



Electrokinetic remediation of heavy metal-contaminated soils under reducing environments

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Abstract

This paper describes the migration of hexavalent chromium, Cr(VI), nickel, Ni(II), and cadmium, Cd(II), in clayey soils that contain different reducing agents under an induced electric potential. Bench-scale electrokinetic experiments were conducted using two different clays, kaolin and glacial till, both with and without a reducing agent. The reducing agent used was either humic acid, ferrous iron, or sulfide, in a concentration of 1000 mg/kg. These soils were then spiked with Cr(VI), Ni(II), and Cd(II) in concentrations of 1000, 500 and 250 mg/kg, respectively, and tested under an induced electric potential of 1 VDC/cm for a duration of over 200 h. The reduction of chromium from Cr(VI) to Cr(III) occurred prior to electrokinetic treatment. The extent of this Cr(VI) reduction was found to be dependent on the type and amount of reducing agents present in the soil. The maximum reduction occurred in the presence of sulfides, while the minimum reduction occurred in the presence of humic acid. The concentration profiles in both soils following electrokinetic treatment showed that Cr(VI) migration was retarded significantly in the presence of sulfides due both to the reduction of Cr(VI) to Cr(III) as well as an increase in soil pH. This low migration of chromium is attributed to: (1) migration of Cr(VI) and the reduced Cr(III) fraction in opposite directions, (2) low Cr(III) migration due to adsorption and precipitation in high pH regions near the cathode in kaolin and throughout the glacial till, and (3) low Cr(VI) migration due to adsorption in low pH regions near the anode in both soils. Ni(II) and Cd(II) migrated towards the cathode in kaolin; however, the migration was significantly retarded in the presence of sulfides due to increased pH through most of the soil. Initial high pH conditions within the glacial till resulted in Ni(II) and Cd(II) precipitation, so the effects of reducing agents were inconsequential. Overall, this study demonstrated that the reducing agents, particularly sulfides, in soils may affect redox chemistry and soil pH, ultimately affecting the electrokinetic remediation process. © 1999 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Electrokinetic remediation, or simply electrokinetics, offers great potential for the remediation of hazardous waste sites, especially those containing fine-grained soils that have been contaminated with heavy metals. It can be used either in-situ or ex-situ and essentially involves the application of a low level DC current or voltage gradient across electrodes that encompass the contaminated soil. As a result, the contaminants are transported towards either the cathode well/reservoir or the anode well/reservoir, depending on their charge.

Numerous studies dealing with the electrokinetic remediation of soils contaminated with cationic metallic contaminants such as lead, copper and cadmium have been reported [1–4]. These studies have demonstrated migration of significant amounts of cationic metallic contaminants towards the cathode region where they are precipitated due to alkaline (high pH) conditions. In addition, these studies showed that the introduction of weak acids such as acetic acid into the cathode well/reservoir can lower the soil pH near the cathode regions, thereby preventing precipitation of the contaminants. The contaminants are allowed to transport into the cathode well/reservoir for subsequent removal by either electroplating or pumping above-ground.

Although most heavy metals exist within the subsurface as cationic species, chromium may exist in the

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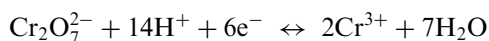
subsurface as either anionic or cationic species, depending on its valence state. Chromium can exist in valence states ranging from -2 to $+6$; however, $+3$ and $+6$ are the only two valence states that prevail under subsurface conditions [5]. Hexavalent chromium (Cr(VI)) is highly mobile and toxic compared to trivalent chromium (Cr(III)). Cr(VI) exists as oxyacids or anions, specifically hydrochromate (HCrO_4^-), dichromate ($\text{Cr}_2\text{O}_7^{2-}$) and chromate (CrO_4^{2-}) and will migrate towards the anode during electrokinetic remediation. On the other hand, Cr(III) exists as a cation, Cr^{3+} , and cationic, neutral and anionic hydroxo complexes, specifically, $\text{Cr}(\text{OH})^{2+}$, $\text{Cr}(\text{OH})_2^+$, $\text{Cr}(\text{OH})_3$, $\text{Cr}(\text{OH})_4^-$, and $\text{Cr}(\text{OH})_5^{2-}$. Cr(III) may also exist as other cationic, neutral and anionic inorganic or organic complexes depending on the ligands present. In acidic regions and at relatively low redox potentials, Cr(III) exists as Cr^{3+} and cationic hydroxo complexes ($\text{Cr}(\text{OH})^{2+}$, $\text{Cr}(\text{OH})_2^+$) and will migrate towards the cathode during electrokinetic remediation. Cr(III) precipitates as its hydroxides ($\text{Cr}(\text{OH})_3$) between a pH of 6.8 and 11.3 while at higher pH values, Cr(III) may form anionic hydroxo complexes ($\text{Cr}(\text{OH})_4^-$, $\text{Cr}(\text{OH})_5^{2-}$). The electrokinetic remediation of chromium-contaminated soils has received the attention of several researchers [6,7]. Recent studies by the authors showed that migration of chromium in clays under an induced electric potential depends on: (1) the initial form (Cr(VI), Cr(III), or a combination of these two), (2) the co-contaminants in the soil, and (3) the soil composition [8–10]. These studies have shown that the removal of chromium from soils by electrokinetics is highly efficient if the chromium exists as Cr(VI). Although most chromium releases into the subsurface have occurred in the Cr(VI) form, Cr(VI) may be reduced to Cr(III) in the presence of naturally occurring reducing agents, including organic matter, ferrous iron, and sulfides in the contaminated soil. The reduction of Cr(VI) to Cr(III) may significantly affect the electrokinetic migration of chromium as well as the migration of coexisting metals such as Ni(II) and Cd(II). Therefore, an evaluation of the Cr(VI) redox chemistry in soils in the presence of various natural reducing agents is essential in order to determine electrokinetic remedial efficiencies at actual field sites.

The objective of this paper is to present the results of a series of bench-scale electrokinetic experiments conducted to assess the migration of multiple heavy metal contamination, specifically Cr(VI), Ni(II) and Cd(II), in soils in the presence of different commonly occurring reducing agents. These experiments were conducted using two different clays, kaolin and glacial till, with three different individual reducing agents, humic acid, ferrous iron, and sulfides. The soils were spiked with Cr(VI), Ni(II), and Cd(II) in proportions that are representative of typical metallic contamination at industrial waste sites. The test results were analyzed for:

- (1) the effects of reducing agents on the Cr(VI) reduction to Cr(III),
- (2) the migration of chromium, in both Cr(VI) and Cr(III) forms, and
- (3) the migration of Ni(II) and Cd(II).

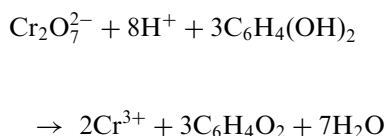
2. Redox chemistry of chromium

Chromium transformation from Cr(VI) to Cr(III) can occur in many different ways. For instance, Cr(VI) which exists in dichromate form, $\text{Cr}_2\text{O}_7^{2-}$, under a low pH and high redox potential conditions can be reduced to Cr(III) as shown in the following reaction:



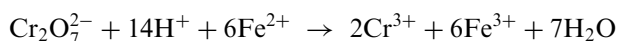
In the subsurface, different naturally occurring substances such as organic matter, ferrous iron, and sulfides can donate electrons and thus reduce Cr(VI) to Cr(III). The extent of reduction and the rate at which the redox reactions occur depends upon the type and amount of the reducing agent and the geochemical conditions (e.g., pH, and type and concentration of ligands).

Saleh et al. [11] conducted experiments to determine the kinetics of chromium transformations and found that the reduction of Cr(VI) by organics was slow and depends on both the type and the amount of organic matter in the soil. For instance, the reduction of dichromate by quinone that represents an organic compound can occur as shown below:



James and Bartlett [12] performed experiments on 38 different soils to study Cr(VI) reduction by organic matter and they found that Cr(VI) reduction is high in low pH soils. Wittbrodt and Palmer [13] reported that the rate of reduction of Cr(VI) in the presence of soil fulvic acid (SFA) increases with a decrease in pH and with an increase in the concentration of SFA.

