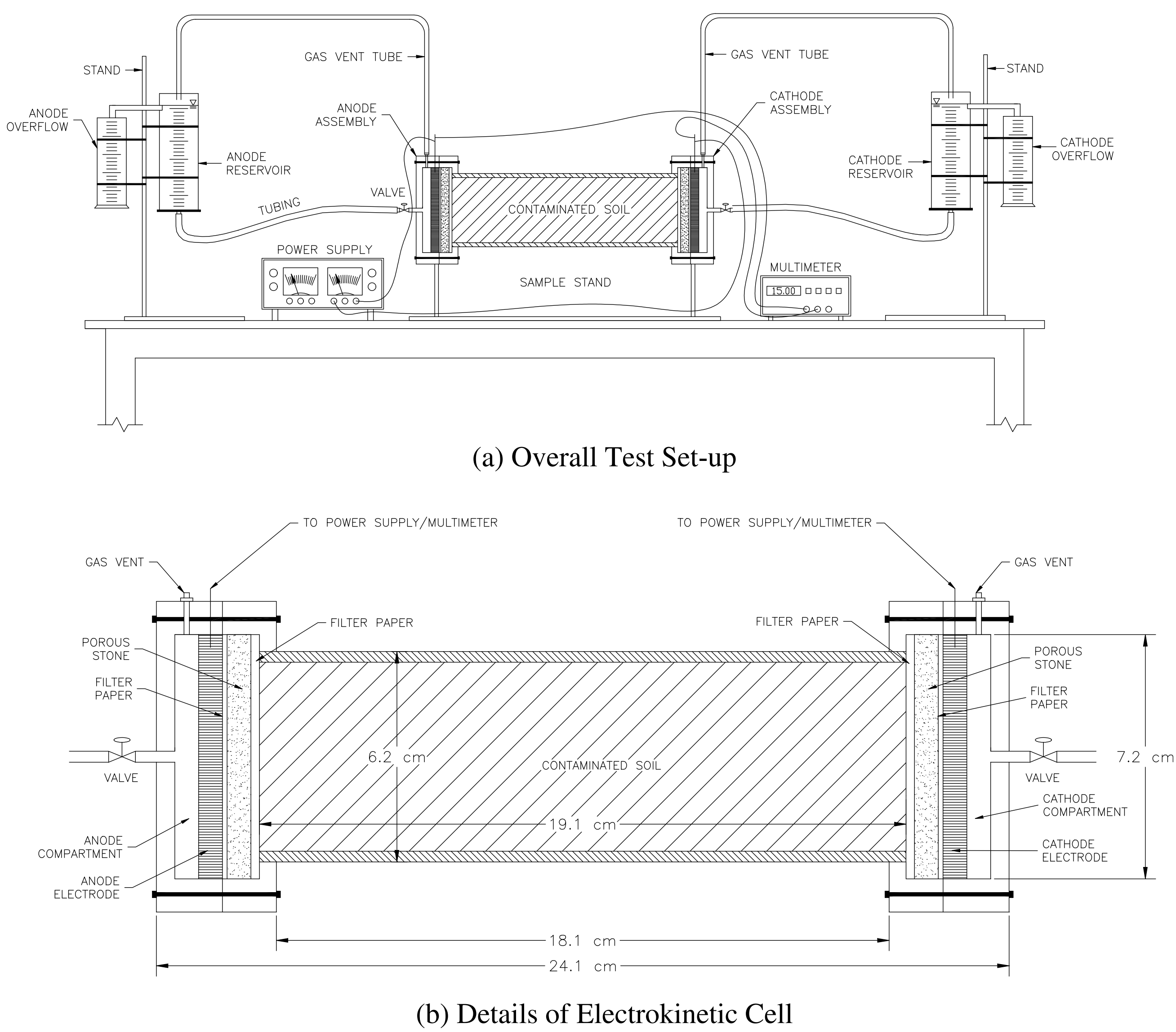

Fig. 1. Bench-scale electrokinetic test setup.

and bounded) to the soil constituents. Some modeling studies showed speciation of contaminants in the soils during electrokinetics, but these studies were often limited to a single contaminant such as lead (Jacobs et al., 1994; Alshawabkeh and Acar, 1996; Yu and Neretnieks, 1996). A detailed assessment of speciation and distribution of contaminants in soils during electrokinetic remediation will provide possible reasons for low contaminant removal under electrokinetics. Furthermore, understanding the contaminant retaining mechanisms in soil–water system during electrokinetics will provide a rational approach to engineer the geochemistry for enhanced contaminant remediation.

This paper presents the results of a systematic laboratory study to assess the transient behavior of chromium, nickel, and cadmium in two different soils during electrokinetic remediation. By studying the contaminant speciation and distribution during electrokinetics, this study provided a better understanding of how the contaminants are held to or within the soil constituents.

2. Experimental methodology

2.1. Electrokinetic test setup

Fig. 1 shows a schematic of the electrokinetic test setup used for all of the tests performed in this study. The detailed description of this setup has been given by Reddy et al. (1997). The setup consisted of an electrokinetic cell, two electrode compartments, two electrode reservoirs, a power source, a multimeter, flow control valves, and gas vents. This setup also incorporated two electrodes, two porous stones, filter papers, and tubing. The setup simulated one-dimensional transport of contaminants under an induced electric potential.

2.2. Materials

Two different clayey soils were selected for this study: kaolin, which is a typical low buffering soil, and glacial till, which is a typical high buffering soil. Kaolin is a commercially available soil and was obtained from the American Clay Minerals Society. Glacial till is a field-derived soil and was obtained from DuPage County, Illinois. These soils have been characterized in detail and have been used in previous investigations (Reddy and Parupudi, 1997; Reddy et al., 1997; Reddy and Chinthamreddy, 1999). Table 1 summarizes the composition and properties of these soils.

The source chemicals used for the heavy metal contaminants of this study were potassium dichromate (K_2CrO_4, ACS certified) for Cr(VI); nickel chloride ($NiCl_2 \cdot 6H_2O$, technical fisher chemical) for Ni(II), and cadmium chloride ($CdCl_2 \cdot 2.5H_2O$, ACS certified) for Cd(II).

2.3. Testing program

A series of laboratory electrokinetic experiments was conducted to investigate the effect of the treatment time (i.e., the time of applying voltage gradient) on the migration behavior of combined contaminants in the in kaolin and glacial till soils. For each type of soil, four electrokinetic experiments with 1, 2, 4, and 10 d of treatment time were performed. In these experiments both soils were spiked with 1000 mg kg^{-1} of Cr(VI), 500 mg kg^{-1} of Ni, and 250 mg kg^{-1} of Cd. In each experiment, a voltage gradient of 1 VDC cm^{-1} was applied. In all experiments, deionized water was used as the electrode solution. The deionized water used for all experiments in this study had pH 5.7, redox = 199 mV, and electrical conductivity (EC) = 0 μS cm^{-1}. The pH and redox potential were measured using an Orion pH-triode probe. The electrical conductivity was measured using an EC glass probe.

