Assessment of electrokinetic removal of heavy metals from soils by sequential extraction analysis

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Abstract

Electrokinetic remediation of metal-contaminated soils is strongly affected by soil-type and chemical species of contaminants. This paper investigates the speciation and extent of migration of heavy metals in soils during electrokinetic remediation. Laboratory electrokinetic experiments were conducted using two diverse soils, kaolin and glacial till, contaminated with chromium as either Cr(III) or Cr(VI). Initial total chromium concentrations were maintained at 1000 mg/kg. In addition, Ni(II) and Cd(II) were used in concentrations of 500 and 250 mg/kg, respectively. The contaminated soils were subjected to a voltage gradient of 1 VDC/cm for over 200 h. The extent of migration of contaminants after the electric potential application was determined. Sequential extractions were performed on the contaminated soils before and after electrokinetic treatment to provide an understanding of the distribution of the contaminants in the soils. The initial speciation of contaminants was found to depend on the soil composition as well as the type and amounts of different contaminants present. When the initial form of chromium was Cr(III), exchangeable and soluble fractions of Cr, Ni, and Cd ranged from 10 to 65% in kaolin; however, these fractions ranged from 0 to 4% in glacial till. When the initial form of chromium was Cr(VI), the exchangeable and soluble fractions of Cr, Ni and Cd ranged from 66 to 80% in kaolin. In glacial till, however, the exchangeable and soluble fraction for Cr was 38% and Ni and Cd fractions were 2 and 10%, respectively. The remainder of the contaminants existed as the complex and precipitate fractions. During electrokinetic remediation, Cr(VI) migrated towards the anode, whereas Cr(III), Ni(II) and Cd(II) migrated towards the cathode. The speciation of contaminants after electrokinetic treatment showed that significant change in exchangeable and soluble fractions occurred. In kaolin, exchangeable and soluble Cr(III), Ni(II), and Cd(II)decreased near the anode and increased near the cathode, whereas exchangeable and soluble Cr(VI) decreased near the cathode and increased near the anode. In glacial till, exchangeable and soluble Cr(III), Ni(II), and Cd(II) were low even before electrokinetic treatment and no significant changes

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were observed after the electrokinetic treatment. However, significant exchangeable and soluble Cr(VI) that was present in glacial till prior to electrokinetic treatment decreased to non-detectable levels near the cathode and increased significantly near the anode. In both kaolin and glacial till, low migration rates occurred as a result of contaminants existing as immobile complexes and precipitates. The overall contaminant removal efficiency was very low (less than 20%) in all tests. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

Numerous sites exist in US, where soils have been contaminated with heavy metals such as chromium, nickel and cadmium as a result of improper waste disposal practices in past. Although, several soil remedial technologies have been developed within the last decade, many have proven to be either ineffective or costly for the in situ remediation of clayey soils. In situ electrokinetic remediation (or electrokinetics) has shown to offer significant potential for the remediation of clays contaminated with heavy metals [1–6].

Electrokinetic remediation involves applying a low dc current or a low potential gradient to electrodes that are inserted into the ground and encompass the contaminated zone. Electrolysis reactions generate hydrogen ions (H^+) and oxygen gas at the anode and hydroxyl ions (OH^-) and hydrogen gas at the cathode. The hydrogen ions in the anode migrate through the soil towards the cathode, whereas the hydroxyl ions in the cathode migrate towards the anode. Depending on the extent of migration of H^+ and OH^-, pH will vary across the soil. These pH changes affect major physico-chemical processes such as adsorption–desorption, precipitation–dissolution and oxidation–reduction, which dictate partitioning and speciation of the contaminants in soils.

In order to remove contaminants from soil by electrokinetics, the contaminants should preferably exist in pore water in soluble ionic form so that they are transported to either the cathode or anode depending on the nature of their charge (i.e. cationic or anionic). Four mechanisms are responsible for the transport of contaminants towards the electrodes: electroosmosis, electromigration, electrophoresis and diffusion [6–8]. Contaminant transport due to electromigration is one to two orders greater than contaminant transport due to the other mechanisms, therefore, electromigration is considered the dominant transport mechanism for ionic species [7]. The contaminants that are accumulated at the electrodes are eventually extracted by methods such as electroplating (or adsorption onto the electrode) and by pumping water near the electrodes.

Since 1993, research has been on-going at the University of Illinois at Chicago to develop a fundamental understanding of different geochemical processes that occur during electrokinetic remediation and to develop enhancement techniques to induce favorable geochemistry and, in turn, increase remedial efficiency. This research has been specifically focused on clayey soils contaminated with chromium, both with and without co-existing heavy metals, including nickel and cadmium. Laboratory bench-scale experiments were conducted using three different clays, kaolin and Na-montmorillonite (both commercial-grade soils) and

glacial till (a field-derived soil) to assess the effect of soil composition on chromium migration under induced electric potential [9]. Experiments were also conducted using kaolin and glacial till to assess: (1) the effect of the initial form of chromium, (2) the synergistic effect of co-contaminants, (3) the effect of naturally occurring reducing agents, and (4) the effect of naturally occurring oxidizing agents on electrokinetic remedial efficiency [10–13]. Results revealed that the migration of chromium, nickel and cadmium depends significantly on soil mineralogy. The overall contaminant removal efficiency was controlled by different geochemical reactions, including oxidation–reduction, adsorption, and precipitation. None of these experiments resulted in substantial contaminant removal. Several other studies also reported low removal efficiency due to precipitation of heavy metals due to high pH in the soil near the cathode regions [1–6].

In order to increase electrokinetic remedial efficiency, the conditioning of electrodes is deemed necessary. Electrode conditioning involves the addition of suitable aqueous solutions into the electrode wells/drains, allowing for their transport into the soils under induced electric potential. The conditioning solutions induce geochemical conditions that favor contaminant migration. In order to develop electrode-conditioning strategies on a rational basis, it is important to assess the forms and distribution of the residual contaminants in soils under induced electric potential without electrode conditioning systems. In this paper, the results of sequential analyses are presented for electrokinetic experiments conducted on two different clayey soils contaminated with chromium, either in the Cr(III) or Cr(VI) form, nickel and cadmium. The forms and distribution of residual contaminants in soils were then determined after electrokinetic treatment. These results were helpful in explaining possible reasons for low contaminant removal under an induced electric potential.