Saleh et al. [11] also found that the reduction of Cr(VI) in presence of ferrous iron (Fe^{2+}) occurs instantaneously as shown by the following reaction:

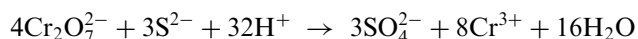


Experimental studies of Cr(VI) reduction in five different subsoils were conducted by Eary and Rai [14] to determine whether the Fe(II) contained in soil minerals could cause Cr(VI) reduction to Cr(III). All of these

soils contained small amounts of Fe(II) and organic matter; however, only the acidic subsoils caused Cr(VI) reduction. The rate of Cr(VI) reduction increased with a decrease in pH below 4. Under acidic conditions, the reduction of Cr(VI) by Fe(II) was as important as the reduction of Cr(VI) by organic matter. Cr(VI) reduction in acidic subsoils resulted in the precipitation of (Fe,Cr)(OH)₃(am), depending on the pH. The amount of hydroxylamine hydrochloride (NH₂OH.HCl) extractable Fe in the acidic subsoils was found to be useful for determining the mole fraction of Fe(III) in the (Fe,Cr)(O-H)₃(am) solid solution, which allowed a prediction of Cr(III) concentrations in acidic solutions to within a logarithmic unit of those observed in experimental soil-water suspensions.

James [15] conducted experiments with Fe(II), steel wool 500 (Fe), leaf litter, and lactic acid; all of which reduced various amounts of Cr(VI). Powell et al. [16] found that the form and quantity of the iron, aquifer material type, and solid to solution ratio have a significant effect on Cr(VI) reduction. Fendorf and Li [17] conducted experiments to determine the role of oxygen in limiting the rate of reduction of Cr(VI) by Fe(II). They found that the reduction rate was unaffected by oxygen when pH is below 8.

Based on laboratory experiments, Saleh et al. [11] concluded that even in the presence of sulfides (S²⁻), the reduction of hexavalent chromium is instantaneous. The stoichiometry between Cr(VI) and sulfides can be expressed by:



James and Bartlett [12] found that sulfates also increase the reduction of Cr(VI) as compared to phosphates and that reduction occurs rapidly in the presence of gallic acid.

The reduction of Cr(VI) into Cr(III) is also affected by several other factors, including soil moisture content, natural soil pH, and soil constituents. Puls et al. [18] concluded that the reduction capacity of a soil depends on the moisture content of the soil. Henderson [19] observed that approximately 30% of Cr(VI) reduced to Cr(III) in a sand aquifer. The reaction rate was observed to be slow at near neutral conditions, a normal characteristic of aquifers. The half life of Cr(VI) was estimated to be 2.5 years while the concentrations of hexavalent chromium were estimated to decrease below the drinking water standard within 10 years. Laboratory experiments conducted by James [15] revealed that even Mn²⁺ can reduce Cr(VI) at pH values greater than 7.2.

Different reducing agents in the soils cause the reduction of anionic Cr(VI) species into cationic Cr(III) species to various degrees. Reddy and Chinthamreddy [8] have demonstrated that Cr(VI) species can be easily transported towards the anode under electric potential

due to their low adsorption onto soil surfaces over a wide pH range. However, cationic Cr(III) species migration towards the cathode under induced electric potential occurs slowly due to higher adsorption of Cr(III) and precipitation as Cr(III) hydroxyl solids under slightly acidic to alkaline conditions. At this point, it is emphasized that even though the reduction of Cr(VI) is expected to occur in the subsurface soils due to the natural reducing agents, the redox conditions may also be affected by the applied electric fields due to significant changes in the pH and redox potentials at the electrodes due to electrolysis reactions. Therefore, a systematic evaluation of the effects of reducing agents on the reduction of Cr(VI) into Cr(III) in soil is essential in order to assess the removal efficiency using electrokinetics. In this study, laboratory experiments were conducted on both kaolin and glacial till to observe the effects of humic acid (representative of organic matter), ferrous iron (Fe(II)), and sulfide (S²⁻) on the migration of Cr(VI), as well as the effects of these reducing agents on the migration of co-existing contaminants, nickel and cadmium, under an induced electric potential.

3. Experimental methods and materials

3.1. Materials

Two different soils, kaolin, a typical low buffering soil, and glacial till, a typical high buffering soil, were used for this study. The mineralogical composition and properties of these soils have been reported by Reddy et al. [10]. Kaolin consists of 100% kaolinite mineral with no organic matter and a cation exchange capacity (CEC) of 1.6 meq/100g. Glacial till consists of 31% quartz, 13% feldspar, 35% carbonates, 15% illite, 4-6% chlorite, 0.5% vermiculite, and trace amounts of smectite. Glacial till also contains 2.8% organic matter and has CEC of 18 meq/100 g.

Two series of electrokinetic experiments were performed for this study. In the first series of experiments, both soil types were contaminated with Cr(VI), Ni(II) and Cd(II) in concentrations of 1000 mg/kg (mg per kg of dry soil), 500 mg/kg, and 250 mg/kg, respectively. Potassium chromate, nickel chloride, and cadmium chloride were used as sources of Cr(VI), Ni(II), and Cd(II), respectively. In the second series of tests, the soils were first spiked with one of the reducing agents, either humic acid, ferrous iron, or sulfides, in concentration of 1000 mg/kg, and then contaminated with Cr(VI), Ni(II), and Cd(II) with concentrations the same as those used in the first series of experiments. Humic acid, ferrous sulfate, and sodium sulfide were used as sources of organic matter, Fe(II), and S²⁻, respectively. Thus, a total of eight experiments, four using kaolin and four using glacial till, were conducted in this study.

3.2. Contaminated soil preparation

For each test, 1100 g of dry soil was used. The chemicals used as reducing agents and contaminants were weighed and dissolved individually in deionized water. Humic acid and sodium sulfide, however, were dissolved in dilute nitric acid. The chemical solution yielding the desired concentration of 1000 mg/kg of a reducing agent was first added to the soil. The soil was mixed carefully and thoroughly with a spatula in a HDPE container. Then, the chemical solutions yielding the desired concentrations of Cr(VI), Ni(II), and Cd(II) were individually added and mixed thoroughly. A total of 375 ml of deionized water (35% moisture content) was added to the kaolin, and 285 ml of deionized water (25% moisture content) was added to the glacial till. These water contents yielded a liquidity index of 50% for both soils, representing typical field moisture conditions.

3.3. Electrokinetic reactor

The electrokinetic reactor used for the experiments for this study is shown in Fig. 1(a) and (b) and has been described in detail by Reddy and Chinthamreddy [8] and Reddy et al. [10]. The reactor consists of an electrokinetic cell, two electrode compartments, two electrode reservoirs, a power supply, a multimeter, flow control valves, and gas vents. This reactor also incorporates two electrodes, two porous stones, filter papers, and tubing. The reactor simulates one-dimensional transport of contaminants under an induced electric potential.

3.4. Testing procedure

The contaminated soil was placed in the electrokinetic cell in layers by compacting uniformly using a hand compactor. The contaminated soil in the cell was allowed to equilibrate for 24 h. The electrode compartments, consisting of graphite electrodes, porous stones, and filter papers, were then connected to both ends of the electrokinetic cell (see Fig. 1). The electrode reservoirs were connected to the compartments which were then filled with potable water (pH=7.7, redox potential=150 mV, electrical conductivity=280 μ S/cm). The initial water elevations in both the reservoirs was kept the same in order to prevent a hydraulic gradient from forming across the soil sample. The electrokinetic cell was then connected to a power supply, and a constant voltage gradient of 1VDC/cm was applied to the soil sample. The current which passed through the soil sample as well as the pH, redox potential, and electrical conductivity (EC) of the aqueous solutions in both the anode and the cathode reservoirs were monitored throughout the duration of the experiment. Water levels and outflow at the electrodes were also monitored to determine the electro-osmotic flow. At the end of test-

ing, aqueous solutions from both the cathode and anode compartment and reservoirs were collected. Then, the reservoirs and the electrode assemblies were carefully disconnected. Soil was extruded from the cell using a mechanical extruder. This soil was then sectioned into five parts; each part was weighed and preserved in a separate sealed glass jar.

3.5. Analytical methods

The pH, redox potential and electrical conductivity of the contaminated soil were measured before and after equilibration. For these measurements, 1:1 soil to deionized water slurry was prepared in accordance with ASTM D4972. Then, the pH and redox potential were measured using an Orion pH-triode probe. The electrical conductivity was measured using an EC glass probe. The same procedures were followed to determine the pH, redox potential and EC of the soil sections after electrokinetic treatment. The pH, redox potential, and electrical conductivity of the aqueous solutions from the electrodes were measured at the end of the electrokinetic testing by directly immersing the above probes into the samples of these solutions.