2.4. Testing procedure

Approximately 1.1 kg of dry soil was used for each test. The required amounts of the chemicals that would yield the desired concentrations of Cr(VI), Ni(II), and Cd(II) were weighed and then dissolved individually in deionized water. These contaminant solutions were then added to the soil and mixed thoroughly with a stainless steel spatula in a high density polyethylene container. A total of 375 mL of deionized water (to yield 35% moisture content) was used

Table 1
Properties of the soils used in this study

Property	Kaolin	Glacial till
Mineralogy (%)	Kaolin: 100	Quartz: 31
	Muscovite: trace	Feldspar: 13
	Illite: trace	Carbonate: 35
		Illite: 15
		Chlorite: 4–6
		Vermiculite: 0.5
		Smectite: trace
Particle size distribution (ASTM D 422)		
Gravel (%)	0	0
Sand (%)	4	20
Silt (%)	18	44
Clay (%)	78	36
Atterberg limits (ASTM D 2487)		
Liquid limit (%)	50.0	21.7
Plastic limit (%)	27.4	11.7
Plasticity index (%)	22.6	10.0
Specific gravity (ASTM D 854)	2.60	2.71
Moisture-unit weight relationships (harvard miniature compaction test)		
Maximum dry unit weight (kN m^{-3})	14.4	18.5
Optimum moisture content (%)	27	14.5
Hydraulic conductivity (or coefficient of permeability) (cm s^{-1})	1.3×10^{-7}	4.1×10^{-8}
Cation exchange capacity (ASTM D 9081) (meq $(100\ g)^{-1}$)	1.0–1.6	13–18
pH (ASTM D 4972)	4.9	8.2
Organic content (ASTM D 2974) (%)	Near 0	2.8
USCS classification (ASTM D 2487)	CL	CL

Table 2
Constant capacitance model parameters for kaolin

Surface area (S_A)		$24\ m^2\ g^{-1}$
Surface site density (N_S)		2.35 sites nm^{-2}
Constant capacitance (C)		$1.0\ F\ m^{-2}$ if I = 0.1 M
		$0.7\ F\ m^{-2}$ if I = 0.01 M
		$0.5\ F\ m^{-2}$ if I = 0.001 M
Ion	Intrinsic constant expression	$\log K^{int}$
Intrinsic constants		
H^+	$SOH + H^+ \leftrightarrow SOH_2^+$	3.8 ± 0.5
	$SOH - H^+ \leftrightarrow SO^-$	-9.4 ± 0.5
Cd^{2+}	$SOH + Cd^{2+} \leftrightarrow SOCd^+ + H^+$	-3.3 ± 1.0
Ni^{2+}	$SOH + Ni^{2+} \leftrightarrow SONi^+ + H^+$	-2.6 ± 0.6
Cr^{3+}	$SOH + Cr^{3+} \leftrightarrow SOCr^{2+} + H^+$	5.0 ± 1.0
CrO_4^{2-}	$SOH + CrO_4^{2-} + 2H^+ \leftrightarrow SOH_2HCrO_4$	12.5 ± 0.5

Table 3
Adsorption model parameters of glacial till

Metal	Freundlich Adsorption Model	n	$\log K_F$
Cadmium	$SOH + (\frac{1}{n})M \leftrightarrow SOH \bullet M$	0.68 ± 0.1	-0.14 ± 0.1
Nickel	$SOH + (\frac{1}{n})M \leftrightarrow SOH \bullet M$	0.89 ± 0.1	0.36 ± 0.2
Trivalent chromium	$SOH + (\frac{1}{n})M \leftrightarrow SOH \bullet M$	0.72 ± 0.2	0.69 ± 0.1
Hexavalent chromium	$SOH + (\frac{1}{n})M \leftrightarrow SOH \bullet M$	1.27 ± 0.1	-1.15 ± 0.05

for kaolin, while 285 mL of deionized water (to yield 25% moisture content) was used for the glacial till.

The contaminated soil was placed in the electrokinetic cell in layers and compacted uniformly. The soil was then allowed to equilibrate for 1 week. The electrode compartments were then connected to the electrokinetic cell at one end and connected to the anode or cathode reservoir at the other end. The reservoirs were then filled with the deionized water. The elevations of the electrode solution in both reservoirs were kept the same so that no hydraulic gradient existed across the specimen. The electrokinetic cell was then connected to the power supply and a constant voltage gradient of 1 VDC cm^{-1} was applied to the soil sample. The electric current across the soil sample as well as the water flow, pH, redox potential, and EC in both the anode and cathode reservoirs were measured at different time periods throughout the duration of the experiments.

At the end of predetermined test duration, aqueous solutions from the anode and cathode reservoirs and the electrode assemblies were collected and volume measurements were made. Then, the reservoirs and the electrode assemblies were disconnected and the soil was extruded from the cell using a mechanical extruder. The soil was sectioned into five parts and each part was weighed and subsequently preserved in glass bottles. For each section, about 10 g of soil was mixed with 10 mL of 0.1 M $CaCl_2$ solution in a glass vial. The mixture was shaken using a mechanical shaker and the solids were allowed to settle. The pH, redox potential, and EC of the soil–water mixture as well as that of the anolyte and catholyte were measured in accordance with ASTM D4972. The moisture content of each soil section was also determined in accordance with the ASTM Standard D2216.