2. Electrokinetic experiments

A comprehensive laboratory electrokinetic experimental program was developed to investigate the geochemical effects on the remediation of soils contaminated with heavy metals [13]. The experimental program included testing of two different clayey soils: kaolin (a low buffering soil) and glacial till (a high buffering soil). Table 1 shows the composition and properties of these soils. The soils were spiked with chromium at a concentration of 1000 mg/kg as either Cr(III) or Cr(VI). Nickel as Ni(II) and cadmium as Cd(II), in concentrations of 500 and 250 mg/kg, respectively were also added in all tests to simulate typical field contamination at electroplating waste sites. Table 2 shows the experimental program, including the test designations (EKK-1, EKK-2, EKGT-1 and EKGT-2). A constant voltage gradient of 1 VDC/cm was applied in all tests for approximately 200 h. Fig. 1 shows a schematic of the electrokinetic test set-up and the specimen dimensions.

For each test, approximately 1100 g of dry soil was first contaminated with the selected heavy metals. The required amounts of source chemicals were weighed and dissolved individually in deionized water. These contaminant solutions were then added to the soil and the soil was mixed thoroughly. Deionized water was used to yield a 35% moisture content in kaolin and a 25% moisture content in glacial till. These moisture contents are selected to simulate typical field moisture conditions. The contaminated soil was then placed in the electrokinetic cell in small layers and each layer was uniformly compacted. A detailed

Table 1
Composition and properties of soils tested

Soil-type	Kaolin	Glacial till
Source	Kga-1a[a]	[b]
Mineralogy	Kaolonite ~100%	Quartz (~31%)
		Feldspar (~13%)
		Carbonate (~35%
		Illite (~15%)
		Chlorite (~4–6%)
		Vermiculite (~0.5%)
		Smectite (trace)
Cation exchange capacity (meq/100 g) (ASTM D9081)	1.6	13.0–18.0
Organic Content (%) (ASTM D2974)	~0	2.8
Initial pH (ASTM D4972)	5.0	7.7–8.3
Percent finer than 0.075 mm, (ASTM D422)	100	84
Atterberg limits (ASTM D2487)		
LL (%)	44	29–31
PL (%)	29	16–17

[a] Washington County, GA, obtained from clay minerals society, MO.
[b] DuPage County, IL, obtained by the authors

description of the preparation of contaminated soils, the electrokinetic set-up and the testing procedure is given in [9,11,13,14].

At the end of testing, the soil specimen was extruded and sectioned into five parts: S-1 (anode 4 cm), S-2 (4–8 cm), S-3 (8–12 cm), S-4 (12–15.5 cm) and S-5 (cathode 15.5). The pH and contaminant concentrations of the initial soil specimen and each soil section were measured. The total concentrations of chromium, nickel and cadmium were determined based on the United States Environmental Protection Agency (USEPA) acid digestion procedure [15]. The details of this analytical procedure have been given in [11,13].

Sequential extraction analyses were performed using the procedure summarized in Table 3 in order to determine the speciation of the contaminants in the soils both before and after the electrokinetic treatment. This procedure was originally developed by Tessier et al. [16] and has been extensively used for the speciation of trace metals in natural soils and sediments into five fractions: (1) exchangeable, (2) bound to carbonates, (3) bound to Fe–Mn oxides, (4) bound to organic matter, and (5) residual. However,

Table 2
Metal spiking scheme for EK-tests

Soil-type	Test designation	Target initial contaminant concentrations (mg/kg)			
		Cr(III)	Cr(VI)	Ni(II)	Cd(II)
Kaolin	EKK-1	1000	–	500	250
	EKK-2	–	1000	500	250
Glacial till	EKGT-1	1000	–	500	250
	EKGT-2	–	1000	500	250

(a) Overall Test Set-up
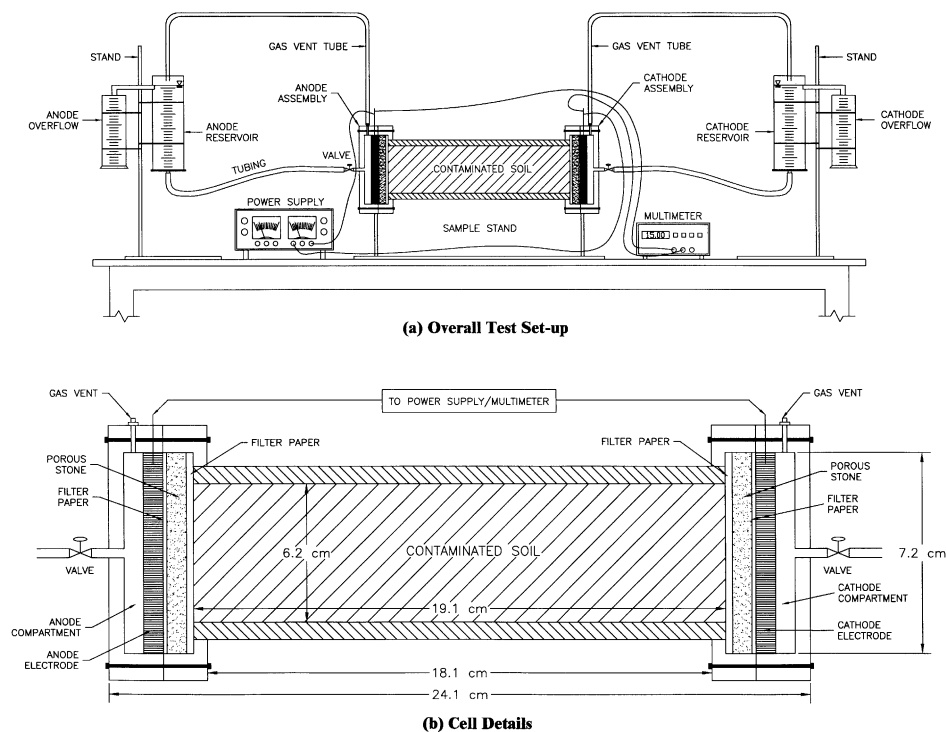

(b) Cell Details

Fig. 1. Schematic of electrokinetic test set-up.

these fraction designations may not apply to freshly and/or heavily contaminated soils and sediments that contain small amounts of organic matter. Therefore, the fractions are denoted as fractions I, II, III, IV and V for the purpose of this study, and are described as follows:

  I. Loosely held contaminants, including the exchangeable and soluble forms, that can be readily extracted (extraction procedure represents mild extracting conditions).
 II. Tightly adsorbed contaminants and those associated with carbonates and easily soluble oxides/hydroxides under slightly acidic conditions (extraction procedure lowers the pH to 5).
III. Additional soluble metal oxides/hydroxides under slightly acidic pH as well as contaminants that are associated with Fe–Mn oxides (extraction procedure uses[III.] large amounts of acetic acid and also causes the reduction of Fe–Mn oxides).
IV. Contaminants associated with easily oxidizable solids or compounds, including organic matter (extraction procedure causes the oxidation of Cr(III) and organic matter).
 V. Contaminants present as consolidated oxides, co-precipitates, and strongly held complexes (e.g. metal sulfides).