The representative specimens from each soil section were tested for moisture content in accordance with ASTM D2216. Representative specimens from each soil section were acid digested in accordance with USEPA procedure 3050 to extract the total chromium, nickel, and cadmium [20]. In addition, separate specimens from each soil section were alkaline digested in accordance with USEPA procedure 3060A to extract the chromium that exists only in Cr(VI) form. The detailed descriptions of these acid and alkaline digestion procedures have been given by Reddy and Chinthamreddy [8]. The concentrations of chromium, nickel and cadmium were determined using an atomic absorption spectrophotometer in accordance with the USEPA Methods 7190 for chromium, 7520 for nickel, and 7130 for cadmium [20].

3.6. Quality assurance

Precautions were taken in order to ensure the accuracy and repeatability of the test results. These precautions included: (1) using new electrodes, porous stones and tubing in each experiment, (2) soaking the apparatus in dilute acid solution for 24 h and rinsing with tap water followed by deionized water to avoid cross contamination between experiments, (3) performing chemical analysis in duplicates, (4) avoiding interference with other elements in atomic absorption spectrophotometer by using nitrous oxide and acetylene flame for chromium and nickel analysis, (5) checking the atomic absorption calibration after testing every five samples, and (6) performing a mass balance analysis for each test. Table 1 summarizes the detailed mass balance analyses for all the tests. From

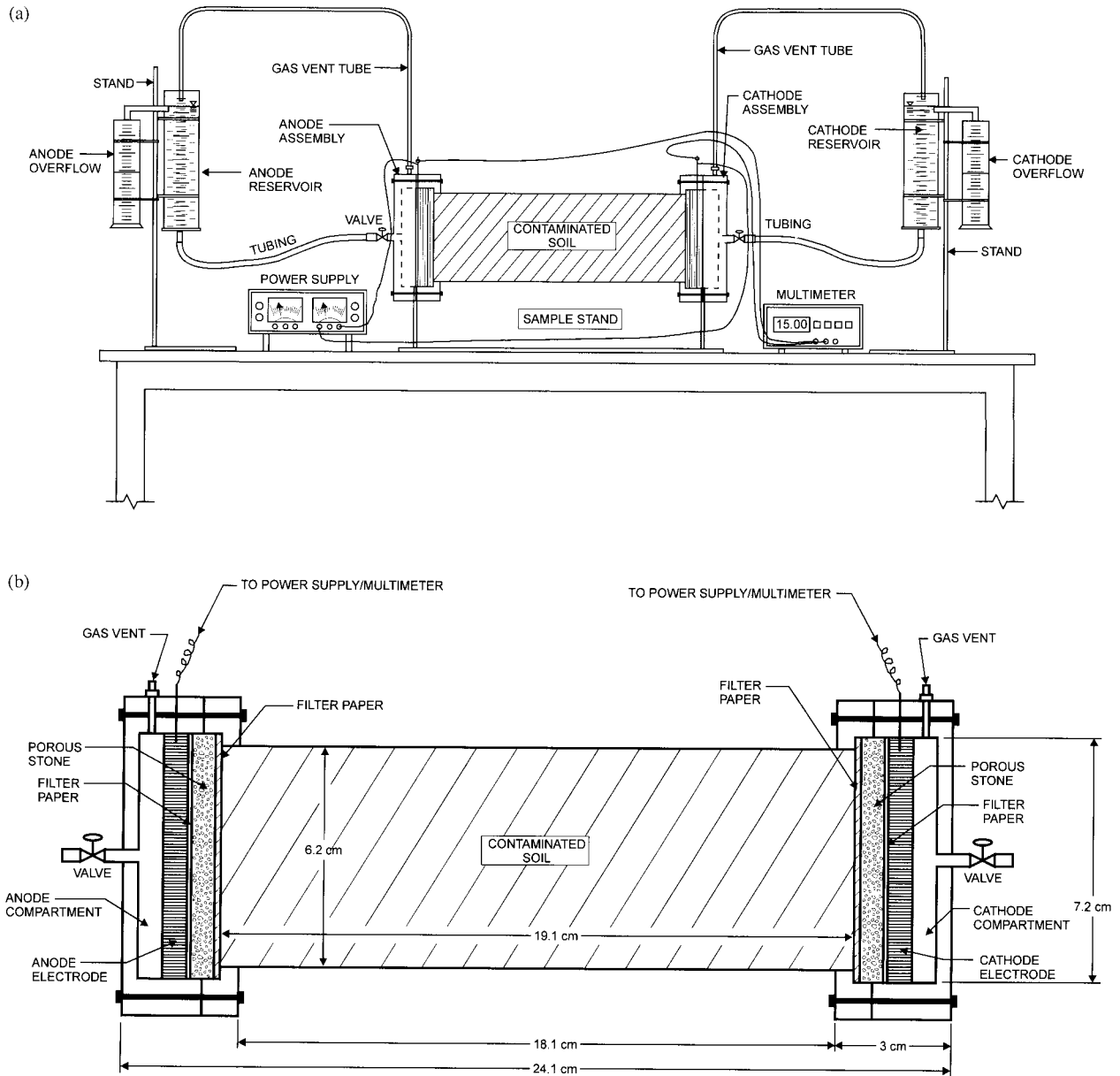


Fig. 1. Schematic of electrokinetic reactor: (a) complete set-up and (b) cell details.

Table 1, it can be seen that the relative mass balance errors are less than 10%. These differences are attributed to the non-uniform contaminant distribution within the selected soil specimens for chemical analysis as well as the contaminant mass that adsorbed to the electrodes and porous stones.

4. Results and discussion

4.1. Initial soil conditions

The initial soil conditions that existed prior to the application of the voltage gradient are shown in Table

2. The initial water content and dry density for tests with each soil were approximately the same, with the average values for moisture content and dry density 37% and 1.36 g/cm³ for kaolin, and 25.5% and 1.63 g/cm³ for glacial till, respectively. The pH of kaolin in the absence of reducing agents was 5.36; the pH was approximately the same in the presence of humic acid. However, the pH was reduced to 3.78 in the presence of ferrous iron, whereas the pH was increased to 11.45 in the presence of sulfides. Ferrous iron acts as a Lewis acid, causing a decrease in the soil pH. The sulfide anion, being a conjugate base to bisulfide (HS⁻), forms metal complexes and consumes hydrogen ions (H⁺), increasing the soil pH. The pH of glacial till was 7.36

Table 1
Mass balance analysis

Soil	Reducing agent	Contaminant	Initial contaminant mass in soil ^a (mg)	Contaminant mass after electrokinetic treatment			Mass balance (%)
				Remaining in soil (mg)	Anode reservoir (mg)	Cathode reservoir (mg)	
Kaolin	None	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 ^b	ND	93
	Humic acid	Cr(total)	688.55	669.22	5.03	0.08	98
		Ni(II)	288.95	291.88	0.22	0.07	101
		Cd(II)	180.54	184.86	ND	ND	102
	Ferrous iron	Cr(total)	730.16	673.84	1.65	0.04	92
		Ni(II)	282.28	279.60	0.42	0.02	99
		Cd(II)	175.98	168.27	0.01	ND	96
	Sulfides	Cr(total)	725.88	665.50	15.95	0.07	94
		Ni(II)	292.79	314.53	2.83	0.05	108
		Cd(II)	170.66	184.12	0.27	ND	108
Glacial Till	None	Cr(total)	944.00	781.94	108.54	0.05	94
		Ni(II)	420.67	379.89	30.73	0.02	98
		Cd(II)	204.85	205.55	0.38	ND	100
	Humic acid	Cr(total)	907.24	715.55	185.67	0.11	99
		Ni(II)	337.16	374.30	1.12	0.03	111
		Cd(II)	205.20	202.71	0.05	ND	99
	Ferrous iron	Cr(total)	991.92	832.00	36.11	0.06	88
		Ni(II)	384.28	376.26	1.38	0.03	98
		Cd(II)	229.99	236.39	0.03	ND	103
	Sulfides	Cr(total)	979.90	778.98	46.38	0.02	84
		Ni(II)	366.82	365.26	5.83	0.03	101
		Cd(II)	221.14	224.18	0.28	ND	102

^a Based on the measured initial concentrations and the actual dry mass of the soil loaded into the electrokinetic cell.