Contaminants in different soil sections were extracted by performing acid digestion in accordance with USEPA 3050 procedure (USEPA, 1986). This extraction procedure allows the total concentrations of total chromium (i.e., Cr(VI) and Cr(III)), nickel, and cadmium to be determined. Alkaline digestion was also performed on soil sections in accordance with the USEPA 3060A procedure to extract only Cr(VI) into the solution. The supernatant (i.e., extracted solution) was analyzed using an atomic absorption spectrophotometer (AAS) to determine the concentrations of chromium, nickel and cadmium in accordance with the USEPA methods 7190, 7520, and 7130, respectively (USEPA, 1986; Reddy and Parupudi, 1997;

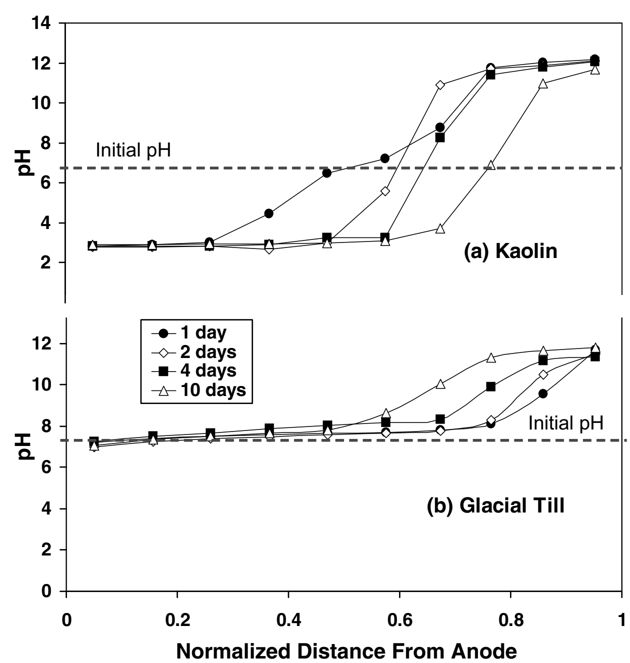

Fig. 2. Time-dependent distribution of pH in soil after elecktrokinetic treatment.

Reddy and Chinthamreddy, 1999). Aqueous samples from the electrode reservoirs were directly tested using AAS for the contaminant concentrations. Cr(III) concentrations were calculated by mass balance, that is by subtracting Cr(VI) concentrations determined by the alkaline digestion from the total chromium concentrations determined by the acid digestion procedure.

In order to ensure the accuracy and repeatability of the test results, the following measures were taken: (1) new electrodes, porous stones, and tubing were used for each experiment, (2) the electrokinetic test setup components were soaked in a dilute acid solution for 24 h and then rinsed with tap water followed by deionized water to avoid cross contamination between the experiments, (3) chemical analyses were performed in duplicate, (4) the interference with other elements in the atomic absorption spectrophotometer was avoided by using nitrous oxide and an acetylene flame for chromium and nickel analyses, (5) the atomic absorption calibration was checked after testing every five samples, and (6) a mass balance analysis was performed for each test. All the tests showed mass balance differences of generally less than 10%.

2.5. Geochemical assessment procedure

In order to assess the geochemical speciation and distribution of the Cr(VI), Ni(II), and Cd(II) during electrokinetics in the soils, the geochemical model MINEQL^{+} (Schecher and McAvoy, 1994) was used. The results of the performed electrokinetic experiments (i.e., metal total concentrations and pH) were implemented in MINEQL^{+} to determine the partitioning of the heavy metals in soils as precipitated, adsorbed, or aqueous form. The surface–aqueous interaction was implemented into the assessment procedure by using the electrostatic and non-electrostatic adsorption models for kaolin and glacial till, respectively. The surface complexation input data was based on series of adsorption experiments conducted using kaolin and

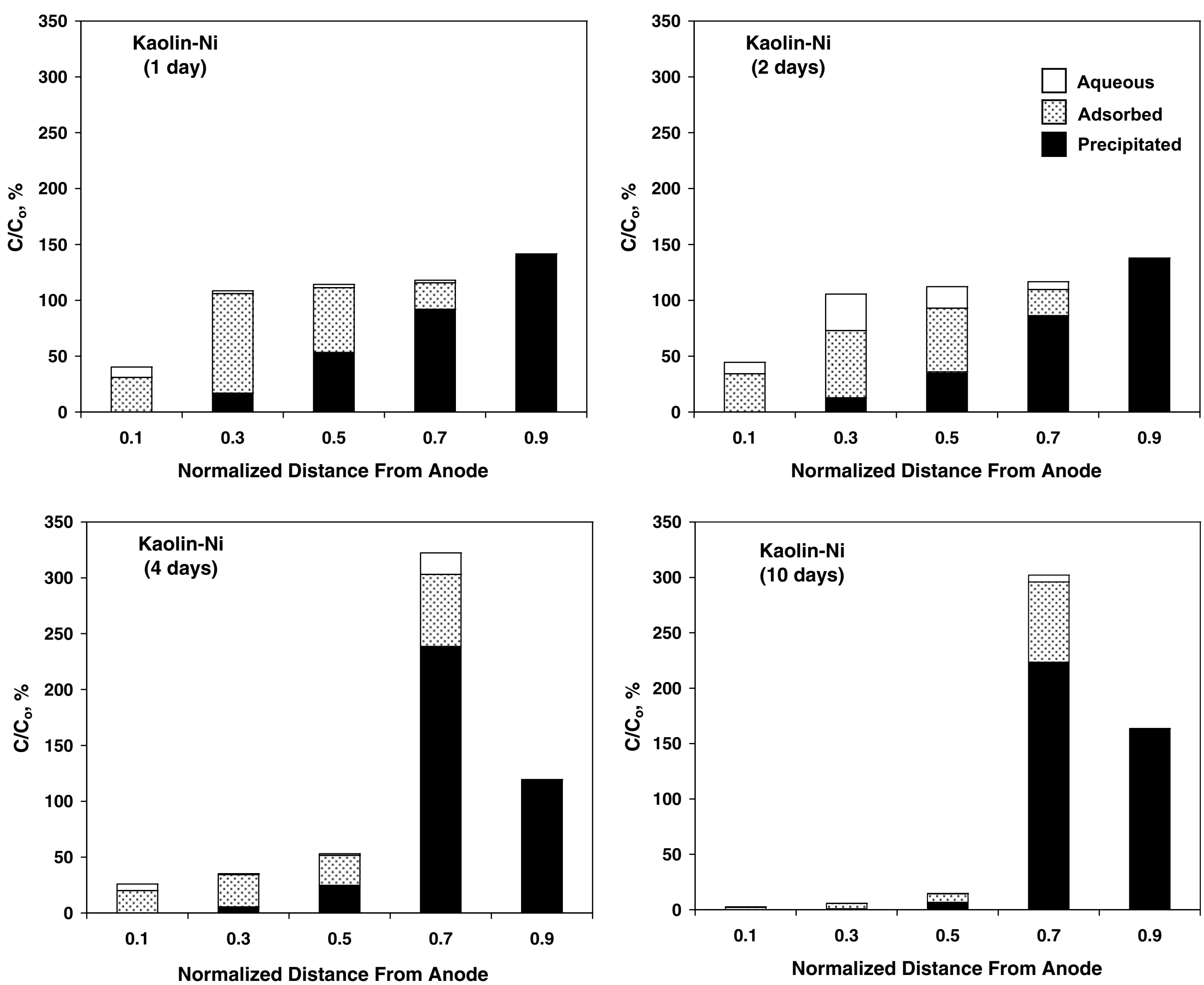

Fig. 3. Time-dependent distribution of nickel in kaolin after electrokinetic treatment.