Table 3
Sequential extraction procedure for speciation of heavy metals

Fraction	Designation	Extraction procedure (per 1 g dry soil sample)
I	Exchangeable	An amount of 8 ml of 1 M sodium acetate solution (pH = 8.2) was added and mixed continuously for 1 h.
II	Carbonates-bound	To the residue from above, 8 ml of 1 M sodium acetate (pH adjusted to 5.0 with acetic acid) was added and mixed continuously for 5 h.
III	Fe–Mn oxides-bound	To the residue from above, 20 ml of 0.04 M hydroxylamine hydrochloride ($NH_2OH.HCl$) was added in 25% (v/v) acetic acid, and heat to 96°C with occasional stirring for 6 h.
IV	Organic-bound	To the residue from above, 3 ml of 0.02 M nitric acid (HNO_3) and 5 ml of 30% hydrogen peroxide (H_2O_2) (pH adjusted to 2.0 with nitric acid), was added and heat to 85°C for 2 h with occasional agitation. Then, 3 ml of 30% H_2O_2 (pH adjusted to 2.0 with HNO_3) was added and mixed continuously for 3 h. Cool the mixture and add 5 ml of 3.2 M ammonium acetate (NH_4OAc) in 20% (v/v) HNO_3. Finally, dilute to 20 ml and mixed continuously for 30 min.
V	Residual	The above four fractions summed-up and subtracted from the total concentration.

3. Results and discussion

3.1. Initial distribution of metals in soils

The distribution of the chromium, nickel, and cadmium in both kaolin and glacial till prior to electrokinetic treatment as determined from the sequential extraction analyses are summarized in Table 4. The pH of kaolin with Cr(III) was 3.83 and with Cr(VI) was 5.36, while the pH of glacial till with Cr(III) was 6.74 and with Cr(VI) was 7.36. The pH of glacial till was high when either Cr(III) or Cr(VI) were present because this soil possesses a high buffering capacity due to its high carbonate content (Table 1).

When chromium was added as Cr(III) in kaolin (EKK-1), 10% existed in exchangeable and soluble form (fraction I), and the remaining chromium was mostly present as tightly adsorbed and solid oxides/hydroxides. Cr(III) forms hydroxo complexes of low solubility, resulting in low amounts of soluble Cr(III) [17]. On the other hand, when Cr(VI) was present in kaolin (EKK-2), 80% existed in exchangeable and soluble form (fraction I), and the remainder as strongly held complexes. Cr(VI) forms oxyanions such as CrO_4^{2-}, $HCrO_4^-$ and $Cr_2O_7^{2-}$; hence it adsorbs minimally to the negatively charged soil surfaces. However, as pH decreases, charge reversal of soil solids may occur, thus increasing the adsorption of Cr(VI) onto soil surfaces [9,17]. A small amount of Cr(VI) is expected to be adsorbed in kaolin at pH of 5.36.

Table 4
Percent distribution of contaminants in soils prior to electrokinetic treatment

Fraction/Test	EKK-1 Cr(III) test	EKK-2 Cr(VI) test	EKGT-1 Cr(III) test	EKGT-2 Cr(VI) test
(a) Chromium (total) (initial concentration = 1000 mg/kg)				
I-Exchangeable	10	80	0	38
II-Carbonate bound	32	15	16	0
III-Fe–Mn oxides bound	17	4	27	0
IV-Organic bound	4	1	2	0
V-Residual	37	0	55	62
(b) Nickel (initial concentration = 500 mg/kg)				
I-Exchangeable	58	66	0	2
II-Carbonate bound	30	19	22	27
III-Fe–Mn oxides bound	10	12	16	15
IV-Organic bound	2	3	2	1
V-Residual	0	0	60	55
(c) Cadmium (initial concentration = 250 mg/kg)				
I-Exchangeable	65	76	4	10
II-Carbonate bound	28	17	37	41
III-Fe–Mn oxides bound	7	5	5	6
IV-Organic bound	0	2	1	1
V-Residual	0	0	53	42

When chromium was present as Cr(III) in glacial till (EKGT-1), exchangeable and soluble forms (fraction I) were not detected, but Cr(III) was distributed as oxides/hydroxides and precipitates. The soil pH of 6.74 caused Cr(III) to either strongly adsorb to the soil surface or precipitate as $Cr(OH)_3$. When chromium was present as Cr(VI) (EKGT-2), 38% was present in exchangeable and soluble forms (fraction I). The high soil pH allows little adsorption of Cr(VI) due to the presence of mostly negatively charged soil surfaces, therefore, the remaining Cr(VI) may have existed as strongly held complexes. In addition, the glacial till contained small amounts of organic matter (Table 1) which may have caused a partial reduction of Cr(VI) to Cr(III). The Cr(III) then precipitated as $Cr(OH)_3$ because of the high soil pH [18].

Significant amounts of both nickel and cadmium were present, 58 and 65%, respectively in exchangeable and soluble form in kaolin which contained Cr(III) (Table 4). The remainder existed as tightly adsorbed forms. Neither of these contaminants was found in strongly held oxides and precipitates. This distribution is mainly attributed to the low soil pH, which caused most of nickel and cadmium to exist as free Ni^{2+} and Cd^{2+}. It is also possible for Ni and Cd to adsorb onto $Cr(OH)_3$ aggregates. When Cr(VI) was present in kaolin, the exchangeable and soluble fractions of Ni and Cd were 66 and 76%, respectively and the remaining Ni and Cd were present as tightly adsorbed fractions. The exchangeable and soluble fractions of Ni and Cd in the presence of Cr(VI) were higher than those observed in the presence of Cr(III), which shows that adsorption of Ni and Cd onto $Cr(OH)_3$ may have occurred when Cr(III) is present, thereby reducing the exchangeable and soluble fractions.

In glacial till, the distribution of both Ni and Cd was similar in the presence of either Cr(III) or Cr(VI). Levels up to 10% existed in exchangeable and soluble form, 22–41%

existed as tightly adsorbed fractions, and the remaining existed in strongly held oxides and precipitates. The soil pH of 6.74–7.36 caused Ni and Cd to adsorb significantly to soil surfaces as well as precipitate as oxides and hydroxides.