^b ND = not detected.

Table 2
Soil conditions prior to electrokinetic treatment

Soil	Reducing agent	Water content (%)	Dry density (g/cm ³)	pH	Redox potential (mV)	Electrical conductivity (μS/cm)	Cr(total) (mg/kg)	Cr(VI) (mg/kg)	Ni(II) (mg/kg)	Cd(II) (mg/kg)
Kaolin	None	41	1.32	5.36	108	809	940	917	356	212
	Humic acid	36	1.39	5.49	285	925	858	820	360	225
	Ferrous iron	37	1.35	3.78	381	1554	938	547	362	226
	Sulfides	35	1.38	11.45	-54	1615	890	122	360	209
Glacial till	None	27	1.64	7.36	178	3370	1000	798	446	209
	Humic acid	25	1.60	7.31	181	2700	984	764	365	222
	Ferrous iron	25	1.60	7.07	203	3230	1074	564	416	249
	Sulfides	25	1.66	9.51	88	3860	1099	347	382	231

when the reducing agents were not present, and pH values of 7.31, 7.07, and 9.51 were observed in the presence of humic acid, ferrous iron, and sulfides, respectively. The pH of the glacial till was higher than kaolin; the high acid buffering capacity of the glacial till due to its high carbonate content prevented significant pH reduction in the presence of humic acid or ferrous iron. From Table 2, it can also be seen that in both soils, when sulfides were present, the redox potentials were substantially lower than the redox potentials when ferrous iron and humic acid were present. The electrical conductivity

values were increased in the presence of reducing agents in kaolin, but these values did not change significantly in glacial till.

As stated previously, the initial concentrations of total chromium, nickel, and cadmium in soils were targeted to be 1000, 500 and 250 mg/kg, respectively. It should be noted that all of the initial chromium was added in the form of Cr(VI). The measured initial concentrations of total chromium, Cr(VI), Ni(II), and Cd(II) in soils are shown in Table 2. The concentrations of Cr(III) were calculated by subtracting Cr(VI)

concentrations from the total chromium concentrations. The measured concentrations of total chromium, Ni(II) and Cd(II) were 858–1099, 360–446 and 209–249 mg/kg, respectively. In general, these initial concentrations are very close to the initial targeted concentrations and the variations in concentrations may be due to the nonuniform distribution of the contaminants in the selected specimens used for the chemical analysis.

Table 2 shows that the Cr(VI) concentrations in the absence of reducing agents were 917 mg/kg for kaolin and 798 mg/kg for glacial till, which indicate that added Cr(VI) in kaolin mostly remained as Cr(VI), while a partial reduction of Cr(VI) into Cr(III) occurred in glacial till. The partial reduction in glacial till may be attributed to the presence of small amounts of naturally occurring reducing agents such as Fe(II) and organic matter. Kaolin is a commercially processed clay and consists only of kaolinite clay minerals; therefore, Cr(VI) reduction did not occur. In the presence of humic acid, the Cr(VI) concentrations were slightly lower than the Cr(VI) concentrations when reducing agents were absent in both soils, indicating that significant additional reduction of Cr(VI) did not occur. The added humic acid may be stoichiometrically too low to cause significant reduction of Cr(VI). In the presence of ferrous iron, the Cr(VI) concentrations were decreased to 547 mg/kg in kaolin and 564 mg/kg in glacial till. In the presence of sulfides, the Cr(VI) concentrations were 122 mg/kg and 347 mg/kg in kaolin and glacial till, respectively. These results show that significant reduction of Cr(VI) occurred in the presence of ferrous iron and sulfides. In the presence of ferrous iron, approximately 42% reduction occurred in kaolin and 47% reduction occurred in glacial till; while in the presence of sulfides, 86% reduction occurred in kaolin and 68% reduction occurred in glacial till. The observed Cr(VI) reduction values are consistent with the redox potential values, indicating that high reducing conditions existed when sulfides were present as compared to the low to moderate reducing conditions resulting from the presence of ferrous iron.

4.2. Monitoring under induced electric potential

For all tests with both kaolin and glacial till, the electric current across the test sample and the electro-osmotic flow were measured at different time periods immediately after the application of the voltage gradient. In addition, the pH, redox potential, and electrical conductivity in both the anode and the cathode reservoirs were measured [21].

In all the tests with both kaolin and glacial till, the current initially increased rapidly, reached a peak within 1–20 h, then decreased, and then finally stabilized at a constant value as seen in Figure 2. In kaolin tests, the maximum current generated ranged from 20 to 75 mA; the

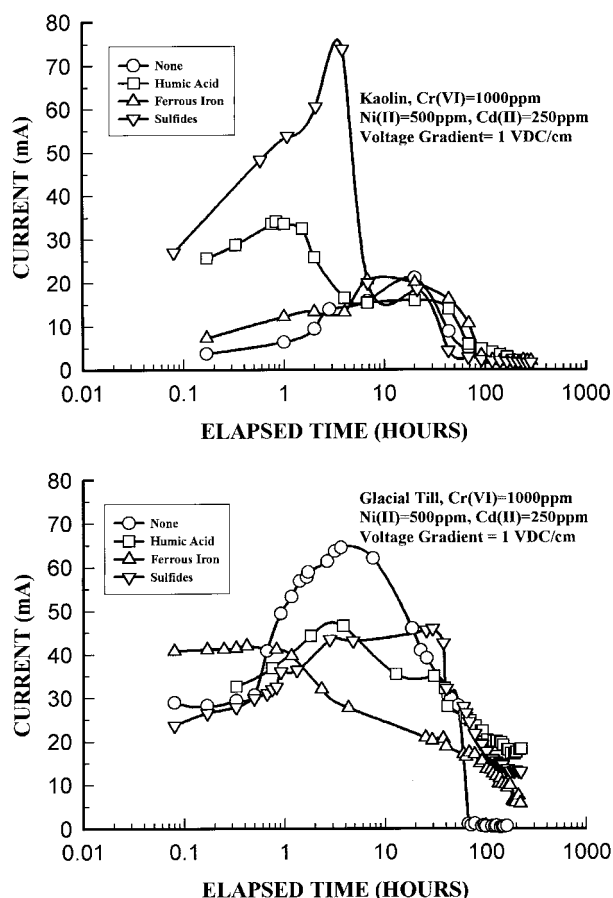


Fig. 2. Electric current measurements: (a) kaolin and (b) glacial till.

lowest current was observed in the absence of reducing agents and the highest current observed when sulfides were present. The reducing agents affected the electric current initially; however, at later stages, the current was stabilized at 0.5–17 mA for all tests. In glacial till tests, high current flow, ranging from 22 to 40 mA, was observed from the beginning of the voltage gradient application. In the absence of reducing agents, the current increased to 65 mA, then gradually decreased, and finally stabilized at 0.1 mA. The current flow in the presence of humic acid and ferrous iron was similar; however, when sulfides were present, the current flow was relatively less as compared to the currents observed in the presence of humic acid and ferrous iron.

Electro-osmotic flow was measured based on the changes in water levels in the anode and cathode reservoirs. The flow was observed towards the cathode in all tests for kaolin and glacial till. In kaolin, the average osmotic flow velocity was approximately 0.018 cm/h in the absence of reducing agents. In the presence of reducing agents, the average flow velocities were 0.026, 0.017, and 0.013 cm/h for humic acid, ferrous iron, and sulfides, respectively. In glacial till, when the reducing agents were absent, the average flow velocity was approximately 0.019 cm/h, and the flow velocity ranged

from 0.023 to 0.027 cm/h in the presence of reducing agents.

The pH of potable water used initially in both the anode and cathode reservoirs measured 7.7 ± 0.1 . Due to the induced electric potential, the pH in the anode reservoir decreased to 2–6, while the pH in the cathode reservoir increased to 7–12. This effect was observed in both soils. The pH of the composite aqueous samples from the anode compartment and reservoir and the cathode compartment and reservoir at the end of the electrokinetic treatment were also measured and are summarized in Table 3. These results show that the pH ranged between 1.54 and 3.4 at the anode and between 10.66 and 13.01 at the cathode for all of the tests. These results indicate that the electrolysis of water occurred at the electrodes [1].