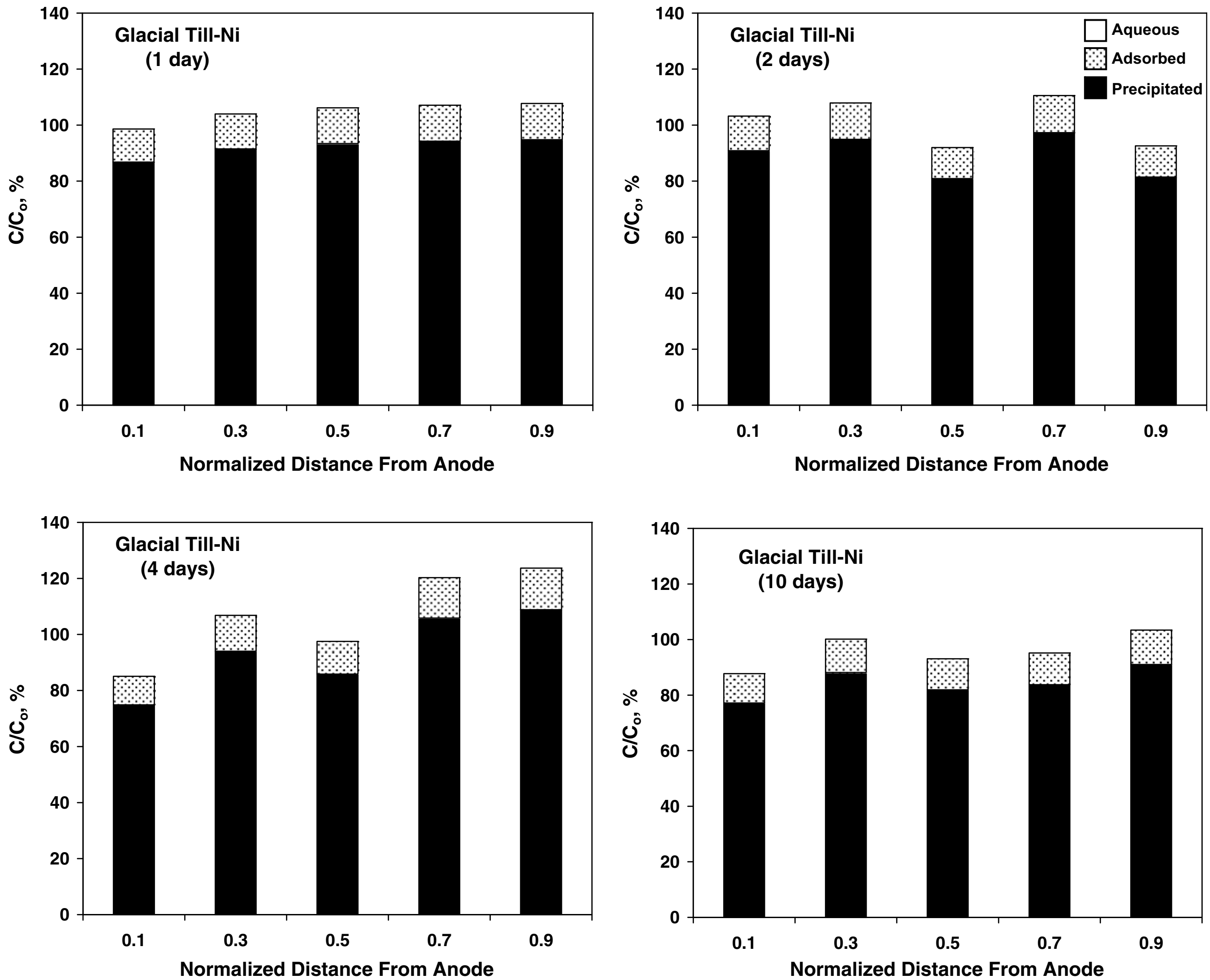

Fig. 4. Time-dependent distribution of nickel in glacial till after electrokinetic remediation.

glacial with Cr(VI), Ni(II), and Cd(II) (Al-Hamdan and Reddy, 2005, 2006). Tables 2 and 3 show the adsorption models and values of model parameters for the two studied soils. All the concentrations were introduced to MINEQL$^+$ as molar basis. The soil solution ratios were entered as 2.2–2.6 kg of soil to 1 l of water based on the measured water content of each section. The oxidation reduction (redox) chemistry was implemented in this study by specifying the redox couple Cr(VI)/Cr(III) and assuming the chromium species are in equilibrium with the O_2/H_2O couple (i.e., oxygen gas is generated at the anode and so water in the soil is oxygenated or oxygen-bearing water) (Stumm and Morgan, 1996). The electrostatic interaction between the ions was taken into consideration by activating the ionic strength correction option provided in MINEQL$^+$ model. MINEQL$^+$ utilizes Davies equation for ionic strength corrections which is valid for a wider range of ionic strength up to 0.5 M (Davis and Masten, 2004). In this study, the maximum calculated ionic strength of the MINEQL$^+$ simulations at pH 2.8 was about 0.108 M.

3. Results and analysis

3.1. Soil pH

Electrolysis of water generated H^+ ions at the anode and OH^- ions at the cathode (Acar and Alshawabkeh, 1993; Reddy et al., 1997). The H^+ ions in the anode migrated with time towards the cathode in kaolin as shown in Fig. 2a. The initial pH of kaolin with the contaminants before applying the electric potential was 6.9. The soil pH decreased to about 2.8 at the region close to the anode on the first day then extended towards the middle of the sample with time. It can be noticed that the initial soil pH (i.e., 6.9) was located at about 0.54, 0.59, 0.63, and 0.78 normalized distances from the anode for 1, 2, 4, and 10 d tests, respectively (Fig. 2a). In other words, the net acid–base front migrated towards the cathode at the rate of 7×10^{-5} at early stages to 3.5×10^{-5} cm s^{-1} V^{-1} at later stages. The point where the acid and OH^- fronts meet moved backwards the cathode, and that is a proof of