Overall, these results show that the initial distribution of heavy metals in the soils is affected by soil-type. The kaolin possesses low cation exchange capacity (CEC), while the glacial till possesses slightly higher CEC due to the presence of illite (Table 1). This implies that lower amounts of exchangeable heavy metals should be expected in kaolin than in glacial till. However, due to the low pH of kaolin (less than 5), heavy metals existed in soluble form, but they precipitated in glacial till due to high pH (over 7). As a result, more heavy metals exist in exchangeable and soluble form in kaolin than in glacial till. The anionic Cr(VI) species exist mostly in soluble form over a wide pH range, consequently, higher amounts of exchangeable and soluble chromium are found in both soils when Cr(VI) is present. Because Cr(III) exists as hydroxo complexes, its solubility is limited, resulting in low amounts of exchangeable and soluble chromium. The distributions of Ni and Cd are similar, with the exchangeable and soluble fractions slightly lower in the presence of Cr(III), possibly due to their adsorption onto $Cr(OH)_3$ solid aggregates. The heavy metals that are present in the exchangeable and soluble fraction are conducive for migration towards the electrodes during the application of electric potential, therefore, they are indicative of potentially higher remedial efficiencies by the electrokinetic process.

3.2. Migration and distribution of heavy metals under induced electric potential

Due to the induced electric potential, the pH in kaolin with both Cr(III) and Cr(VI) decreased near the anode and increased near the cathode (Fig. 2). These pH changes are due to electrolysis of water at the electrodes due to the induced electric potential. The H^+ ions generated at the anode migrate towards the cathode (negative) and OH^- ions generated at the cathode migrate towards the anode (positive), causing the pH of the soil to decrease to a value between 2 and 3 near the anode and to increase between 11 and 12 near the cathode. However, the pH of glacial till for both Cr(III) and Cr(VI) remained relatively high throughout the soil with pH values ranging from 5 to 6 near the anode and from 11 to 12 near cathode (Fig. 2). This is because the H^+ ions generated at the anode were neutralized by the high carbonate content, while the OH^- ions migrated from the cathode into the soil to increase the soil pH in the cathode region. The different pH distributions in both soils caused by the induced electric potential will have profound effects on the distribution and migration of the contaminants.

Among the different contaminant transport processes that occur during the application of electric potential, including electroosmosis, electromigration, electrophoresis, and diffusion, the transport of metallic contaminants occurs predominantly through electromigration [7]. The cationic contaminants, Cr(III), Ni(II) and Cd(II), migrate towards the cathode, while the anionic contaminant, Cr(VI), migrates towards the anode. Such a migration of Cr(III), Cr(VI), Ni(II) and Cd(II) in the soils during the electric potential application is evident from the total concentration profiles shown in Figs. 3–8. A detailed assessment of the migration behaviors of these contaminants is given elsewhere [13].

Fig. 3(a) shows the distribution of chromium in kaolin which initially contained all chromium in the Cr(III) form. Chromium existed as hydroxide complexes and precipitates
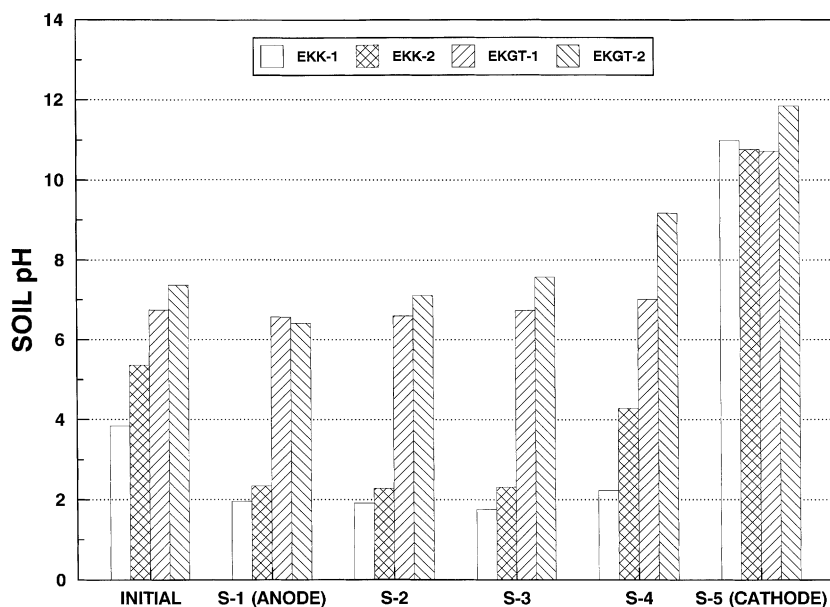
Fig. 2. pH distributions within the soils (S-1: section 1 near the anode; S-2: section 2; S-3: section 3; S-4: section 4; S-5: section 5 near the cathode).

after the application of the electric potential. Exchangeable and soluble Cr(III) fractions migrated towards the cathode. In addition, due to lowering of the soil pH near the anode, chromium hydroxide complexes and precipitates may have solubilized and then migrated towards the cathode. Chromium accumulated near the cathode possibly as hydroxide complexes and precipitates due to increased pH in this region. The chromium thus became immobile, preventing migration to the cathode.

The distribution of chromium in glacial till differed significantly after treatment (Fig. 3(b)). Because of high soil pH initially as well as after the electrokinetic treatment, chromium remained as hydroxide complexes and precipitates. Since glacial till has a high carbonate content, chromium may have adsorbed to the carbonates. The presence of chromium in immobile form prevented migration to the cathode during the application of the electric potential.