The redox potential of potable water used in the reservoirs prior to the application of the electric potential was 150 ± 25 mV. Under induced electric potential, the redox potential in the anode reservoir increased to 250 mV for kaolin tests and to 450–500 mV for glacial till tests. The redox potential in the cathode reservoir decreased to -110 mV for kaolin tests and to -100 to 30 mV for glacial till tests. Table 3 shows that the redox potential of the composite aqueous solutions from the electrode compartment and reservoir ranged from 390 to 515 mV at the anode, and from -144 to -12 mV at the cathode. Overall, these results show that highly oxidizing conditions existed at the anode and highly reducing conditions existed at the cathode. The observed redox potentials at the electrodes are consistent with the expected redox reactions that are associated with the electrolysis of water [1].

The potable water which was used initially in the anode and cathode reservoirs had an EC value of 280 ± 20 $\mu\text{S}/\text{cm}$. The EC measured in the anode reservoir gradually increased to 400 $\mu\text{S}/\text{cm}$ for all tests on kaolin; however, in glacial till, the EC at the anode increased with test duration to different maximum values depending on the reducing agent. After 200 h,

EC values were approximately equal to 9000 $\mu\text{S}/\text{cm}$ in the absence of reducing agents, 20,000 $\mu\text{S}/\text{cm}$ when humic acid was present; 11,000 $\mu\text{S}/\text{cm}$ when ferrous iron was present; and 30,000 $\mu\text{S}/\text{cm}$ when sulfides were present. At the cathode, the EC significantly increased with test duration for both kaolin and glacial till. In kaolin, the maximum EC values at cathode were approximately 9000 $\mu\text{S}/\text{cm}$ both in the absence of reducing agents and when humic acid was present, 3000 $\mu\text{S}/\text{cm}$ when ferrous iron was present, and 4800 $\mu\text{S}/\text{cm}$ when sulfides were present. In glacial till, the maximum EC values were 3000 $\mu\text{S}/\text{cm}$ in the absence of reducing agents, 13,000 $\mu\text{S}/\text{cm}$ when humic acid was present, 7000 $\mu\text{S}/\text{cm}$ when ferrous iron was present, and 37,000 $\mu\text{S}/\text{cm}$ when sulfides were present. The EC values measured in the composite aqueous samples from the electrode reservoir and compartment, as shown in Table 3, indicate that during kaolin tests, the EC values ranged from 556 to 650 $\mu\text{S}/\text{cm}$ at the anode, and from 8430 $\mu\text{S}/\text{cm}$ to 9600 $\mu\text{S}/\text{cm}$ at the cathode. However, the EC values for glacial till tests ranged from 12,440 to 32,300 $\mu\text{S}/\text{cm}$ at the anode, and from 6110 to 11,640 $\mu\text{S}/\text{cm}$ at the cathode. These EC values indicate that in kaolin tests significant ions were present in the cathode, but in the glacial till tests significant ions were present in both the anode and the cathode.

4.3. pH, redox potential and EC profiles

Fig. 3 shows the pH profiles for both kaolin and glacial till after the electrokinetic testing. In kaolin, the pH profiles for the test without reducing agents as well as for the tests with humic acid and ferrous iron were approximately the same. As compared to the initial pH values shown in Table 2, the pH was reduced to approximately 2–4 throughout the kaolin, except near the cathode, where pH was increased to 10–12. The pH profile for the test with sulfides, however, differed significantly. The initial pH for this test was 11.45. The pH profile shows that the pH remained the same from the

Table 3
Conditions at electrodes after electrokinetic treatment

Soil	Reducing agent in soil	Anode compartment and reservoir			Cathode compartment and reservoir		
		pH	Redox potential (mV)	Electrical conductivity ($\mu\text{S}/\text{cm}$)	pH	Redox potential (mV)	Electrical conductivity ($\mu\text{S}/\text{cm}$)
Kaolin	None	2.30	468	2610	12.43	-112	10130
	Humic acid	3.16	390	556	12.27	-110	9600
	Ferrous iron	3.4	404	650	10.66	-12	8430
	Sulfides	2.06	480	620	12.3	-105	8700
Glacial Till	None	1.89	493	11540	12.09	-94	3720
	Humic acid	1.86	497	21150	12.81	-133	11640
	Ferrous iron	2.9	398	12440	12.51	-120	6750
	Sulfides	1.54	515	6110	13.01	-144	32300

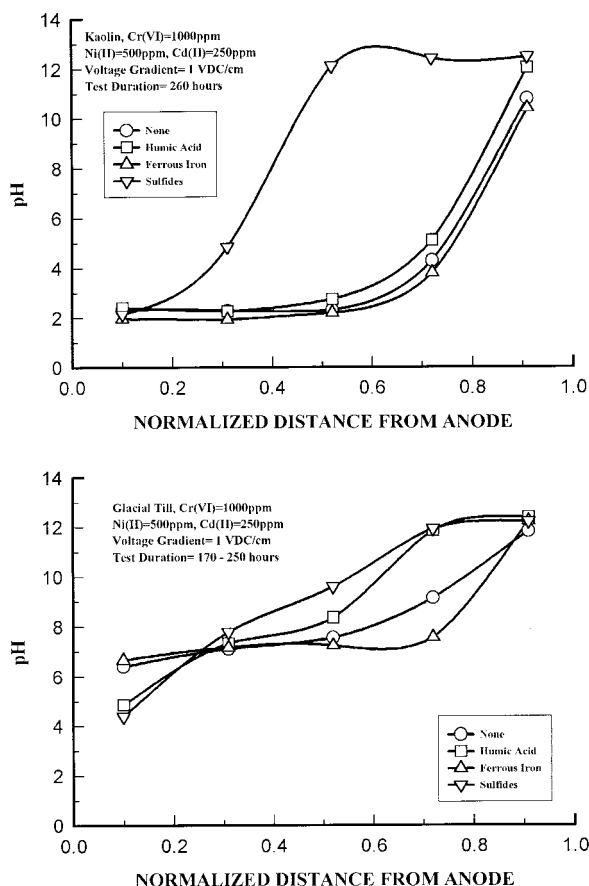


Fig. 3. pH profiles: (a) kaolin and (b) glacial till.

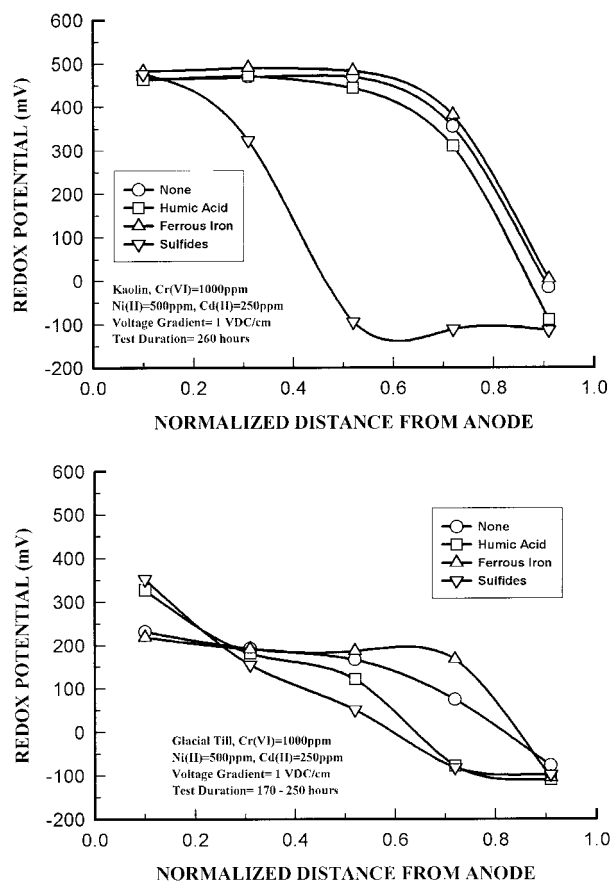


Fig. 4. Redox potential profiles: (a) kaolin and (b) glacial till.

cathode to the middle of the soil, but then decreased to 2 near the anode. In glacial till, the pH varied from 4.5 to 6 near the anode to 12 near the cathode for all tests. As compared to the initial pH values for both kaolin and glacial till, as shown in Table 2, the soil pH decreased near the anode region and increased near the cathode region. In general, alkaline conditions existed throughout the glacial till. The high pH in glacial till as compared to kaolin is attributed to the high acid buffering capacity resulting from its high carbonate content.