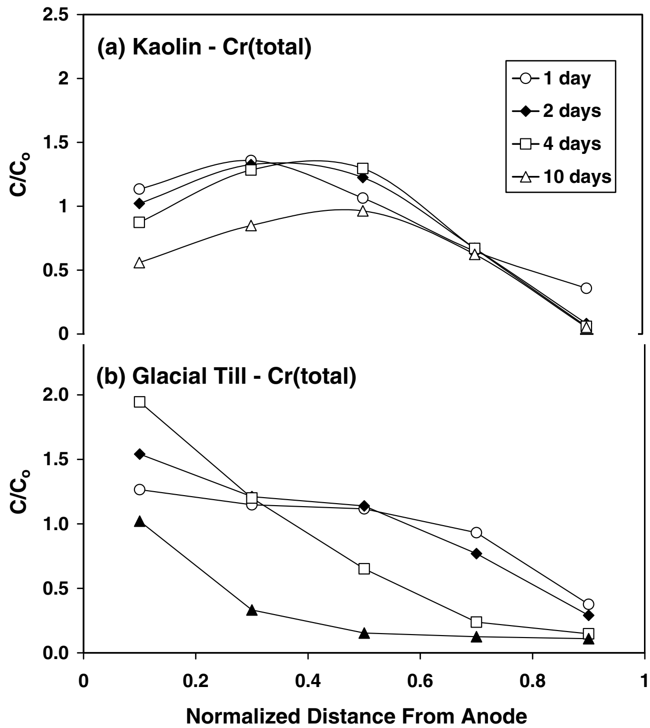

Fig. 5. Time-dependent distribution of total chromium in soil after elecktrokinetic treatment.

higher mobility of H^+ ions in soils than OH^- ions. Moreover, because H^+ possess higher mobility than OH^-, and the H^+ ions are also transported with electroosmotic flow while the OH^- ions are hindered from transport due to electroosmotic flow in opposite direction, then the number of sustaining H^+ ions to the point where the two fronts meet push the OH^- front back (i.e., the rate of advance of the acid front is higher than the base). Therefore, the soil pH eventually stabilized at a point when the net rate OH^- and H^+ are the same.

For the glacial till that has a high buffering capacity, Fig. 2b shows clearly that the base front (OH^-) generated at the cathode migrated towards the anode. However, acid front (H^+) generated at the anode was immediately neutralized by the soil and hence no acid front was generated in the soil. The pH of the soil did not change in the area close to the anode (i.e., pH 7.6), while it increased with time in the area close to the cathode. Therefore, the carbonates in glacial till provided buffering and significantly influenced the pH changes in the soil, consequently affecting the heavy metal transport behavior during electrokinetics. The pH in the anode region did not change even after 10 d treatment.

3.2. Metal migration

The MINEQL$^+$ results showed that cadmium and nickel have similar behavior in kaolin and glacial till during electrokinetic remediation (Al-Hamdan, 2002). Therefore, only nickel and chromium results are presented herein. For the initial soil conditions before applying the electric gradient, MINEQL$^+$ results showed that in kaolin Ni was totally adsorbed to the soil surfaces prior to the electrokinetic treatment. In glacial till, most of the nickel precipitated as $Ni(OH)_2$ and some of Ni was adsorbed to the solid surfaces. Most of the hexavalent chromium initially existed as aqueous form within kaolin and glacial till. In kaolin, 42% of the aqueous form of the chromium was as CrO_4^{2-}, 30% as $Cr_2O_7^{2-}$, and 28% as $HCrO_4^-$. In glacial till, 94% of the aqueous form of chromium was as CrO_4^{2-}, 1% as $Cr_2O_7^{2-}$, and 4.7% as $HCrO_4^-$. Some of the chromium was initially adsorbed to the soils.

The experimental results determined the distribution of the metals throughout the soil sample after electrokinetic treatment (i.e., ratio of the total metal concentration at each section after electrokinetics to its initial concentration before electrokinetics). The MINEQL$^+$ model was used to predict the proportions of aqueous, adsorbed, and precipitated forms of the metals at equilibrium using the total elemental composition of the soil at the end of the electrokinetic treatment. The transient behavior of nickel in kaolin during electrokinetics is shown in Fig. 3. The treatment time had a significant effect on the extent of nickel migration toward the cathode. For the first day, a slight migration of nickel occurred because the pH front did not move far enough (i.e., pH 6 for the soil located after 0.4 as normalized distance from the anode), keeping the nickel be adsorbed or precipitated in most of the soil. The same was observed for 2 d. As the acid front advanced towards the cathode with time, soil pH was lowered and the nickel was desorbed. As a result, nickel migrated towards the cathode and finally accumulated either as precipitates or adsorbates at the sections close to the cathode where the high pH conditions exist. In glacial till, there was no effect of treatment time on nickel distribution (see Fig. 4). Because of the high pH conditions even under prolonged treatment time, nickel existed as precipitated and adsorbed forms and no migration resulted.

The time-dependent profiles of normalized total chromium for kaolin and glacial till after electrokinetic tests are shown in Fig. 5a and b, respectively. In both tested soils, and for all treatment times, the total concentrations of chromium were higher near the anode and in the middle of soil sample and lower near the cathode region. These concentration variations indicate that chromium migrated from the cathode region toward the anode region. However, the chromium migration was more significant in glacial till than in kaolin. Figs. 6 and 7 show that adsorption was the hindering mechanism for the removal of Cr(VI) from kaolin and glacial till, respectively. The adsorption of Cr(VI) in kaolin was higher than in glacial till because of the low pH conditions that existed in kaolin compared to those in glacial till. Moreover, the high pH conditions of glacial till caused Cr(VI) to exist in the aqueous form. For kaolin, increasing treatment time from 1 to 4 d showed slow migration of Cr(VI) towards the anode, while further increase in treatment time to 10 d showed substantial migration of Cr(VI) towards the anode.