The distribution of chromium in kaolin and glacial till when initially present as Cr(VI) is shown in Fig. 4(a) and (b), respectively. The distribution is drastically different from that observed when chromium was initially present as Cr(III). Because of the anionic nature of Cr(VI), it exists predominantly in exchangeable and soluble form and was able to migrate towards the anode in both kaolin and glacial till. Most of the chromium present in the cathode region migrated towards the anode in both soils. In kaolin, migration of Cr(VI) towards the anode is retarded due to the high adsorption of Cr(VI) onto the soil surfaces at low pH conditions. Also, Cr(VI) was partially reduced into Cr(III) in the anode region, forming hydroxo complexes [13]. However, in glacial till, chromium migration towards the anode was significant due to low adsorption of Cr(VI) as a result of high soil pH. The
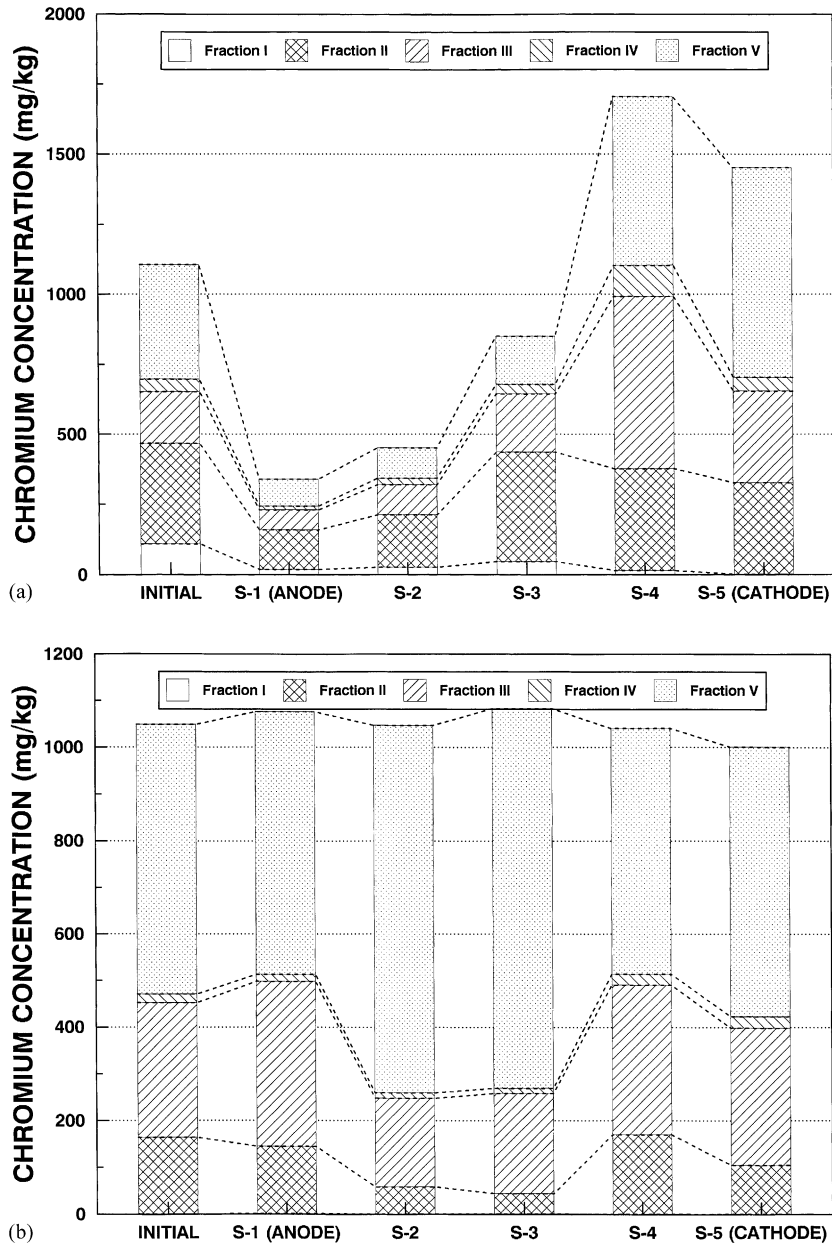