Fig. 4 shows the redox potential in kaolin remained approximately constant (+500 mV) from the anode to the middle regions, but then decreased rapidly towards the cathode with values ranging from -50 to +50 mV in the absence of reducing agents. The high redox potential for most of the soil from the anode to the middle regions indicates highly oxidizing conditions, while the low redox potential in the cathode region indicates reducing conditions. The redox potential variation for tests with humic acid and ferrous iron were approximately the same as that found for tests without reducing agents. However, when sulfides were present, the redox potential was reduced from 500 mV near the anode to -100 mV in the middle but remained constant towards the cathode. These redox potentials show that

oxidizing conditions were prevalent near the anode and that reducing conditions were prevalent from the middle to the cathode. As compared to the initial soil redox potentials for these tests (Table 2), significant changes in redox potentials occurred in the soil due to the induced electric potential. In glacial till, the redox potentials decreased from +230 mV near the anode to -60 mV near the cathode for tests without reducing agents as well as for tests with ferrous iron. When humic acid or sulfides were present, the redox potentials reduced from +350 mV near the anode to -100 mV near the cathode. These results show that the redox conditions in glacial till also changed to highly oxidizing conditions near the anode and to reducing conditions near the cathode due to the induced electric potential.

Fig. 5 shows the EC values in kaolin were very low at the cathode but increased gradually towards the anode for all tests except when sulfides were present. For sulfides, the EC value was high near the cathode, decreased towards the anode, and then increased near the anode. In glacial till, the EC values were lower than those observed in the kaolin. Slightly higher values were observed near the anode and cathode electrodes as compared to the EC values found in the middle of the sample. The EC values are proportional to ionic

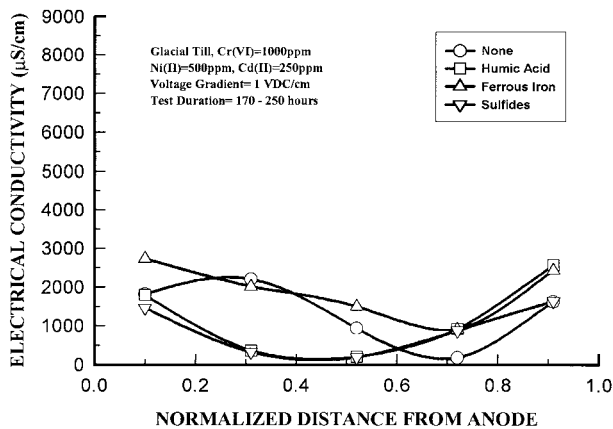
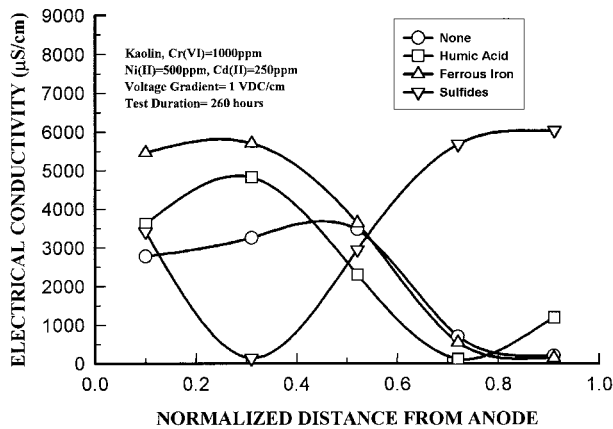


Fig. 5. Electrical conductivity profiles: (a) kaolin and (b) glacial till.

concentrations, including the ions resulting from the electrolysis of water and the ions naturally present in the soils, particularly in the glacial till.

4.4. Chromium migration

Fig. 6 shows the total chromium concentration profiles for kaolin and glacial till after electrokinetic testing. In kaolin, the total chromium concentrations were lower near the anode and cathode regions and higher in the middle of the sample. These concentration variations indicate that chromium migrated from the cathode regions into the middle of the sample, while chromium near the anode migrated into the anode. Chromium concentrations were detected in the anode, as seen in Table 1, which confirms the fact that chromium migration did indeed occur. In glacial till, chromium concentrations increased from the cathode towards the anode, indicating significant chromium migration towards the anode. The chromium concentrations measured in the anode in the test with glacial till were higher than those concentrations measured for tests using kaolin. The effect of reducing agents on chromium migration is also apparent from these concentration profiles. The results show that the presence of humic acid did not retard

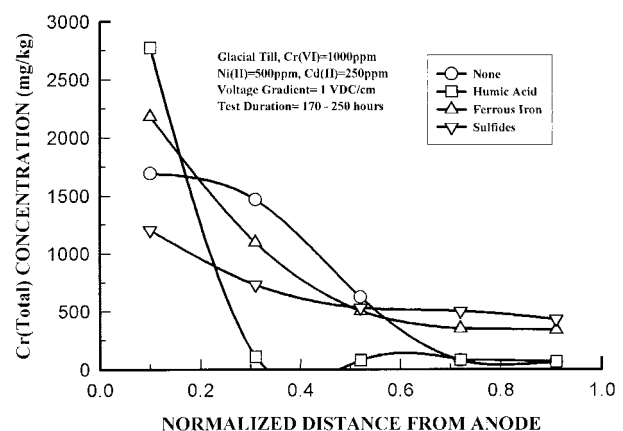
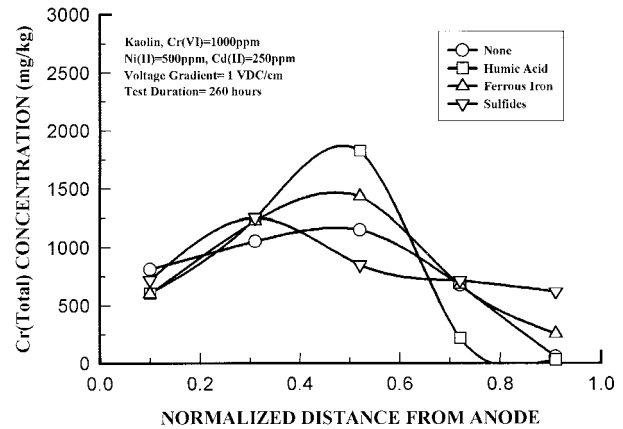


Fig. 6. Total chromium concentration profiles: (a) kaolin and (b) glacial till.

chromium migration in either soil; instead it enhanced chromium migration towards the anode. The presence of ferrous iron caused low to moderate retardation of chromium migration, while the presence of sulfides caused even higher retardation of chromium migration in both soils.

Table 1 shows that significant amounts of Cr(VI) migrated into the anode reservoir in glacial till, but in kaolin small amounts were detected in the anode. Traces of chromium detected in the cathode in both soils may be attributed to the transport of Cr(III) species that resulted from the reduction of Cr(VI) as well as the diffusion of chromium. Although chromium migrated towards the anode, most of the chromium remained within the soil for all tests.

In order to delineate the effects of reducing agents on chromium speciation, the concentrations of Cr(VI) in each soil section were also measured. Since the total chromium exists as a combination of Cr(VI) and Cr(III), the Cr(III) concentrations were computed by subtracting the Cr(VI) concentrations from the total chromium concentrations. The measured Cr(VI) concentration profiles are shown in Fig. 7, while the calculated Cr(III) concentration profiles are shown in Fig. 8 for both kaolin and glacial till. It should be noted that a