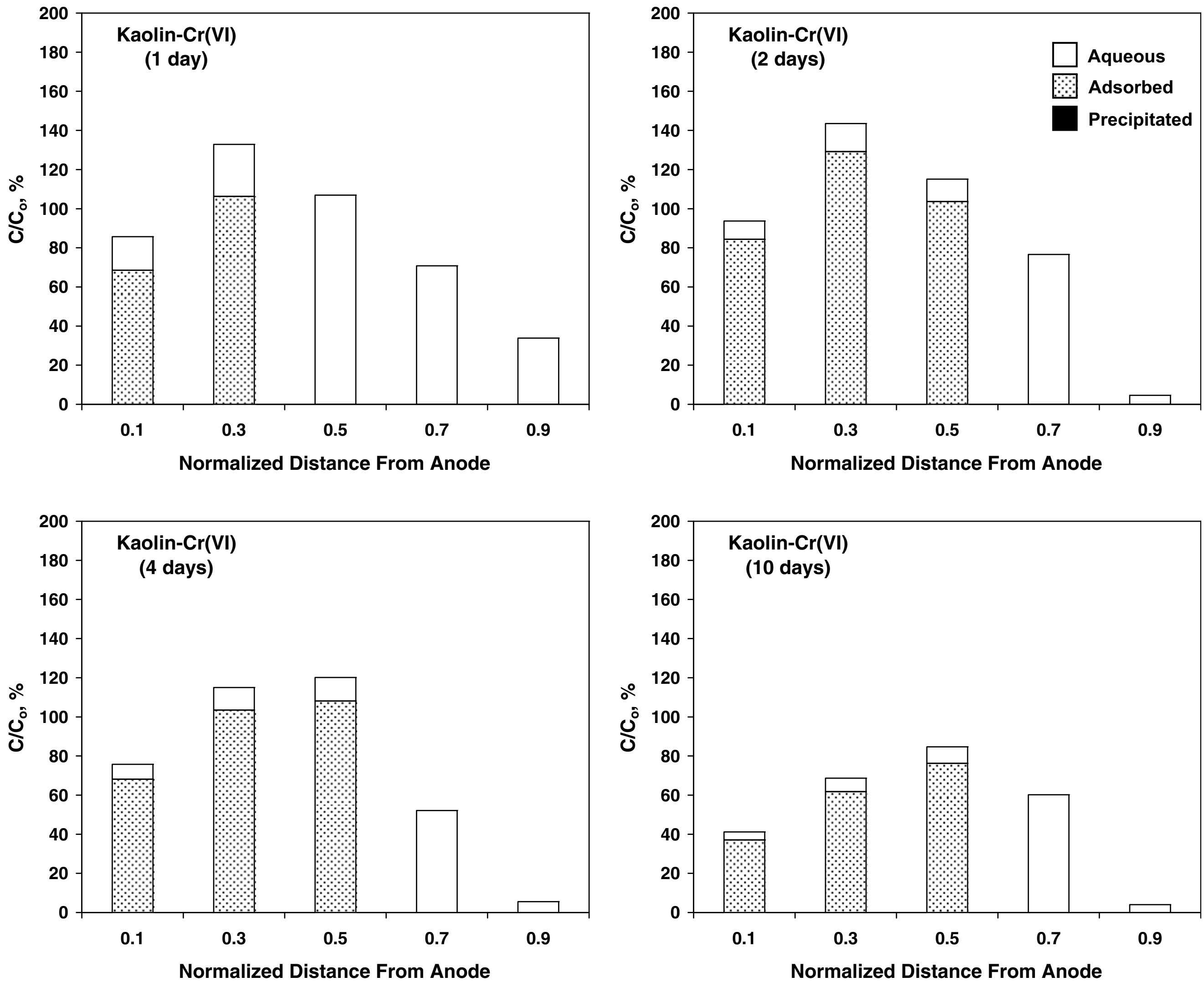

Fig. 6. Time-dependent distribution of hexavalent chromium in kaolin after electrokinetic treatment.

These results demonstrated that chromium migration increases with increased duration; however, at later stages, soil pH is significantly lowered near the anode resulting higher adsorption and slower migration of Cr(VI). For glacial till, 1–2 d tests had similar residual chromium concentrations, however increased treatment time to 4 and 10 d reduced the concentrations. The concentrations for 10 d test were much lower than 4 d test. These results suggest that further increased test duration may lead to further decrease in residual chromium concentrations in glacial till.

Initially chromium was introduced as Cr(VI), but the experimental results showed a partial reduction of Cr(VI) to Cr(III). In kaolin, the concentrations of Cr(III) in the soil at the end of electrokinetic treatment ranged from 0 to 252 mg kg^{-1} in the sections close to the cathode and anode. In glacial till, Cr(III) concentrations ranged from 96 to 367 mg kg^{-1} in the sections close to the cathode and anode. The reduction of Cr(VI) to Cr(III) could be attributed to the oxygen and hydrogen gases that were generated at the electrodes which can alter the redox conditions of the pore water (i.e., the oxidation and reduction of water limits the electron activity in the natural system). Such conditions change the redox state of the metals (Stumm and Morgan, 1996). In all tests, the measured redox potential values in the reservoirs showed that oxidizing conditions prevailed in the anode (i.e., ranged from 217 to 314 mV), while reducing conditions prevailed in the cathode (i.e., ranged from −315 to −345 mV). In kaolin tests, the redox potential values in the soil after electrokinetic treatment ranged from 258 to 273 mV in the sections close to the anode (i.e., in the area between 0 and 40% as normalized distance from the anode), while it ranged from −285 to 28 mV in the sections close to the cathode. In glacial till tests, the redox potential values in the soil after electrokinetic treatment were negative ranged from −1 to −261 mV throughout the soil except at the sections close to the anode where the redox ranged from 0 to 22 mV. In general, when the redox potential is above 200 mV, the system is considered slightly oxidizing, and when it is above 800 mV, it is considered highly oxidizing. Furthermore, when the redox potential is below 200 mV,