Fig. 3. Chromium distribution in soils contaminated with Cr(III), Ni(II) and Cd(II): (a) kaolin (EKK-1); (b) glacial till (EKGT-1).
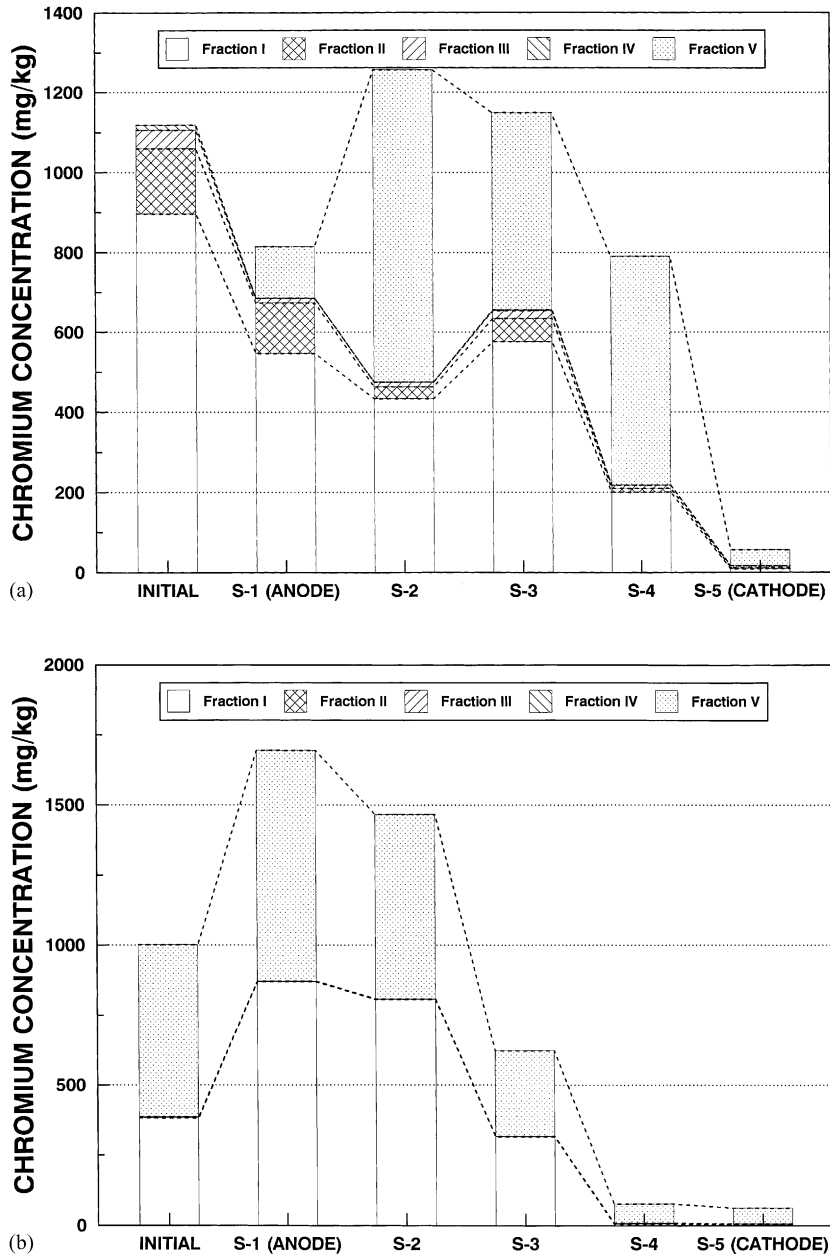
Fig. 4. Chromium distribution in soils contaminated with Cr(VI), Ni(II) and Cd(II): (a) kaolin (EKK-2); (b) glacial till (EKGT-2).
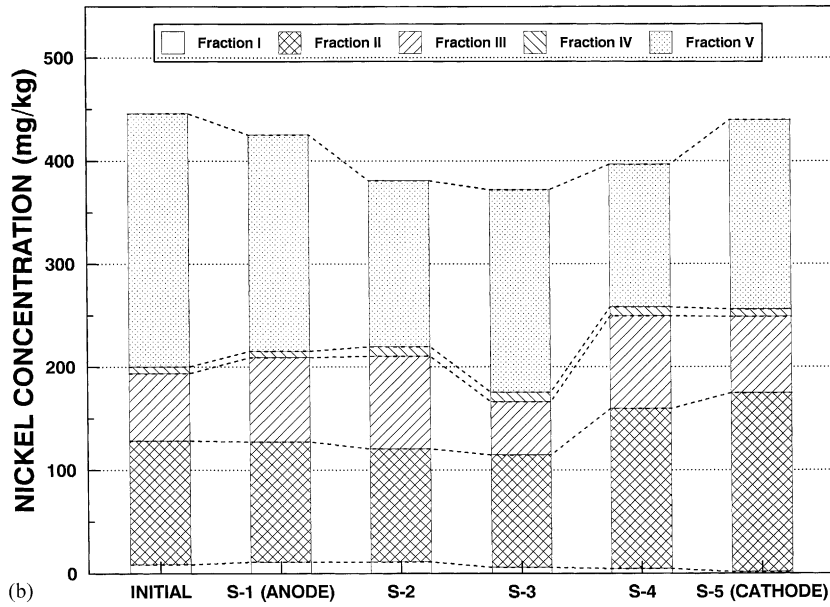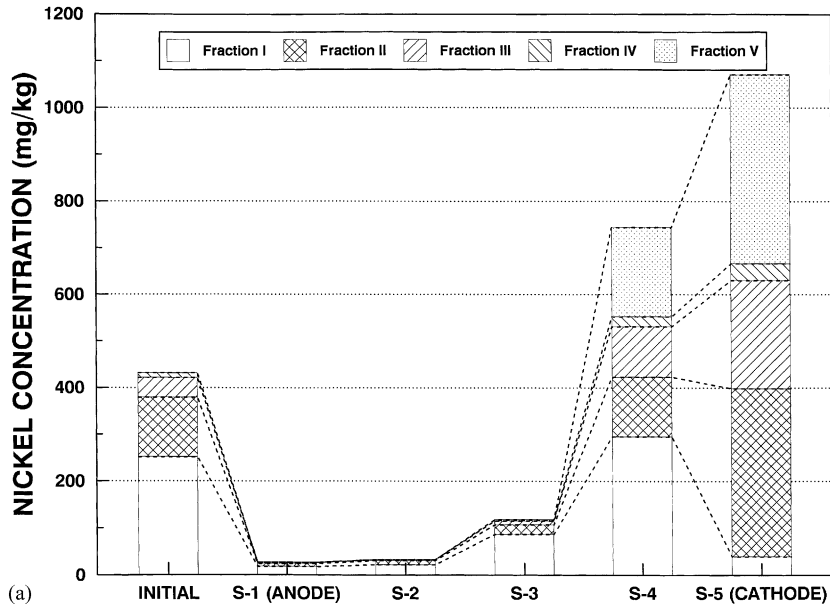
Fig. 5. Nickel distribution in soils contaminated with Cr(III), Ni(II) and Cd(II): (a) kaolin (EKK-1); (b) glacial till (EKGT-1).
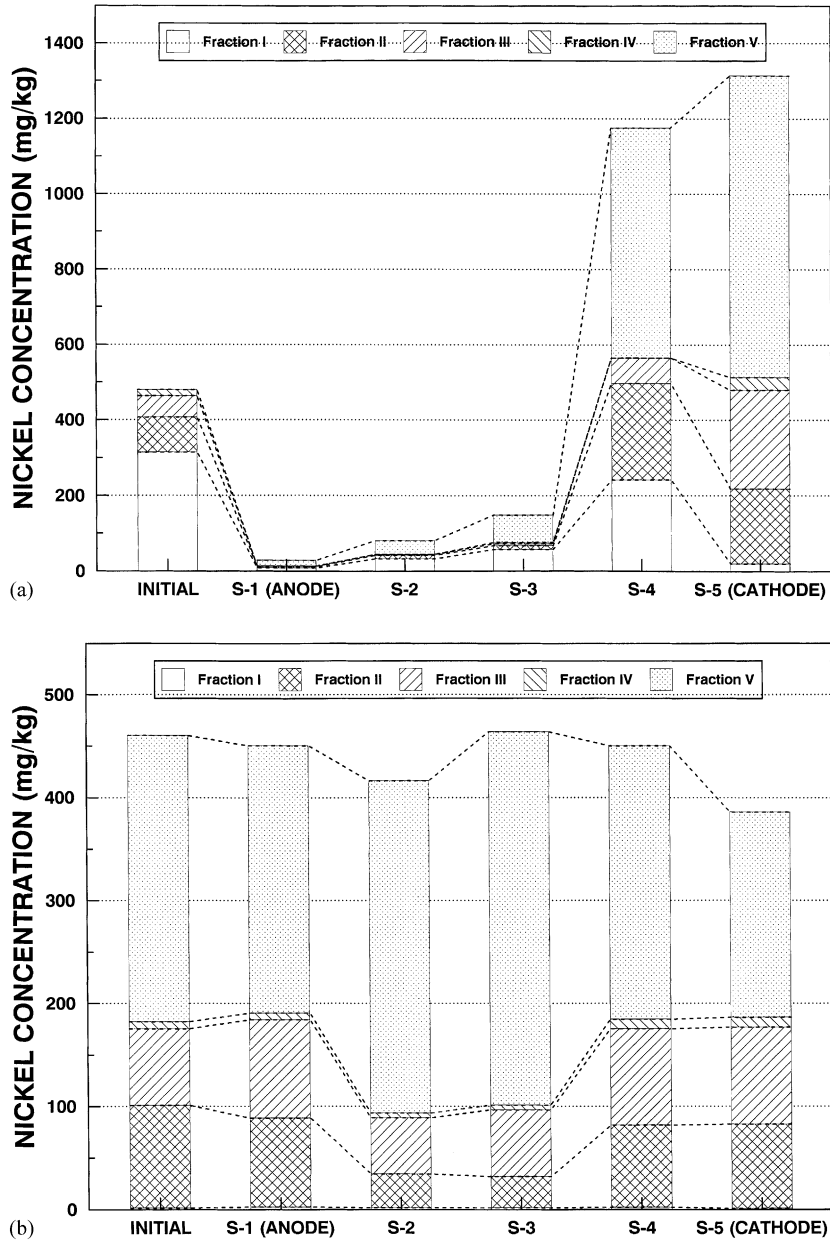
Fig. 6. Nickel distribution in soils contaminated with Cr(VI), Ni(II) and Cd(II): (a) kaolin (EKK-2); (b) glacial till (EKGT-2).
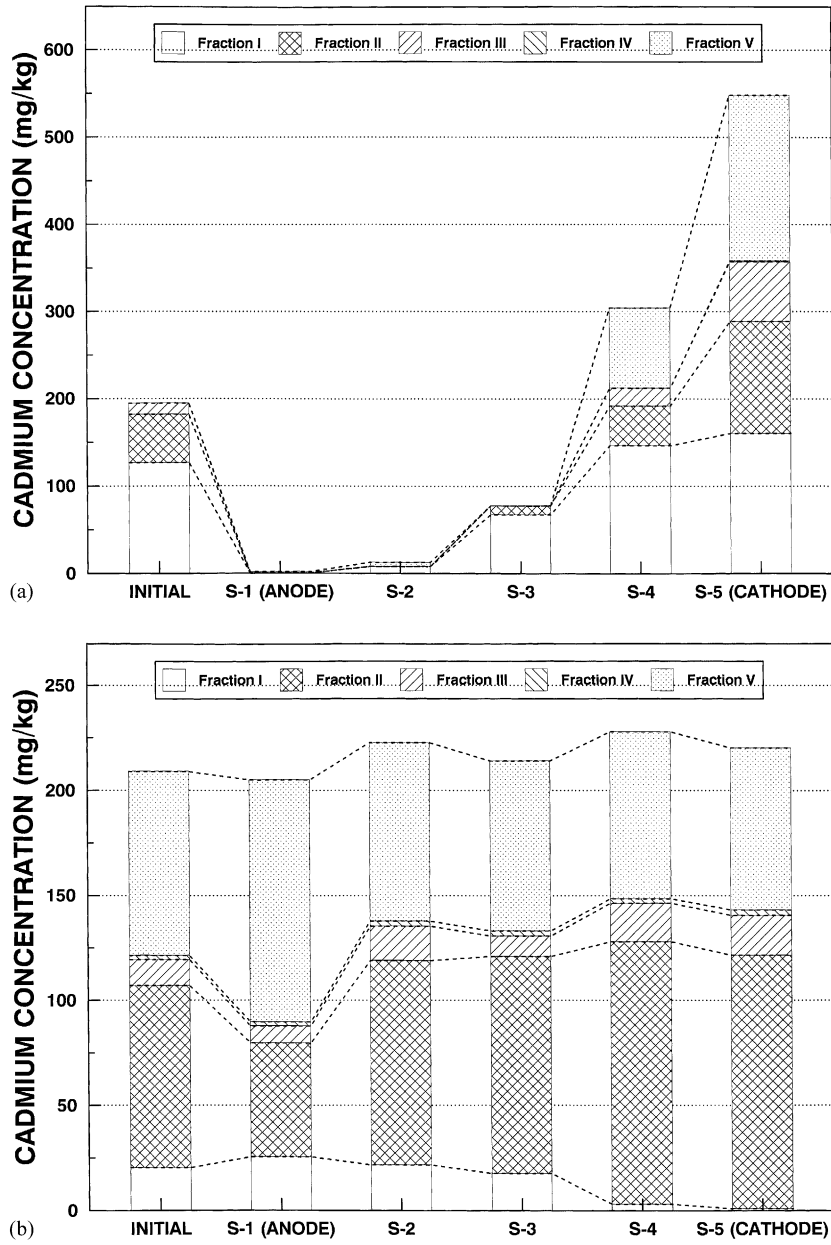
Fig. 7. Cadmium distribution in soils contaminated with Cr(III), Ni(II) and Cd(II): (a) kaolin (EKK-1); (b) glacial till (EKGT-1).
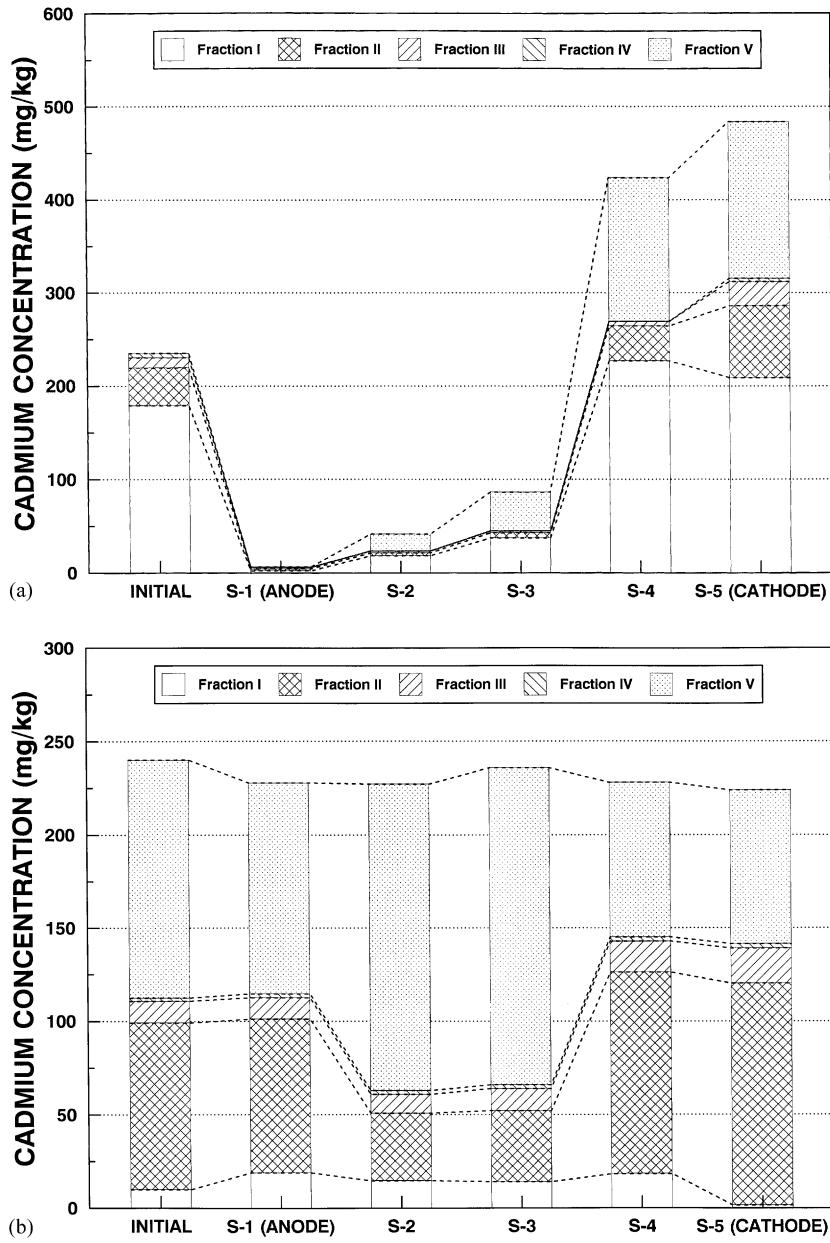
Fig. 8. Cadmium distribution in soils contaminated with Cr(VI), Ni(II) and Cd(II): (a) kaolin (EKK-2); (b) glacial till (EKGT-2).