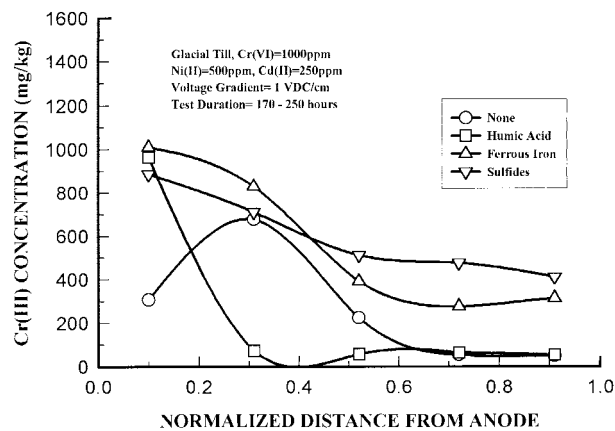
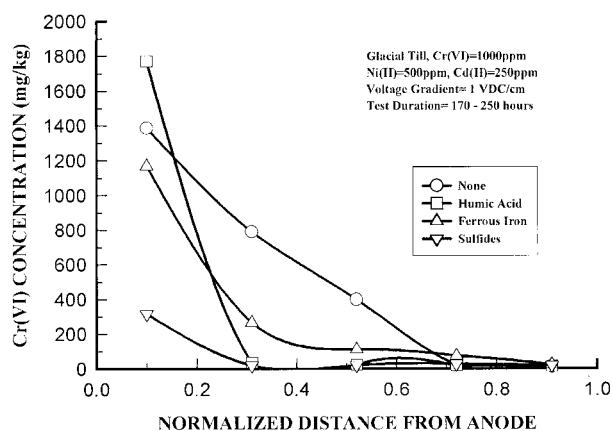
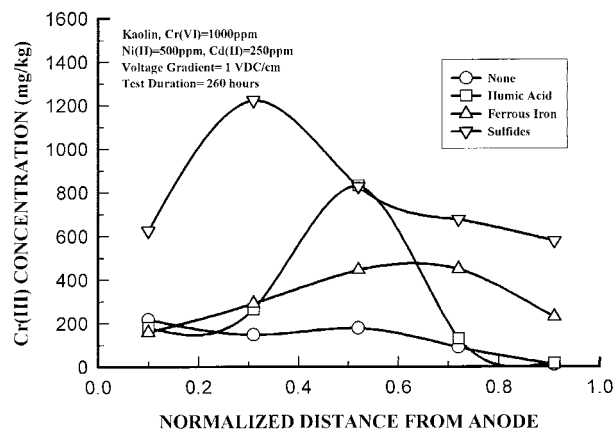
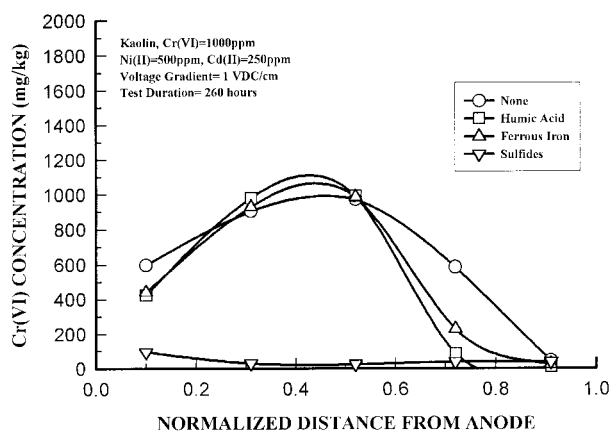


Fig. 7. Cr(VI) concentration profiles: (a) kaolin and (b) glacial till.

Fig. 8. Cr(III) concentration profiles: (a) kaolin and (b) glacial till.

total chromium concentration of 860–1100 mg/kg was initially introduced in the form of only Cr(VI) in all tests. Fig. 7 shows that Cr(VI) migration occurred towards the anode for both kaolin and glacial till. The migration of Cr(VI) was significant in glacial till as compared to the Cr(VI) migration that was observed in kaolin. Fig. 8 shows that although chromium was introduced as Cr(VI), it was reduced to Cr(III) in all tests to various degrees, depending on the redox conditions that existed due to the presence of reducing agents and the imposed electric potential. The extent of Cr(VI) reduction into Cr(III) has affected the overall chromium removal.

Due to the applied electric potential, the electrolysis of water created oxidizing conditions at the anode and reducing conditions near the cathode. These redox conditions at the electrodes altered the pH and redox potential throughout the soil, as shown in Figs. 3 and 4. These changes of pH and redox potential throughout the soil impacted the proportions of Cr(VI) and Cr(III) as well as the migration of Cr(VI) and Cr(III). Figs. 7 and 8 show that Cr(VI) was reduced to Cr(III) in both kaolin and glacial till, even when reducing agents were not present, because of the redox conditions induced by the electric potential. The Cr(VI) reduction was higher in glacial till than in kaolin and the reduction increased

towards the anode. In the presence of humic acid, additional Cr(VI) reduction was minimal in both kaolin and glacial till. In the presence of ferrous iron, Cr(VI) reduction was significant in both kaolin and glacial till. The Cr(VI) reduction to Cr(III) was the highest in the presence of sulfides in both soils. For both soils, higher Cr(III) concentrations were observed near the anode. This higher Cr(VI) reduction is attributed to acidic conditions during which the rate of Cr(VI) reduction is increased due to the availability of excess H^+ to participate in the redox reactions [14]. The reduced Cr(III) tends to migrate towards the cathode, resulting in high Cr(III) concentrations in the section near the anode. Low Cr(VI) migration towards the anode was observed in kaolin, resulting in low Cr(VI) reduction, and consequently lower concentrations of Cr(III) near the anode.

The Cr(VI) adsorption onto the soil solids decreases with an increase in soil pH [10]. Because of high pH conditions, low Cr(VI) adsorption occurs throughout the glacial till and in the regions near the cathode in kaolin. As a result of this low adsorption, Cr(VI) exists in dissolved phase, leading to higher migration under induced electric potential. Because of low pH near the anode in kaolin, Cr(VI) adsorption was higher, causing low Cr(VI) migration. Because of its anionic form, Cr(VI) migration occurred towards the anode in both

soils (see Fig. 7). In contrast, any Cr(III) resulting from the reduction of Cr(VI) exists mostly in cationic form and tries to migrate towards the cathode. Cr(III) adsorption at low pH conditions is low and increases with an increase in pH. Precipitation occurs at pH values exceeding 7. The opposite migration of Cr(VI) and Cr(III) is responsible for the low removal of both species. As seen in Fig. 8, significant reduction of Cr(VI) to Cr(III) occurred in the presence of sulfides and due to the high pH conditions that exist near the cathode; the Cr(III) precipitated without any migration. The precipitation of reduced Cr(III) in presence of ferrous iron in high pH regions is also responsible for low chromium migration. In the presence of soluble humic acid, Cr(VI) reduction was minimal and the observed enhanced chromium migration towards the anode in both soils can be attributed to the formation of anionic organic chromium complexes.

The experimental results show that the speciation of chromium in the presence of naturally occurring reducing agents within the soil as well as changes in redox conditions caused by the induced electric potential will dictate the electrokinetic removal efficiency of chromium. The type and amount of reducing agents can significantly affect Cr(VI) reduction, and suitable electrode conditioning systems that favor high removal of both Cr(VI) and Cr(III) should be investigated in order to counteract the retarding effects of the reducing agents.

4.5. Nickel migration

Fig. 9 shows the Ni(II) concentration profiles for both kaolin and glacial till at the end of the electrokinetic treatment. These results show that significant migration of Ni(II) occurred within kaolin both with the absence of reducing agents as well as during the presence of humic acid or ferrous iron. Ni(II) migrated from the anode regions towards the cathode and accumulated near the cathode. In the test using kaolin with sulfides present, the Ni(II) concentration profile shows that Ni(II) migrated from the first section near the anode and accumulated in the second section, but the concentrations in the other sections towards the cathode were approximately equal to the initial concentrations, indicating that Ni(II) migration did not occur within these sections. The mass balance analysis for all kaolin tests shown in Table 1 indicates that negligible amounts of Ni(II) migrated into the cathode compartment, very small amounts of Ni(II) migrated into the anode compartment, and most of the Ni(II) remained in the soil. The trace amounts of Ni(II) into the anode may be due to diffusion since most of the Ni(II) in the soil near the anode exists in the dissolved phase; it also be due to possible formation of anionic Ni(II) complexes that had migrated into the anode.

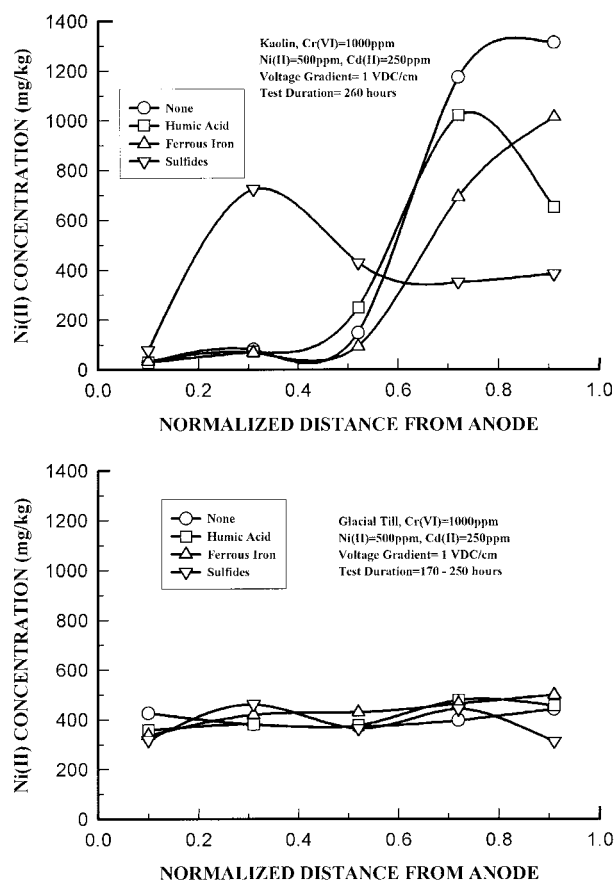


Fig. 9. Ni(II) concentration profiles: (a) kaolin and (b) glacial till.