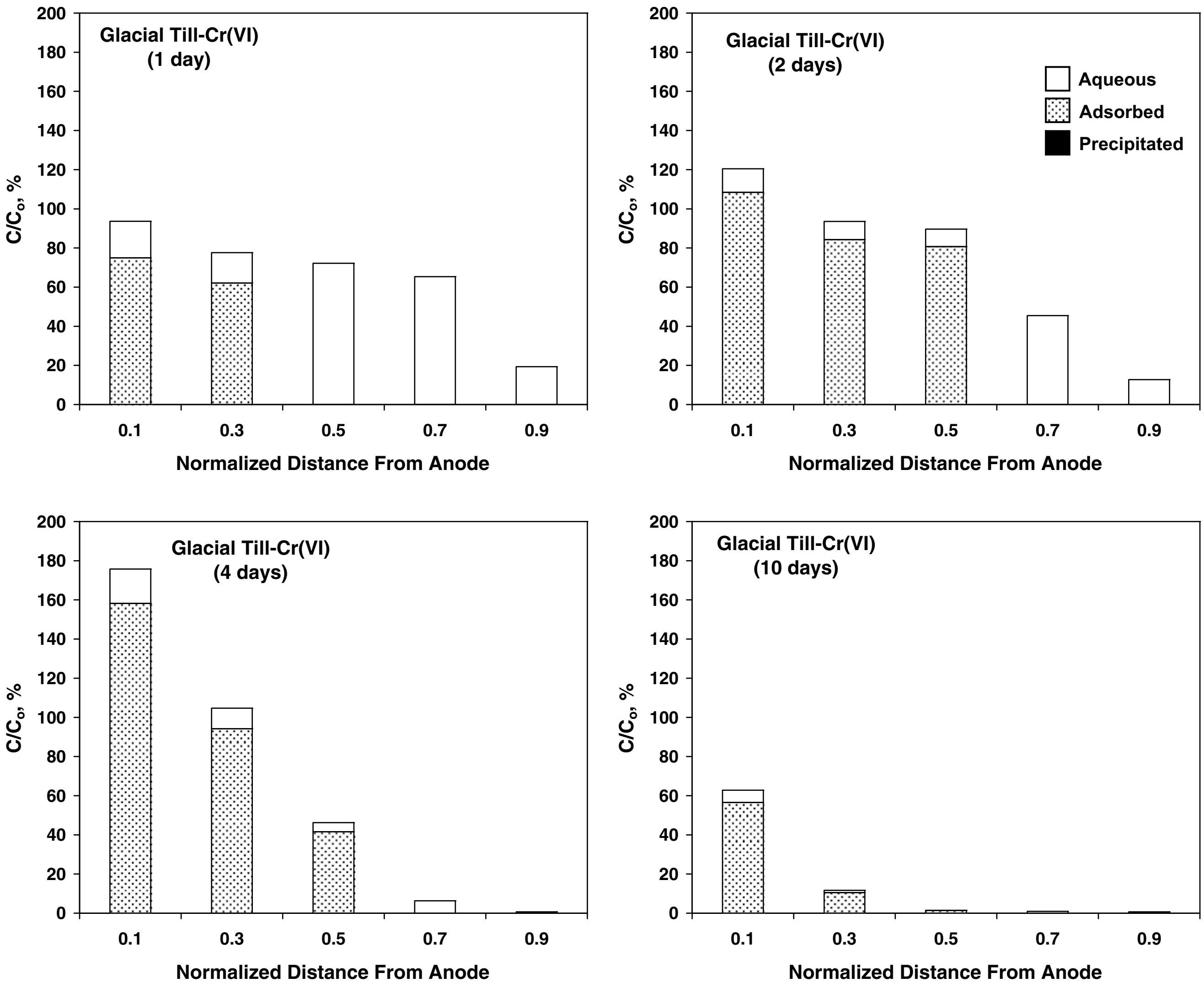

Fig. 7. Time-dependent distribution of hexavalent chromium in glacial till after electrokinetic treatment.

it indicates slightly reducing conditions, and when it gets below 100 mV, it is considered a highly reducing environment (Sposito, 1989). Therefore, the reduction of the Cr(VI) to Cr(III) during electrokinetic treatment was more significant in glacial till than in kaolin. Furthermore, the natural presence of iron in the tested glacial till (i.e., total iron = 10000 mg kg^{-1}, EPA method 7380) may have caused more Cr(VI) reduction in glacial till than in kaolin. However, the rate of Cr(VI) reduction increases with a decrease in pH below 4 (Eary and Rai, 1991). Such low pH conditions may have occurred in glacial till only in the soil that directly in contact with the anode reservoir.

The presence of Cr(III) in the both soils may also attributed to the specific extraction procedure adopted to determine Cr(VI) concentration in the soil. Cr(VI) concentrations were obtained using USEPA method 3060A which is the best available method for determining Cr(VI) in the soil. This method may not be highly effective in removing all of the Cr(VI) from the soil, hence, lesser amount of Cr(VI) obtained than the actual concentration may have resulted higher Cr(III) values (i.e., Cr(III) concentrations were calculated by subtracting Cr(VI) from Cr(total)).

3.3. Current

Fig. 8 shows the measured current for all of the tests performed to different treatment durations. The current passing through the soil is dependent on the conductivity of the soil, which in turn depends on the concentration of the ionic species present in the pore fluid. The higher the ionic concentration, the higher will be the current passing through the soil. In this study, the voltage difference was kept constant between the electrodes and the current was allowed to vary.

All the tests performed using kaolin exhibited similar current variation as seen in Fig. 8a. The current reached a peak in 25 h, then, the current decreased and finally stabilized at a low value after 100 h. The initial increase in the current was due to initial low soil pH and subsequent lowering of soil pH near the anode regions due to

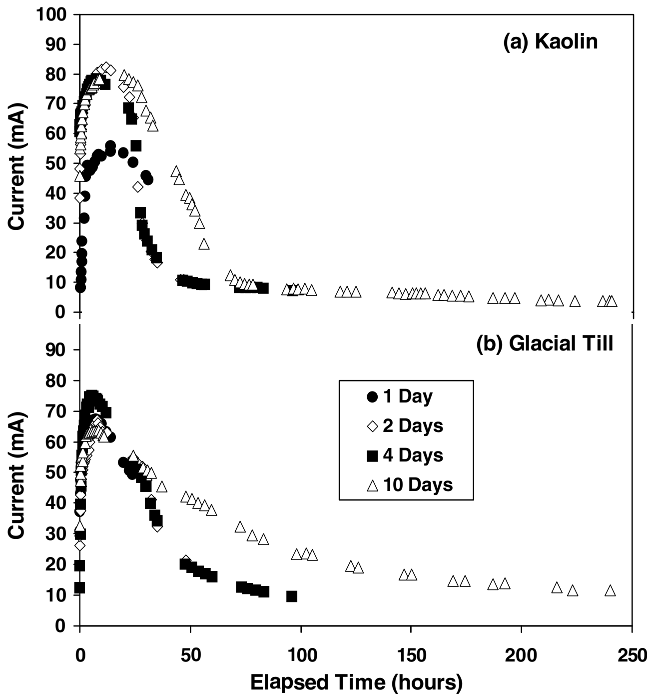

Fig. 8. Current variation during electrokinetic treatment.

electromigration of H^+ generated at the anode by the electrolysis of deionized water. Under low pH conditions, the conductivity of the soil was high due to the presence of more contaminants in the pore water in ionic form. The conductivity of the soil reduced with decreasing concentration of dissolved ionic species. The ionic concentration decreased when adsorption and/or precipitation of metals occurred in the soil due to increased soil pH near the cathode region due to the OH^- generated at the cathode by the electrolysis of deionized water. Thus, nickel and cadmium adsorption and precipitation were responsible for lower current measured at later stages of electrokinetic treatment.

As seen in Fig. 8b, current variation in glacial till tests is similar to that observed in kaolin tests. However, in the glacial till tests, the current reached its highest value in the first few hours and then decreased and stabilized. The decrease in current was gradual in glacial till tests. Glacial till contained large amounts of calcium carbonate that caused the soil to posses a high buffering capacity. Moreover, the pH of glacial till was about 7.8, thus, the cationic contaminants precipitated throughout the soil and decreased the soil conductivity. Glacial till is a field soil and it contains many dissolved species other than the spiked contaminants, leading to higher final stabilized current as compared to kaolin.