chromium that accumulated near the anode region existed as the exchangeable and soluble fraction as well as tightly held complexes and precipitates. A partial reduction of Cr(VI) to Cr(III) may have been responsible for the formation of precipitates in the anode region [13]. The amount of Cr(VI) reduction to Cr(III) was higher in glacial till as compared to that observed in kaolin, resulting in higher amounts of immobile hydroxo complexes and precipitates near the anode. These results show that application of electric potential for extended periods may allow the removal of chromium that is present in exchangeable and soluble form, however, residuals may remain as immobile complexes and precipitates.

Fig. 5(a) and (b) show the distribution of Ni(II) in the presence of Cr(III) remaining in kaolin and glacial till, respectively following electrokinetic treatment. In kaolin, Ni was removed from sections near the anode and accumulated near the cathode. This indicates that exchangeable and soluble Ni easily migrated from the anode region. In addition, due to lowering of soil pH in the anode region, Ni that existed as hydroxo complexes may have solubilized, resulting in additional migration towards the cathode. The accumulated Ni in the cathode region mostly existed as hydroxo complexes and precipitates due to increased pH, thus migration into the cathode was restricted. The extended application of the electric potential would not have caused migration of Ni into the cathode. fractions II to V indicate that some of the Ni complexes/precipitates may be easily soluble with lowering of pH, while the others may be strongly held. The distribution of Ni in glacial till is quite different from that observed in kaolin (Fig. 5(b)). Initially Ni was distributed as hydroxo complexes/precipitates with no exchangeable fraction present. The soil pH remained high even after the application of the electric potential, thus the distribution of Ni did not change. Because Ni existed in immobile forms, no migration into the cathode occurred.