The observed migration of Ni(II) in kaolin may be explained based on the pH profile shown in Fig. 3. For all tests except those when sulfides were present, the pH was less than 4, except in the vicinity of the cathode where values were above 10. Thus, Ni(II) existed in dissolved form in regions of low pH and easily migrated towards the cathode. When reaching the high pH region near the cathode, Ni(II) was precipitated. In the presence of sulfides, the pH was approximately 2 in the first section near the anode, then increased to 4.5 in the second section, and remained approximately constant at 12 in other sections towards the cathode. Because of low pH in the first section, Ni(II) existed in dissolved phase and migrated towards the cathode. When the Ni(II) entered and precipitated within the high pH conditions of the second section, high concentrations resulted. In other sections near the cathode, Ni(II) was precipitated without any migration because of high soil pH.

The Ni(II) concentration profiles in glacial till reveal that negligible migration of Ni(II) occurred in all tests. The mass balance analysis results in Table 1 show that negligible amounts of Ni(II) migrated into the cathode, small amounts migrated into anode, and most of Ni(II) remained in the soil. The small amounts of Ni(II) detected in the anode may be due to the formation of anionic Ni(II) complexes that had migrated into the

anode. The low pH in the soil near the anode and the resulting diffusion of dissolved Ni(II) may also be responsible for the detected amounts. The amount of Ni(II) detected in the anode was relatively higher in glacial till as compared to kaolin; this may have resulted from higher transport of anionic complexes in glacial till than in kaolin. From the pH profile in Fig. 3, the pH in the glacial till ranged from 4 to 6.5 near the anode to over 12 at the cathode. Because of the high pH conditions that existed throughout the soil, Ni(II) precipitated instead of migrating.

Among the different reducing agents, the presence of sulfides in the soil affected the redox chemistry and increased the soil pH significantly, and consequently, retarded Ni(II) migration. However, for all tests with and without the presence of a reducing agent, the high pH conditions that existed near the cathode in kaolin and also throughout the glacial till caused Ni(II) to precipitate, preventing removal of Ni(II) from the soils. These results show that conditioning of the electrodes with acids or complexing agents is required in order to enhance the mobility of the contaminants in the soil, thereby assisting in the transport of these contaminants into the electrode compartments. In this manner, the achievement of higher contaminant removal from the soils may be realized.

4.6. Cadmium migration

Fig. 10 shows the Cd(II) concentration profiles for kaolin and glacial till. These concentration profiles show that Cd(II) migration under induced electric potential was very similar to the migration that was observed for Ni(II). The extent of Cd(II) migration was affected by the pH profile across the soils. In kaolin, without a reducing agent as well as in the presence of humic acid and ferrous iron as reducing agents, low pH conditions existed throughout most of the soil except near the cathode. The Cd(II) existed in the dissolved phase at low pH regions; therefore, it was transported toward the cathode. However, upon entering the high pH region near the cathode, the Cd(II) was precipitated, preventing migration of Cd(II) into the cathode compartment. Within kaolin in the presence of sulfides, low pH conditions existed only in very close proximity to the anode, while high pH conditions existed throughout the rest of the soil. Thus, the migration of Cd(II) occurred from the anode region while precipitation occurred in regions of high pH. Results in Table 1 show that insignificant migration of Cd(II) occurred into the electrodes while most of the Cd(II) remained in the soil.

In glacial till, Cd(II) precipitated due to high pH conditions that existed throughout the soil, both with and without reducing agents. This precipitation prevented migration of Cd(II) within the soil. Table 1 also shows that most of the Cd(II) initially loaded into the

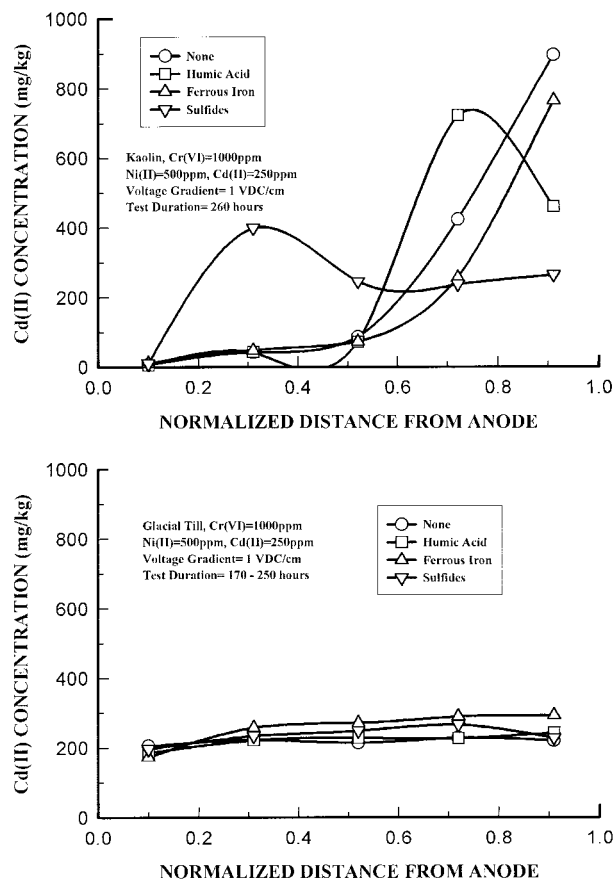


Fig. 10. Cd(II) concentration profiles: (a) kaolin and (b) glacial till.

soil remained in the soil; therefore, the effects of the reducing agents were inconsequential on the Cd(II) migration in glacial till. Overall, the results also indicate that suitable electrode conditioning systems are needed, similar to those required for Ni(II) removal, to remove Cd(II) from both kaolin and glacial till under induced electric potential. Different conditioning strategies may be required, depending upon soil compositional differences.

5. Conclusions

Based on the results of bench-scale electrokinetic experiments using both kaolin and glacial till containing various reducing agents, the following conclusions can be drawn:

1. A partial reduction of Cr(VI) into Cr(III) occurs in soils in the presence of reducing agents even before electrokinetic treatment begins. For a constant concentration of 1000 mg/kg, the amount of Cr(VI) reduced into Cr(III) was highest when sulfides were present, lowest for humic acid, and intermediary for ferrous iron.
2. Under induced electric potential, a partial reduction of chromium from Cr(VI) into Cr(III) was

observed in the soils, even in the absence of any reducing agents. This reduction may be attributed to the redox reactions that occur at the electrodes due to the electrolysis of water.

3. The pH and redox conditions that existed in the soils after the electrokinetic treatment were affected by the presence of reducing agents. The effect of sulfides on chromium migration was more pronounced than the other reducing agents (humic acid and ferrous iron). In the presence of sulfides, significant reduction of Cr(VI) to Cr(III) as well as significant increase in soil pH occurred, resulting low chromium migration in both soils.
4. For the reducing agent concentrations less than or equal to 1000 mg/kg, the effects of humic acid and ferrous iron did not affect the overall migration of either Ni(II) or Cd(II). However, the introduction of sulfides into kaolim caused significant increase in pH, resulting in low migration of Ni(II) and Cd(II) due to the precipitation of these contaminants. In high buffering soils such as glacial till, these contaminants did not migrate because of the high pH conditions that existed throughout the soil.
5. This study shows that significant removal of the contaminants from the soils was not achieved. Therefore, additional research is needed to determine strategies by which contaminant migration may be enhanced and ultimately lead to significant contaminant removal. The selection of the enhancement strategies for each particular situation must take into account individual soil composition, including the type and amount of the reducing agents as well as the different contaminants that are present within the soil.

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