For all the tests, the current variation was similar in that it increased initially and then decreased with test duration; however, it stabilized within the short duration of 4 d and remained uncharged under prolonged electric potential application.

3.4. Electroosmotic flow

Cumulative electroosmotic flow volume during electric potential application for all the tests are shown in Fig. 9a and b for kaolin and glacial till, respectively. The cumulative electroosmotic flow was calculated by measuring the volume change in the electrode reservoirs. All the tests (1, 2, 4, and 10 d) showed similar electroosmotic flow trend for both soils in that the flow increased with the test duration. The flow rate was higher during the initial stages, but it decreased significantly at later stages. Most of the flow occurred within 4 d of test duration. The surface charge of the soil particles (zeta potential), the pore fluid properties, and the electrical gradient vary through the soil, resulting non-uniform electroosmotic flow. Moreover, these physical/chemical changes in the soil may cause the electroosmotic flow to reverse direction or even cease. As the ions electromigrate towards the electrodes, they transfer momentum to the solution molecules, and the flow is related to the net amount of ionic migration towards an electrode location. Therefore, the high current observed in the tests correlated to the elevated electroosmotic flow. Furthermore, since the flow in the tests was directed towards the cathode, it indicates that the net amount of electromigration was towards the cathode for all the tests, and this suggests that dominant ions present in the soils were in the form of cations or cationic complexes. Although the electroosmotic flow in the tests for both soils showed a similar flow trend, the flow rates in the glacial till tests were lower than those in the kaolin tests. During the

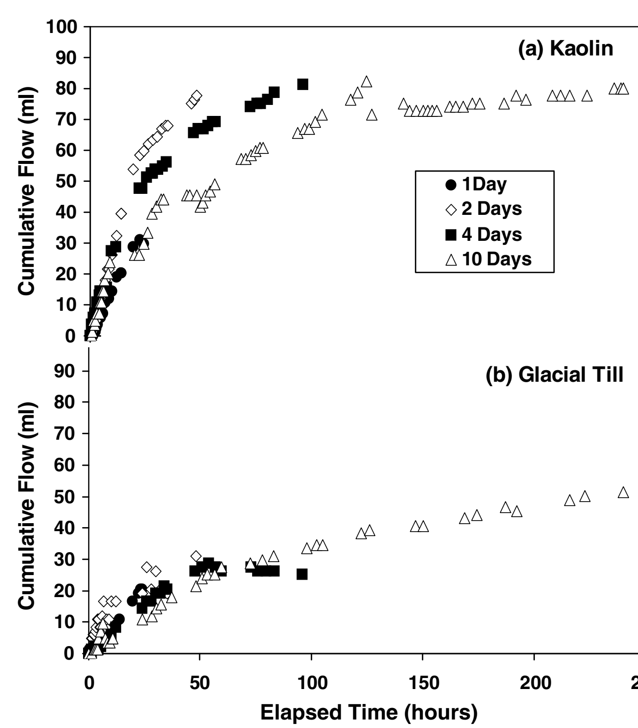

Fig. 9. Electroosmotic flow volume variation during electrokinetic treatment.

first 60 h of the tests, the coefficient of electroosmotic conductivity (K_e) was calculated to be around 2.2×10^{-4}–7.4×10^{-4} and 9.2×10^{-5}–4.6×10^{-4} $cm^2\ s^{-1}\ V^{-1}$ for kaolin and glacial till, respectively. After the first 60 h, the flow rate reduced to a lower K_e value of 8.8×10^{-5}–2.4×10^{-4} and 3.9×10^{-5}–1.5×10^{-4} $cm^2\ s^{-1}\ V^{-1}$ for kaolin and glacial till, respectively. This flow behavior also suggests that there were less mobile ions in glacial till than in kaolin, which is attributed to the precipitation of the cationic metals in glacial till under the high pH conditions.

4. Summary and conclusions

Electrokinetic laboratory experiments were performed using two different clayey soils, kaolin and glacial till, to investigate the transient migration behavior of heavy metals, Cr(VI), Ni(II), and Cd(II), under applied electric potential. The geochemical model MINEQL$^+$ was used to determine the speciation of heavy metals distributed through the soil after electrokinetic treatment. The results showed that in kaolin, the acid front advanced towards the cathode faster than the base front towards the anode, leading to a development of an acidic condition through most of the soil. In glacial till, however, because of its high buffering capacity, the development of the acid front was hindered, which resulted in alkaline conditions throughout the soil during electrokinetic remediation.

In kaolin, the duration of applied voltage gradient had a pronounced effect on the migration of nickel and cadmium. The extent of Ni(II) and Cd(II) migration towards the cathode increased in kaolin as the treatment time increased. However, the effect of treatment time was noticeable to a certain extent after which it diminished because of the generated soil conditions by the cathode that hindered the nickel and cadmium migration. Unlike kaolin, in glacial till the treatment time had no effect on nickel and cadmium migration because of its high buffering capacity.

In both kaolin and glacial till, the extent of Cr(VI) migration towards the anode increased as the treatment time increased. However, Cr(VI) migration was higher in glacial till as compared to kaolin because of the high pH conditions that existed in glacial till. Some Cr(VI) was reduced to Cr(III) in both soils. The Cr(VI) reduction rate to Cr(III) as well as the Cr(III) migration were significantly affected by the treatment time, leading to different chromium distributions throughout the soil.

During electrokinetic treatment, the current passing through the soil increased with treatment duration; however, it stabilized within the short duration of four days and remained unchanged under prolonged electric potential application. In both kaolin and glacial till, the flow rate sharply increased in earlier stages of treatment and stabilized at later stages because of the dynamic changes in pore chemistry and soil solid surface characteristics occurring during the application of electric potential. Electrokinetic process in the soils continuously alter the soil conditions, leading the electroosmotic flow to change and stabilize with time due to the reduction of the soluble ions in the system as a result of adsorption and precipitation processes.

Overall, this study showed that the current, electroosmotic flow, pH, and contaminant migration are affected by the treatment duration. Increased treatment time enhances migration of contaminants in kaolin, but the removal of contaminants was low due to adsorption/precipitation of the contaminants near the electrode regions. Increased treatment time enhanced migration and removal of Cr(VI) in glacial till, however, no effects were observed on Ni(II) and Cd(II) migration and removal. Moreover, the extent of contaminants migration is strongly dependent on their initial speciation prior electrokinetic treatment, polarity of the contaminant, treatment duration, and type of soil.

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