The effects of chromium either in the Cr(VI) or Cr(III) form on Ni distribution after the application of electric potential are negligible (Figs. 5(a), 5(b), 6(a) and 6(b)). Ni that existed in exchangeable and soluble form in kaolin migrated towards the cathode and then existed as immobile hydroxo complexes/precipitates. In glacial till, Ni was distributed as hydroxo complexes/precipitates initially and this distribution was unaffected by the application of electric potential. Fig. 7(a) and (b) show the distribution of Cd in kaolin and glacial till, respectively when these soils contained Cr(III). The Cd distribution in both soils is similar to that observed for Ni. In kaolin, exchangeable and soluble Cd migrated from the anode regions and then accumulated in the cathode region. Because of high pH, Cd near the cathode existed as precipitates, but a significant amount of Cd also existed in exchangeable and soluble form. The presence of the latter fraction may be attributed to the higher solubility of Cd and also competitive adsorption/precipitation of Ni as compared to Cd [18]. In glacial till, Cd existed mostly as hydroxo complexes/precipitates. A small amount of Cd that was initially present as exchangeable and soluble fraction did not migrate under induced electric potential. Although, small amounts of the exchangeable and soluble fraction were present near the anode, it was not present in the sections near the cathode due to increased pH. The distribution of Cd in kaolin and glacial till with added Cr(VI) is shown in Fig. 8(a) and (b). The distribution of Cd in both soils is unaffected regardless of the form of chromium present.

The distributions of the heavy metals based on the sequential extraction analyses show that greater migration of metals occurred under induced electric potential if the metals initially existed in exchangeable and soluble form (fraction I). Significant amounts of Cr(III), Ni(II)

and Cd(II) were present as fraction I in kaolin, causing higher migration of these metals during electrokinetic treatment. Significant Cr(VI) was present as fraction I in both kaolin and glacial till, which resulted in higher migration during electrokinetic treatment. The lower migration of metals resulted from their existence as immobile complexes/precipitates (fractions II, III, IV and V).

The distribution of the heavy metals suggests that electrode-conditioning systems capable of dissolving heavy metals out of complexes/precipitates should be investigated. The speciation results also show that under mildly acidic conditions metal hydroxides can be partially solubilized, allowing for migration to occur under electric potential. However, effective solubilization of the majority of the metal hydroxides is required in order to obtain high electrokinetic removal efficiencies.

In addition to speciation testing, the authors are currently conducting diffraction testing and using scanning/transmission electron photographs to develop a further understanding of changes in soil composition and surface morphology before and after electrokinetic treatment. A compilation of these results will provide a fundamental approach for geochemical modeling and assist in the development of effective electrokinetic remediation systems.

4. Summary and conclusions

The following conclusions may be drawn based on the results of this study:

1. Under an induced electric potential, the anionic Cr(VI) migrated towards the anode, while the cationic Cr(III), Ni(II), and Cd(II) migrated towards the cathode. The extent of migration of these metals was dependent on their initial speciation prior to the electrokinetic treatment. Higher rates of contaminant migration occurred when the contaminants existed in exchangeable form. The presence of precipitates and complexes may be responsible for retarding contaminant migration.
2. The initial speciation of contaminants was found to depend on the soil composition as well as the type and amounts of contaminants present. In tests with Cr(III), exchangeable and soluble fractions of Cr, Ni, and Cd ranged from 10 to 65% in kaolin, however, these fractions were 0–4% in glacial till. When the initial form of chromium was Cr(VI), the exchangeable and soluble fractions of Cr, Ni and Cd ranged from 66 to 80% in kaolin. In glacial till, however, the exchangeable and soluble fraction for Cr was 38% and Ni and Cd fractions were 2 and 10%, respectively. The remainder of the contaminants existed as strongly held complex/precipitate fractions.
3. Significant changes in exchangeable and soluble fractions occurred after electrokinetic treatment. In kaolin, exchangeable and soluble Cr(III), Ni(II), and Cd(II) decreased near the anode and increased near the cathode, whereas exchangeable and soluble Cr(VI) decreased near the cathode and increased near the anode. In glacial till, exchangeable and soluble Cr(III), Ni(II), and Cd(II) were low even before electrokinetic treatment and no significant changes were observed after treatment. However, significant exchangeable and soluble Cr(VI) present in glacial till prior to electrokinetic treatment decreased to non-detectable levels near the cathode and increased significantly near the anode. In both kaolin and glacial till, low migration rates occurred as a result of contaminants existing as immobile complexes and precipitates.

This study shows that additional research is warranted to develop electrode-conditioning systems that enhance contaminant removal. Electrode conditioning may involve using solutions such as acids and chelating agents rather than water at the electrodes.

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